

Synthesis and Characterization of Linear and Crosslinked Mono-Sulfonated Poly(arylene ether sulfone)s for Reverse Osmosis Applications

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SCHOLARLY ABSTRACT

Synthesis and Characterization of Linear and Crosslinked Mono-Sulfonated Poly(arylene ether sulfone)s for Reverse Osmosis Applications

Trevor I. Schumacher

Sulfonated poly(arylene ether sulfone)s can exhibit several ideal features as potential desalination membranes for reverse osmosis applications, including chlorine resistance, low surface fouling, and high water flux. However, this class of polymer membranes has suffered from two major drawbacks that jeopardize effective levels of salt rejection in order to achieve high water flux. In mixed salt feed sources, monovalent salt rejection decreases when divalent cations such as Ca^{2+} bind with the anionic sulfonate groups to cause charge screening, and this can lead to too much salt passage for the membranes to be competitive with interfacially produced polyamides. Sulfonate fixed charge concentration must be high enough for sufficient membrane water uptake to obtain high membrane water flux, but if the water uptake is too high, this permits increased salt passage. The research described in this dissertation attempts to address both of these challenges through the design of a sulfonated monomer that strategically spaces the ionic groups along the polymer backbone chains to inhibit divalent ion binding. Free radical crosslinking further tunes the hydrated free volume in the RO membranes.

A mono-sulfonated comonomer, sodium 3-sulfonate-4,4'-dichlorodiphenylsulfone (*ms*-DCDPS), was synthesized by stoichiometrically controlled electrophilic aromatic sulfonation of 4,4'-dichlorodiphenylsulfone (DCDPS). HPLC-UV revealed complete isolation of *ms*-DCDPS

free of by-products after the 1st recrystallization and ¹H NMR analysis confirmed the structure. A standard calibration curve was developed to accurately determine the leftover quantity of excess NaCl that was used for precipitation during the work-up procedures. A series of linear sulfonated poly(arylene ether sulfone)s with varying *ms*-DCDPS incorporation was synthesized. ¹H NMR confirmed the structure of the polymers and size-exclusion chromatography confirmed that the intended molecular weights were achieved. The copolymers were cast into dense films and the mechanical and transport properties were measured in their fully hydrated states. Tensile tests revealed mechanically robust, tough membranes with glassy elastic moduli and high strains at break. The dense membrane prepared from sulfonated poly(arylene ether sulfone) with 51% of the repeat units sulfonated had NaCl rejection = 99.3% measured at 400 psi and 2000 ppm NaCl with a water permeability coefficient of $0.57 \times 10^{-6} \text{ cm}^2/\text{s}$. The salt rejection remained greater than 99% when a mixed salt feed source containing Ca²⁺ in the 0-200 ppm range together with the 2000 ppm NaCl was introduced.

Crosslinked mono-sulfonated oligomers were synthesized with targeted molecular weights by utilizing stoichiometric quantities of monomers with the desired degrees of sulfonation, and the endgroups were functionalized with tetrafluorostyrene. These end-functionalized sulfonated oligomers were crosslinked by both thermal and UV free radical methods in the presence of initiators without any additional crosslinking agents. Reaction conditions were thoroughly investigated and optimized to produce highly crosslinked membranes that yielded gel fractions greater than 87%, as measured by solvent extraction in dimethylacetamide. The hydrated crosslinked membranes were tested for both mechanical and transport properties, and the results were compared to their linear membrane counterparts. Crosslinking decreased the hydrated free volume and reduced water uptakes when compared to linear sulfonated membranes. Tensile tests

of the fully hydrated crosslinked membranes showed good mechanical properties. The transport properties of a dense UV crosslinked membrane prepared with a 10,000 g/mol oligomer having 50% of the repeat units sulfonated was tested under RO cross-flow conditions at 400 psi and 2000 ppm NaCl in the feed. The membrane demonstrated a salt rejection = 98.4% with a water permeability coefficient of $0.49 \times 10^{-6} \text{ cm}^2/\text{s}$.

GENERAL AUDIENCE ABSTRACT

Synthesis and Characterization of Linear and Crosslinked Mono-Sulfonated Poly(arylene ether sulfone)s for Reverse Osmosis Applications

Trevor I. Schumacher

Billions of individuals across the world lack clean, affordable drinking water, and the unavailability of fresh drinking water can be attributed to both physical and economic reasons. Several techniques have been utilized to produce potable water for human consumption that include both water desalination and recycling procedures. Water desalination is a process that allows for purifying salt contaminated water into drinking water. The two major desalination processes involve either distillation or passage through polymer membranes. Distillation separates water from salt by heating liquid water to form a gas, and collecting the vapor as condensate while impurities remain in the heated bulk material. Polymer membranes separate impurities through filtration where membranes allow water to pass through a physical barrier while rejecting the unwanted contaminants, including salt.

Reverse osmosis desalination is the most common membrane separation process. Reverse osmosis membranes are comprised of either short-chain crosslinked oligomers or long-chain linear polymers. Commercial reverse osmosis membranes are largely poly(amide)s where a thin film is formed in an interfacial reaction. The membranes allow for almost quantitative salt rejection with high water fluxes. But, these membranes degrade over time from periodic cleaning with chlorine disinfectants.

This dissertation primarily focuses on the implementation of an alternative polymer membrane material known as a mono-sulfonated polysulfone that strategically distributes the fixed sulfonate charged groups along the polymer backbone. These reverse osmosis mono-sulfonated polysulfones display comparable salt rejection with better chemical resistance than commercial poly(amide)-based membranes, and could potentially offer a replacement in the market.

Dedicated to my loving parents and sisters

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great deal with structural analysis confirmation, and Eui Soung Jang determined the water/salt transport properties.

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ATTRIBUTION

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TABLE OF CONTENTS

CHAPTER 1: LITERATURE REVIEW	1
1.1 Potential Water Crisis	1
1.2. Desalination Processes and Applications	3
1.2.1. Thermal Separation Processes.....	6
1.2.1.1. Multi-Stage Flash Distillation	7
1.2.1.2. Multi-effect Distillation	8
1.2.1.3. Vapor Compression Distillation.....	9
1.2.2. Membrane Separation Processes.....	10
1.2.2.1. Microfiltration and Ultrafiltration	11
1.2.2.2. Nanofiltration	12
1.2.2.3. Reverse Osmosis.....	13
1.2.2.4. Electrodialysis	15
1.3. Reverse Osmosis Transport Properties	17
1.3.1. Water Transport.....	18
1.3.2. Salt Transport.....	20
1.3.3. Membrane Selectivity.....	21
1.4. RO Membrane Design and Fabrication	22
1.5. Reverse Osmosis Materials	25
1.5.1. Cellulose Acetate.....	27
1.5.2. Polyamide Thin-Film Composites.....	29
1.5.3. Polyfurans	34
1.6. Poly(arylene ether sulfone)s for Reverse Osmosis Applications	35
1.6.1. Synthesis of Poly(arylene ether sulfone)s.....	37
1.6.1.1. Nucleophilic Aromatic Substitution (S_NAr).....	37
1.6.1.2. Electrophilic Aromatic Substitution (S_EAr).....	40
1.7. Sulfonated Poly(arylene ether sulfone)s for Reverse Osmosis Applications	41
1.7.1. Post-sulfonation Synthesis of Sulfonated Poly(arylene ether sulfone)s.....	41
1.7.2. Direct Polymerization of Sulfonated Poly(arylene ether sulfone)s for Reverse Osmosis	45
1.8. Crosslinking Sulfonated Poly(arylene ether sulfone)s	52
1.8.1. Polycondensation Crosslinking.....	53
1.8.2. Thermal Free Radical Crosslinking.....	59
1.8.3. UV Free Radical Crosslinking	64

CHAPTER 2: SYNTHESIS OF STATISTICAL SULFONATED POLY(ARYLENE ETHER SULFONES)S VIA DIRECT POLYMERIZATION WITH A MONO-SULFONATED MONOMER.....	86
2.1 Abstract	86
2.2 Introduction.....	87
2.3 Experimental	89
2.4 Results and Discussion	94
2.5 Conclusions.....	105
2.6 References.....	106
2.7 Supplementary Material	108
 CHAPTER 3: THERMAL AND UV FREE RADICAL CROSSLINKING OF SULFONATED POLY(ARYLENE ETHER SULFONE) TELECHELIC OLIGOMERS FOR POTENTIAL WATER DESALINATION MEMBRANE APPLICATIONS	 110
3.1 Abstract	111
3.2 Introduction.....	111
3.3 Experimental	115
3.4 Results and Discussion	122
3.5 Conclusions.....	148
3.6 References.....	149
 CHAPTER 4: CONCLUSIONS AND SUGGESTED FUTURE WORK	 152
4.1. Conclusions.....	152
4.2. Suggested Future Work	154
4.3. References.....	159

LIST OF FIGURES

Figure 1. 1. Global map displaying water scarcity as of 2012 ⁵	2
Figure 1. 2. Comparison of desalination processes. Chart A shows the average daily production capacity for desalination processes. Chart B displays the number of operational desalination facilities worldwide.....	5
Figure 1. 3. Multi-stage flash distillation for desalination of seawater ⁴⁴	7
Figure 1. 4. Typical arrangement of multi-effect evaporative distillation for desalination of seawater ⁴⁴	8
Figure 1. 5. Conventional design of vapor compression distillation for desalination of seawater. Used with permission of John Wiley and Sons ⁴⁷	9
Figure 1. 6. General representation of pore-flow and solution-diffusion models ⁴⁹	10
Figure 1. 7. Overview of rejection capabilities for MF, UF, NF, and RO membranes for desalination ⁵²	11
Figure 1. 8. Schematic diagram of reverse osmosis for desalination. Used with permission from the Royal Society of Chemistry ⁷⁴	14
Figure 1. 9. Common configuration of an electrodialysis cell for desalination ⁸²	15
Figure 1. 10. Crosslinked polystyrene-divinylbenzene matrices for CEMs and AEMs utilized for ED desalination.....	16
Figure 1. 11. Tradeoff between water/NaCl permeability selectivity vs water permeability with an upper bound line ⁹¹	21
Figure 1. 12. Diagrams of symmetric and asymmetric membranes	23
Figure 1. 13. SEM cross section of a thin-film composite membrane with a polyamide dense skin layer and polysulfone porous support ¹⁰⁶	25
Figure 1. 14. AFM image of FT-30 polyamide TFC displaying surface roughness ¹³⁹	34
Figure 1. 15. Resonance stability in poly(arylene ether sulfone) linkages.....	35
Figure 1. 16. Commercial poly(arylene ether sulfone) examples.....	36
Figure 1. 17. Chemical structure of di-sulfonated poly(arylene ether sulfone)s	48
Figure 1. 18. Effect of chlorine exposure on salt rejection for both polyamide SW-30HR and di-sulfonated poly(arylene ether sulfone). ¹²³	50
Figure 1. 19. AFM surface images of (a) a commercial polyamide BW-30 Dow Filmtech© membrane and (b) a di-sulfonated poly(arylene ether sulfone) TFC. ¹⁸⁸	51
Figure 1. 20. Chemical structures for linear and crosslinked sulfonated poly(arylene ether sulfone)s	54
Figure 1. 21. (A) Salt rejection versus water permeability for linear and epoxy crosslinked PAES copolymers that contained biphenol; (B) salt rejection versus water permeability for linear and epoxy crosslinked PAES copolymers that contained bisphenol A. Number next to data point = IEC	56
Figure 1. 22. Chemical structure of crosslinks between sulfonated poly(arylene ether sulfone) polymer chains by disproportionation or S-alkylation methods.....	58
Figure 1. 23. Sulfonated poly(arylene ether sulfone)s endcapped with functional endgroups or polymer chain side groups for thermal free radical crosslinking	62
Figure 1. 24. Non-sulfonated and sulfonated poly(arylene ether sulfone)s for free radical UV-crosslinking.....	68

Figure 1. 25. Telechelic nonsulfonated and sulfonated poly(arylene ether sulfone)s for free radical UV-crosslinking	70
Figure 2. 1. ^1H NMR overlay spectra of non-sulfonated and sulfonated monomers.....	96
Figure 2. 2. ^{13}C NMR spectrum of <i>ms</i> -DCDPS.....	97
Figure 2. 3. UV-Vis spectra of <i>ms</i> -DCDPS after successive recrystallizations at a concentration of 3×10^{-5} M in methanol.....	98
Figure 2. 4. ^1H NMR spectrum of high molecular weight polymer ($x = 0.5$).....	100
Figure 2. 5. Hydrated uniaxial mechanical properties and molecular structures of high molecular weight non-sulfonated PAES in purple, di-sulfonated PAES in red, and mono-sulfonated PAES in blue.....	102
Figure 2.S.1. HPLC-UV standard calibration curve of purified <i>ms</i> -DCDPS.....	108
Figure 2.S.2. SEC light scattering chromatogram of sulfonated poly(arylene ether sulfone). 50% of the repeat units mono-sulfonated (high molecular weight).....	109
Figure 3. 1. ^1H NMR overlay of targeted 10,000 g/mol oligomers with 50% of the repeat units containing the monosulfonated <i>ms</i> -DCDPS.....	124
Figure 3. 2. ^{19}F NMR overlay of targeted 10,000 g/mol oligomers with 50% incorporation of <i>ms</i> -DCDPS repeat unit and pentafluorostyrene	125
Figure 3. 3. SEC chromatograms of targeted 2,000 and 10,000 g/mol oligomers with 50% incorporation of <i>ms</i> -DCDPS repeat units and with biphenol endgroups.....	126
Figure 3. 4. Gel fractions vs. the amount of polymer dissolved in one mL of DMAc of networks prepared by thermally crosslinking telechelic 2,000 and 10,000 kDa oligomers endcapped with tetrafluorostyrene end groups. 50% of the repeat units in each polymer contained <i>ms</i> -DCDPS.	129
Figure 3. 5. Gel fractions upon thermal crosslinking as a function of initiator concentration using the 10 kDa oligomer with 50% incorporation of the <i>ms</i> -DCDPS repeat unit.....	131
Figure 3. 6. Thermal free radical polymerization with crosslinking of a 2,000 g/mole oligomer with tetrafluorostyrene end groups as a function of time with <i>in-situ</i> FT-IR.....	133
Figure 3. 7. Gel fractions vs. thermal curing time at 80°C of a 2,000 g/mol tetrafluorostyrene terminated oligomer that had 50% of the units containing <i>ms</i> -DCDPS	134
Figure 3. 8. UV spectra of the 2,000 g/mol oligomer containing 50% incorporation of <i>ms</i> -DCDPS repeat units, pentafluorostyrene, DMAc and DEG.....	136
Figure 3. 9. Effects of TPO concentration on crosslinking a 10,000 g/mol oligomer with 50% of the repeat units containing the <i>ms</i> -DCDPS	138
Figure 3. 10. Gel fractions after curing a tetrafluorostyrene encapped 10,000 g/mole oligomer with UV light at 365 nm and 65°C as a function of curing energy.....	140
Figure 3. 11. UV curing with varying TPO initiator concentration at low curing energies of the 10,000 g/mol tetrafluorostyrene oligomer with 50% incorporation of <i>ms</i> -DCDPS repeat unit..	142
Figure 3. 12. Gel fractions of networks prepared with a 10,000 g/mole oligomer with 50% incorporation of <i>ms</i> -DCDPS repeat units in DMAc/DEG (90/10 v/v) as a function of curing energy	143
Figure 3. 13. Hydrated uniaxial mechanical properties of linear high molecular weight mono-sulfonated PAES (<i>ms</i> -PAES-xx) and crosslinked mono-sulfonated oligomers (<i>xl-ms</i> -PAES-xx).	147

Figure 4. 1. Effects of NaCl salt rejection with Ca^{2+} concentration in feed source. (A) Sulfonated Udel® at 400 PSI (B) Di-sulfonated poly(arylene ether sulfone) and polyamide TFC. Used with permission from Elsevier ^{3,4}	152
Figure 4. 2. Post-sulfonated hydroquinone and biphenol based poly(arylene ether sulfone)s...	155
Figure 4. 3. Sulfonated and carboxylated monomers for potential reverse osmosis applications	158
Figure 4. 4. General diagram of two methods for creating asymmetric crosslinked membranes. Used with permission from Elsevier ¹³	159

LIST OF TABLES

Table 1. 1 Comparison of energy, water cost, recovery rate, capacity, and TDS parameters for desalination processes. ^{22,27,31–36}	6
Table 1. 2. Water transport and salt rejections for polymeric RO membranes	26
Table 1. 3. Reverse osmosis transport and physical properties of disulfonated poly(arylene ether sulfone) films with varying degrees of sulfonation in their salt and acid forms ¹²³	49
Table 1. 4. Comparison of ion exchange compacity, water permeability, and salt rejection for linear and epoxy crosslinked sulfonated poly(arylene ether sulfone)s ^{94,95,193,203}	55
 Table 2. 1. Directly polymerized sulfonated poly(arylene ether sulfone) (PAES) ion exchange capacity (IEC), water uptake (WU), and hydrated mechanical properties. <i>ns</i> -PAES is the non-sulfonated PAES, <i>ds</i> -PAES is a sulfonated PAES containing a di-sulfonated monomer (<i>ds</i> -DCDPS) and <i>ms</i> -PAES is a sulfonated PAES containing the mono-sulfonated monomer (<i>ms</i> -DCDPS).....	101
Table 2. 2. Transport properties of <i>ds</i> -PAES-32, <i>ms</i> -PAES-51, and <i>ms</i> -PAES-61	103
 Table 2.S.1. NaCl concentration in <i>ms</i> -DCDPS by UV-Vis spectroscopy in comparison to HPLC with UV detection	108
Table 2.S.2. Molecular Weights of Sulfonated Poly(arylene ether sulfone)s	108
 Table 3. 1. Molecular weight analyses for oligomers with targeted number average molecular weights of 2,000 and 10,000 g/mol and with 50% and 60% sulfonated repeat units	127
Table 3. 2. Thermal curing effects of polymer concentration with respect to Gel Fraction (%) of both 2 and 10 kDa oligomers with 50% incorporation of <i>ms</i> -DCDPS repeat units	130
Table 3. 3. Thermal curing effects of initiator concentration with respect to gel fraction of a 10 kDa tetrafluorostyrene terminated oligomer containing 50% of <i>ms</i> -DCDPS repeat units	132
Table 3. 4. Gel fractions as a function of thermal curing time at 80°C under nitrogen with a 2 kDa oligomer containing 50% incorporation of the <i>ms</i> -DCDPS repeat unit.....	135
Table 3. 5. Gel fractions vs. TPO initiator concentration during curing of a 10,000 g/mole oligomer with 50% incorporation of repeat units containing <i>ms</i> -DCDPS	139
Table 3. 6 Gel fractions after curing a tetrafluorostyrene encapped 10,000 g/mol oligomer with 50% of the repeat units containing <i>ms</i> -DCDPS with varying energies	141
Table 3. 7. UV curing with varying initiator concentration at low curing energy exposure of the 10,000 g/mol oligomer with 50% incorporation of <i>ms</i> -DCDPS repeat unit	142
Table 3. 8. Gel fractions after UV curing of a 10,000 g/mole oligomer containing <i>ms</i> -DCDPS in 50% of the repeat units in DMAc/DEG (90/10 v/v)	144
Table 3. 9. UV curing a 10,000 and a blend of 2000 and 10,000 g/mole oligomers containing <i>ms</i> -DCDPS in 50% in DMAc/DEG (90/10 v/v) results in efficient curing at low curing energies..	144
Table 3. 10. Directly polymerized sulfonated poly(arylene ether sulfone) (PAES) ion exchange capacity (IEC), water uptake (WU), and hydrated mechanical properties. <i>ms</i> -PAES-xx are the linear sulfonated PAES containing the mono-sulfonated monomer (<i>ms</i> -DCDPS), and <i>xl-ms</i> -PAES-xx are the crosslinked sulfonated PAES containing the mono-sulfonated monomer (<i>ms</i> -	

DCDPS). xx denotes the mol. percentage of mono-sulfonated monomer incorporated in the oligomer.	146
Table 3. 11. Water transport and salt rejection properties of crosslinked oligomers and linear polymers. <i>ms</i> -PAES-xx is the linear sulfonated PAES containing the mono-sulfonated monomer (<i>ms</i> -DCDPS), and xl- <i>ms</i> -PAES-xx is the crosslinked sulfonated PAES containing the mono-sulfonated monomer (<i>ms</i> -DCDPS). xx denotes the mol. percentage of mono-sulfonated monomer incorporated in the oligomer.	147

LIST OF SCHEMES

Scheme 1. 1. Synthesis of cellulose acetate.....	27
Scheme 1. 2. Synthesis and fabrication of crosslinked aromatic polyamide TFC RO membranes, commercially known as FT-30	31
Scheme 1. 3. Chlorination of a polyamide TFC by irreversible direct attack and Orton rearrangement	33
Scheme 1. 4. Polymerization of crosslinked polyfuran via acid-catalyzed polycondensation	35
Scheme 1. 5. Mechanism of nucleophilic aromatic substitution.....	37
Scheme 1. 6. Synthesis of poly(arylene ether sulfone) with a strong base via S _N Ar	38
Scheme 1. 7. Synthesis of polysulfone (Udel®)	39
Scheme 1. 8. Electrophilic aromatic substitution sulfonylation.....	40
Scheme 1. 9. Post-sulfonation of Udel® by chlorosulfonic acid and a sulfur trioxide complex..	42
Scheme 1. 10. Post-sulfonation of PAES containing activated hydroquinone rings	43
Scheme 1. 11. Synthesis of di-sulfonated 4,4'-dichlorodiphenylsulfone	46
Scheme 1. 12. Direct polymerization of di-sulfonated PAES with ds-DCDPS monomer and various bisphenols.....	47
Scheme 1. 13. Sulfonamide crosslinking of linear sulfonated poly(arylene ether sulfone) copolymers	57
Scheme 1. 14. Radical crosslinking of poly(arylene ether sulfone) oligomers with maleimide endgroup functionality	60
Scheme 1. 15. Mechanistic steps for free radical photopolymerization.....	64
Scheme 1. 16. Formation of radical species by homolytic bond cleavage for HCPK and TPO...65	
 Scheme 2. 1. Synthesis of <i>ms</i> -DCDPS	95
Scheme 2. 2. Polymerization of poly(arylene ether sulfone)s	99
 Scheme 3. 1. Polymerization of telechelic sulfonated poly(arylene ether sulfone) oligomers with tetrafluorostyrene end groups	123
Scheme 3. 2. Thermal free radical crosslinking of tetrafluorostyrene functional oligomers.....	128
Scheme 3. 3. Overall reaction for UV curing of tetrafluorostyrene endcapped oligomers	137
 Scheme 4. 1. Polymerization and post-sulfonation of dihydroxynaphthalene based poly(arylene ether sulfone)	156
Scheme 4. 2. Carboxylated and phosphonated poly(arylene ether sulfone)s.....	157

Chapter 1: Literature Review

1.1 Potential Water Crisis

With the world's growing population and urbanization, the lack of sufficient fresh water presents a global water shortage. This issue pertains to individuals in both developed and developing nations across the planet. Water covers 75% of the Earth's surface and 97% of this water consists of undrinkable saline water situated in oceans and seas. Approximately 2.5% is fresh water trapped in glaciers and icecaps, leaving just a small amount of ~0.5% as viable fresh water from ponds, lakes, springs, and aquifers.^{1,2}

Seven hundred and eighty-five million people live without potable drinking water and over 2 billion encounter drinking water with fecal matter contaminated on a daily basis.³ Approximately 4 billion people experience water scarcity for at least one month during the year, which results from either economic or physical origins.⁴ Economic scarcity implies an inadequate fresh water supply due to financial constraints due to the need for investment in infrastructure, whereas physical scarcity refers to the demand for water surpassing the available water supply in a given area. Central American, Caribbean, and Central African countries experience economic water scarcity. The United States, Australia, and North Africa suffer from physical water scarcity. The world map shows the overall global locations that are affected by economic, physical, and approaching water scarcity, as shown in Figure 1.1.⁵

The World Economic Forum (WEF) disclosed the water crisis as the number one global threat to humanity, and the water crisis remains a top five global risk in their comprehensive assessment report as of 2018.^{6,7} The availability of fresh water continues to diminish as the total accessible withdrawals outpace the renewable water sources in certain areas. Water withdrawals

can be categorized into 3 primary sectors including agriculture, industry, and municipal needs. Agriculture singlehandedly accounts for 69% of the world's total water withdrawals, with industrial and municipal requirements accounting for 19 and 12%, respectively.^{8,9}

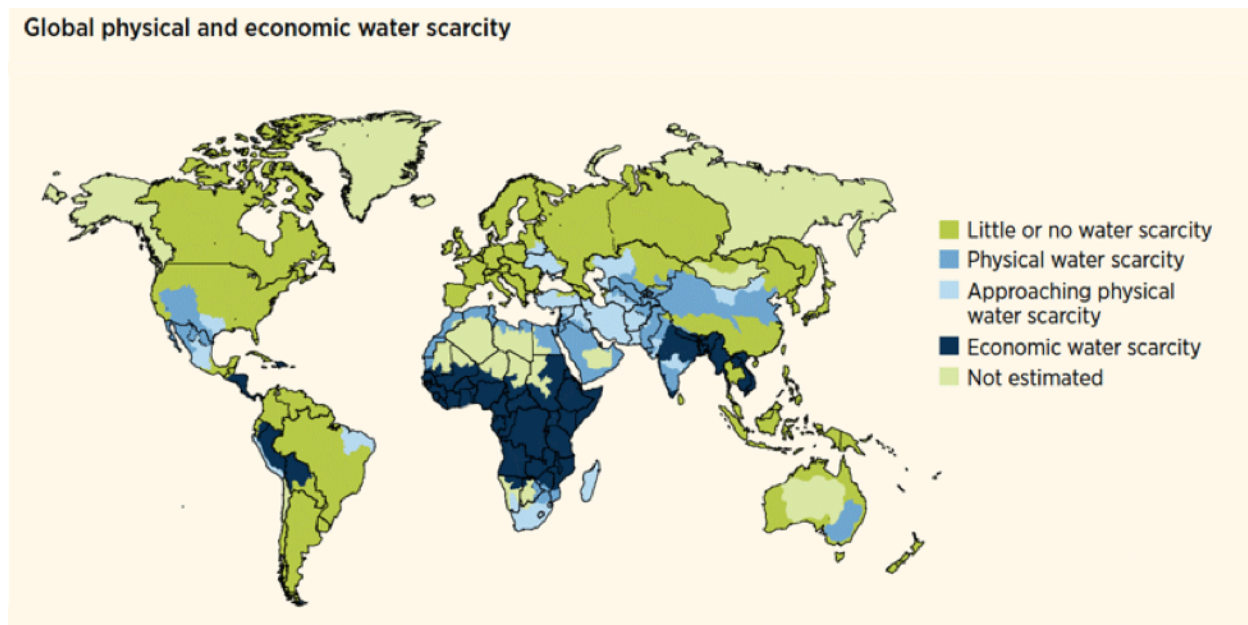


Figure 1. 1. Global map displaying water scarcity as of 2012. Used with permission from the United Nations Education, Scientific and Cultural Organization.⁵

Population growth, progress in living standards, drought, and contamination are the primary driving forces behind the increasing threat of water scarcity. Presently, the world population is 7.7 billion and it is predicted to increase to an alarming 9.7 billion by 2050.¹⁰ The increase in population will require an amplification in water withdrawals to accommodate drinking water, sanitation needs, and food production.¹¹ Scientists forecast that agricultural production will necessitate a 19% water withdrawal rise by the year 2050.¹² Migration and urban population growth strain water resources that are already used to more extreme stress. Urbanization leads to the depletion of fresh water sources that can affect the surrounding environment.¹³ For example,

the Colorado River remains under considerable water stress as a result of diverting to hydroelectric dams, assisting the irrigation of crops in California, and also meeting the water demands for desert cities such as Phoenix.¹⁴ Industry/energy water consumption rises with the increased manufacturing and the concomitant increase in electrical output, especially in developing nations.¹⁵ The earth's climate constantly changes and leads to water scarcity occurring in areas exposed to prolonged drought conditions. Australia, South Africa, and parts of the United States are commonly afflicted by drought-generated water scarcity.^{16,17} Finally, industrial hazardous chemical waste dumping, mining, agriculture fertilizer runoffs, and other toxins pollute fresh water resources and can lead to unsuitable drinking water.¹⁸ A case study examination of downhill fresh water from mountaintop mining operations in the Appalachian region revealed an abnormal amount of dissolved trace metals and inorganic ions, including selenium, magnesium, and sulfate ions.¹⁹

Available fresh water resources, such as lakes, rivers, and springs cannot overcome the driving forces for global water scarcity. Management of water resources through water conservation cannot fully avoid water shortages. Thus, other means for freshwater production need to be implemented to completely alleviate global water stress. Water recycling and desalination techniques have been implemented to address the water crisis.^{20–22} Considerable private and government research funding have led to economical, cost-friendly, and innovative desalination techniques for purified water.²³

1.2. Desalination Processes and Applications

Since World War II, considerable research and development has been commissioned for water desalination technologies in regions with physical and/or economic water scarcity.

Desalination involves the removal of minerals and salts from a water feed source to produce potable fresh water. The World Health Organization has detailed guidelines for safe drinking water and concludes that the total dissolved solids (TDS) must be less than 1000 mg/L.²⁴ Therefore, desalination facilities must remove enough TDS from the water supply to accommodate this standard. Desalination feed sources include seawater, brackish water, and surface water and wastewater. Brackish water has a TDS range of 1000-10,000 mg/L, while seawater possesses a much higher TDS range of 10,000-60,000 mg/L.²⁵ Approximately 57% of desalinated water today comes from seawater, whereas 23.5 % is from brackish water. The remaining amount is from surface water and wastewater.²⁶ Currently, there are about 16,000 operational desalination plants with a daily capacity of 95.4 million m³/day worldwide.²⁷ The daily capacity is predicted to increase at a 9% annual rate until 2030.²⁸ Selection for a desalination operation depends on location, water feed source, and energy demands.

Thermal separation and physical separation stand as the two main categories for desalination processes to help with drinkable water demands. Thermal separation consists of a phase change through the distillation of water from salt ions and includes multi-stage flash (MSF), multi-effect evaporation (MED), and vapor compression distillation as the major modes. Physical separation, or membrane separation, entails the filtering of salt ions from water by either nanofiltration (NF), electrodialysis (ED), or reverse osmosis (RO). Although distillation has been known for hundreds of years, large scale thermal desalination was not implemented until the 1950s.²⁹ Thermal separation remains the dominant process for Middle Eastern countries, excluding Israel. Membrane separation plants (RO) exponentially expanded in the 1980s with the introduction of better-quality membranes.³⁰ The United States, Spain, and Israel mainly employ membrane separation facilities. The opening of membrane separation facilities continues to

outpace the development of distillation plants. Multi-stage flash distillation and Reverse Osmosis are the most commonly used desalination methods and comprise more than 87% of desalinated water production capacity. Alone, reverse osmosis generates 65.5 million m³/day of desalinated water which comprises 69% of global market production (Figure 1.2).²⁷

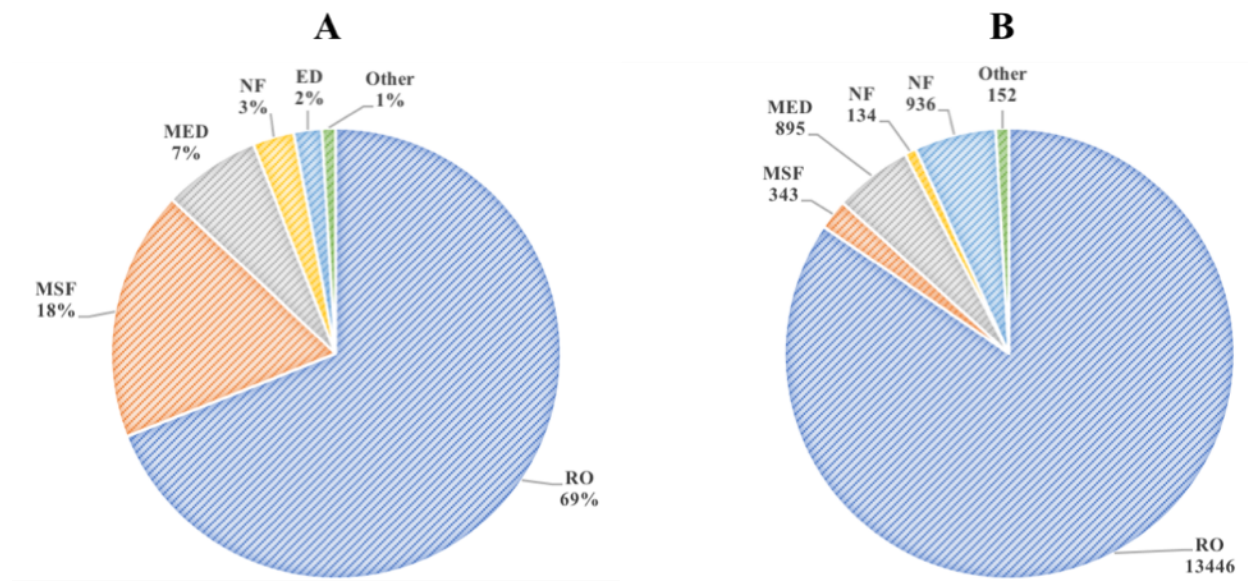


Figure 1. 2. Comparison of desalination processes. Chart A shows the average daily production capacity for desalination processes. Chart B displays the number of operational desalination facilities worldwide.²⁷

Thermal and membrane desalination processes possess advantages and disadvantages over each other and Table 1.1 reflects some of these fundamental aspects. Thermal separation requires a tremendously larger amount of energy input due to the required phase change from liquid to gas during the distillation procedure. The energy requirements and construction costs for distillation plants lead to higher average costs of water relative to RO or ED. Membrane separation yields better recovery rates; however, distillation produces cleaner water with lower total dissolved solids. Both processes suffer from fouling that requires repeated maintenance. Research and

development of new materials, plant design, and antifouling advancements have lowered energy consumption and water prices while increasing recovery rates for both distillation and membrane separation processes. Continued research must be implemented in order to prevent future water scarcity.

Table 1. 1 Comparison of energy, water cost, recovery rate, capacity, and TDS parameters for desalination processes.^{22,27,31–36}

	Reverse Osmosis (Seawater)	Reverse Osmosis (Brackish)	Electro- dialysis (Brackish)	Multi- Stage Flash	Multi- effect Distillation	Vapor Compression Distillation
Energy Use (kWh/m ³)	4-12	2-6	0.2-2.1	20-58	15-58	8-33
Cost of water (\$/m ³)	0.45-0.92	0.20-0.35	0.58	1.1-1.5	0.66-86	0.87-0.92
Recovery Rate (%)	30-60	60-75	80-95	25-50	0-60	~50
Worldwide Capacity (%)	69		2	18	7	<1
TDS (mg/L)	<500	<200	140-600	<50	<10	<10

1.2.1. Thermal Separation Processes

Large scale desalination processes are for the most part geographically employed in desert areas such as the Middle East. The desalination methods distill water from the feed source, leaving behind a concentrated brine solution. Distillation, relative to RO and ED, requires considerably more thermal energy to produce drinking water. Most processes are stationed in unison with power plants to maximize efficiency.³⁷ Combined systems such as MSF-vapor compression distillation

systems have been developed to keep thermal energy consumption to a minimum.^{38,39} The geographical location of these plants with little to virtually no rain/cloud coverage could also lead to their utilization of solar energy to drive fuel costs down.⁴⁰

MSF, MED, and vapor compression distillation processes suffer from scaling and fouling. Scaling occurs by deposition of insoluble salts from the concentrated brine solutions onto internal surfaces, such as piping and heating elements. Scale formation, particularly calcium sulfate, conducts heat poorly and decreases performance efficiency.⁴¹ Seawater and high temperatures corrode the internal system elements over time. Antiscalants, bulk boiling, reduced pressure, and innovations in plant design have minimized scaling impact, but this still remains an underlying concern for thermal separation facilities.^{42,43}

1.2.1.1. Multi-Stage Flash Distillation

Multi-stage flash distillation involves evaporation and condensation of water, and occurs over several successive stages (Figure 1.3).^{44,45} The seawater feed source is pumped through the condenser piping through all stages and enables preheating. A steam source introduced to the

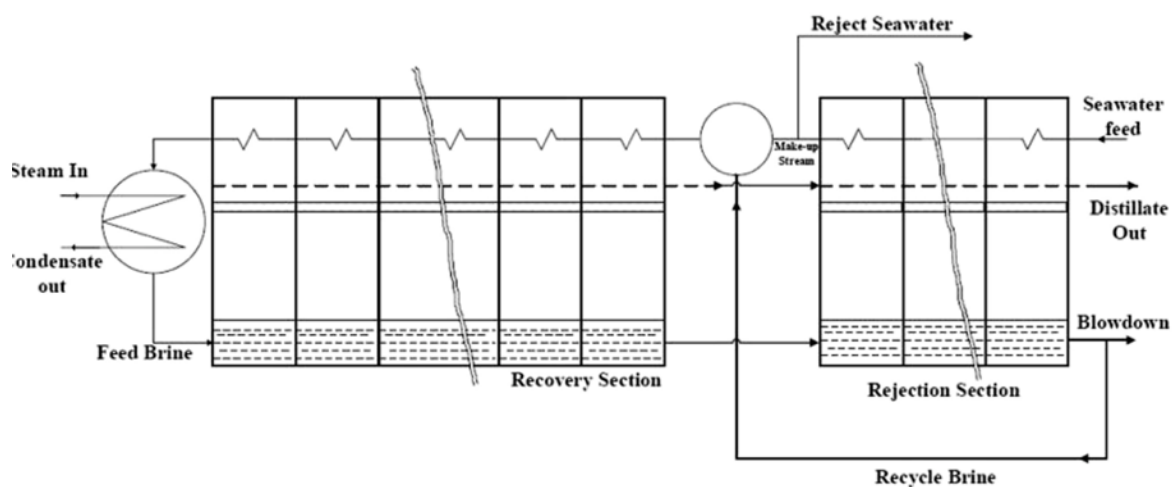


Figure 1. 3. Multi-stage flash distillation for desalination of seawater. Used with permission from Elsevier.⁴⁴

1st stage of MSF then heats the seawater. The reduced pressure of the system causes the heated seawater to rapidly boil and evaporate and then condense. Chambers at the top collect the distillate as purified desalinated water and simultaneously pump it to a reservoir. The brine solution moves from each consecutive stage becoming further concentrated with lower pressures, and ultimately is pumped back to the source or collected as waste.

1.2.1.2. Multi-effect Distillation

Multi-effect distillation (MED) requires less thermal energy input as compared to MSF and the overall process is shown in Figure 1.4.^{44,46} The seawater feed source is pumped to the first “effect” consisting of steam heated tubes. The seawater source is sprayed onto the tubes and rapidly

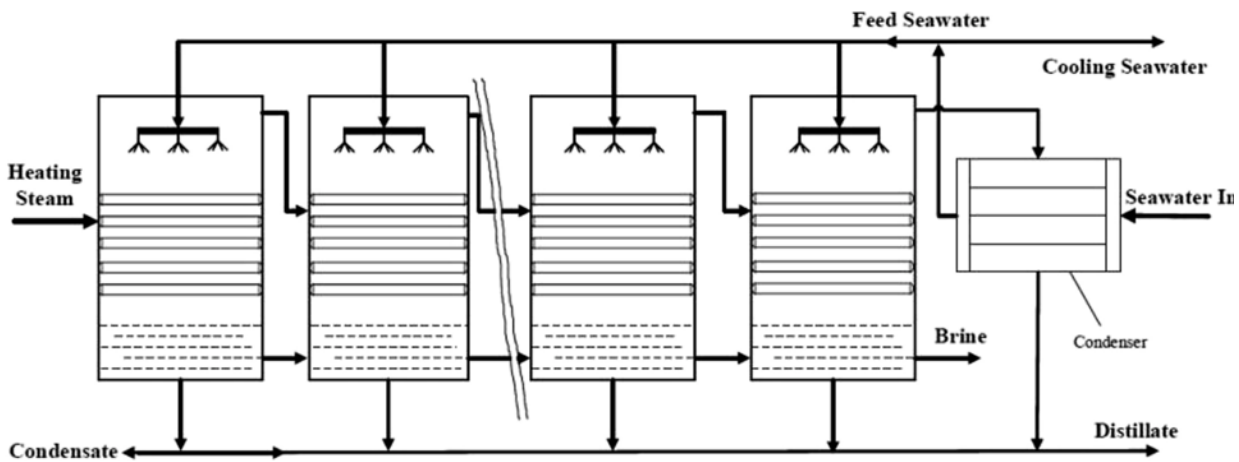


Figure 1. 4. Typical arrangement of multi-effect evaporative distillation for desalination of seawater. Used with permission from Elsevier.⁴⁴

evaporates into high temperature vapor, with a brine solution forming at the bottom of the section. Water vapor passes to the next effect through evaporator tubes and simultaneously heats the sprayed seawater while condensing into distillate (purified desalinated water). The overall process

repeats with many effects where the vapor of the previous effect is cooled and condensed by the seawater feed source. The pressure of the system is reduced between each effect to increase evaporation of the feed source. Reservoirs collect and store the desalinated seawater. Concentrated brine pumps into the next effect from the proceeding effect, and the highly concentrated brine from the last effect is disposed.

Vapor compression distillation has a lower energy requirement than MED and allows for higher recovery rates. Figure 1.5 displays the overall process for mechanical vapor compression distillation.^{47,48} Seawater as the feed source is pumped into a chamber and is boiled with a heating element. A baffle system collects the vapor and a turbine compresses the vapor. The compression increases both pressure and temperature of the water vapor. The steam passes through a heat exchanger located in the boiling chamber to thermally recycle energy and aid in evaporation of the boiling chamber brine solution. The water vapor heats the incoming seawater feed source prior

Figure 1. 5. Conventional design of vapor compression distillation for desalination of seawater. Used with permission of John Wiley and Sons.⁴⁷

to the boiling chamber and condenses into distillate. The distillate is collected in a reservoir and the concentrated brine solution is removed from the boiling chamber.

1.2.2. Membrane Separation Processes

Water filtration by membranes occurs through the physical separation of contaminants from water without chemical alteration to produce purified water. Membranes present a physical interface that regulates and allows for the permeation of water while preventing the chemical contaminant that interacts with the barrier to flow through the membrane. The mechanism of membrane permeation occurs by either pore-flow or solution-diffusion models (Figure 1.6).⁴⁹

The pore-flow model describes a microporous structure which allows for the desired permeate to flow through pores while rejecting the larger unwanted species. Membrane pores are relatively larger than the permeate and typically do not change in size, shape or position with respect to the permeate flux time-scale.⁵⁰ Microfiltration, ultrafiltration, and nanofiltration membranes operate by the pore-flow model. The solution-diffusion model utilizes a membrane material that permits the desirable permeate to infuse and then diffuse through the material at faster

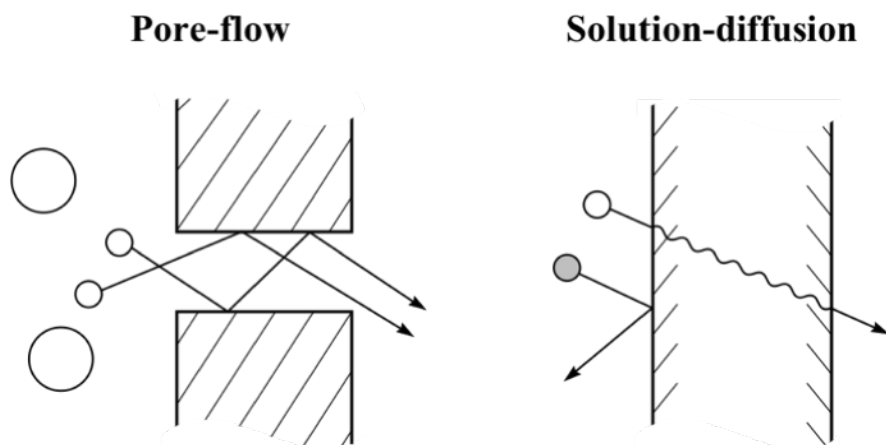


Figure 1. 6. General representation of pore-flow and solution-diffusion models. Used with permission of John Wiley and Sons.⁴⁹

rates while the undesirable permeate is excluded due to slower absorption and diffusion rates.⁵¹ The permeate diffuses through a chemical potential gradient within the membrane from higher to lower concentration. Electrodialysis and reverse osmosis desalination processes use the solution-diffusion model. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis operate by means of a hydrostatic pressure driving force for separation, whereas electrodialysis uses an electric potential gradient driving force for filtration. Figure 1.7 displays the overall performance and separation capabilities for common contaminants in MF, UF, NF, and RO membranes.⁵²

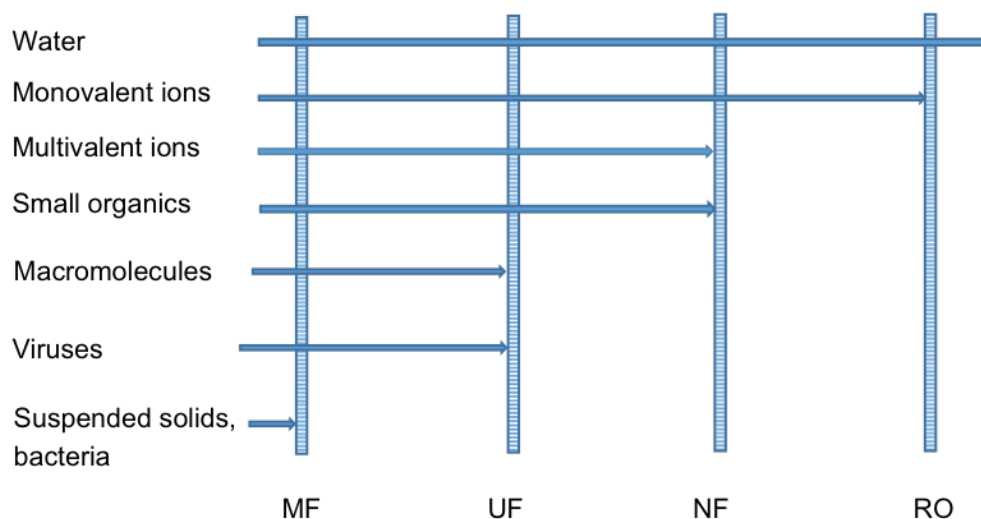


Figure 1. 7. Overview of rejection capabilities for MF, UF, NF, and RO membranes for desalination. Used with permission from Elsevier.⁵²

1.2.2.1. Microfiltration and Ultrafiltration

Microfiltration (MF) and ultrafiltration (UF) membranes were first synthesized from cellulose nitrate in the early 1900s. These membranes were used in laboratories for filtering and isolating microorganisms and particulate matter during the 1920s, became commercially available in the 1940s, and were finally utilized in large-scale industrial applications beginning in the 1960-

1970s.^{53,54} Microfiltration membranes have a pore diameter range between 0.1 - 10 μm , and ultrafiltration membranes have pore sizes that range between 0.001 – 0.1 μm or a molecular weight cutoff between 2000-25,000 Da. Symmetric and asymmetric membranes can be fabricated for both MF and UF methods. Asymmetric membranes allow for higher flux with lower economic costs.⁵⁵ Microfiltration and ultrafiltration membranes are currently prepared from cellulose acetate, polysulfones, polyamides, polyolefins, polytetrafluoroethylene, poly(vinylidene fluoride), and polyacrylonitrile copolymers.⁵⁴ Material choice depends on application and cost. Microfiltration membranes are typically used as cartridge filters and UF membranes are utilized as hollow-fiber or spiral-wound modules with pressurized cross-flow.⁵⁶ MF membranes operate at pressures lower than ~50 psi.⁵² Microfiltration has been developed for applications in the oil refinery industry to separate oil/water emulsions.⁵⁷ UF membranes operate at pressures between 15-75 psi, producing 20-200 GFD (gallons/ft²/day).⁵⁸ UF membranes can be used to separate enzymes, dairy whey, and paper pulp from water.⁵⁹⁻⁶¹ MF and UF membranes are implemented for pretreatment of feed source water for NF, RO, and ED desalination. As with all membranes, MF and UF are prone to blockage and fouling from permeates in the source water, but this can be controlled by several factors such as constant-flux operation, reverse flow, turbidity, hydrophilic surfaces on either the polymer matrix or derived from surface modification to reduce adhesion, and routine cleaning.⁶²

1.2.2.2. Nanofiltration

Nanofiltration (NF) membranes first gained considerable interest in the 1980s and achieved commercial success in the early 1990s for desalination and organic molecule separation applications.⁶³ Nanofiltration membranes have been described as “poor RO membranes” and mutually agreed upon defining characteristics remain up for debate. NF membranes can have pore size diameters up to 2 nm with a molecular weight cutoff between the range of 150 – 2000 Da for

neutral species. Typical operating conditions subject NF membranes to pressures between 60 – 200 psi yielding 15 – 60 GFD.⁵² NF membranes need less energy input than reverse osmosis or electrodialysis. Presently, pharmaceutical, wastewater recycling, chemical, textile, and oil refinery industries employ NF membranes for effective separation of chemicals including antibiotics, dyes, hormones, pesticides, and organic solvents.^{64–67} Most NF membranes show an intrinsic ability to separate divalent ions from monovalent ions with passage of monovalent ions greater than 30%. NF membranes have salt rejections that rely on molecular size and donnan effects inherent to the material.^{68,69} The dairy industry implements nanofiltration to separate whey proteins and sugars from excess monovalent ions (lithium, sodium, potassium, cesium) to improve the taste of the final product.⁴⁴ Brackish water can be effectively desalinated to acceptable drinking water standards by means of NF membranes; however, the same membranes fail to properly desalinate seawater to the drinking water requirements due to the high salt concentration of seawater. For the most part, both RO and ED utilize NF membranes for pretreating feed source water. Commercial NF membranes are comprised of crosslinked aromatic polyamide thin-film composites synthesized via an interfacial polymerization.⁶³ Similar to MF and UF, NF membranes experience scaling/fouling that reduce the overall efficiency of the membranes, and similar prevention techniques are aimed at prolonging their longevity and performance.⁷⁰

1.2.2.3. Reverse Osmosis

Reverse Osmosis (RO) first achieved commercial/industrial success in the beginning of the 1960s with the introduction of asymmetric cellulose acetate membranes. However, the most significant achievement occurred in the late 1970s with the development of fully aromatic polyamide thin film composite (TFC) membranes that are still the primary choice for RO desalination.^{70,71} These polyamide TFCs show salt rejections of ~99% with high permeate flux.

Plant design and new membranes have lowered the energy consumption towards the theoretical limit.⁷² RO effectively desalinates water by applying pressure against the salt water feed source onto a semipermeable membrane. Pressures are typically greater than 200 psi to overcome the osmotic pressure of the system.⁵² The semipermeable membrane allows for the water permeate to diffuse across the interface while rejecting salt ions to produce clean drinking water (Figure 1.8). State of the art RO desalination processes operate primarily with cross flow spiral wound modules but hollow fiber modules could potentially be utilized.⁷³

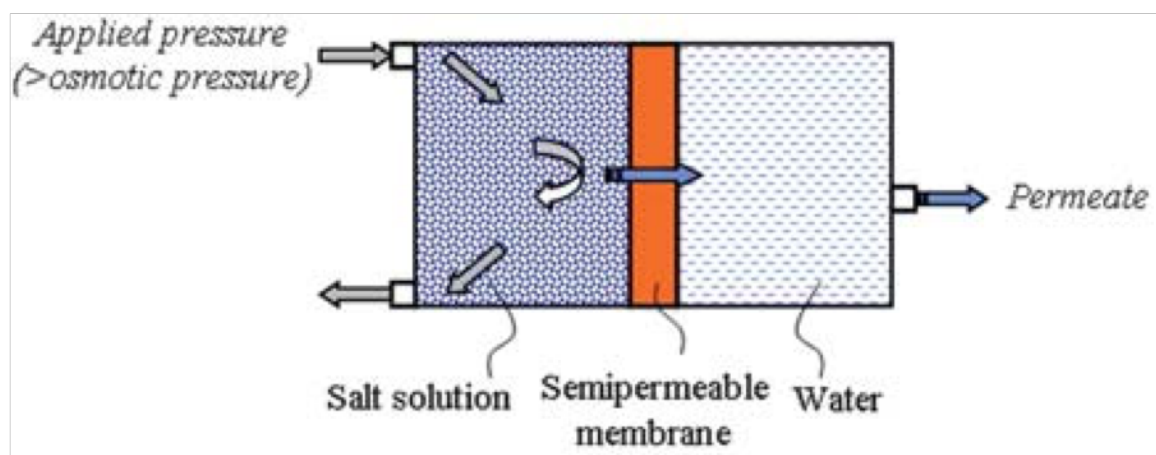


Figure 1. 8. Schematic diagram of reverse osmosis for desalination. Used with permission from the Royal Society of Chemistry.⁷⁴

Semipermeable membranes can be classified into two categories: neutral or charged. Neutral membranes reject salt ions through the repulsion of ionic species by the lower dielectric constant of the membrane. Charged membranes reject salt ions by Donnan rejection where the electrostatic forces from fixed charges on the membrane reject co-ions.⁷⁵ RO membrane industrial applications include desalination, waste-water recycling, purification of water for food and beverage and pharmaceutical applications, and organic molecule separations.^{76–78} Typical

Commercial RO membranes are prepared with cellulose acetate, aromatic polyamides, and polysulfone support layers. Membranes are designed to be as thin as possible to maximize water transport while withstanding high pressures. The fabrication of these materials into structures with high surface area/volume ratios is challenging.⁷⁹ Polyamide and cellulose acetate membranes can undergo considerable scaling and fouling. Pretreatment of water, surface modification, and cleaning of these membranes prolong performance and longevity. However, considerable research continues seeking new polymeric materials with better water transport properties, chemical resistance, and antifouling/antiscaling characteristics.⁸⁰

1.2.2.4. Electrodialysis

Electrodialysis (ED) methods for desalinating water were successfully commercialized in the 1950s and 1960s with the advent of new polymer materials and system design.⁸¹ ED can be used to desalinate water with higher recovery rates and lower costs than RO.^{22,35} ED employs an

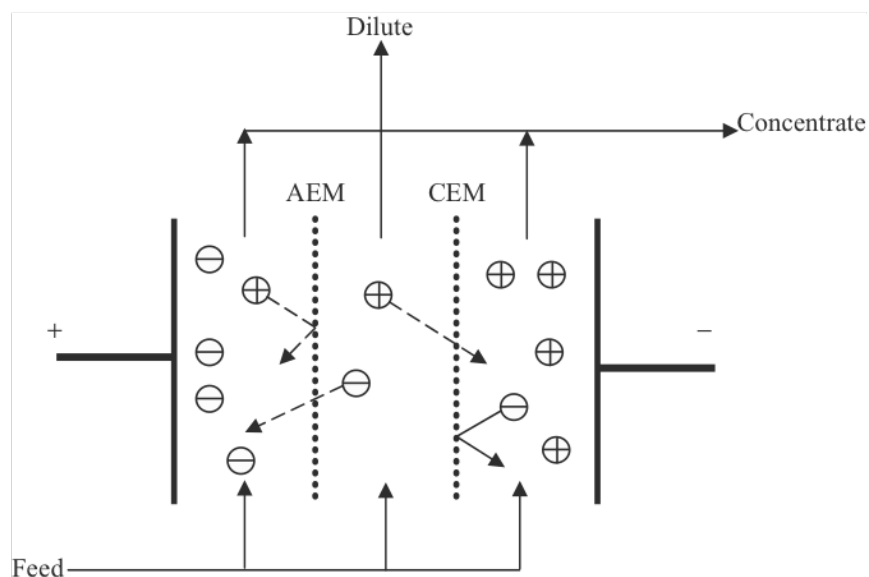


Figure 1. 9. Common configuration of an electrodialysis cell for desalination. Used with permission from Elsevier.⁸²

electrical potential gradient to separate salts to effectively produce drinking water. An electrodialysis cell comprises alternating cation and anion exchange membranes, resulting in three types of regions separating the membranes (Figure 1.9). Saline feed water is pumped through the cells while a cathode and anode provide the poles for the electrical gradient. Cationic species migrate through the cation exchange membrane towards the cathode while rejecting anionic species. Anionic species migrate through the anionic exchange membranes towards the anode while rejecting cationic species. This process forms concentrated brine streams and a dilute stream of purified water. ED processes use several stacks of the alternating CEM and AEM cells to maximize efficiency.⁸³ ED can be utilized to desalinate both brackish and seawater, but the high salinity of seawater requires too much energy to be economical. Modern ED membranes can be made from crosslinked polystyrene-divinylbenzene polymeric matrices as shown in Figure 1.10. CEMs are functionalized with anions such as sulfonate groups, whereas AEMs usually have quaternary ammonium fixed charges.⁸⁴ ED does not generally require as much pretreatment of the

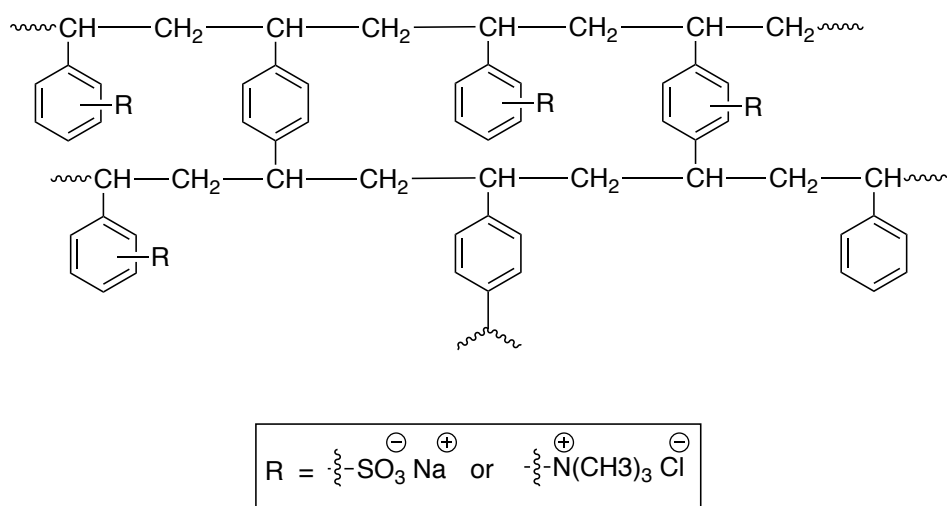


Figure 1. 10. Crosslinked polystyrene-divinylbenzene matrices for CEMs and AEMs utilized for ED desalination.

feed water as is needed for RO membranes. ED membranes suffer from both scaling and fouling. Scaling can be minimized through electrical reversal of the polarity.⁸⁵ Advancements in electrodialysis metathesis have been implemented through the use of selective CEM and AEM membranes for transporting monovalent ions.⁸⁶ These selective membranes allow for concentrating soluble monovalent and insoluble divalent salt streams. Research continues for the development of thinner, more robust membrane materials with better ion conductivity and selectivity.

1.3. Reverse Osmosis Transport Properties

Water and salt permeate through reverse osmosis membranes by solution-diffusion. RO membranes are fabricated from polymeric materials into thin film composites comprised of a dense non-porous layer at the top of a porous substrate, or into asymmetric membranes with a dense separation layer at the top. Polymers inherently contain free volume.⁸⁷ Free volume allows for passage of permeates by the opening and closing of gaps from the unoccupied (free) volume due to the thermal motion of the polymer chains.⁸⁸ RO membranes desalinate water by allowing water to permeate through the polymer while rejecting salt ions by dielectric and/or electrostatic effects.^{89,90} Effective commercial RO membranes have salt rejections of approximately 99%. This occurs due to differences in permeate diffusion rates as well as solubility within the polymer matrix. Fick's law describes the diffusion of water through a hydrated membrane and shows that water transport through the membrane is inversely proportional to thickness (equation 1.1), where J_i = permeate flux ($\text{g}/\text{cm}^2\text{s}$), D_i = the permeate diffusion coefficient (cm^2/s), c_i = the concentration of permeate at either 0 or l , and l = thickness (cm).⁴⁹ When water flux through the membrane is measured, one measures the volume of water passing through the membrane per unit of surface

area within a given time in units of grams of water per cm² of surface area per second. While the amount of water transporting through the membrane per second is strongly dependent on thickness, the flux data is not normalized for thickness.

$$J_i = \frac{D_i \left(c_{i_o(m)} - c_{i_l(m)} \right)}{l} \quad \text{Equation 1.1}$$

1.3.1. Water Transport

It is desirable for a RO membrane to have a high flux to transport water at a fast rate. This allows for one to use less surface area of the membrane material and to lower pressure demands to reduce the needed energy input. Reverse osmosis requires applied pressure to drive the water through the membrane that overcomes the osmotic pressure, thus producing a concentration gradient permitting water to permeate from low to high concentration. Equation 1.1 can be manipulated to portray the water flux occurring through a RO membrane that is under pressure in an equilibrium state (equation 1.2), where J_W = water flux (g/(cm²s), D_W = the water diffusion coefficient (cm²/s), $C_{W,F}^m$ = the water equilibrium concentration in the membrane (g/cm³), L = thickness of the membrane (cm), V = partial molar volume of water (cm³/mol), R = gas constant (81.3 cm³ bar/(mol K)), T = absolute temperature (K), ΔP = pressure difference, and $\Delta\pi$ = the osmotic pressure difference.⁹¹ According to equation 1.2, higher water diffusion coefficients,

$$J_W = \frac{D_W C_{W,F}^m}{L} \frac{V}{RT} (\Delta P - \Delta\pi) \quad \text{Equation 1.2}$$

thinner membranes, and greater pressure lead to an increase in water flux. However, water diffusivities through polymer membranes are typically low.⁹² Water permeability is related to the water diffusion coefficient and water solubility coefficient of the material (equation 1.3), where P_W = water permeability (cm^2s) , K_W = water solubility coefficient (g/cm^3), and D_W = the water diffusion coefficient (cm^2/s). The water solubility coefficient is determined by equation 1.4, where K_W = the water solubility coefficient (g/cm^3 of swollen polymer), $C_{W,F}^m$ = the water equilibrium concentration in the membrane (g/cm^3), and $C_{W,F}$ = the water concentration of the feed solution (g/cm^3).

$$P_W = K_W D_W \quad \text{Equation 1.3}$$

$$K_W = \frac{C_{W,F}^m}{C_{W,F}} \quad \text{Equation 1.4}$$

It should be noted that water permeance is not an intrinsic property of the membrane.⁹³ Water permeability can be increased by increasing the water absorption of the polymer material through increased hydrophilicity, but an increase in water sorption strongly correlates to an increase in salt absorption. This reduces the separation of water from salt. Several measures can be implemented to reduce the water uptake of a membrane by lowering the available free volume for solution diffusion. Crosslinking, self-assembled morphologies of block copolymers, and semi-crystalline

regions can reduce dimensional swelling of the polymeric material, lowering the overall water absorption of the RO membrane.^{94–97}

1.3.2. Salt Transport

Good RO membranes demand high water flux with low salt flux to achieve salt rejections greater than 99.0%. Equation 1.5 describes salt passage through RO membranes, where J_S = the salt flux (g/cm²s), P_S = salt permeability (cm²/s), L = membrane thickness (cm), $C_{S,F}^m$ = salt equilibrium concentration in the membrane (g/cm³), and $C_{S,F}$ = salt concentration of the solution (g/cm³). Decreasing salt permeability and increasing membrane thickness minimize salt flux. However, membrane thickness needs to be small for water flux to be high, and therefore salt permeability remains the critical factor for salt passage. Equation 1.6 describes salt permeability, where P_S = salt permeability (cm²/s), K_S = the salt solubility coefficient (g/cm³), and D_S = the salt diffusion coefficient (cm²/s). Salt diffusivity and salt solubility in the membrane should be much lower than the diffusivity and solubility of water in the membrane. Increasing the feed pressure decreases the permeate salt concentration,⁹¹ so the experimental conditions influence salt passage and rejection.

$$J_S = \frac{P_S}{L} (C_{S,F} - C_{S,P}) \quad \text{Equation 1.5}$$

$$P_S = K_S D_S \quad \text{Equation 1.6}$$

1.3.3. Membrane Selectivity

Equation 1.7 describes the ideal selectivity with regard to permeabilities of water versus salt, where $\alpha_{W/S}$ = ideal water/salt permeability selectivity, K_W/K_S = water/salt solubility selectivity and D_W/D_S = the water/salt diffusivity selectivity. High water permeability and low

$$\alpha_{W/S} = \frac{P_W}{P_S} = \frac{K_W}{K_S} \times \frac{D_W}{D_S} \quad \text{Equation 1.7}$$

salt permeability are ideal to achieve effective RO membranes. But a strong correlation exists between water/salt permeability selectivity and water permeability with respect to reverse osmosis membranes, similar to gas selectivity with gas permeability. This correlation shows that high

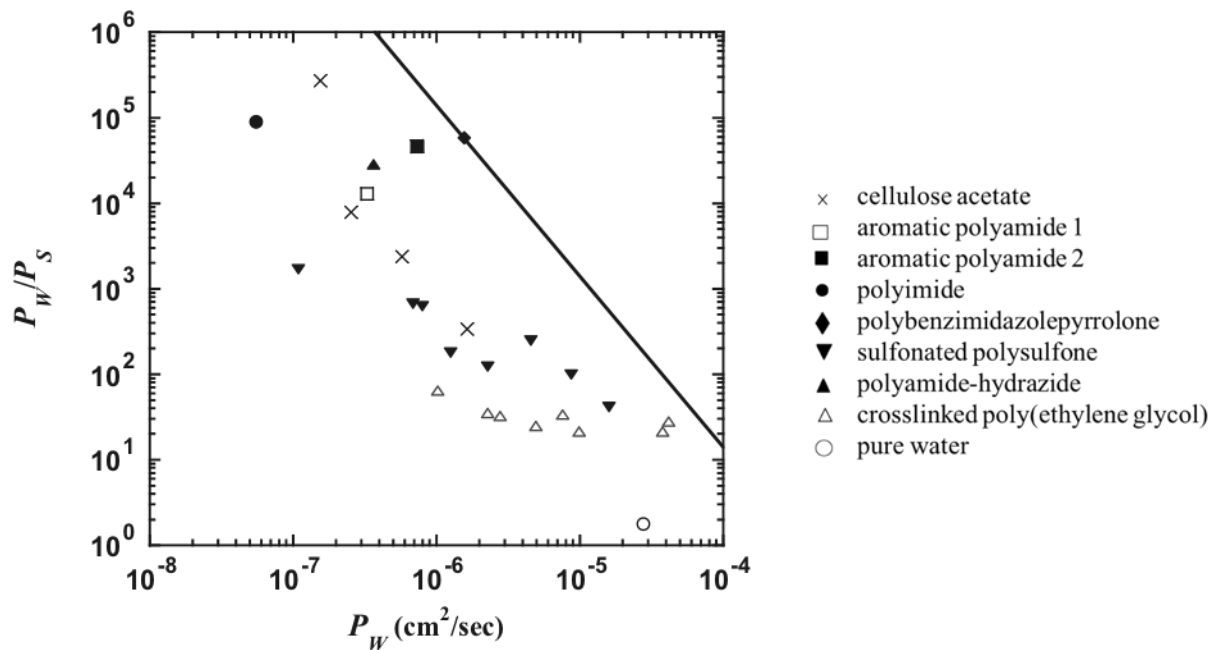


Figure 1. 11. Tradeoff between water/NaCl permeability selectivity vs water permeability with an upper bound line. Used with permission from Elsevier.⁹¹

selectivity leads to lower water permeability, and low selectivity leads to higher water permeability. Geise *et al.* reported this tradeoff as shown in Figure 1.11. The plot consists of several dense RO membranes prepared with varied polymeric materials. The cellulose acetate and polyimide membranes display a high degree of selectivity, but with poor water permeability. Crosslinked poly(ethylene glycol) and di-sulfonated poly(arylene ether sulfone)s present extremely high water permeability, but inferior selectivity. The overall plot reveals an upper bound relationship through the polybenzimidazolepyrrolone data point. Current RO research focuses on developing new polymers with high selectivity and high water permeability to overcome/raise the upper bound limit.

1.4. RO Membrane Design and Fabrication

Membranes can be either symmetric or asymmetric. Symmetric membranes have a uniform structure with porous or dense (nonporous) compositions, whereas asymmetric membranes occur in a gradient form with porous or thin-film composite configurations (Figure 1.12). Loeb and Sourirajan developed the first asymmetric films in 1960 from cellulose acetate. This breakthrough led to large increases in water flux relative to previous RO membranes.⁹⁸ The next RO milestone was achieved by Cadotte and Riley with the development of thin-film composites (TFC) by synthesizing the thin top barrier layer in situ.⁹⁹ TFCs improved salt rejection to greater than 99.0% with high water flux. Practical RO membranes must display the following qualities: high selectivity, high flux, mechanical stability, chemical resistance, temperature tolerance, processability, reproducibility and good economics.

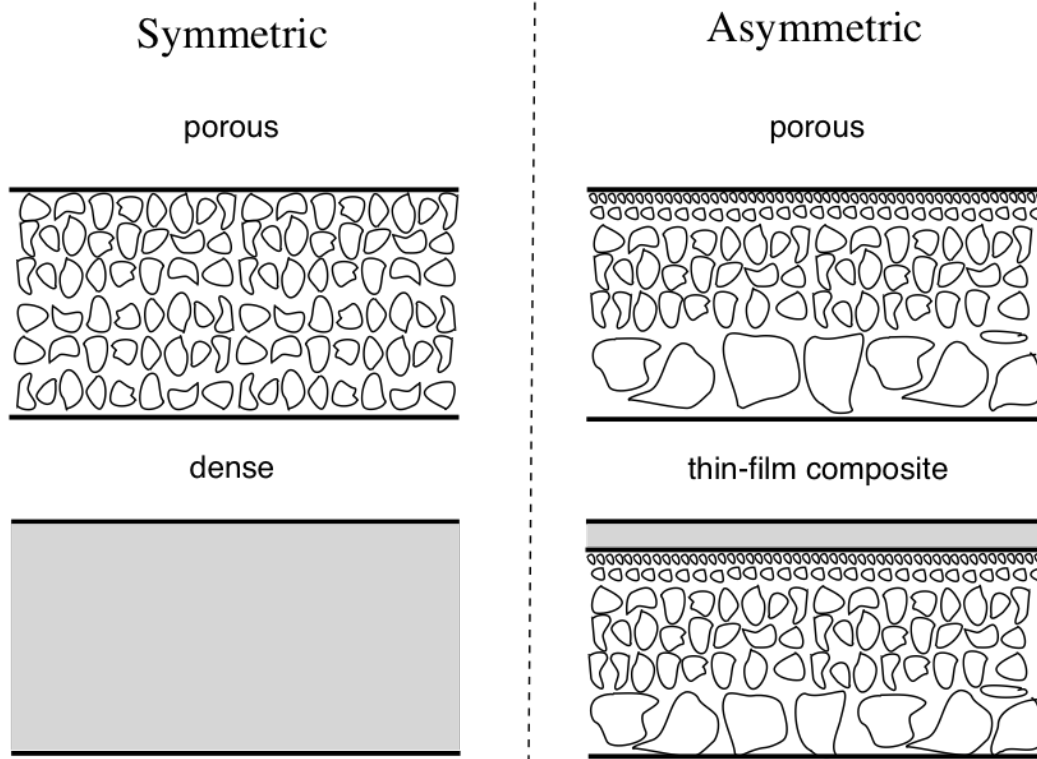


Figure 1. 12. Diagrams of symmetric and asymmetric membranes.

Symmetric dense membranes can be fabricated through solution casting with evaporation or by melt extrusion processes.¹⁰⁰ The manufacturing procedure typically results in membranes with thickness greater than $\sim 5 \mu\text{m}$ to prevent defects or pinholes in the membrane.⁴⁹ Dense membranes allow for high selectivity with low water flux, making them ineffective for RO desalination. Electrodialysis utilizes dense membranes with polymeric matrices containing highly functionalized charged moieties.

Integrally-skinned asymmetric membranes have a selective polymer thin-skin layer with a porous polymer substructure layer derived from the same polymer. The thin-skin layer permits higher water flux than dense membranes due to the very thin dimensions. The casting procedure uses a concentrated polymer solution that is immersed into a polymer nonsolvent where the polymer precipitates.⁵⁴ The skin and porous structure form in seconds. Pore size can be adjusted

through additives that can include other polymers or added salts.¹⁰¹ Polymer molecular weight, solvent/non-solvents, additives, temperature, evaporation rate, casting thickness, and drying procedures affect membrane formation and structure.¹⁰²

Thin-film composites have become the preferred structure for industrial RO desalination due to the interfacial in situ manufacturing procedure of the barrier layer that allows for extremely thin separation layers. TFCs consist of a selective “skin” surface polymer resting on or near the top of a polymeric porous support layer. TFCs also employ a woven or non-woven polymer bottom layer to obtain sufficient mechanical support to resist failure from the pressures that are necessary during RO desalination. Skin layer thickness is minimized to 100-500 nm, allowing for high water flux while retaining high selectivity.¹⁰³ The porous support layer provides the scaffold for the interfacial process and also adds mechanical stability to the skin layer. TFCs possess several advantages over integrally-skinned asymmetric films, including individual selection of the skin layer and porous support polymeric materials, and the thin-skin layer uses less material, so the cost of the skin material becomes less of an issue.¹⁰⁴

TFC skin layers can be applied to the porous support layer by solution-coating or a pre-formed polymer or by interfacial in situ polymerization of the top layer. TFCs from solution-coating often suffer from skin-layer defects arising from surface pores in the underlying porous support. The dilute casting solution can penetrate into the supporting layer pores and either damages the porous support or is unable to successfully cover the entire surface. Sealing layers applied between the skin layer and the porous support or a very high molecular weight polymer in the casting solution may reduce such effects.¹⁰⁵ Interfacial polymerization involves saturating the support layer in an aqueous solution of monomer. The saturated material is then immersed into a non-aqueous solvent that is immiscible with water and that contains another monomer. A thin layer

forms during the polymerization and the excess monomer can be washed away.⁷¹ The cross-section of a thin-film composite comprised of an interfacially polymerized aromatic polyamide with a polysulfone support layer is shown in Figure 1.13.¹⁰⁶

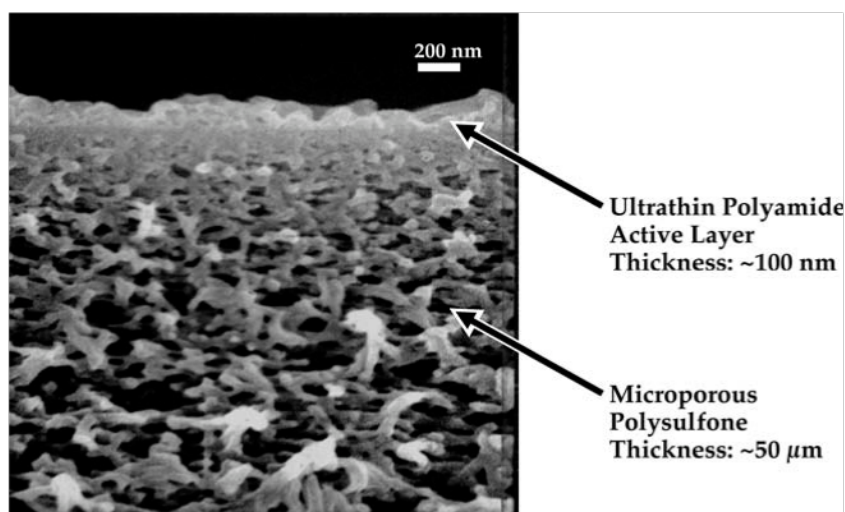


Figure 1. 13. SEM cross section of a thin-film composite membrane with a polyamide dense skin layer and polysulfone porous support. Used with permission from Wiley Periodicals, Inc.¹⁰⁶

1.5. Reverse Osmosis Materials

Several polymeric materials have been investigated and implemented commercially as reverse osmosis membranes for desalination. Polymeric membranes should display high water flux, high salt rejection, good mechanical properties, and chemical resistance. Single-stage RO membranes must generate water permeate with less than ~ 1000 mg/L of salt to be competitive.¹⁰⁷ Currently employed RO membranes suffer from both fouling and scaling. Fouling occurs from the chemical composition of the feed source water or through chemical products implemented for periodic cleaning. Pretreatment of feed water supports ideal conditions for RO membranes. Pretreatment can include filtering of suspended particles, use of disinfectants and scale inhibitors,

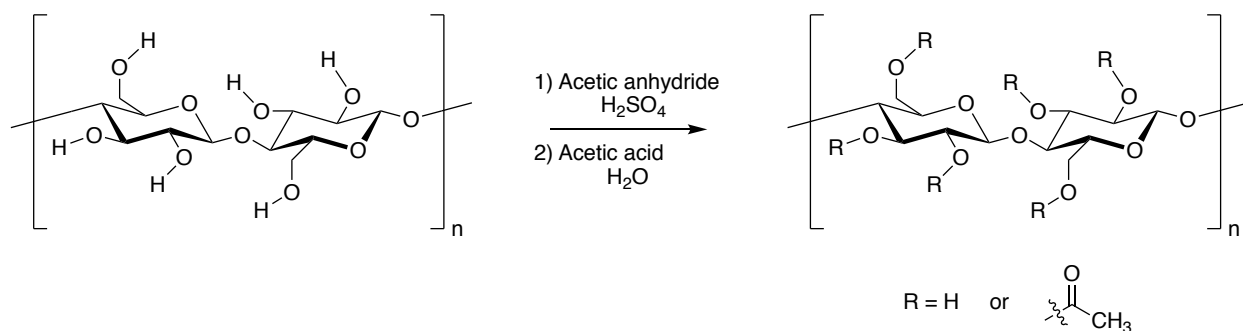
pH adjustment, and coagulation-flocculation.^{108,109} Routine cleaning of the membrane to prevent biofouling with bleach-like products exposes the membrane to high levels of chlorine disinfectants that can cause chemical deterioration of the polymer.¹¹⁰ Some RO polymeric materials are designed to be chlorine tolerant and to be stable over a wide pH range, and they can have structurally smooth surfaces to minimize scale formation while retaining high water flux and selectivity.¹¹¹ Ionic polymers are promising candidates for RO materials, especially sulfonated polysulfones.^{112,113} These RO ionic polymers can be tailored for effectiveness by means of composition, ion-exchange capacity, water uptake, topology, and membrane fabrication. Table 2 displays water flux and salt rejection for several RO polymeric materials. Aromatic polyamide TFCs are the most commonly implemented RO membranes due to their high water flux and selectivity. The design for new materials should have comparable or greater water transport and selectivity properties to be used in commercial RO desalination plants.

Table 1. 2. Water transport and salt rejections for polymeric RO membranes

Material	Water Flux (m ³ m ⁻² d ⁻¹)	Salt Rejection (%)	Test Conditions
cellulose acetate ¹¹⁴	0.35	99.0	100 bar 4% NaCl feed
polyfurane (NS-200) ¹¹⁵	0.8	99.8	100 bar 3.5% NaCl feed
polyamide FT-30 ¹¹⁶	1.0	99.0	15 bar 0.2% NaCl feed
sulfonated polysulfone ¹¹⁷	0.06	98.0	69 bar 3.5% NaCl feed

1.5.1. Cellulose Acetate

Cellulose acetate (CA) is manufactured by reacting cellulose with acetic anhydride, acetic acid, and sulfuric acid (Scheme 1.1).¹¹⁸ The degree of substitution of the cellulose is controlled by degree of back hydrolysis. Cellulose acetate was first implemented as a reverse osmosis membrane in the 1950s.¹¹⁹ Dense membranes were cast from a solution of acetone with a film thickness as small as 10 μm . The membranes displayed a relatively high salt rejection of 98%, but yielded a very low water flux of $0.00024 \text{ m}^3\text{m}^{-2}\text{d}^{-1}$.¹²⁰ Testing conditions consisted of 58.6 bar pressure with a 0.1 M NaCl feed source.



Scheme 1. 1. Synthesis of cellulose acetate

Loeb and Sourirajan developed an integrally-skinned asymmetric cellulose acetate membrane in the late 1950s.¹¹⁴ The membrane was formed by casting a solution containing cellulose acetate, magnesium perchlorate, and acetone. The film side exposed to air formed a skin layer and immersion into water created the porous substructure. Magnesium perchlorate aided in the control of pore size and formation of the substructure, and annealing in hot water further eliminated surface porosity. The Loeb-Sourirajan membranes had a salt rejection of 99% with water flux equal to $0.35 \text{ m}^3\text{m}^{-2}\text{d}^{-1}$.¹¹⁴ These asymmetric membranes displayed an increase in water

flux on the order of magnitudes from previous dense films. The overall membrane thickness was $\sim 100\text{ }\mu\text{m}$, but the dense skin layer was found to be just 100-200 nm in thickness.¹²¹ The membranes were introduced commercially in 1961 for reverse osmosis desalination.

The degree of substitution (DS) affects water transport and salt rejection of cellulose acetate membranes. Cellulose triacetate (CTA) RO membranes, or fully substituted cellulose acetate, display salt rejections greater than 99.6%, but suffer from extremely low water flux. Typically, RO commercial cellulose acetate membranes comprised blends of CA (DS = 2.7) and a minor amount of CTA (DS = ~ 3.0).⁴⁹ The membranes are economical to manufacture and are used in some seawater desalination applications due to their high selectivity, mechanical strength, and chemical resistance. These CA membranes display chemical resistance to chlorine chemicals and other oxidants. CA membranes have shown the capacity to tolerate water feed sources with a chlorine feed concentration up to 5 ppm over constant operation.¹²²

Pretreatment of feed source water is necessary for RO cellulose acetate membranes to reduce fouling. Chlorination of feed water prevents biofouling from microorganisms that can potentially destroy the cellulose polymer.^{123,124} CA membranes are very sensitive to pH because of hydrolysis. Hydrolysis can alter the molecular weight and also the degree of substitution. Typical operating conditions include a pH range of 4 – 6 and operation at room temperature to prevent hydrolysis of the membrane.¹²⁵ Another serious issue arises with decreasing water flux from compaction of the CA membrane under continual high pressure.^{123,126} Water flux decreases due to viscoelastic creep of the dense skin layer into the porous substructure, creating a larger dense skin layer.¹²⁷ Reducing pressure minimizes the effects and prolongs the performance of CA membranes. Surface modification and other post-treatments have been shown to improve fouling.

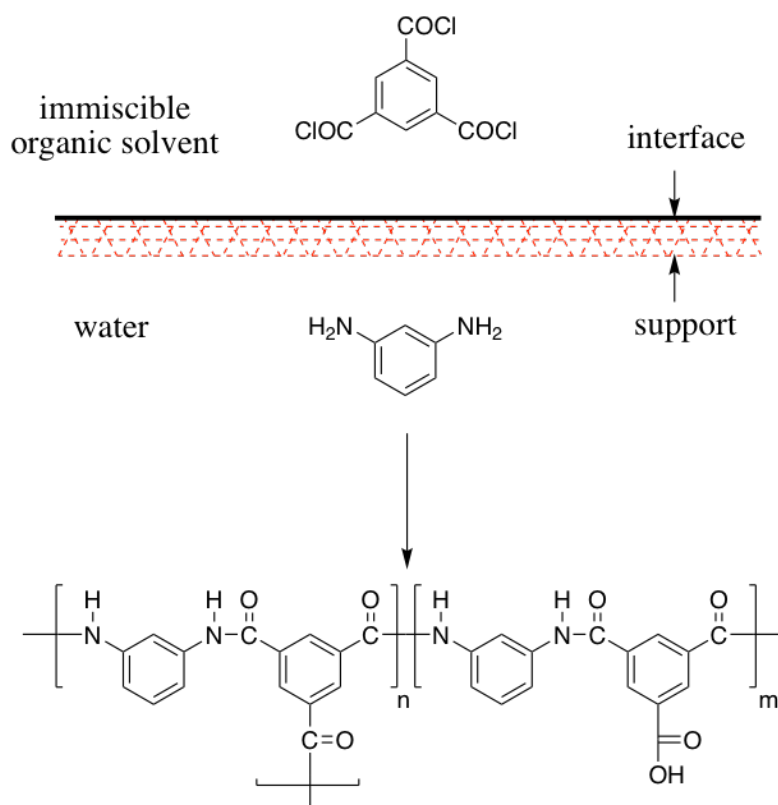
1.5.2. Polyamide Thin-Film Composites

John Cadotte created the first polyamide thin film composite for reverse osmosis desalination at North Star Research Institute during the late 1970s.^{128,129} The process involved soaking a porous polysulfone support layer in an aqueous solution containing linear polyethylenimine. The saturated support layer was then immersed into an organic solution of either di- or tri-functional monomer (acid chloride or isocyanate). The thin-skin layer was formed through interfacial crosslinking of the monomers between the two immiscible solution phases. These first synthesized TFCs displayed high selectivity (99.5% salt rejection) and high water flux, which made them more effective than cellulose acetate RO membranes.¹³⁰ These TFC membranes also display several ideal qualities including ease of fabrication and operation over a wider pH and temperature range. The independent layers of the TFCs relative to the previous asymmetric membranes also allowed for more control over the morphology, and post-modification was possible and with overall low economics.⁷³ This early research on the TFCs led to the commercialization of polyamide-based RO membranes and remains the principal choice for commercial RO desalination applications today.

Polyamide thin-film composites consist of at least two components, a selective skin layer and a porous substructure. The porous substructure is typically made from either polysulfone or poly(vinylidene fluoride).¹³¹ The porous structure must exhibit mechanical strength, chemical resistance, and high surface porosity. Mechanical strength helps to withstand the pressures that occur during RO, and chemical resistance prevents membrane deterioration from the feed source water/cleaning chemicals. High surface porosity decreases resistance to water transport. Small pores permit a smoother surface and less penetration of the selective skin by the thin dense selective coating layer.⁵⁴ For example, polysulfone microporous support layers are created through

immersion precipitation. Linear polysulfone is dissolved in an organic solvent and then cast on a woven or non-woven fabric (the fabric provides more mechanical support). The film is submerged into a miscible solvent for the casting solvent but a non-solvent for the polysulfone, usually water, and the porous structure is formed through precipitation of the polysulfone. Additives including salt can be added to manipulate and control the pore size.^{132,133}

Cadotte created “FT-30” at FilmTec in 1980, and the polymeric material continues to be the most widely implemented polyamide TFC today.¹¹⁶ The synthesis and fabrication of FT-30 follows a similar procedure to the earlier PEI TFC membranes (Scheme 1.2). An aqueous solution of *m*-phenylene diamine is introduced to the surface of a polysulfone support layer. An immiscible organic solvent containing trimesoyl chloride is then cast on top of the aqueous layer. An interfacial polymerization only occurs between the monomers at the aqueous/organic solvent interface, and a crosslinked thin-selective layer forms within seconds. The monomers are initially unable to cross the liquid interface for further polymerization because of low aqueous monomer diffusion. Subsequently the dense crosslinked layer formation prevents any further diffusion due to the physical interface barrier between the solutions. Residual diamine monomer that was able to diffuse into the organic phase continues to react until completion.¹³⁴ The interfacial technique creates a 100 – 200 nm average thickness of the dense selective layer for FT-30 membranes. Monomer choice, polymer concentration, solvent choice, and curing conditions are implemented to tune water transport properties for polyamide thin-film composites.¹⁰⁴



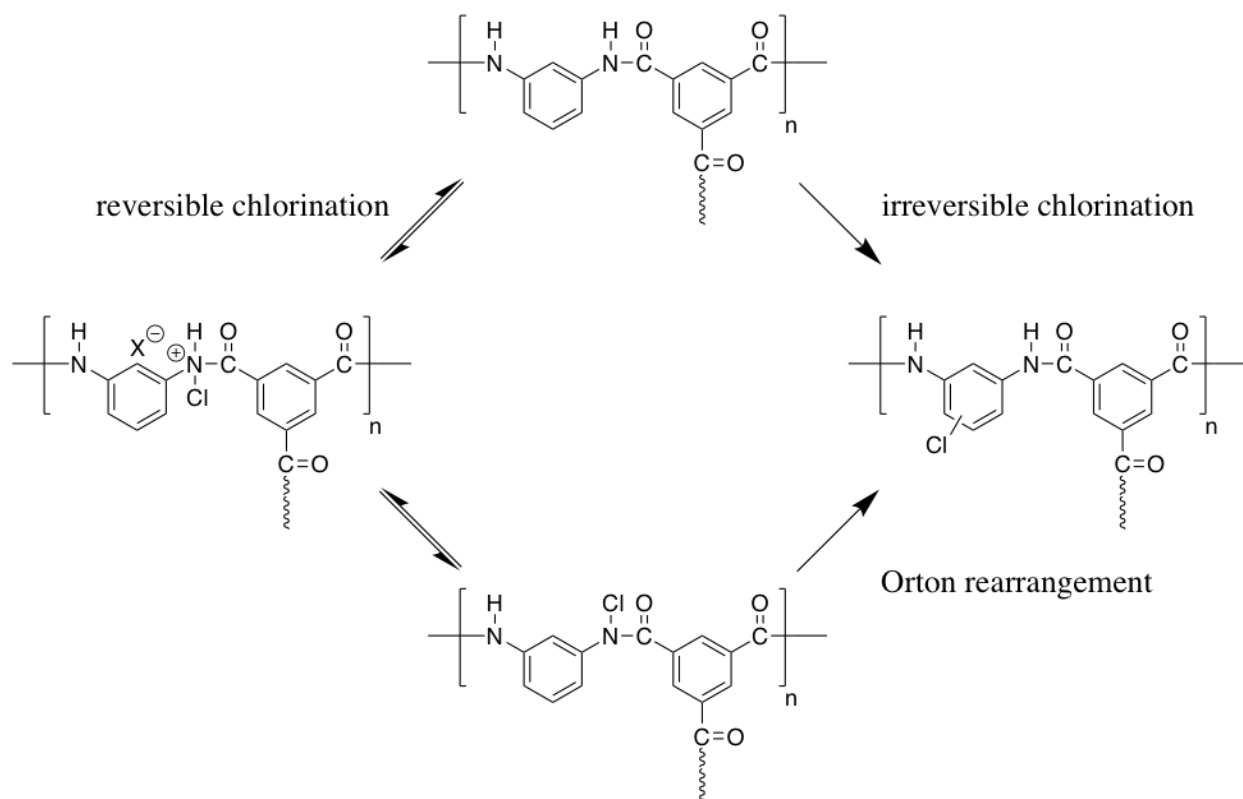
Scheme 1. 2. Synthesis and fabrication of crosslinked aromatic polyamide TFC RO membranes, commercially known as FT-30

Polyamide TFCs are susceptible to fouling during long term desalination applications. Fouling occurs through biological microorganisms, chemical composition of the water feed source, scaling, and cleaning disinfectants. Repetitive chlorine exposure damages the amide or urea polymeric linkages.^{79,123} Membrane surface roughness promotes scaling. These two major issues lead to a decrease in desalination performance. Pretreatment of water, system design, and post surface treatments help decrease fouling, but overall fouling remains a chief concern with polyamide TFC RO membranes.

Polyamide TFCs encounter chlorine exposure through feed source water or cleaning disinfectants. Feed source water requires the addition of chlorine to eliminate bacteria and other micro-organisms.¹²⁴ This treatment largely prevents biofouling of the membrane, but increases

chlorine concentration. After sufficient treatment time, the addition of sodium bisulfite reduces the chlorine disinfectants to tolerable levels before the water comes into contact with the polyamide TFC.¹³⁵ Although water pretreatment helps to decrease fouling, the membranes require routine cleaning to prolong water transport and selectivity performance. Cleaning solutions typically involve bleach that contains chlorine, sodium and calcium hypochlorite salts, and other oxidants such as peroxides.¹³⁶ The concentrations are kept to a minimum to reduce chlorination or oxidation, but repetitive application produces membrane degradation. Aromatic polyamide TFCs tolerate chlorine levels in the range between 500 – 2000 ppm-h.⁷⁹

Chlorination of the polyamide occurs by two distinct mechanisms: direct irreversible chlorination, or by an Orton rearrangement following reversible chlorination (Scheme 1.3).^{23,137} Irreversible chlorination occurs through an electrophilic aromatic substitution where a chlorine electrophile attacks and then substitutes onto the aromatic ring. Reversible chlorination involves chlorination of the aromatic nitrogen atom in the amide linkages, and occurs at a slower rate. A high degree of crosslinking slows chlorination of the aromatic secondary amines.¹³⁸ After a high degree of chlorination, degradation of the membrane occurs by either delamination of the skin layer or through hydrolysis. Delamination involves the physical separation of the polyamide skin layer from the porous support layer.¹³⁷ Chlorination on the aromatic ring electronically withdraws electron density away from the amide linkage and potentially allows for hydrolysis. During the cleaning procedure, pH becomes greater than 11 and leads to chain scission of the amide linkages by hydrolysis. Post surface modification of the polyamide layer could possibly stop chlorination and research continues for a solution.



Scheme 1. 3. Chlorination of a polyamide TFC by irreversible direct attack and Orton rearrangement

Interfacial polymerization of polyamide thin-film composites produces extreme surface roughness, and the partial diffusion of the diamine monomer across the organic/aqueous liquid-liquid interface leads to valleys and peaks.¹³⁴ Residual monomer continues to polymerize after the dense film forms. Figure 1.14 shows the surface of a commonly employed aromatic polyamide membrane, FT-30, and researchers measured an average peak height ($\bar{Z}$) of 146 nm.¹³⁹ The roughness promotes biofouling and also scaling. Essentially, the ridges and voids create “dead zones” where deposition on the surface materializes at a faster rate. Then the fouling spreads across the rest of the surface.^{140,141} Increased turbidity and surface coatings can minimize surface fouling. Operational design by cross-flow pathways increases the feed source turbidity and promotes less anchoring of the foulants. A smooth coating or sealant layer decreases surface roughness and

minimizes dead zones.^{80,142} Coatings should not affect the water transport properties and research continues on developing the ideal coating layer.

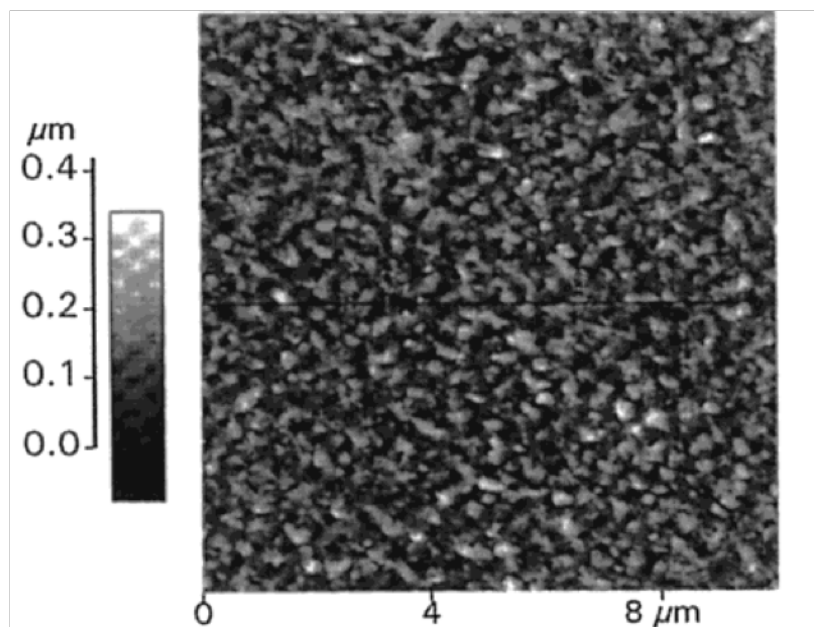
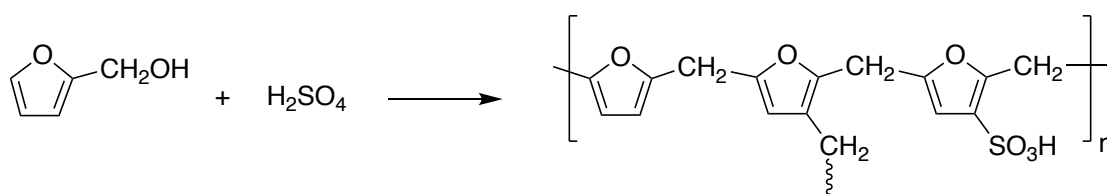


Figure 1. 14. AFM image of FT-30 polyamide TFC displaying surface roughness. Used with permission from the American Chemical Society.¹³⁹

1.5.3. Polyfurans

John Cadotte developed polyfuran thin-film composite membranes (NS-200) at North Star Research Institute in 1972.¹¹⁵ The process involved dip-coating a porous polysulfone substructure into an aqueous solution of furfuryl alcohol and sulfuric acid. The application of heat initiates an acid-catalyzed polymerization and produces a crosslinked network as the dense thin skin layer (Scheme 1.4). Polyfuran membranes display high selectivity of 99.9% salt rejection with water flux up to $491 \text{ m}^3\text{m}^{-2}\text{d}^{-1}$.⁹⁹ Test conditions consisted of a synthetic seawater and pressure = 69 bar. These membranes display the highest known selectivity/flux ratio for RO membranes. Toray

Industries commercialized a polyfuran-based RO membrane (PEC-1000) in the 1980s. The membrane incorporates a co-monomer, 1,3,5-tris(hydroxyethyl)isocyanuric acid.¹⁴³ However, the membrane was short-lived and taken off the market because of the rapid loss of performance. Polyfuran membranes are highly sensitive to chlorine and degradation occurs by hydrolysis, oxidation, and irreversible swelling upon hydration.^{73,99} Overall, the membranes lacked the chemical resistance to be implemented as commercial RO membranes.



Scheme 1. 4. Polymerization of crosslinked polyfuran via acid-catalyzed polycondensation

1.6. Poly(arylene ether sulfone)s for Reverse Osmosis Applications

Poly(arylene ether sulfone)s (PAES) are a class of amorphous engineering thermoplastics that display several high-performance qualities, including high thermal stability, good mechanical

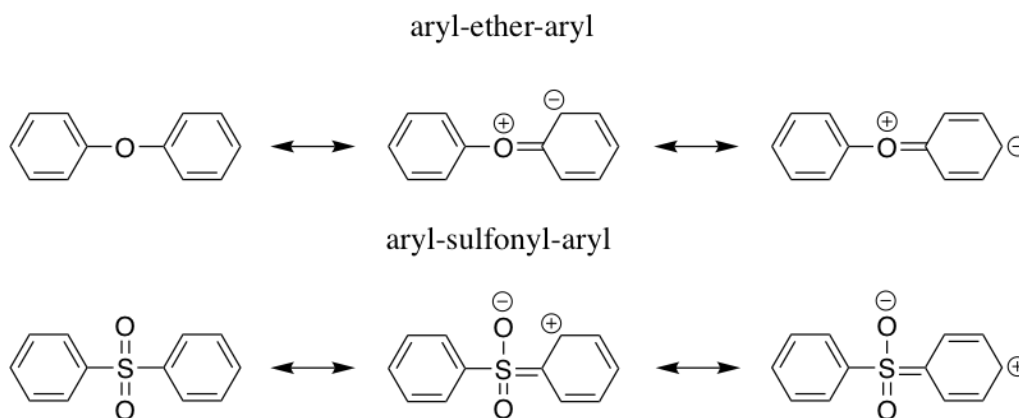


Figure 1. 15. Resonance stability in poly(arylene ether sulfone) linkages.

properties, high glass-transition, and chemical resistance.^{144–148} Both aryl-ether-aryl and aryl-sulfonyl-aryl linkages provide resonance stability within the polymer (Figure 1.15). The aryl-ether-aryl linkages allow for flexibility and resist hydrolysis.^{149,150} The aryl-sulfonyl-aryl linkages demonstrate rigidity and are highly oxidation resistant. PAES can attribute their exceptional physical, thermal, chemical properties from resonance. These characteristics have led to considerable research and commercial applications for PAES. Material application domains include automotive and aviation, extrusion processing, electronics, flame-retardants, fuel cells, and desalination membranes.^{151–155} Figure 1.16 displays the most common commercial PAES: Victrex[®], Udel[®], and Radel[®]. The polymerization of poly(arylene ether sulfone)s occurs by three distinct synthesis routes involving nucleophilic aromatic substitution, electrophilic aromatic substitution, and metal-catalyzed coupling.^{144,145,156–158}

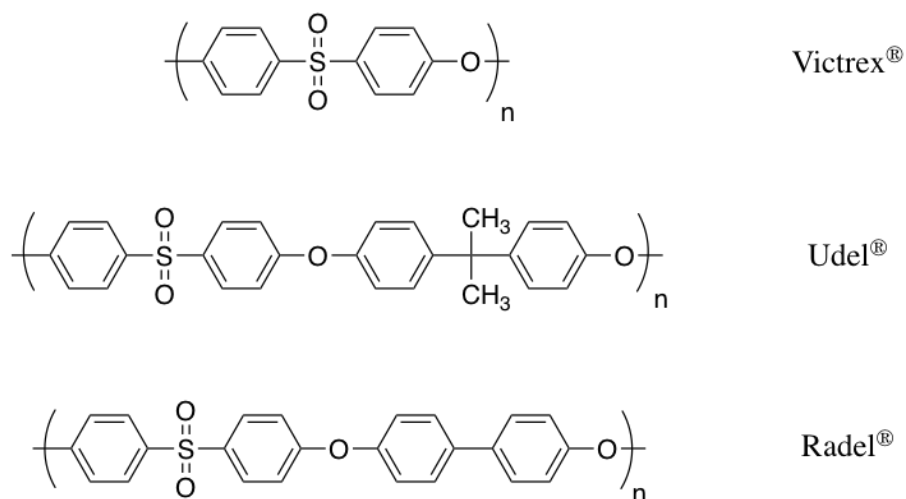
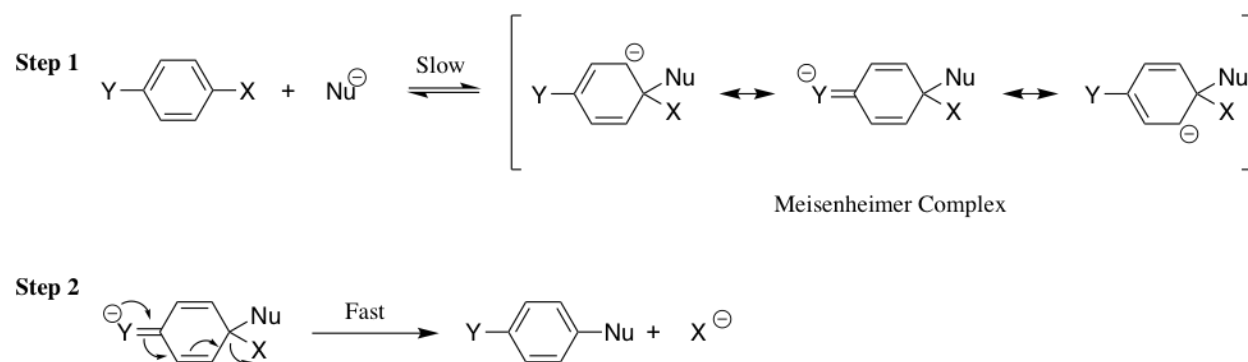


Figure 1. 16. Commercial poly(arylene ether sulfone) examples

1.6.1. Synthesis of Poly(arylene ether sulfone)s

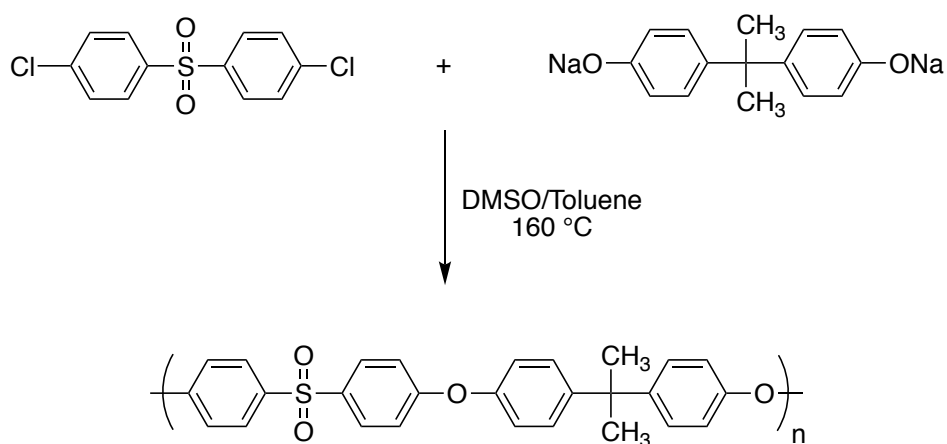
1.6.1.1. Nucleophilic Aromatic Substitution (S_NAr)

S_NAr involves the displacement of an activated leaving group by a nucleophile (Scheme 1.5). In the case of PAES, the electron withdrawing aryl-sulfonyl group activates the halide position for attack. In the first step, the electron rich nucleophile attacks an electron deficient aryl-halide carbon forming a resonance stabilized complex known as a Meisenheimer complex.^{159,160} In the second step, the leaving group (halide) detaches from the Meisenheimer complex and restores aromaticity to the phenyl ring. The rate-determining step is the first step and the order of reactivity confirms the mechanism. The reactivity increases with more electron withdrawing halide groups ($F \gg Cl > Br > I$).¹⁶¹ The aryl-carbon becomes more susceptible to nucleophilic attack with increasing aryl-halide electrophilicity, and also leads to more resonance stability through inductive electron-withdrawing effects. Increasing strength of the activating group and nucleophile, higher temperature, and solvent choice improve S_NAr reaction kinetics.¹⁶² Polymerization using S_NAr generally occurs through either *para* or *ortho* aryl-halide positions because the *meta* position is less reactive, but research has shown that *meta*-activated aryl-fluorine can be sufficient for displacement.¹⁶³



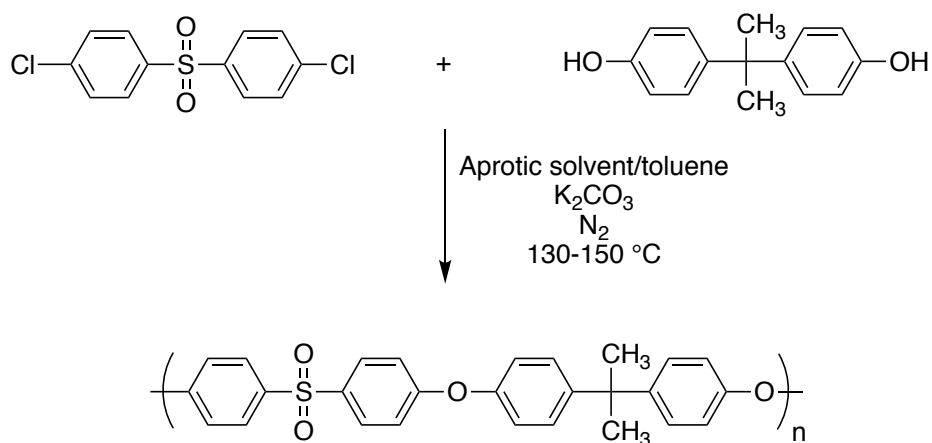
Scheme 1. 5. Mechanism of nucleophilic aromatic substitution

Commercial poly(arylene ether sulfone) synthesis involves a polycondensation reaction between an activated-dihalide and dihydroxy monomer through a nucleophilic aromatic substitution mechanism. Johnson *et al.* developed this method at Union Carbide in 1965 (Scheme 1.5).^{144,164} The reaction involved polycondensation between bisphenol-A and 4,4'-dichlorodiphenylsulfone. Bisphenol-A and sodium hydroxide (1:2 molar ratio) were added to a solution of DMSO/chlorobenzene. The strong base removes the protons from the hydroxy groups forming disodium bisphenolate and water. Chlorobenzene azeotropically removes water which prevents possible side reactions from occurring by hydrolysis. Chlorobenzene was removed from the system and the dihalide monomer was added to the system where polymerization occurred between the monomers by a polycondensation S_NAr mechanism. The reaction is highly efficient and practical for industrial applications, but the use of strong base can lead to adverse effects, especially for targeted high molecular weight PAES. Strong bases can hydrolyze the dihalide monomers and must be stoichiometrically equivalent. Also the solubility of disodium bisphenolate monomers is very low in polar aprotic solvents.



Scheme 1. 6. Synthesis of poly(arylene ether sulfone) with a strong base via S_NAr

Clendinning *et al.* first described the use of weak bases for polymerization to form PAES.¹⁶⁴ McGrath *et al.* investigated reaction conditions and parameters using sodium and potassium carbonate bases for implementation instead of stronger bases.¹⁶⁵ Findings showed weak bases to be a viable alternative, with potassium carbonate being the best choice. The weak bases do not require stoichiometric equivalences and reduce the chance of hydrolysis. Water removal and an inert atmosphere also diminish possible hydrolysis of the aryl halides. Anhydrous polar aprotic solvents such as NMP, DMAc, DMF, and DMSO aid with resonance stability and phenolate monomer solubility. A minor drawback of using the weaker carbonate bases is the slower reaction rate.¹⁶² Higher boiling point solvents can be used to achieve faster polymerizations which can reduce reaction times. For example, sulfolane is utilized commercially for PAES production due to its boiling point of 285 °C, but sulfolane is extremely hygroscopic so precaution must be taken.¹⁶⁴ A general polysulfone polymerization is shown in Scheme 1.7.



Scheme 1. 7. Synthesis of polysulfone (Udel®)

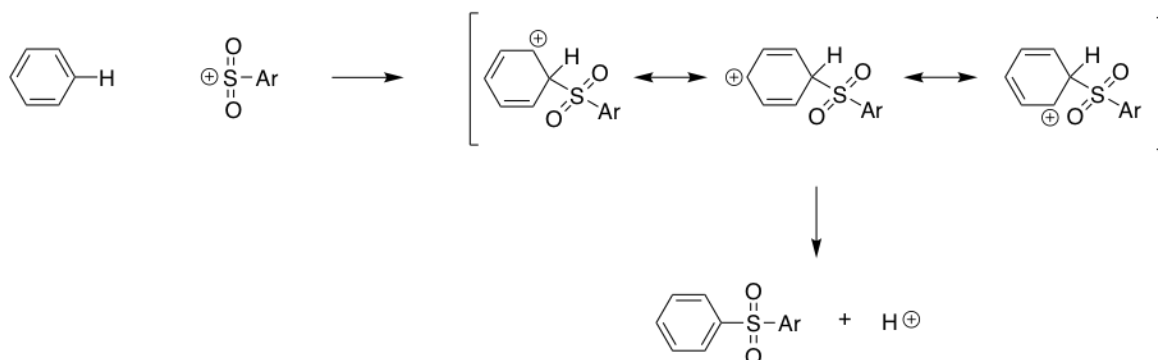
1.6.1.2. Electrophilic Aromatic Substitution (S_EAr)

S_EAr involves the displacement of a leaving group by an electrophile (Scheme 1.8). For PAES, polymerization occurs through a two-step mechanism. In the first step, a Friedel-Craft catalyst (AlCl₃, FeCl₃, BF₃) reacts with an arylsulfonyl chloride to generate a sulfonylium cation electrophile and attacks an aromatic carbon producing a resonance stabilized intermediate complex, known as a Wheland complex.^{166,167} In the second step, the proton leaving group departs from the Wheland complex, which restores aromaticity to the ring. The rate determining step is the first step of the mechanism. Substitution primarily occurs at the *ortho* or *para* position on the aromatic ring, and strong electron-donating groups increase substitution on those positions. High catalyst concentration, increased reaction temperature, and very reactive monomers increase the reaction rate. However, high catalyst concentration and temperature increase side reactions and create irregular structures through side reactions including crosslinking.¹⁶⁸ PAES can be produced

Step 1



Step 2



Scheme 1. 8. Electrophilic aromatic substitution sulfonylation

by both AB and AA/BB type monomers through S_EAr .¹⁶⁹ Starting in 1967, 3M commercially produced Astrel 360® implementing the S_EAr polymerization route.¹⁶⁴ The PAES can be made in either bulk or solution methods. However, due to difficulties associated with the S_EAr and the difficulties in removing the catalysts, nucleophilic aromatic substitution is the preferred synthetic route for commercially manufactured poly(arylene ether sulfone)s.

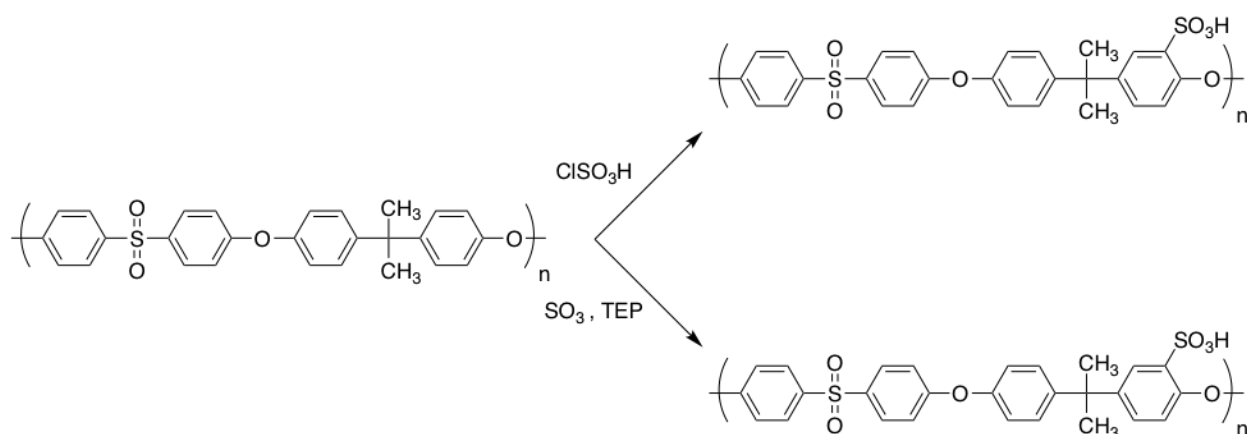
1.7. Sulfonated Poly(arylene ether sulfone)s for Reverse Osmosis Applications

Poly(arylene ether sulfone)s display some ideal characteristics for reverse osmosis applications, including chlorine tolerance, biofouling resistance, and good thermal and mechanical properties.^{145,148,170} However, the inherent hydrophobicity of the polysulfones makes them unsuitable for RO selective skin layers because water permeability would be exceedingly low.¹⁷¹ Therefore, considerable research has been conducted with the objective of modifying the chemical structure of PAES to increase hydrophilicity.¹⁵¹ One method that has attracted considerable interest involves the sulfonation of PAES. Sulfonated PAES show good water transport properties and high salt rejection, while retaining both chemical and physical properties. Synthesis of sulfonated PAES can follow two distinct routes that involve either post-sulfonation of the polymers or direct polymerization of sulfonated monomers.

1.7.1. Post-sulfonation Synthesis of Sulfonated Poly(arylene ether sulfone)s

Sulfonated poly(arylene ether sulfone)s were initially fabricated by post-sulfonation of linear polymers derived from the polymerization of bisphenol-A with 4,4-dichlorodiphenylsulfone

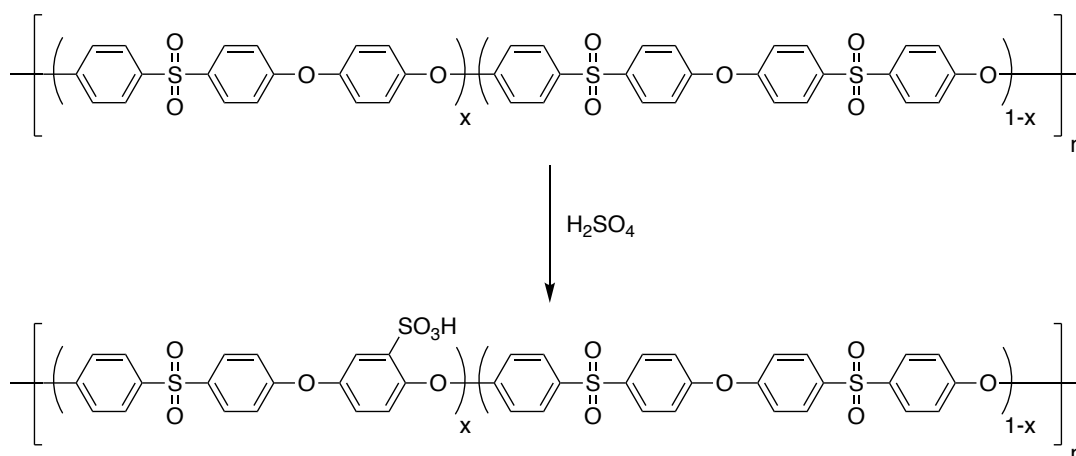
(DCDPS), also known Udel®. Quentin *et al.* described one of the first synthetic sulfonation routes involving reaction of PAES with chlorosulfonic acid (Scheme 1.9).¹⁷² Sulfonation took place primarily at the activated *ortho*-position in relation to the aromatic ether bond of bisphenol A. The degree of sulfonation could be somewhat controlled by stoichiometric quantities of chlorosulfonic acid. Several membranes with varying degrees of sulfonation were examined for RO transport properties. Test conditions included a 3.5% salt feed source at a pressure of 100 bar. The highest salt rejection was found with a dense membrane having an IEC = 0.98 meq/g. RO test results revealed a reasonably high salt rejection of 97.5% but with a low water flux of 0.07 m³m⁻²d⁻¹.^{112,172} The synthetic route allowed for targeting the degree of sulfonation, but the harsh reaction conditions caused undesirable side effects. Chlorosulfonic acid promotes both hydrolysis and potential crosslinking/branching of polymer chains.^{173,174} Hydrolysis occurs through the aryl-ether-aryl linkages and decreases the molecular weight by chain scission. Sulfonic acid moieties on the polymer chain can form sulfonyl chlorides and subsequently crosslink/branch with other unreacted bisphenol-A repeat units.



Scheme 1. 9. Post-sulfonation of Udel® by chlorosulfonic acid and a sulfur trioxide complex

Noshay and Robeson post-sulfonated PAES by implementing an alternative route using a sulfur trioxide/triethyl phosphate complex at room temperature (Scheme 1.8), and some whar targeted degrees of sulfonation could be obtained by adjusting the stoichiometric quantities of SO₃ and TEP.¹⁷⁵ The sulfonation occurs under moderate reaction conditions and limits side reactions compared to the chlorosulfonic acid synthesis route. The mechanism is an electrophilic aromatic substitution reaction that primarily sulfonates the activated *ortho*-carbon of the bisphenol-A phenyl ring. RO test results revealed salt rejection greater than 95% with good water flux (flux unreported) for a membrane that displayed a 50% degree of sulfonation of available activated groups.¹⁷⁵ Test conditions consisted of a 0.1% salt feed source at a pressure of 103 bar. This alternative sulfonation route produced sulfonated PAES with little to no polymer chain defects but the degree of sulfonation and microstructure were difficult to control. It was reported that the overall reaction was undesirable as it was extremely exothermic, and the handling of toxic SO₃ was difficult.^{174,176}

Rose *et al.* developed a controlled sulfonation route by regulating the amount of available activated phenyl rings for electrophilic sulfonation within the polymer backbone.^{177–179} The linear



Scheme 1. 10. Post-sulfonation of PAES containing activated hydroquinone rings

PAES were derived from hydroquinone, bisphenol-S, and 4,4'-dichlorodiphenylsulfone (Scheme 1.10). Then the polymer was sulfonated by dissolution in sulfuric acid (98% w/v) at room temperature over several days, where successful sulfonation of all activated rings occurred after approximately two hours without side reactions or molecular weight deterioration. These sulfonated PAES displayed high water flux with salt rejections greater than 90%.

Kerres *et al.* reported the sulfonation of deactivated phenyl rings by a metalation route.¹⁸⁰ First, n-butyllithium was used to lithiate a deactivated phenyl ring, then the polymer was sulfonated with sulfur dioxide and lastly oxidized to form the sulfonic acid moiety. Targeted degrees of sulfonation were controlled by stoichiometric quantities of the metalation reactant. Linear and crosslinked membranes displayed good salt rejection.

Allegrezza *et al.* explored the potential of post-sulfonated Udel® PAES for reverse osmosis applications.^{181,182} The sulfonated PAES thin film composite membranes showed relatively high salt rejections between 95 – 97% with high water flux 1.22-2.04 m³m⁻²d⁻¹. RO Test conditions included 0.01 and 0.025% NaCl feed water sources with a pressure = 27.6 bar. The research also demonstrated that the membranes performed well over a continuous operational pH range of 4-11 and a feed source chlorine concentration of 5 ppm, which is much higher than polyamide TFCs can withstand (<0.1 ppm). The membranes also showed the ability to resist degradation when exposed to chlorine-based cleaning products with a maximum chlorine tolerance of 100 ppm. However, the membranes displayed poor NaCl salt rejections with mixed Ca²⁺ salt feeds. The fixed charges from the sulfonate groups in the polymer membrane preferentially associate with the divalent cation, allowing for increased passage of the more mobile and weakly attracted monovalent ions.

Overall, post-sulfonating poly(arylene ether sulfone)s restricts control and distribution of sulfonate moieties to activated aromatic rings. Sulfonation reaction conditions typically lead to polymer chain degradation as well as the potential for unwanted side reactions. Although post-sulfonated PAES demonstrate excellent chlorine tolerance, low salt rejection with mixed salts remains a principal concern for commercial RO membrane implementation.

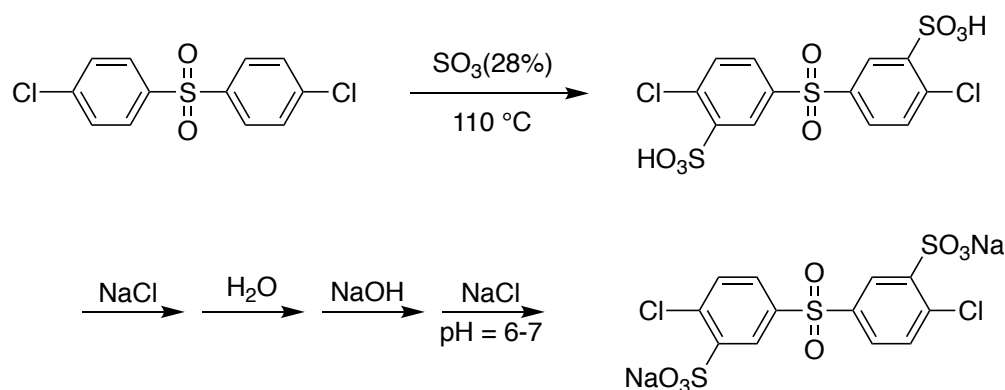
1.7.2. Direct Polymerization of Sulfonated Poly(arylene ether sulfone)s for Reverse Osmosis

Pre-sulfonated monomers used for the direct polymerization of sulfonated poly(arylene ether sulfone)s have been the subject of many studies in recent years. Pre-sulfonated monomers allow for better control and distribution of sulfonate groups throughout the polymer backbone without potential deterioration of molecular weight as observed with conventional post-sulfonation approaches. Pre-sulfonated monomers also permit the incorporation of sulfonate moieties onto deactivated aromatic phenyl rings in PAES and allow for potentially better chemical stability and water transport properties for reverse osmosis applications.

Robeson and Matzner described the use of 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (ds-DCDPS).¹⁵⁴ This work utilized the compound as a flame retardant in thermoplastic polymer blends of polyacrylates. Ueda *et al.* used ds-DCDPS as a monomer to synthesize PAES copolymers including both 4,4'-dichlorodiphenylsulfone and bisphenol-A.¹⁸³ McGrath *et al.* developed an easier method for synthesis and isolation of the di-sulfonated monomer, and investigated sulfonated PAES copolymers with controlled quantities of the ds-DCDPS with DCDPS and different bisphenols.¹⁸⁴

Sulfonation of the DCDPS occurs through an electrophilic aromatic substitution utilizing fuming sulfuric acid at an elevated temperature (Scheme 1.11). The aryl-sulfonyl group is *meta*-

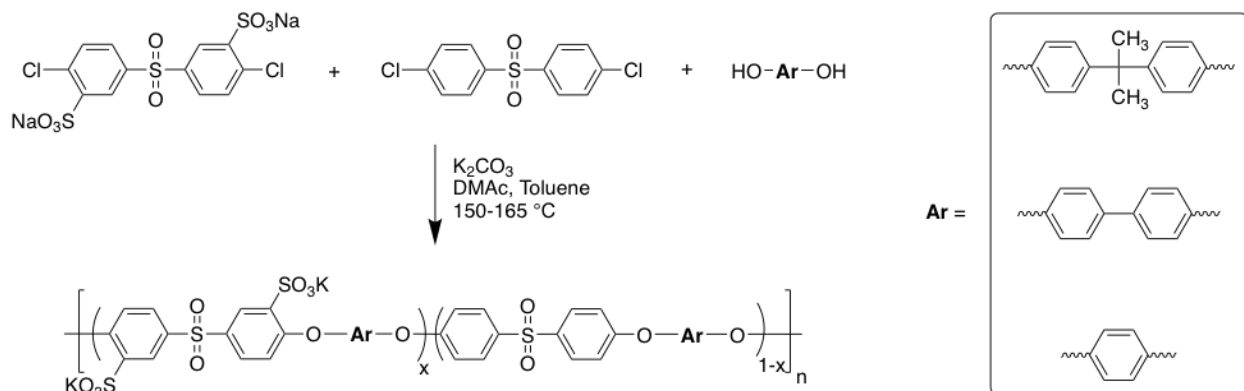
directing while the aryl-chloro group is *para/ortho*-directing. Complete substitution occurred on both aromatic rings at the *ortho* position in relation to the aryl-chloro group. The isolation procedure involved salt-induced precipitation, neutralization by sodium hydroxide, and recrystallization from an ethanol/water solution. The procedure allowed for a yield of greater than 80%. UV-Vis spectroscopy was later implemented to quantify excess salt content by establishing a calibration curve and ultimately eliminated the need for repetitive recrystallizations to obtain a reagent grade monomer.¹⁸⁵



Scheme 1.11. Synthesis of di-sulfonated 4,4'-dichlorodiphenylsulfone

The synthesis of sulfonated poly(arylene ether sulfone)s occurred through the direct polymerization of the di-sulfonated monomer, DCDPS, and a bisphenol (Scheme 1.12) by a nucleophilic aromatic substitution mechanism. This direct polymerization route enabled precise control over the degree of sulfonation and produced statistical copolymers with regard to the positions of the sulfonate ions within the polymer chains. The copolymerization was highly reproducible and removed any concern of polymer degradation as seen in post-sulfonation. The location of sulfonate moieties on deactivated rings yielded higher chemical stability through

inductive effects by the strong sulfonyl electron withdrawing group, and creates better hydrolytic stability.¹⁸⁶



Scheme 1. 12. Direct polymerization of di-sulfonated PAES with ds-DCDPS monomer and various bisphenols

Freeman and McGrath *et al.* investigated these directly sulfonated poly(arylene ether sulfone) copolymers for potential reverse osmosis applications.^{123,187,188} Thin-film composite membranes were studied for transport properties, chlorine resistance, and surface morphology. The membranes consisted of statistical copolymers with varying degrees of sulfonation comprising both hydrophilic and hydrophobic repeat units (Figure 1.17). The hydrophobic repeat unit consisted of either biphenol, bisphenol A or dihydroxy-triphenylphosphine oxide (TPPO) with DCDPS.

Membrane hydrophilicity could be tailored by varying the amount of di-sulfonated monomer incorporation, as well as the chemical composition/comonomer choice. Water uptake, ion-exchange capacity, and water permeability increased while salt rejection decreased with higher degrees of sulfonation because the polymer became more polar (Table 1.3). The rising polarity allows for more plasticization of the polymer chains by water and causes dimensional swelling of

the membranes. The swelling of the membrane leads to higher free volume, producing an increase in both water and salt permeability that lowers water/salt selectivity.^{189,190}

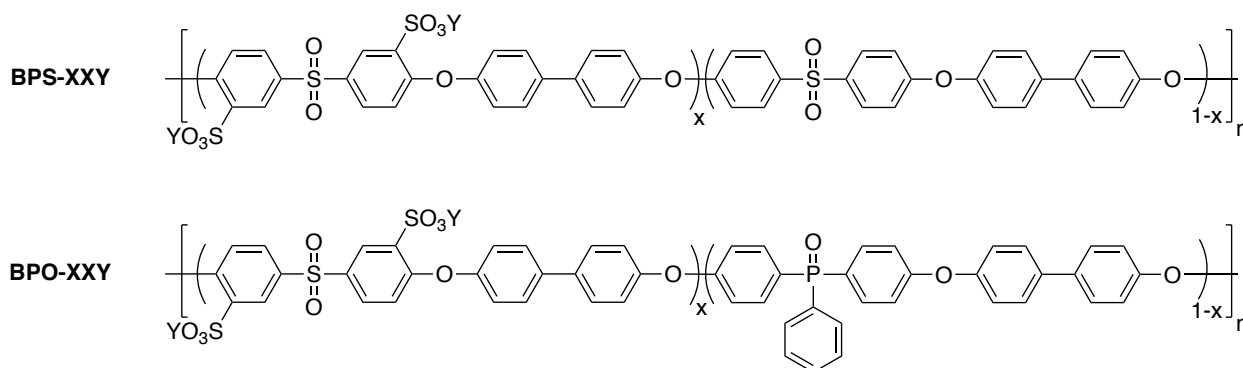


Figure 1. 17. Chemical structure of di-sulfonated poly(arylene ether sulfone)s. XX = mol % and Y = N (salt form) or H (acidic form)

It was found that the acidic forms of these polymers displayed noticeably higher water permeability and lower salt rejection than their salt form counterparts. The acid moieties increase the polarity of the polymer chains, while the salt counter ion shields the sulfonate anion.¹⁹¹ Another interesting aspect involved the differences in properties with the comonomer choice. The BPO-40Y PAES contained triphenylphosphine oxide groups and biphenol in the hydrophobic segments with ds-DCDPS and biphenol in the hydrophilic segments. The “40” denotes that 40% of the repeat units were disulfonated. The BPS-40Y PAES contained DCDPS and biphenol in the hydrophobic segments with the same hydrophilic segments as the BPO polymers. The BPS polymers had higher IECs than the BPO polymers at the 40% sulfonation level and demonstrated higher water permeability and lower salt rejections as would be expected. Triphenylphosphine oxide groups are inherently more polar than biphenol groups and may allow for stronger interactions with sulfonate

moieties between polymer chains. The interaction produces lower dimensional swelling of the membrane and possibly a lower free volume.

Table 1. 3. Reverse osmosis transport and physical properties of disulfonated poly(arylene ether sulfone) films with varying degrees of sulfonation in their salt and acid forms¹²³

Polymer**	Water uptake (%)	IEC (meq/g)	H ₂ O permeability (Lμmm ⁻² h ⁻¹ bar ⁻¹)	NaCl rejection (%)
BPS-20N	4.5	0.92	0.03	99.2
BPS-40N	17.3	1.78	0.62	92.5
BPO-40N	15.7	1.56	0.43	97.5
BPS-20H	18.1	0.92	0.21	98.7
BPS-40H	59.5	1.78	4.21	85.9
BPO-40H	25.6	1.56	0.76	95.3

*Test conditions: Measured at 25 °C using cross-flow (pressure = 27.6 bar, 2000 NaCl ppm)

**"N" in the nomenclature refers to the polymers in their sodium salt forms

"H" refers to the polymers in their acidified form

Poly(arylene ether sulfone) membranes made by direct polymerization of the disulfonated monomer had similar transport properties to the post-sulfonated Udel® materials reported in Allegrezza's work.^{181,182} BPS-40H displayed lower salt rejections with divalent salt feeds than with sodium chloride. The membranes exhibited a NaCl rejection = 85.9%, whereas a lower rejection was observed for CaCl₂ = 69.4%. The difference was attributed to shielding effects that lowered the Donnan repulsive force exerted by the anionic sulfonates.¹⁸¹ BPS-40H membranes also showed excellent chlorine tolerance in comparison to the commercial polyamide SW30HR (FilmTech). The BPS-40H membrane maintained a NaCl salt rejection of 89.6% over the entirety of the continuous chlorine exposure experiment. However under the same experimental conditions, the NaCl salt rejection of the polyamide membrane decreased by 20% after 10,000 ppm-h, and ultimately declined to an overall NaCl salt rejection of 40% after a chlorine exposure of just 15,000

ppm-h (Figure 1.17). BPS-40H permeate flux did not change significantly in the chlorine exposure experiment, but the polyamide flux increased from about 0.6 to 2.2 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. These findings confirmed comparable chlorine resistance of directly polymerized sulfonated poly(arylene ether sulfone)s as compared to the post-sulfonated PAES RO membranes previously investigated by Allegrezza *et al.*. Thus, sulfonated PAES could provide better economics by excluding typical feed source pretreatment requirements of polyamide TFCs.

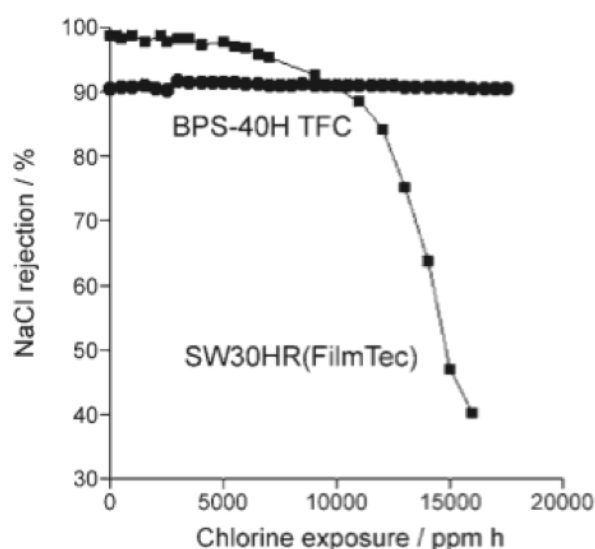


Figure 1. 18. Effect of chlorine exposure on salt rejection for both polyamide SW-30HR and di-sulfonated poly(arylene ether sulfone). *Test conditions: Measured at 25 °C using cross-flow (pressure = 27.6 bar, 2000 ppm NaCl, 500 ppm chlorine, pH = 9.5). Used with permission from Wiley Interscience Inc.¹²³

Direct polymerization of sulfonated PAES and their fabrication into the barrier layer of a TFC demonstrate ideal surface topology for RO applications. AFM images showcase the membrane surfaces of a commercial interfacially polymerized polyamide TFC and a solution cast di-sulfonated poly(arylene ether sulfone) TFC (Figure 1.19).¹⁸⁸ The interfacial polyamides have extremely rough surfaces whereas the sulfonated PAES possesses a considerably smoother surface

where smoothness is independent of the degree of sulfonation. The desirable smooth surface decreases “dead zones” and the reduction in roughness likely reduces surface fouling and scaling. McGrath *et al.* discovered that the ratio of free to bound water increased with increasing IEC in statistical sulfonated PAES copolymers, and that free water only developed after reaching a critical IEC.^{192–194} Free water is necessary for high water permeability, but water uptake of the membrane increases non-linearly after reaching the IEC critical point and allows for increased salt permeability. McGrath *et al.* also found that membranes consisting of statistical sulfonated copolymers with high degrees of sulfonation exhibit different permeabilities when membranes are converted from their salt form to the acidic form at elevated temperatures.¹⁹² This suggested that the polymer/water reorients and AFM suggested that the membrane morphology changes with polymer with higher IEC. RO membranes should have sufficient water permeability without jeopardizing salt rejection. Therefore, considerable research has been performed with sulfonated PAES to maximize IEC while minimizing water uptake to obtain desirable water/salt transport properties.^{195,196}

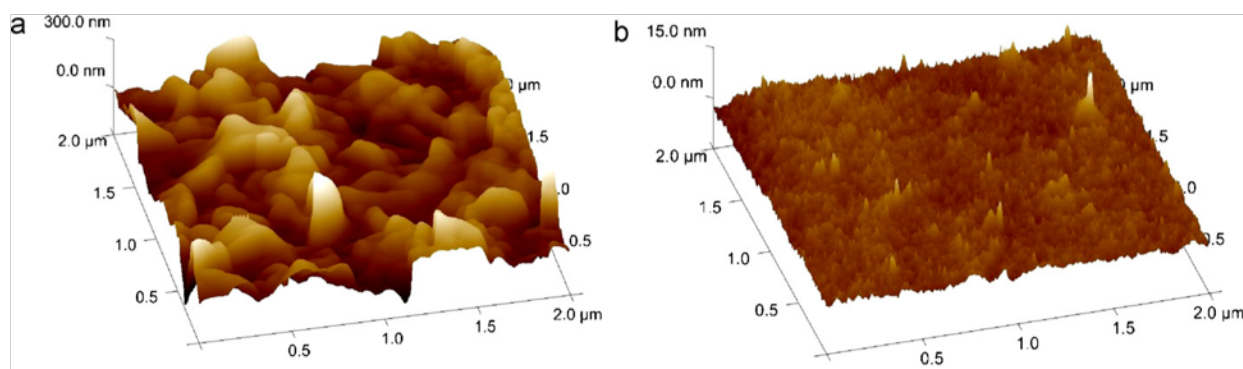


Figure 1. 19. AFM surface images of (a) a commercial polyamide BW-30 Dow Filmtech© membrane and (b) a di-sulfonated poly(arylene ether sulfone) TFC. Used with permission from Elsevier.¹⁸⁸

1.8. Crosslinking Sulfonated Poly(arylene ether sulfone)s

Sulfonated poly(arylene ether sulfone) RO membranes reject salt through size exclusion and electrostatic repulsions created by anionic fixed charged groups that are directly attached to the polymer backbone known as Donnan rejection. The negative charges of the sulfonate groups repel anions by negative/negative repulsive forces, and also prevent the passage of cations by positive/negative attractive forces. Salt passage only occurs when the fixed charged groups fail to completely reject the anions which allows for adsorption and permeation of both the negative co-ions with positive counter-ions.¹⁸¹

Sulfonate fixed charge groups allow for ion adsorption within the membrane and an equilibrium forms between the sulfonated polymer and salt feed source.⁵¹ The counter-ion adsorption concentration is greater than the co-ion adsorption concentration in the polymer membrane because the counter-ions must electronically balance both the fixed charged groups and adsorbed co-ions.¹⁹⁷ The adsorption equilibrium causes an ion disproportion between the sulfonated polymer and the salt feed source, which produces a Donnan potential at the polymer/salt feed source interphase that prohibits further co-ion adsorption.¹⁹⁸ A higher Donnan potential allows for better salt rejection, and increasing the sulfonate fixed charge concentration in poly(arylene ether sulfone)s should result in a stronger Donnan potential. However as previously discussed, the water uptake increases with increasing ion-exchange capacity for linear sulfonated PAES.^{106,189,193} The increase in water uptake decreases the water/salt permeability selectivity because of larger free volume formation from dimensional swelling.

Covalent crosslinking of sulfonated poly(arylene ether sulfone)s can decrease water uptake by restricting the dimensional swelling of the membrane.^{94,199} The chemical crosslinks essentially anchor the polymer chains within the membrane matrix, limiting chain mobility and decreasing

water plasticization effects. Crosslinking potentially allows for better water/salt transport properties, resulting from higher sulfonate fixed charge concentration incorporation while reducing water uptake. Crosslinking reactions employ sulfonated PAES oligomers of targeted molecular weights and crosslinking occurs through either pendent moieties within the polymer chains or functional endgroups. Crosslink density can be adjusted for better water transport and mechanical properties by using different molecular size oligomers and also by implementing crosslinking agents. Covalently crosslinked sulfonated poly(arylene ether sulfone) RO membranes can be achieved by either polycondensation or polyaddition synthetic mechanisms. The crosslinking reaction occurs *in-situ* during the membrane formation. Overall, crosslinking offers many benefits for improving the performance of sulfonated poly(arylene ether sulfone)s as potential commercial RO membranes.

1.8.1. Polycondensation Crosslinking

McGrath *et al.* first investigated the crosslinking of poly(arylene ether sulfone)s using an epoxy-based reaction scheme in the 1980s.²⁰⁰ The preliminary research focused on utilizing the PAES oligomers as epoxy-resin network modifiers to improve chemical resistance and toughness for commercial epoxy materials. PAES oligomers with targeted molecular weights were synthesized with either bisphenol-A or *m*-aminophenol endcapping groups.^{201,202} Molecular weight was controlled through stoichiometric manipulation using the Carother's equation. The oligomers were crosslinked with a bisphenol-A diglycidyl epoxy resin and 4,4'-diaminodiphenylsulfone. Initial findings displayed high levels of cross-linking with better toughness. These findings would lay the ground work for future research of epoxy crosslinked sulfonated poly(arylene ether sulfone)s as potential RO membranes.

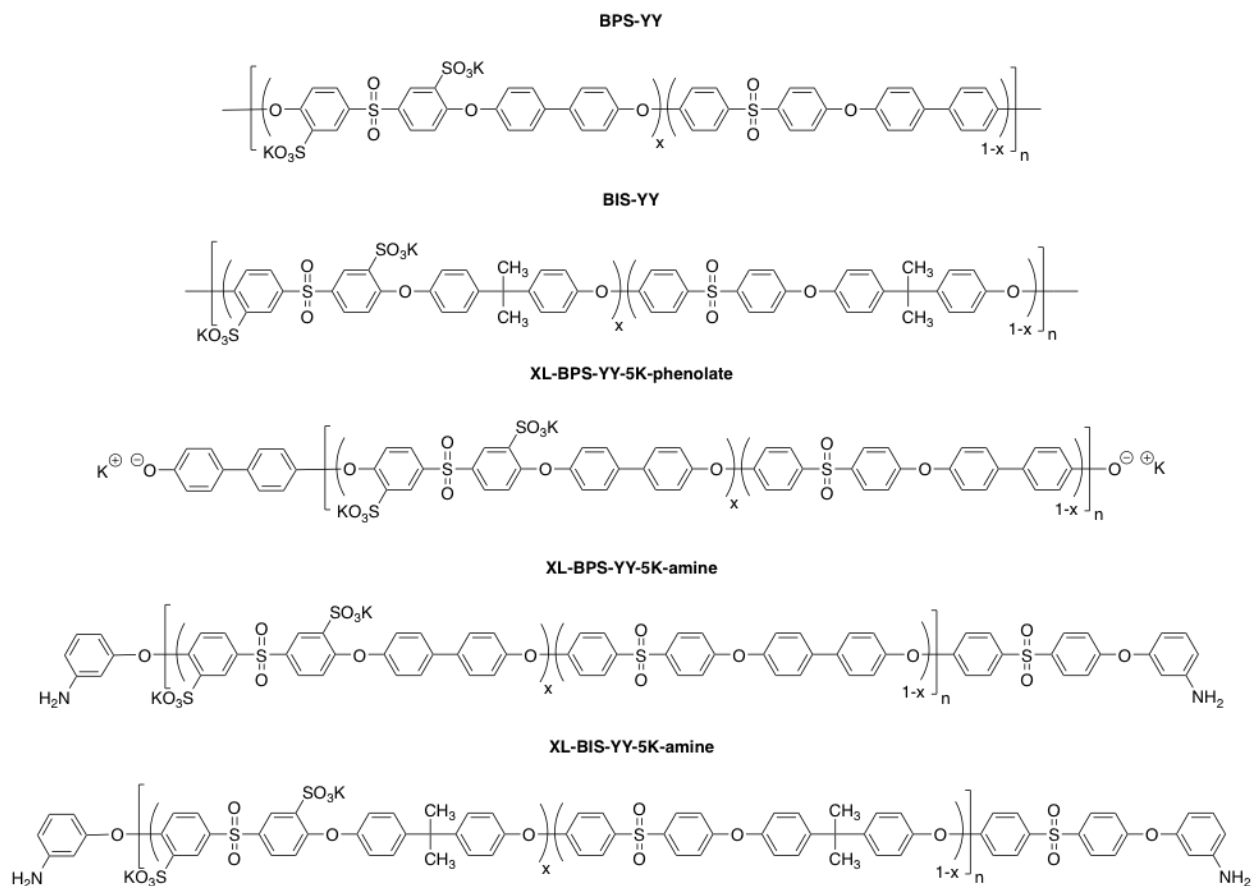


Figure 1. 20. Chemical structures for linear and crosslinked sulfonated poly(arylene ether sulfone)s (XL= crosslinked, BPS and BIS = biphenol and bisphenol, YY = molar quantity of di-sulfonated incorporation, 5K = molecular weight, phenolate/amine = endgroup).

Riffle *et al.* investigated epoxy-crosslinked sulfonated poly(arylene ether sulfone)s as RO membrane candidates.⁹⁴ Sulfonated PAES oligomers with targeted molecular weights were synthesized by direct polymerization of 4,4'-biphenol, dichlorodiphenylsulfone and di-sulfonated 4,4'-dichlorodiphenylsulfone. Stoichiometrically offsetting with excess biphenol allowed for complete phenolate endgroup functionalization (Figure 1.21). Membranes were formed through the *in-situ* crosslinking of the oligomers at elevated temperatures with a tetrafunctional epoxide crosslinking agent (tetraglycidyl bis(*p*-aminophenyl)methane) and triphenylphosphine as a

catalyst. It was found that longer reaction times led to higher degrees of crosslinking with lower water uptake. The phenolate-epoxy crosslinked dense RO membrane comprised of 50% di-sulfonated repeat unit incorporation displayed high salt rejection = 97.2% with water permeability = 1.4 L μ mm⁻²h⁻¹bar⁻¹ (Table 1.4).

Table 1. 4. Comparison of ion exchange capacity, water permeability, and salt rejection for linear and epoxy crosslinked sulfonated poly(arylene ether sulfone)s^{94,95,193,203}

Polymer	IEC (meq/g)	Water Permeability (L μ mm ⁻² h ⁻¹ bar ⁻¹)	NaCl Rejection (%)
BPS-35*	1.52	0.34	94.5
BIS-40*	1.49	1.1	93.1
XL-BPS-50-5K-phenolate**	2.08	1.4	97.2
XL-BPS-40-5K-amine*	1.60	0.43	97.9
XL-BIS-50-5K-amine*	1.48	0.36	96.6

*Test conditions: feed source water = 2000 ppm NaCl, pressure = 27.6 bar, temperature = 25 °C

**Test conditions: feed source water = 2000 ppm NaCl, pressure = 69.9 bar, temperature = 25 °C

McGrath *et al.* further explored epoxy-crosslinked sulfonated poly(arylene ether sulfone)s as potential dense RO membranes. The sulfonated PAES oligomers with targeted molecular weights were synthesized using either 4,4'-biphenol or bisphenol-A, and functionalized with *m*-aminophenol groups (Figure 1.21).^{95,203} A series of RO membranes with varying degrees of sulfonation were fabricated using a similar procedure as discussed for the phenolate-epoxy crosslinked membranes. The membranes were analyzed for water and salt transport properties. Both the biphenol and bisphenol A sulfonated epoxy-crosslinked membranes displayed higher salt rejection, 96.6 and 97.9%, respectively, than their sulfonated linear counterparts salt rejection = 94.5% and 93.1%, respectively, (Table 1.4). The XL-BPS-40-5K-amine crosslinked membrane

with 40% degree of disulfonation demonstrated water permeability = $0.36 \text{ L}\mu\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$, which is quite similar to the linear BPS-35 water permeability = $0.34 \text{ L}\mu\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$.

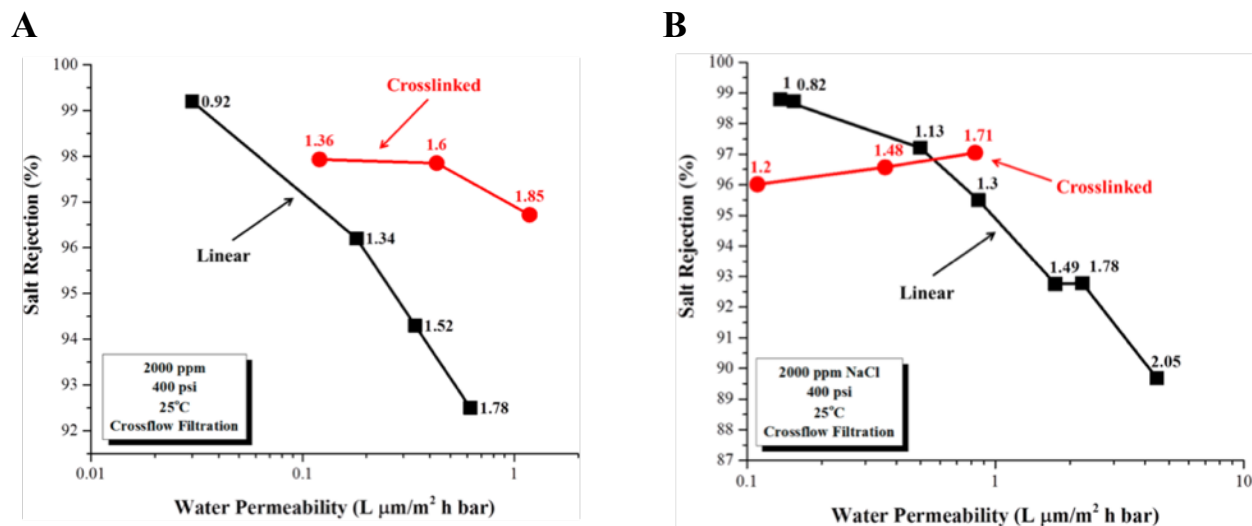
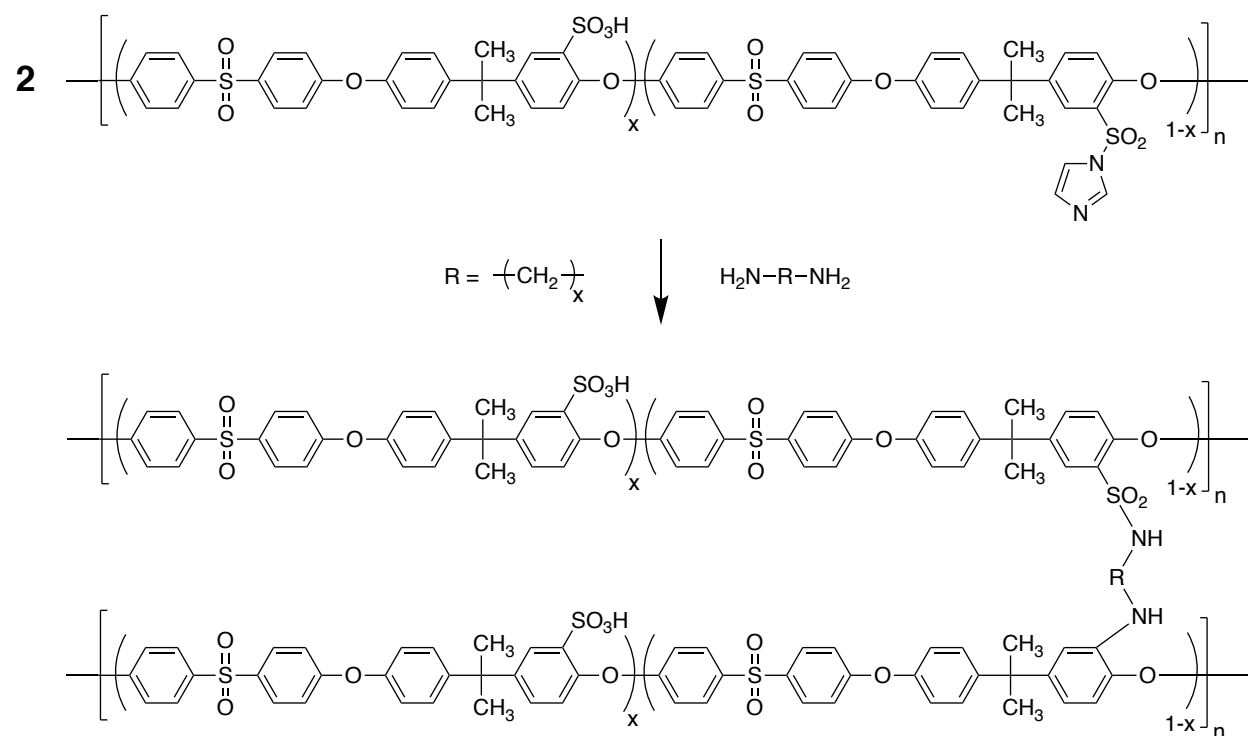


Figure 1. 21. (A) Salt rejection versus water permeability for linear and epoxy crosslinked PAES copolymers that contained biphenol; (B) salt rejection versus water permeability for linear and epoxy crosslinked PAES copolymers that contained bisphenol A. Number next to data point = IEC. Used with permission from Elsevier.²⁰³

Linear sulfonated poly(arylene ether sulfone) copolymers exhibit a strong relationship between water and salt transport properties and the degree of sulfonation. Both water permeability and salt permeability increase with increasing sulfonation. Figure 1.21 presents the salt rejection versus water permeability trends for linear and epoxy-crosslinked copolymers. As expected, the salt rejections of the linear sulfonated copolymers decreased considerably with increasing IEC and water permeability. The crosslinked sulfonated copolymers displayed significantly higher salt rejections with increasing IEC than their linear counterparts. Crosslinking reduced the dimensional swelling of the membranes, thus lowering water uptakes, and this generated higher fixed charge concentrations. Thus, the crosslinked networks were more effective at rejecting salt than the linear copolymer membranes. The crosslinked sulfonated copolymers that contained bisphenol A (Figure

1.21 B) showed both higher water permeability and salt rejection with increasing IEC. This upward salt rejection trend was attributed to lower swelling with better fixed charge concentration than the crosslinked copolymers that contained biphenol. Epoxy-crosslinking improved RO water and salt transport properties, but the long reaction time required for the crosslinking reactions is a detriment.

Nolte *et al.* reported the crosslinking of post-sulfonated poly(arylene ether sulfone)s as potential proton exchange membranes for fuel cell applications.²⁰⁴ Udel® and Victrex® were sulfonated to obtain the targeted degrees of sulfonation. Crosslinking and membrane formation occurred *in-situ* over approximately 8 hours at elevated temperature. The sulfonic acid groups of the linear polymers were partially functionalized with 1,1'-carbonyl imidazole to form N-



Scheme 1. 13. Sulfonamide crosslinking of linear sulfonated poly(arylene ether sulfone) copolymers

sulfonylimidazole, and simultaneously crosslinked with 4,4'-diaminodiphenylsulfone that converted into sulfonamide crosslinks (Scheme 1.13). Crosslinking reduced the dimensional swelling of the membrane by 50% in relation to its linear counterpart.

Kerres *et al.* fabricated crosslinked membrane blends consisting of both sulfonated and sulfinated poly(arylene ether sulfone) polymers.^{205,206} Sulfonate and sulfinate polymers were synthesized to certain degrees of sulfonation or sulfination by post-functionalization of Udel®, and subsequently crosslinked. Covalent crosslinking occurred inter- or intramolecularly between sulfinite groups while the sulfonated polymer chains became entangled in the network during membrane formation. Chemical compatibility allowed for the formation of transparent films. The investigations found two distinct crosslinking routes, including disproportionation and S-alkylation (Figure 1.22). Disproportionation crosslinking takes place between the sulfinic acids of polymer chains that bear these groups. S-alkylation crosslinking occurs between sulfinite groups and dihalogenoalkane crosslinking agents. Both crosslinking methods produced membranes that demonstrated lower dimensional swelling than comparable linear poly(arylene ether sulfone) membranes.

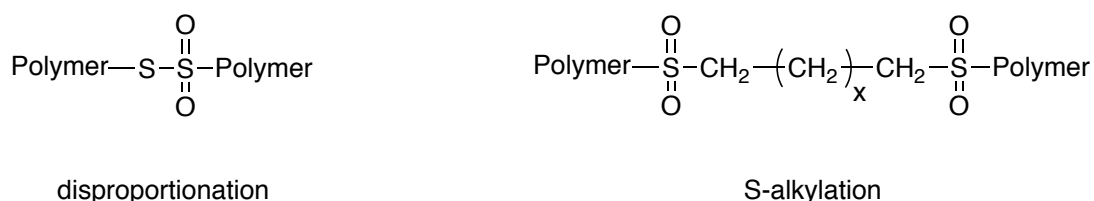


Figure 1. 22. Chemical structure of crosslinks between sulfinite poly(arylene ether sulfone) polymer chains by disproportionation or S-alkylation methods

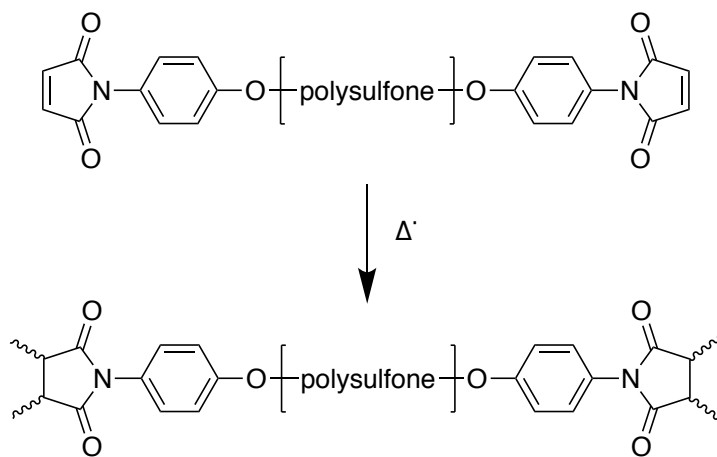
In recent years, several other covalent crosslinking methods have been developed for polycondensation crosslinking of sulfonated poly(arylene ether sulfone)s. Xiao *et al.* reported crosslinking between sulfonated PAES with glycol, glycerol, and poly(vinyl alcohol).²⁰⁷ The sulfonic acid groups reacted with the alcohol groups under mild reaction conditions. Zhang *et al.* developed poly(ethylene glycol) crosslinked sulfonated poly(arylene ether sulfone) membranes.²⁰⁸ Initial findings showed that these membranes had high salt rejection of divalent ions (96 % - MgSO_4), but low salt rejection of monovalent ions (55% - NaCl). Other promising crosslinking reactions have involved the polymerization of PAES with monomers that possess protected moieties such as protected phenol groups.²⁰⁹ Later, the moieties were deprotected to allow for the formation of crosslinked membranes. Functional groups that can form crosslinks can also be inserted into PAES polymer chains through halomethylation (bromo or chloro) onto aromatic rings.^{176,210}

1.8.2. Thermal Free Radical Crosslinking

Thermal free radical crosslinking of sulfonated poly(arylene ether sulfone)s occurs through the crosslinking of double bonds which can be either located within the polymer chains or by functional endgroup incorporation. Thermal radical crosslinking requires elevated temperature and crosslinking can occur through two distinct free radical generating mechanisms: 1) thermal double bond decomposition, 2) thermal decomposition of initiators into radicals.²¹¹ Typically, radical initiators allow for lower temperatures during crosslinking, where radical generation kinetics are temperature dependent. Thermal free radical polymerization encompasses three main steps: initiation, propagation, and termination.²¹² Propagation must be faster than termination to achieve a high degree of crosslinking for sulfonated poly(aryl ether sulfone)s. Several factors can influence

crosslinking: polymer concentration, initiator concentration, crosslinking agents, amount of available double bonds, atmosphere, and reaction time/temperature influence the degree of crosslinking.^{213,214} Thermal free radical crosslinking of PAES can create isotropic dense membranes and several different methods have shown promising results.

Kwiatkowski *et al.* reported crosslinking of poly(arylene ether sulfone)s with functional arylimide endgroups.²¹⁵ PAES with targeted molecular weights were synthesized by endcapping with *p*-aminophenol endgroups. The amines were then reacted with maleic anhydride, followed by *in-situ* imidization to form arylimide endgroups (Scheme 1.13). The maleimide endgroups were then crosslinked by polyaddition with temperatures above 150 °C forming a network. The reaction rate was shown to increase upon using a thermal initiator. Overall, the reaction produced satisfactory degrees of crosslinking with good mechanical properties.



Scheme 1. 14. Radical crosslinking of poly(arylene ether sulfone) oligomers with maleimide endgroup functionality

Sundell *et al.* used a similar procedure to crosslink sulfonated poly(arylene ether sulfone)s, but employed *meta*-aminophenol because it was more oxidatively stable than *para*-aminophenol.⁹⁵

The oligomers were endcapped with either maleimide or 4-phenylethynyl phthalic anhydride endgroups (Figure 1.23). The oligomers were thermally cured at various high temperatures without initiator to induce crosslinking. The films showed high gel fractions, but they were mechanically brittle and difficult to delaminate from the glass surfaces on which they were cast. The elevated temperature reaction resulted in brown films with bubbles present throughout the films.

Functionalized sulfonated poly(arylene ether sulfone)s with allyl and propargyl endgroups have been reported (Figure 1.23).^{216,217} Targeted molecular weight sulfonated oligomers were first directly polymerized with phenolate endgroups and then modified with allyl chloride or propargyl bromide. The oligomers were thermally cured without initiator at ramped temperatures of 120 °C (2 hours), 160 °C (2 hours), and 220 °C (4 hours). The crosslinked membranes displayed gel fractions greater than 80 % and were tested as proton exchange membranes. The crosslinking diminished dimensional swelling and reduced water uptake.

Callender *et al.* successfully modified highly fluorinated poly(arylene ether sulfone) oligomers containing tetrafluorostyrene endgroups at low temperatures for optical waveguide applications (Figure 1.23).²¹⁸ The fluorinated styrenic groups were crosslinked with 1 wt% of dicumyl peroxide initiator at elevated temperatures in a polymer solution (20% w/v). Crosslinked films revealed an 18 °C increase in the glass transition temperature in relation to linear polymers of the same composition.

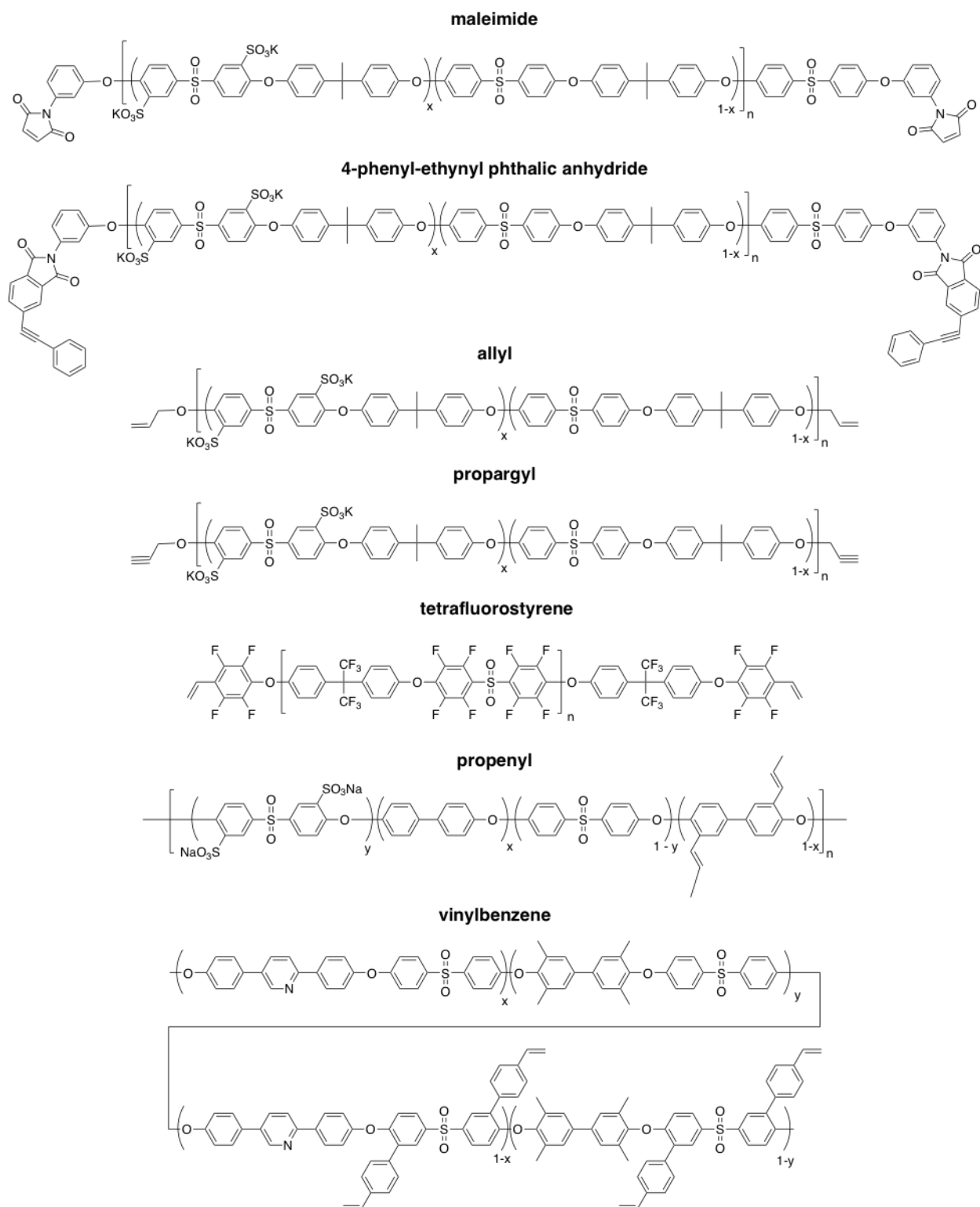


Figure 1. 23. Sulfonated poly(arylene ether sulfone)s endcapped with functional endgroups or polymer chain side groups for thermal free radical crosslinking

Synthesis of crosslinkable sulfonated poly(arylene ether sulfone)s by incorporating propenyl moieties attached to the phenyl rings of the biphenol monomer repeat unit within the polymer chain as investigated (Figure 1.23).²¹⁹ The initial oligomer was directly polymerized with 3,3'-diallyl-4,4'-dihydroxybiphenyl and the endgroups were later converted to propenyl functionality. The sulfonated oligomers were crosslinked with 3 wt% of benzoyl peroxide and membranes were formed *in-situ* at elevated temperatures. The membranes were investigated for potential direct methanol fuel cell applications. Water uptake decreased from 43 to 21% and dimensional swelling of the membrane was reduced from 22 to 11% with increase of the 3,3'-diallyl-4,4'-dihydroxybiphenyl unit from 0 to 30%.

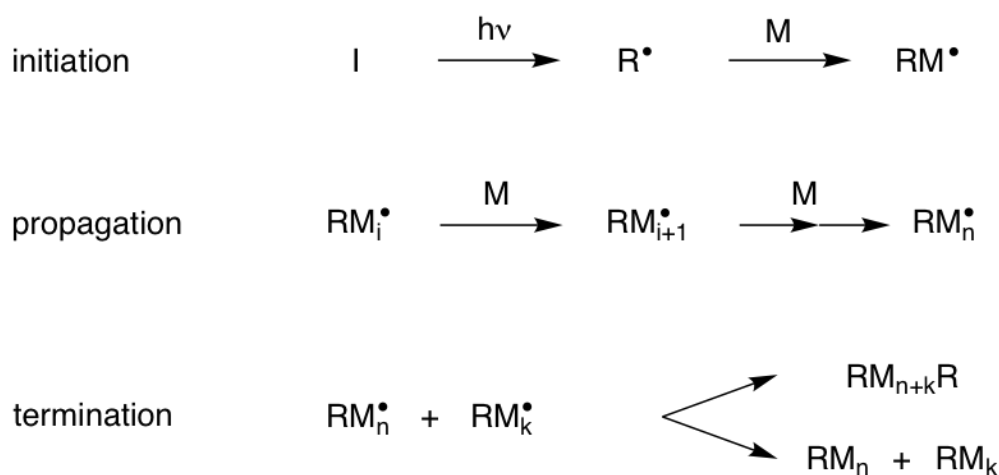
Kallitsis *et al.* also reported the direct polymerization of PAES copolymers possessing crosslinkable pendent functional groups that were located throughout the oligomer backbone chains (Figure 1.23).²²⁰ The synthesis involved functionalization of 4,4'-difluorodiphenylsulfone with difunctional vinylbenzene moieties and then polymerization of polysulfone oligomers bearing pyridine groups. A series of oligomers with differing quantities of the crosslinking repeat unit were thermally crosslinked without initiator. Both the glass transition temperature and crosslink density increased with increasing vinylbenzene content.

Overall, the literature demonstrates that sulfonated poly(arylene ether sulfone)s can be thermally crosslinked by a free radical mechanism through incorporating either crosslinkable functional end groups or by appending crosslinkable moieties on the polymer chain repeat units. Thermal crosslinking permits high degrees of crosslinking, which lowers dimensional swelling and increases the fixed charge concentration. However, thermal crosslinking generally requires longer reaction times than are required for polyamide thin film composites, which makes them non-ideal for commercial reverse osmosis applications. Increasing reaction temperature and

employing thermal initiators can be used to improve the reaction rate, but the process conditions dry the membrane causing mechanical failure and brittleness.²²¹

1.8.3. UV Free Radical Crosslinking

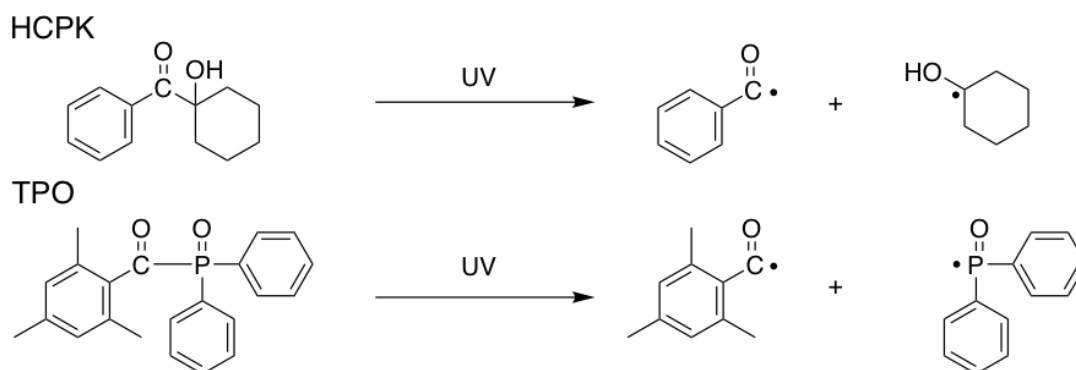
Industrial applications employ photopolymerization reactions in several areas that include adhesives, coatings, sealants, inks, and membranes.^{222,223} Photo-crosslinking involves the photopolymerization of crosslinkable polymeric materials into networks, and primarily utilizes free radical or cationic synthetic mechanisms.²²⁴ Similar to thermal free radical crosslinking, UV free radical crosslinking comprises three steps: initiation, propagation, and termination (Scheme 1.14).



Scheme 1. 15. Mechanistic steps for free radical photopolymerization

Generally speaking, photo-crosslinkable functional groups are incapable of forming free radical species without using tremendously large quantities of radiation. Therefore, UV-curable polymer formulations require photo-initiators to induce crosslinking. Upon UV-exposure,

photolabile initiators generate free radicals through direct homolytic cleavage or indirect secondary pathways.²²⁴ The free radical species then reacts with functional crosslinkable double bonds on the polymer chains which produces another radical. These radicals propagate with other double bonds and this continues until termination occurs. Photo-initiators consist of several different chemical classes that include: azo compounds, ketones, aldehydes, benzoyl-phosphine oxides, and disulfides.²²⁵ Ketone based initiators are predominantly used in industrial applications. Initiator choice for photo-curing is completely dependent on the system because the polymeric material or solvent can potentially absorb the UV-radiation depending on the available light source and wavelength. Ideally, UV-curing should be performed under a light source outside the absorbance wavelength of the oligomer and solvent and paired with an initiator. Photo-initiators



Scheme 1.16. Formation of radical species by homolytic bond cleavage for HCPK and TPO

are more effective with specific UV-wavelength ranges by absorbing more UV-radiation. Higher molar absorptivity requires lower initiator concentrations for equal curing times and energies and also minimizes cure gradients that can occur in the polymeric network. For example, 2,4,6-trimethylbenzoyl diphenylphosphine oxide (TPO) has a high molar absorbance in the range between 360 – 395 nm, whereas 1-hydroxy-cyclohexylphenyl ketone (HCPK) exhibits high molar

absorbance at 240 – 250 nm and lower absorbance at 320 – 350 nm.²²⁶ Scheme 1.24 displays the structures and generated radical species for TPO and HCPK.

UV free radical crosslinking processes demonstrate several advantages when compared to thermal free radical crosslinking.^{227,228} UV crosslinking usually occurs with faster rates where networks form in seconds or minutes, as compared to hours for similar thermal crosslinking methods. UV crosslinking can occur at room temperature and potentially allow for continuous processing, whereas thermal crosslinking requires elevated temperatures over extended periods. These advantages make UV-curing more cost-effective than thermal curing because it allows for faster processing time and lower energy requirements. UV-curing fabrication design also permits the implementation of temperature sensitive materials and facilitates larger surface applications (membranes). UV crosslinking also allows for spatial resolution because initiation only occurs in areas exposed to the UV radiation.

UV curing suffers from primarily two major drawbacks: limited light penetration and oxygen inhibition. Polymers, monomers, crosslinking agents, photo-initiators, and solvent can potentially absorb UV-radiation and this minimizes the depth to which light can penetrate.²²⁹ This causes the formation of gradients throughout the system and affects the inherent properties of the crosslinked material. Consideration must be taken for materials that are used and their concentrations for network formation. Fabrication of thin films with high UV irradiation energies can increase penetration. Oxygen inhibition remains another major drawback for the development of UV-curing processes, especially for thin-film fabrication.²³⁰ If oxygen is present, free radical species react with oxygen, forming oxygen radicals that drastically inhibit crosslinking. Inert atmospheres such as nitrogen or argon can avoid the detrimental effects of oxygen inhibition. However, Joe DeSimone developed continuous liquid interface production (CLIP) and this process

utilizes oxygen inhibition as an advantage for 3D printing complex structures from UV-curable resins.²³¹ His research could be implemented to produce thin films by employing oxygen inhibition.

UV-crosslinking polymer systems are predominantly based on free radical photopolymerizations of acrylates and methacrylates.²³² Crosslinking agents with multifunctionality, their chemical structure, and the lengths of oligomers enable one to design for high degrees of crosslinking. In recent years, several methods have been investigated to crosslink both non-sulfonated and sulfonated poly(arylene ether sulfone)s as coatings or membranes by UV-curable processes. PAES UV-crosslinking includes synthetic routes with monomers, pendent functional groups, and functional endgroups.

Lee *et al.* reported the crosslinking of poly(arylene ether sulfone) by incorporating 4,4'-dihydroxychalcone (DHC) as a monomer with a crosslinkable double bond (Figure 1.24).²³³ Oligomers with varying amounts of DHC were cast as films onto a glass surface and heated to remove solvent. The films crosslinked after exposure to UV radiation for 200 seconds. The resultant films were crosslinked networks with double bond conversions between 50 – 80%, and gel fractions also confirmed these findings.

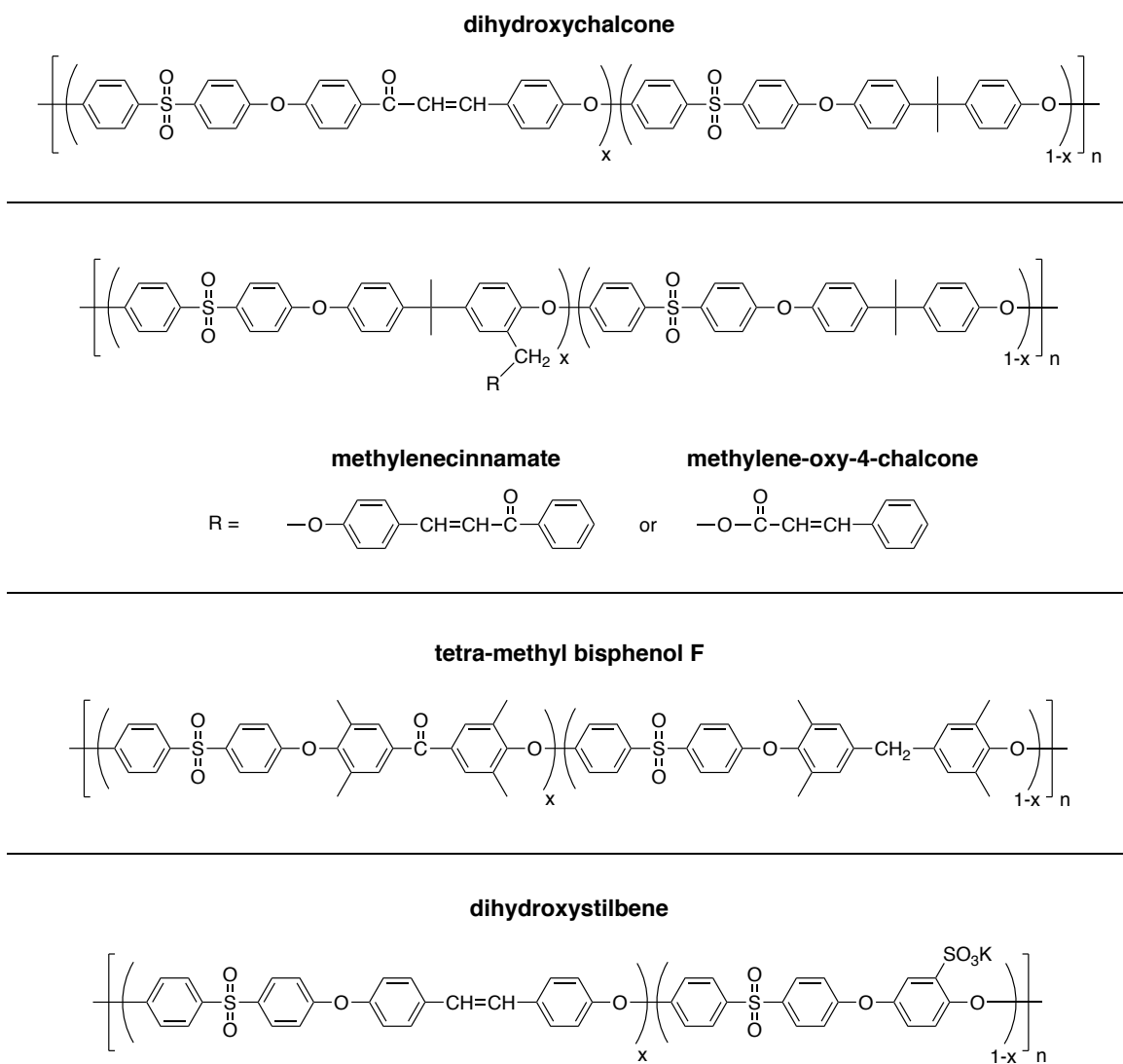


Figure 1. 24. Non-sulfonated and sulfonated poly(arylene ether sulfone)s for free radical UV-crosslinking

Poly(arylene ether sulfone)s bearing crosslinkable pendent groups have also displayed high degrees of crosslinking. Bisphenol A aromatic rings were partially chloromethylated and subsequently functionalized with crosslinkable moieties comprising either methylene-oxy-4-chalcone or methylene cinnamate (Figure 1.24).²³⁴ Membranes were formed by film-casting polymer solutions at elevated temperature, followed by self-crosslinking by UV-curing over 300

seconds. Methylene-oxy-4-chalcone films displayed a double bond conversion of 78.5%, whereas the methylene cinnamate films yielded a considerably lower conversion of 32.9%. However, both crosslinked networks showed gel fractions greater than 96.5% in all organic solvents that were tested.

McGrath *et al.* also explored crosslinking of poly(arylene ether sulfone)s as membranes for potential oxygen/nitrogen gas separation applications.²³⁵ Crosslinkable PAES were synthesized with tetramethyl bisphenol-F and methylene bridges were partially oxidized to carbonyls. Membranes were created by solution-casting at high temperatures and UV-cured for 1 hour on each film side. The polymer chains crosslinked through benzylic hydrogen abstraction by benzophenone as the photo-initiator. The films displayed high crosslinking with gel fractions over 80%.

Sulfonated poly(arylene ether sulfone)s have been successfully UV-crosslinked for potential fuel cell applications.²³⁴ Sulfonated polymers were directly polymerized using 4,4'-dihydroxystilbene, potassium hydroquinone sulfonate, and 4,4'-difluorodiphenylsulfone. The films were UV-crosslinked by using benzophenone to initiate the double bonds of the stilbene repeat unit. FT-IR analysis confirmed the disappearance of double bonds and crosslinked films revealed high gel fractions in several solvents.

Poly(arylene ether sulfone)s can also be UV-cured by incorporating crosslinkable functional endgroups. Yagci *et al.* explored crosslinkable telechelic PAES for water-ultrafiltration membranes (Figure 1.25).²³⁶ Targeted molecular weight oligomers were endcapped with phenolate endgroups and then reacted with methacryloyl chloride to form methacrylate endgroups. Crosslinked membranes were formed by a two-step solution casting procedure comprised of UV-curing aided with a photo-initiator and non-solvent induced phase separation (NIPS). The order of

steps were analyzed for potential impact on the degree of crosslinking and pore formation. NIPS followed by UV-curing (NIPS-UV) demonstrated a double-bond conversion of 41% with an average pore size of 2 μm . UV-curing followed by NIPS (UV-NIPS) yielded a double-bond conversion of 62% with an average pore size range between 0.8 – 1.8 μm . Membranes showed water permeability values of 2.5 and 9.5 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for NIPS-UV and UV-NIPS, respectively.

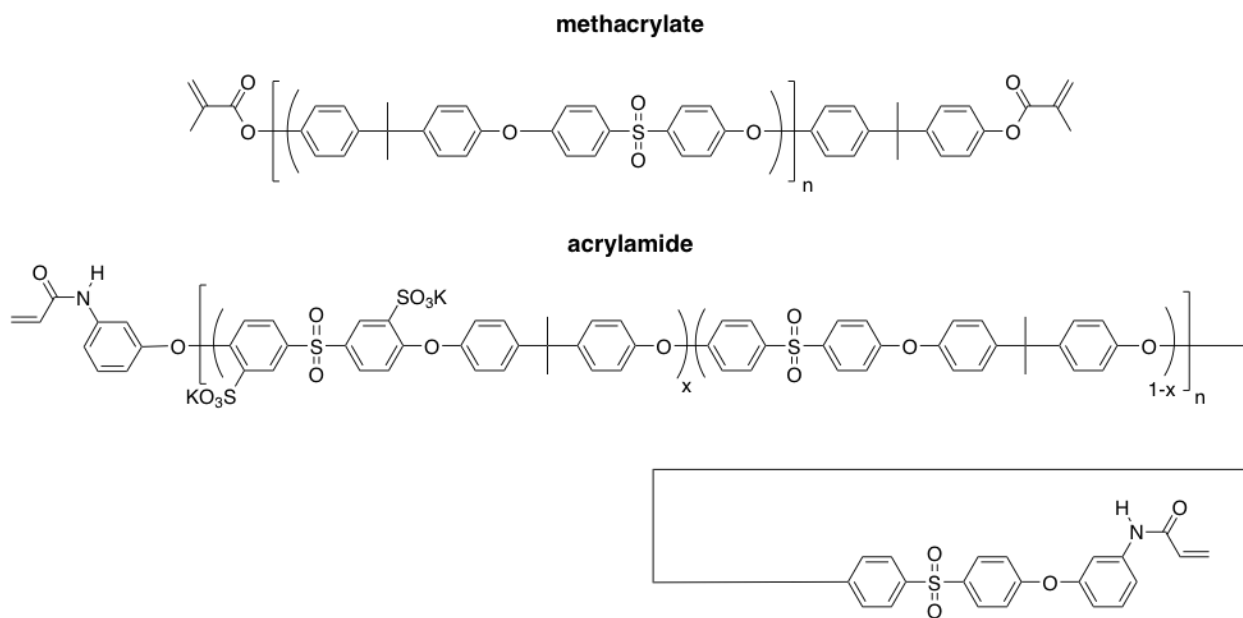


Figure 1. 25. Telechelic nonsulfonated and sulfonated poly(arylene ether sulfone)s for free radical UV-crosslinking

McGrath *et al.* explored UV-crosslinkable telechelic sulfonated poly(arylene ether sulfone)s with acrylate endgroups for potential reverse osmosis applications.²³⁷ Sulfonated PAES were endcapped with acrylamide endgroups by reaction of *m*-aminophenol endgroups with acryloyl chloride (Figure 1.25). Crosslinked films were prepared by solution-casting the polymers and photo-initiator with or without different crosslinking agents, followed by UV-curing. Initial findings revealed low gel fractions between 13 – 45% for membranes that did not have crosslinking moieties, whereas appending the cross-linking agent resulted in high gel fractions up to 98%.

Membrane surfaces also revealed two orders of magnitude less root-mean square roughness than commercial interfacially polymerized membranes.

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CHAPTER 2: SYNTHESIS OF STATISTICAL SULFONATED POLY(ARYLENE ETHER SULFONE)S VIA DIRECT POLYMERIZATION WITH A MONO-SULFONATED MONOMER

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2.1 Abstract

A mono-sulfonated monomer, sodium 3-sulfonate-4,4'-dichlorodiphenylsulfone (*ms*-DCDPS), was synthesized via electrophilic aromatic sulfonation on dichlorodiphenylsulfone (DCDPS). HPLC-UV revealed complete isolation of the mono-sulfonated monomer from byproducts upon the 1st recrystallization with minor NaCl content (*ms*-DCDPS wt% = 94.66, NaCl = 5.34 wt%). A series of sulfonated poly(arylene ether sulfone)s was synthesized by direct copolymerization of *ms*-DCDPS, DCDPS, and 4,4'-biphenol. Copolymer membranes cast from these copolymers had a high degree of toughness in their fully hydrated state. The copolymer with

51% of the repeat units sulfonated exhibited >99% salt rejection at 400 psi and 2000 ppm of NaCl in the feedwater, and Na⁺ passage was unaffected from mixed mono/di-valent feed sources with Ca²⁺ concentrations reaching 200 ppm.

2.2 Introduction

Sulfonated poly(arylene ether sulfone)s belong to a class of high-performance engineering polymers that are synthesized through polycondensation reactions.¹ In general, these polymers display good mechanical properties, high thermal stability, excellent resistance against both oxidation and hydrolysis, and excellent electrical resistance.^{2,3,4,5} These inherent characteristics suggest their potential for membrane applications including water desalination by reverse osmosis or electrodialysis, and as proton exchange membranes for fuel cells.^{6,7,8} Sulfonation of polysulfones can be achieved through either incorporation of pre-sulfonated monomers or via post-sulfonation of the polymers after polymerization.

Early reports of sulfonated poly(arylene ether sulfone)s describe post-sulfonation of the polymers derived from reaction of bisphenol A with dichlorodiphenylsulfone (DCDPS) that is commonly known as UDEL®.⁹ The sulfonations utilized mild conditions such as reacting with sulfur trioxide that was at least partially complexed with triethylphosphate. Sulfonation likely occurred primarily at the position ortho to the aromatic ether bond of bisphenol A since that position was activated toward the electrophilic aromatic sulfonation. However, to achieve control over the level of sulfonation and the distribution of sulfonate ions along the chain, post-sulfonation is restricted to polymer structures where only activated aromatic rings toward electrophilic aromatic sulfonation react. The sulfonation procedure may also lead to polymer degradation.¹⁰ Thus, polymerization of pre-sulfonated monomers has gained significant interest in order to

counter the issues associated with post-sulfonation for developing sulfonated poly(arylene ether sulfone)s.

Robeson and Matzner reported the use of 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (*ds*-DCDPS) as a flame retardant blended with thermoplastic polymers including polyarylates.¹¹ Ueda *et al.* used this compound as a di-sulfonated dihalide monomer to synthesize copolymers containing DCDPS and bisphenol A.¹² McGrath *et al.* investigated sulfonated poly(arylene ether sulfone) copolymers by direct polymerization of controlled amounts of the *ds*-DCDPS monomer with DCDPS and biphenol or bisphenol A.¹³ The direct polymerization route utilizing the di-sulfonated monomer allowed for rigorous control over the degree of sulfonation, led to copolymers with strictly random microstructures with regard to the positions of the sulfonate ions, and eliminated any concerns regarding degradation of molecular weights during post-sulfonation reactions.

Allegrezza *et al.* explored post-sulfonated UDEL® poly(arylene ether sulfone)s as a potential reverse osmosis membrane as an alternative to aromatic polyamide thin film composites.¹⁴ The polyamide membranes displayed good salt rejection and high water flux, but suffered from polymer degradation when periodically introduced to chlorine disinfectants during cleaning procedures. The polyamide linked rings undergo *N*-chlorination followed by hydrolysis or chlorination of the ring via an Orton rearrangement which also leads to hydrolysis susceptibility.^{15,16} Thus considerable research has been conducted searching for an alternative polymer membrane material. Sulfonated poly(arylene ether sulfone)s demonstrate high salt rejection and water permeability, good resistance to fouling and scaling, a wide pH range of operation, and high stability against degradation to chlorine exposure.¹⁴ All of these excellent traits

suggest the potential for sulfonated poly(arylene ether sulfone)s as reverse osmosis or electrodialysis membranes.

Direct polymerization of sulfonated poly(arylene ether sulfone)s with incorporation of *ds*-DCDPS provided materials with promising transport properties in reverse osmosis studies with high water permeability and salt rejection.¹⁷ This work has led to our current research which involves the development of a new monomer, 3-monosulfonate-4,4'-dichlorodiphenylsulfone (*ms*-DCDPS). We believe copolymers containing the mono-sulfonated monomer may lead to improved transport properties relative to copolymers derived from the di-sulfonated counterpart monomer. The present study describes the mono-sulfonated monomer synthesis, workup, purity determination, and polymerization, and compares mechanical and transport properties to copolymers containing the *ds*-DCDPS monomer.

2.3 Experimental

Materials

4,4'-Dichlorodiphenylsulfone (DCDPS) provided by Solvay Advanced Polymers was recrystallized from toluene, and dried *in vacuo* at 120 °C for 48 h. 4,4'-Biphenol was provided by Eastman Chemical Company, recrystallized from toluene/ethanol, and dried *in vacuo* at 120 °C for 48 h. Fuming sulfuric acid (30%), acetic acid and trifluoroacetic acid were purchased from Sigma-Aldrich and used as received. Potassium carbonate was purchased from Sigma-Aldrich and dried *in vacuo* at 160 °C for 72 h. Acetonitrile was purchased from Thermo Fisher and used as received. Calcium hydride and sodium chloride were purchased from Alfa-Aesar and used as received. Chloroform, toluene, ethanol, and isopropanol were purchased from Fisher Scientific

and used as received. *N,N*-Dimethylacetamide was purchased from Chem-Impex International, distilled from calcium hydride, and stored over molecular sieves.

Characterization

Nuclear Magnetic Resonance Spectroscopy (NMR). ^1H and ^{13}C NMR spectra were acquired with a Varian Unity Plus 400 MHz spectrometer operating at 400 MHz for ^1H spectra and 100 MHz for ^{13}C spectra. Chemical shifts are reported in ppm relative to an internal solvent resonance. All spectra were acquired with 10% (w/v) solutions in $\text{DMSO-}d_6$.

UV-Visible Spectroscopy (UV-Vis). Purity of the *ms*-DCDPS monomer was determined using an Agilent Cary 100 Bio UV-Vis spectrophotometer. All measurements were conducted in a 1-cm path length quartz cuvette at room temperature in methanol. All absorbance measurements were acquired at 210 nm. The monomer was recrystallized 3X from water to obtain a pure monomer that was used to establish a calibration curve through serial dilutions according to Beer's Law ($A=\epsilon bc$).

High Performance Liquid Chromatography (HPLC-UV). HPLC-UV separations were performed using an X-Bridge C_{18} (250 x 4.6 mm, 5 μm ps) column from Waters Corporation (Milford, MA). A C_{18} security guard column from Phenomenex (Torrance, CA) was used to protect the column from any particulates. An Agilent 1100 series HPLC equipped with a quaternary pump, auto-sampler, UV detection at 254 nm, and an oven heater set to 40 °C was used. The mobile phases for all separations were H_2O + 0.1% trifluoroacetic acid (A) and acetonitrile + 0.1% trifluoroacetic acid (B). The following gradient was used for the separations: Time 0 – 95/5% A/B, Time 10 – 5/95% A/B, Time 12 – 5/95% A/B, Time 12.1 – 95/5% A/B, Time 15 – 95/5% A/B. HPLC flow was set to 1 mL/min and 5 μL of standards and samples were injected for each analysis.

Size Exclusion Chromatography (SEC). Molecular weight analysis was conducted using an Agilent 1260 Infinity system, which included an isocratic pump, autosampler, online degasser, and column oven equipped with 3 Agilent PLgel 10-mm Mixed B-LS 300 x 7.5 mm columns (polystyrene/divinylbenzene) connected in series with a guard column. A multi-angle laser light scattering detector (DAWN-HELEOS II, Wyatt Technology Corp.), operating at a wavelength of 658 nm, and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corp.) provided online results. Both the columns and detectors were operated at 50 °C. The mobile phase comprised DMAc containing 0.1 M LiCl. The system was adjusted for delay and band broadening using a polystyrene standard ($M_n = 18.3$ kg/mol). ASTRA 6 software was implemented for data acquisition and analysis. Refractive indices were calculated online assuming 100% recovery.

Synthesis

Synthesis of 3-monosulfonate-4,4'-dichlorodiphenylsulfone monomer (ms-DCDPS). DCDPS (0.6965 moles, 200.0 g) and 30% fuming sulfuric acid (0.662 moles SO_3 , 65 mL) were charged to a 500-mL, three neck, round bottom flask equipped with a mechanical stirrer and two glass stoppers. Dissolution occurred at room temperature, then the reaction vessel was immersed in a preheated silicone oil bath at 85 °C and stirred for 6.0 h. The reaction mixture was cooled to 0 °C and slowly added into deionized water (1500 mL) with ice (1500 g), while stirring vigorously. The reaction mixture was heated to 60 °C and NaCl (600 g) was slowly added to precipitate the reaction contents. The precipitate was filtered via vacuum filtration. The filtrate was added to deionized water (3000 mL) and neutralized with 10 M aqueous NaOH to pH = 7. NaCl (400 g) was added to precipitate the reaction contents. The precipitate was vacuum filtered, then dissolved in deionized water (3000 mL). The dissolved product was portioned into 3 (1000 mL) samples,

placed in a separatory funnel, and washed with chloroform 5X (300 mL each) to remove the starting material. The aqueous layers were collected and the product was recrystallized from the aqueous solution. The product was filtered and dried *in vacuo* at 125 °C for 72 h to afford a white, crystalline monomer with a yield of 55%. MP = 221 °C.

Synthesis of a linear high molecular weight polymer with 50% of the repeat units containing the mono-sulfonated monomer (ms-DCDPS). DCDPS (13.43 mmol, 3.855 g), *ms*-DCDPS (13.43 mmol, 5.225 g in the sodium form), 4,4'-biphenol (26.86 mmol, 5.000 g), potassium carbonate (32.23 mmol, 3.711 g), dimethylacetamide (82 mL), and toluene (20 mL) were charged to a 250-mL, three neck, round bottom flask equipped with a mechanical stirrer, Dean-Stark trap, condenser, and nitrogen inlet. The reaction vessel was immersed in a silicone oil bath and heated to 150 °C for 4 h while stirring to remove water from the system via the toluene-water azeotrope. The toluene and water were drained from the Dean-Stark trap and the oil bath temperature was increased to 180 °C and maintained for 48 h. The reaction was diluted with dimethylacetamide (40 mL) and allowed to cool to room temperature. The reaction mixture was filtered and precipitated into stirring isopropyl alcohol (1200 mL), resulting in a white polymer. The polymer was filtered and stirred in deionized water (1500 mL) at 80 °C overnight to remove salts and residual DMAc. The polymer was filtered and dried *in vacuo* at 140 °C for 48 h to obtain a 91% yield.

Membrane Casting and Characterization

The copolymers in their sodium salt forms (0.7 g) were dissolved in DMAc (12 mL), and then filtered through a 0.45 µm Teflon syringe filter. The solutions were cast onto 4" × 4" clean glass substrates and dried under an infrared lamp at 50-60 °C for 8 h. Afterwards, the membranes

were placed in a vacuum oven under vacuum at ~150 °C for 6 h. The membranes were extracted in room temperature water for 12 h to remove the residual solvent and to aid in delamination from the glass plates.

Water Uptake. Water uptakes of each membranes in its sodium salt form were as gravimetrically. For water uptake measurements of the membranes in the sodium salt form, membranes in the K⁺ salt form were soaked in 2M NaCl solution for 2 days. These membranes were extracted with DI water to remove free NaCl from the membrane and then weighed. The water uptake of the membranes was calculated according to Equation 1, where mass dry and mass wet refer to the masses of the dry and the wet membranes, respectively.

$$\text{Water Uptake (\%)} = \frac{Mass_{wet} - Mass_{dry}}{Mass_{dry}} \times 100 \quad (1)$$

Ion Exchange Capacity (IEC). IECs were measured on the acid form of the membranes by soaking them (in their salt form) in boiling 1M H₂SO₄ for 2 h, followed by immersion in boiling DI water for an additional 2 h. The membranes were dried under vacuum at 110 °C for 8 h. These dry membranes in their acid form were weighed, then soaked in aqueous 1M NaCl solution for 48 h to convert them to their salt form. Each membrane in solution was titrated with aqueous 0.1N NaOH solution. The IEC of each membrane in units of meq/g of dry membrane was calculated from Equation 2

$$IEC = \frac{V * N}{M} \times 1000 \quad (2)$$

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

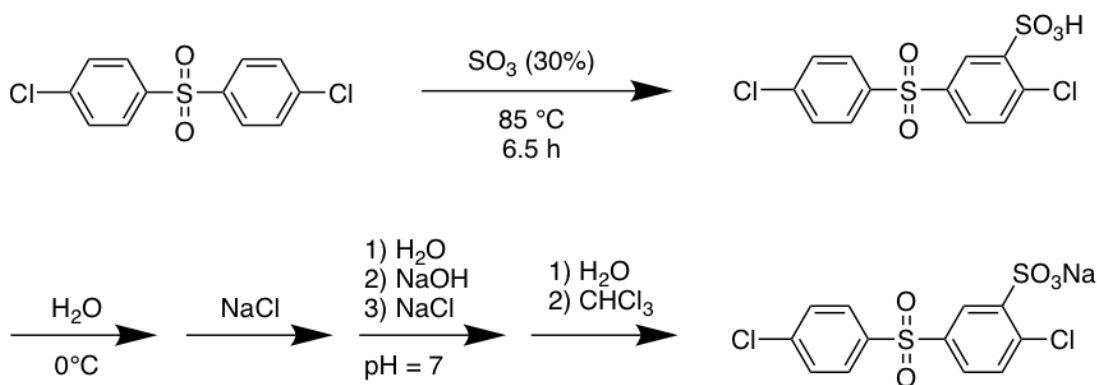
Transport Property Measurements. Transport properties of the membranes synthesized in this work were measured using a cross-flow filtration system.¹⁸ The concentration of the feed solution was 2000 ppm NaCl. The applied transmembrane pressure was 400 psi and the flowrate was 3.8 L/min (1 gpm). The feed solution temperature was maintained at 25 °C using a NesLab RTE 7 circulating bath (Thermo Electron Corporation, Waltham, MA). The pH of the solution was adjusted to approximately 7 using a sodium bicarbonate solution. The mass and conductivity of the permeate samples were measured to determine water permeability ($\text{L } \mu\text{m m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ or $\text{cm}^2 \text{ s}^{-1}$), salt permeability ($\text{cm}^2 \text{ s}^{-1}$), salt rejection (%), and water/NaCl selectivity.

Tensile Tests of Hydrated Membranes. The membranes were cut into dogbone samples with a gauge width of 3.18 mm and gauge length of 25 mm, Type V according to ASTM D638-14, using a Cricut Explore One™ stencil cutter. Four samples with uniform thickness of 60-70 μm from each membrane were tested. The thicknesses of the dogbones were measured at four points along the gauge length using a Mitutoyo digimatic micrometer model MDC-1" SXF. A hydrated testing cell was secured onto the Instron to test samples under fully hydrated conditions. The wet samples were loaded into the cell of the Instron and the cell was filled with DI water. The samples were immersed in DI water for at least 24 h prior to testing and allowed to equilibrate in the Instron in the water for 3 min. Uniaxial load tests were performed using an Instron ElectroPuls E1000 testing machine equipped with a 250-N Dynacell load cell. The crosshead displacement rate was 10 mm/min and the initial grip separation was 25 mm. The hydrated stress-strain curves were smoothed using a 6-point moving average.

2.4 Results and Discussion

Synthesis and characterization of the mono-sulfonated monomer (ms-DCDPS). The ms-DCDPS monomer was synthesized and isolated as shown in Scheme 1. Sulfonation occurred by

electrophilic aromatic substitution with fuming sulfuric acid and substitution took place only at the meta position relative to the sulfone moiety due to the directing nature of both the sulfone and chlorine groups. A stoichiometric balance with a 1:1 molar ratio of DCDPS starting material to sulfur trioxide was utilized to limit di-sulfonation. The reaction contents were isolated from the highly acidic solution by precipitation rather than utilizing substantial quantities of base for neutralization. The DCDPS starting material was removed by washing the precipitate with chloroform and the *ds*-DCDPS product was removed through recrystallization from water.



Scheme 2. 1. Synthesis of *ms*-DCDPS

^1H NMR, ^{13}C NMR, HPLC-UV, and elemental analysis confirmed the chemical structure of the purified *ms*-DCDPS monomer.¹⁸ An ^1H NMR overlay as shown in Figure 1 displays the three products in this reaction which include the non-sulfonated DCDPS, *ds*-DCDPS, and purified *ms*-DCDPS monomer. The spectra reveal that the isolation procedure removes the unwanted non-sulfonated DCDPS and *ds*-DCDPS materials. ^1H NMR analysis revealed the following chemical shifts: δ 7.66 (3H, m); 7.91 (3H, m); 8.30 (1H, d). ^{13}C NMR supported the ^1H NMR spectral

analysis. The ^{13}C spectrum of the mono-sulfonated monomer displayed 10 distinct peaks as shown in Figure 2 with the following chemical shifts: δ 127.95, 129.46, 129.74, 130.55, 132.76, 137.28, 139.00, 139.56, 139.76, 146.79. Elemental analysis also confirmed the *ms*-DCDPS structure: Elem. Anal. Calcd. for $\text{C}_{12}\text{H}_7\text{S}_2\text{O}_5\text{NaCl}_2$: C, 36.39; H, 1.78; S, 16.21; O, 20.23; Na, 6.47; Cl, 18.90. Elem. Anal. Found C, 36.07; H, 1.178; S, 14.76; O, 19.29; Na, N/A; Cl, 18.47.

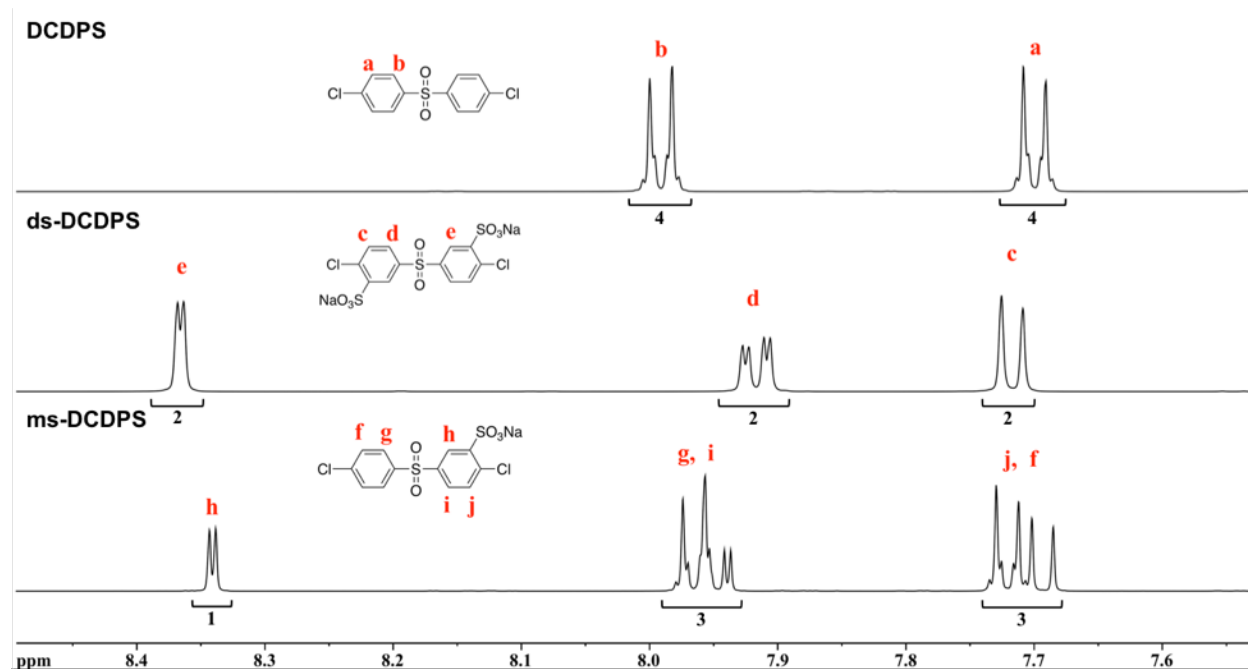


Figure 2. 1. ^1H NMR overlay spectra of non-sulfonated and sulfonated monomers

However, residual NaCl remained and had to be quantified in order to synthesize high molecular weight polymers based on the Carother's equation. It was reasoned that the presence of NaCl should not affect the overall polymerization reaction as long as it was accounted for in controlling the monomer stoichiometry. This approach alleviated the necessity of conducting excessive recrystallizations to remove the salt.

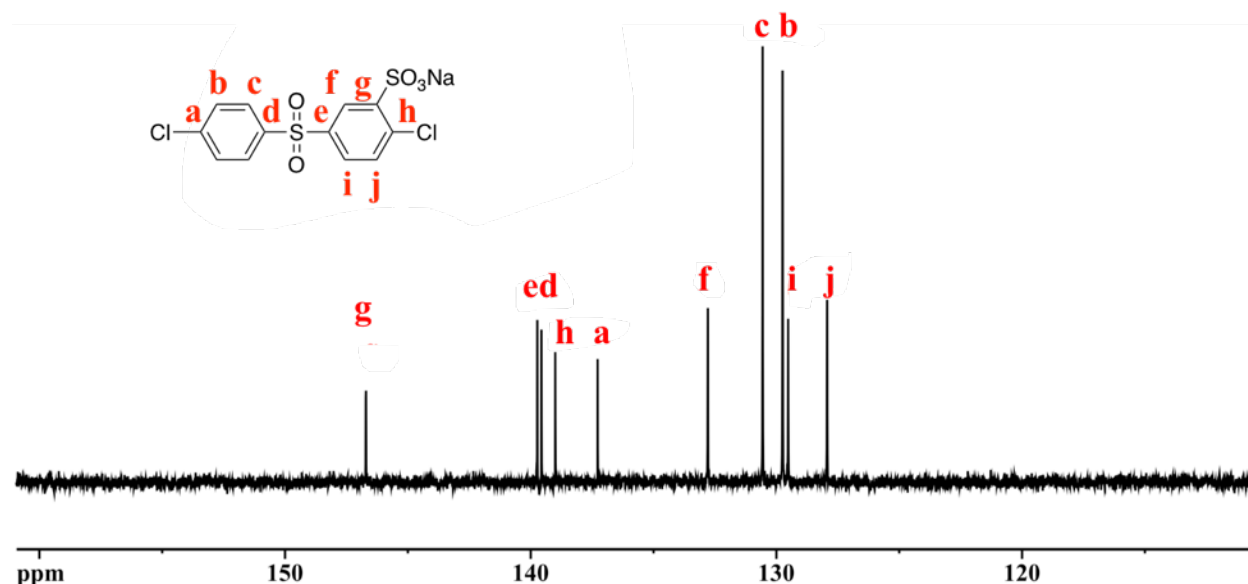


Figure 2. 2. ^{13}C NMR spectrum of *ms*-DCDPS

UV-Visible spectroscopy and HPLC with UV detection and quantification (HPLC-UV) were used to determine the NaCl content of the mono-sulfonated monomer. The first step was to isolate a pure sample of the mono-sulfonated monomer through multiple recrystallizations from DI water, then calibrate its UV spectra with concentration via Beer's Law using a procedure similar to that used by Li *et al.*¹⁹ The recrystallizations were conducted at a concentration of 3×10^{-5} M. The absorbance at 210 nm was calibrated as a function of concentration. The absorbance at 210 nm remained constant after the 3rd recrystallization as shown in Figure 3. An HPLC-UV method was developed to distinguish between the desired *ms*-DCDPS monomer and any non-sulfonated or di-sulfonated impurities while also analyzing for the NaCl content. UV-Visible spectroscopy revealed 6.00 wt% NaCl, whereas HPLC-UV revealed 5.34 wt% with only the mono-sulfonated monomer (Table S1 and Figure S1). HPLC-UV demonstrated better accuracy with a $R^2 = 0.99$.

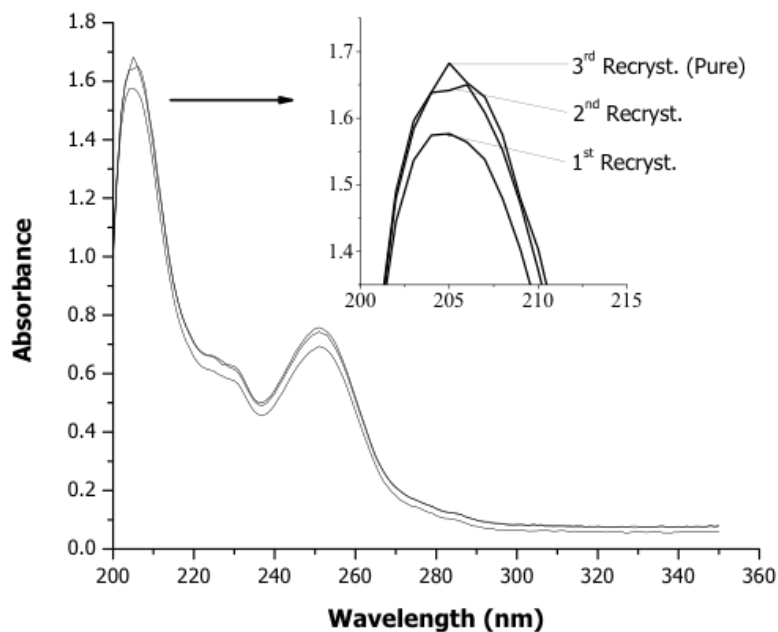
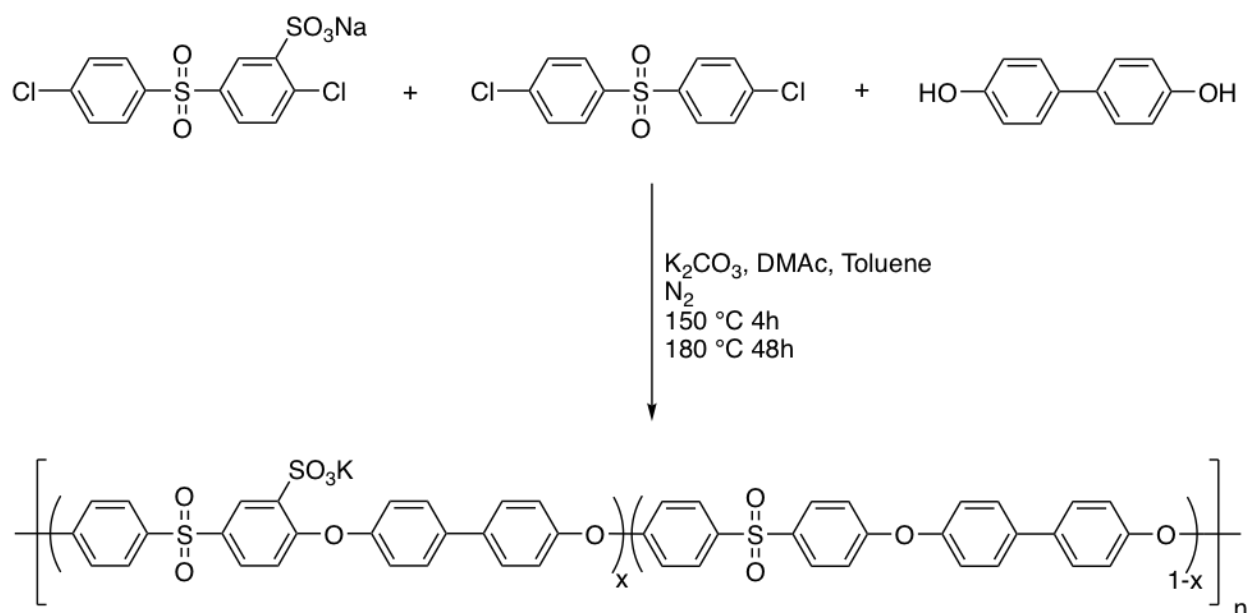


Figure 2. 3. UV-Vis spectra of *ms*-DCDPS after successive recrystallizations at a concentration of 3×10^{-5} M in methanol

Synthesis and Characterization of Sulfonated Poly(arylene ether sulfone) Copolymers

Sulfonated poly(arylene ether sulfone) copolymers were synthesized by direct polymerization of *ms*-DCDPS, DCDPS, and biphenol by nucleophilic aromatic polycondensation (Scheme 2). The Carother's equation was used to determine the stoichiometric monomer quantities needed with the residual NaCl salt present in the mono-sulfonated monomer (HPLC-UV 5.34 wt%). The reactants initially were azeotropically dried with toluene to remove any water that might detrimentally affect the molecular weight in the overall polymerization. High molecular weights were observed for polymerizations containing a 1:1 molar ratio between the biphenol and dihalide monomers, where the ratios of *ms*-DCDPS to DCDPS were varied.



Scheme 2. 2. Polymerization of poly(arylene ether sulfone)s

^1H NMR analysis was implemented to confirm the polymer structure (Figure 4). The integration of proton *c* assigned to the proton adjacent to the sulfonate ion was set to 1 with the integrals of the other peaks relative to *c*. For the copolymer with 50% of the *ms*-DCDPS and 50% of DCDPS, the integrals showed that 100% biphenol, and 50% of each of the mono-sulfonated and non-sulfonated monomers were present as expected.

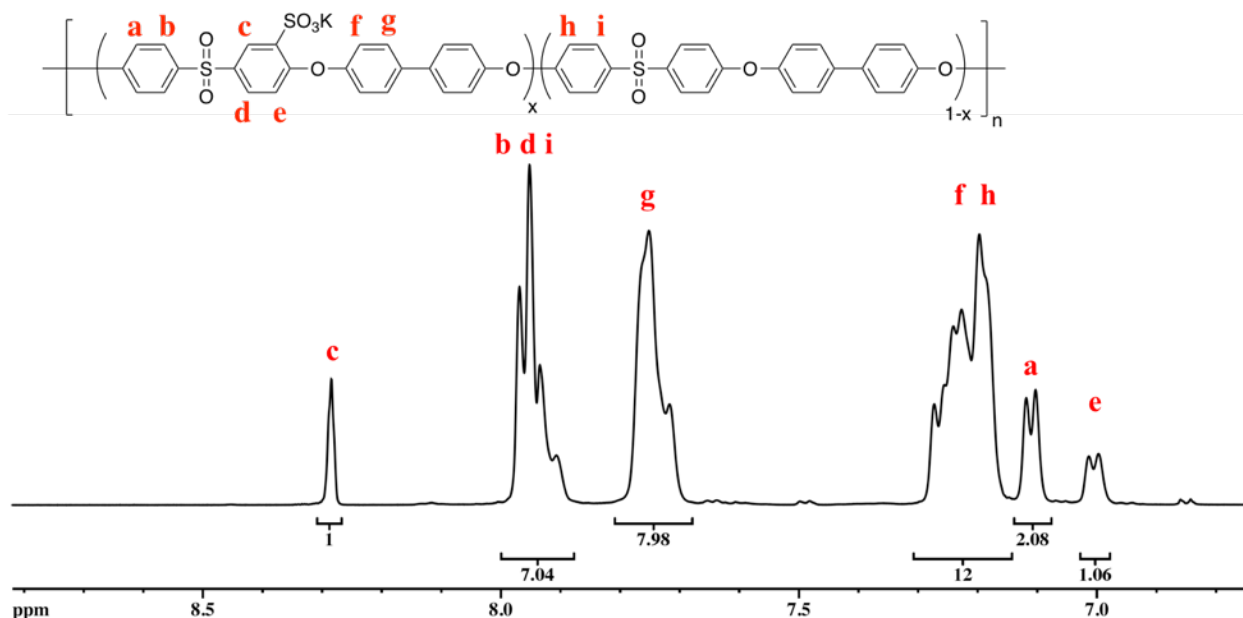


Figure 2. 4. ^1H NMR spectrum of high molecular weight polymer ($x = 0.5$)

SEC analysis was conducted in dry DMAc containing 0.1 M LiCl as the mobile phase. The SEC traces displayed unimodal distributions and the polymers appeared to be free of cyclic species, as shown in Figure S2. The target high molecular weight polymer with 50% of the units mono-sulfonated had a $M_n = 87.5$ kDa as shown in Table S2. The molecular weight results confirmed the validity of both the UV-Vis and HPLC-UV procedures for determining the purity of the *ms*-DCDPS monomer and also demonstrated that the direct polymerizations were not affected by the excess NaCl content.

As expected, water uptake of the membranes generally increases with increasing IEC (Table 1). It was been previously shown that the ionic polymer electrolyte membranes absorb more water when they are in their sulfonic acid form rather than in the salt form.²⁰ However, at a given IEC, the copolymers containing the mono-sulfonated units unexpectedly absorb less water than their di-sulfonated counterparts. For example, the di-sulfonated copolymer with 27% of the repeat units di-sulfonated (IEC of 1.18 meq/g) absorbed 27% water by weight, while the mono-sulfonated

copolymer with 51% of the units mono-sulfonated (IEC of 1.16 meq/g) only absorbs 16% water. Also, the di-sulfonated copolymer with 32% of the units di-sulfonated (IEC of 1.37 meq/g) absorbs 32 wt% of water, while the mono-sulfonated counterpart with 61% of the units mono-sulfonated (IEC of 1.36 meq/g) only absorbs 22 wt% of water. The only structural differences between these polymers is the spacing between the fixed ions, and thus the differences in water uptake are hypothesized to reflect differences in the distribution of water inside the membranes. The molecular weights are shown in Table S2.

Table 2. 1. Directly polymerized sulfonated poly(arylene ether sulfone) (PAES) ion exchange capacity (IEC), water uptake (WU), and hydrated mechanical properties. *ns*-PAES is the non-sulfonated PAES, *ds*-PAES is a sulfonated PAES containing a di-sulfonated monomer (*ds*-DCDPS) and *ms*-PAES is a sulfonated PAES containing the mono-sulfonated monomer (*ms*-DCDPS)

Membrane Name	Average IEC* (meq/g)	Average WU (%)	Average Elastic Modulus (MPa)	Average Yield Stress (MPa)
<i>ns</i> -PAES	0.00	2.6±1.1	1560±100	55.6±1.7
<i>ds</i> -PAES-22	0.99	19±2.6	1070±55	27.2±2.2
<i>ds</i> -PAES-27	1.18	27±4.8	812±130	25.7±6.1
<i>ds</i> -PAES-32	1.37	32±2.7	834±69	28.1±0.7
<i>ms</i> -PAES-51	1.16	16±1.0	816±53	21.8±0.9
<i>ms</i> -PAES-61	1.36**	22±1.5	762±56	23.0±2.3

*IEC values based on the targeted degree of sulfonation

**Determined by titration

The hydrated mechanical properties of all of these copolymers are typical of engineering thermoplastics with a well-defined yield strength and high elongation to break (Figure 5). They also all exhibit glassy polymeric characteristics in their fully hydrated states at room temperature.

The non-sulfonated polymer was tested as a control for the remaining sets of sulfonated polymers. The water uptake for the non-sulfonated polymer was measured to be 2.6% which, as expected, yielded both the highest elastic modulus (1560 MPa) and yield stress (55.6 MPa) (Table 1).

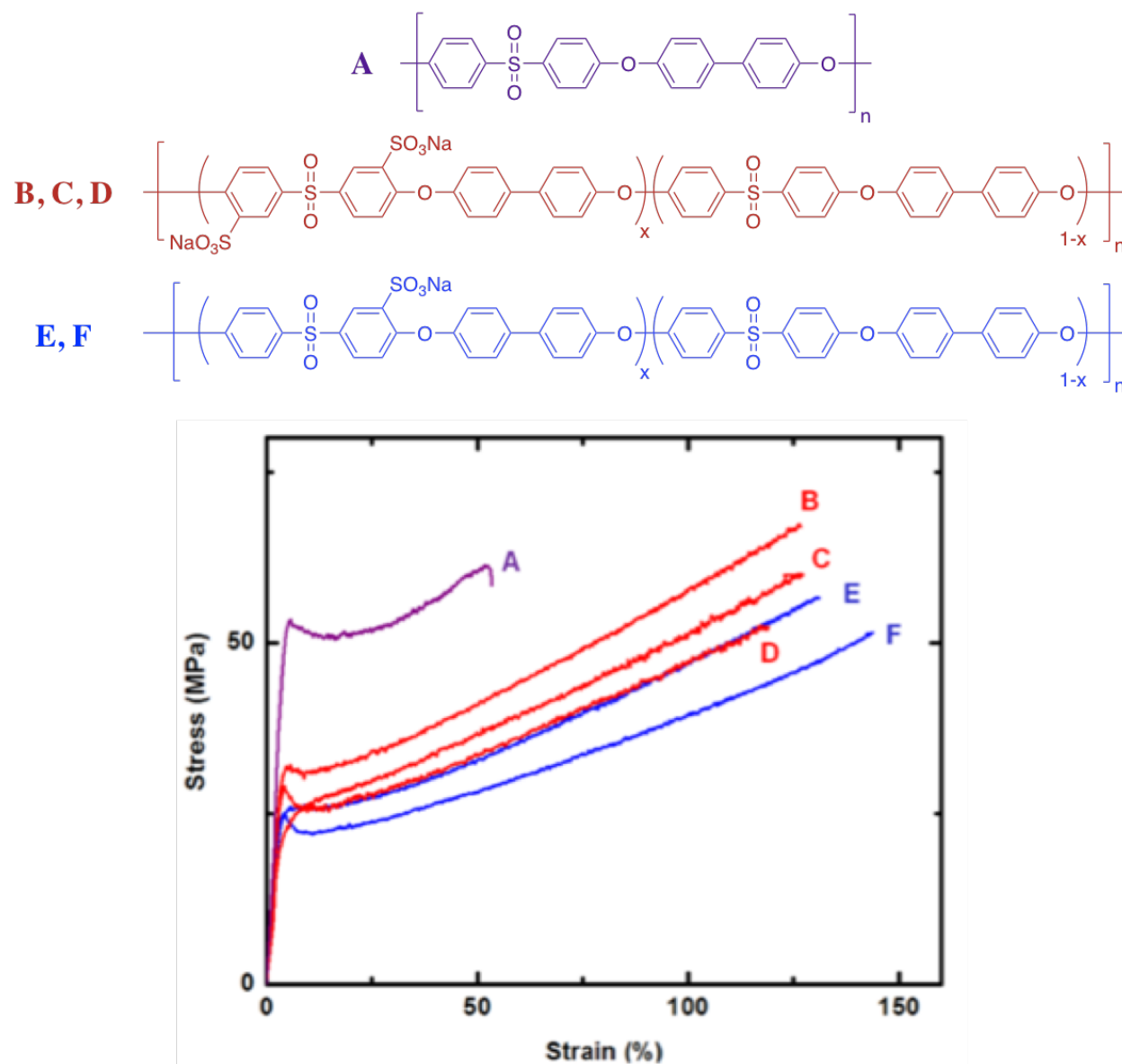


Figure 2. 5. Hydrated uniaxial mechanical properties and molecular structures of high molecular weight non-sulfonated PAES in purple, di-sulfonated PAES in red, and mono-sulfonated PAES in blue. Legend: A) *ns*-PAES; B) *ds*-PAES-22; C) *ds*-PAES-27; D) *ds*-PAES-32; E) *ms*-PAES-51 and F) *ms*-PAES-61; where “*ns*” - non-sulfonated, “*ds*” - di-sulfonated, and “*ms*” - mono-sulfonated

Within the two sets of directly polymerized sulfonated copolymers with increasing degrees of sulfonation, there was a decrease in both the elastic modulus and the yield stress of the polymers as the degree of sulfonation was increased. This is likely primarily due to the affinity of water for the polar sulfonate ions. This phenomenon can be attributed to water plasticization of the sulfonated polymers that correlates with their water uptake.

The transport properties of the copolymers containing the mono-sulfonated monomer with 51 and 61% of the repeat units sulfonated (i.e., *ms*-PAES-51 and -61) were compared to the copolymer that contained the di-sulfonated monomer with 32% of the repeat units di-sulfonated (i.e., *ds*-PAES-32) in Table 2. The fixed charge concentrations, defined as the moles of fixed charge groups per liter of sorbed water in the swollen polymer for *ms*-PAES-51, -61, and *ds*-PAES-32, are 4.28, 7.25 and 6.18 respectively. Generally, ion exchange membranes with higher fixed charge concentration exhibit stronger co-ion exclusion (i.e., Donnan exclusion).²¹ As shown in Table 2, the salt rejection of *ms*-PAES-51 is 99.25%, the highest among the three membranes due to strong Donnan exclusion. This is expected, however, since the water uptake of *ms*-PAES-51 is relatively low, and its water permeability is also lower than the other membranes.

Table 2. 2. Transport properties of *ds*-PAES-32, *ms*-PAES-51, and *ms*-PAES-61

Membrane Name	Salt Rejection (%)	Water Permeability, P_w (cm ² /s)	Salt Permeability, P_s (cm ² /s)	Permeability Selectivity (P_w/P_s)
<i>ms</i> -PAES-51	99.25±0.14	$(0.57±0.02) \times 10^{-6}$	$(8.31±1.20) \times 10^{-11}$	$(6.86±1.0) \times 10^3$
<i>ms</i> -PAES-61	98.65±0.63	$(2.09±0.26) \times 10^{-6}$	$(5.37±2.19) \times 10^{-10}$	$(3.90±1.59) \times 10^3$
<i>ds</i> -PAES-32	97.49±0.24	$(2.96±0.09) \times 10^{-6}$	$(1.48±0.12) \times 10^{-9}$	$(2.00±0.16) \times 10^3$

In the past, sulfonated poly(arylene ether sulfone)s have shown sensitivity towards a mixed monovalent/divalent cation feed source. Allegrezza *et al.* found that monovalent Na^+ rejection decreases with increasing divalent Ca^{2+} concentration for post-sulfonated Udel® polymer membranes.¹⁴ Sulfonated copolymers in the present work were analyzed for divalent cation sensitivity by subjecting both *ms*-PAES-51 and *ds*-PAES-32 copolymer membranes to a mixed monovalent/divalent feed source consisting of Na^+ and Ca^{2+} (Figure 2.6). The *ds*-PAES-32 copolymer membrane demonstrated increased Na^+ salt passage with increasing Ca^{2+} concentration,

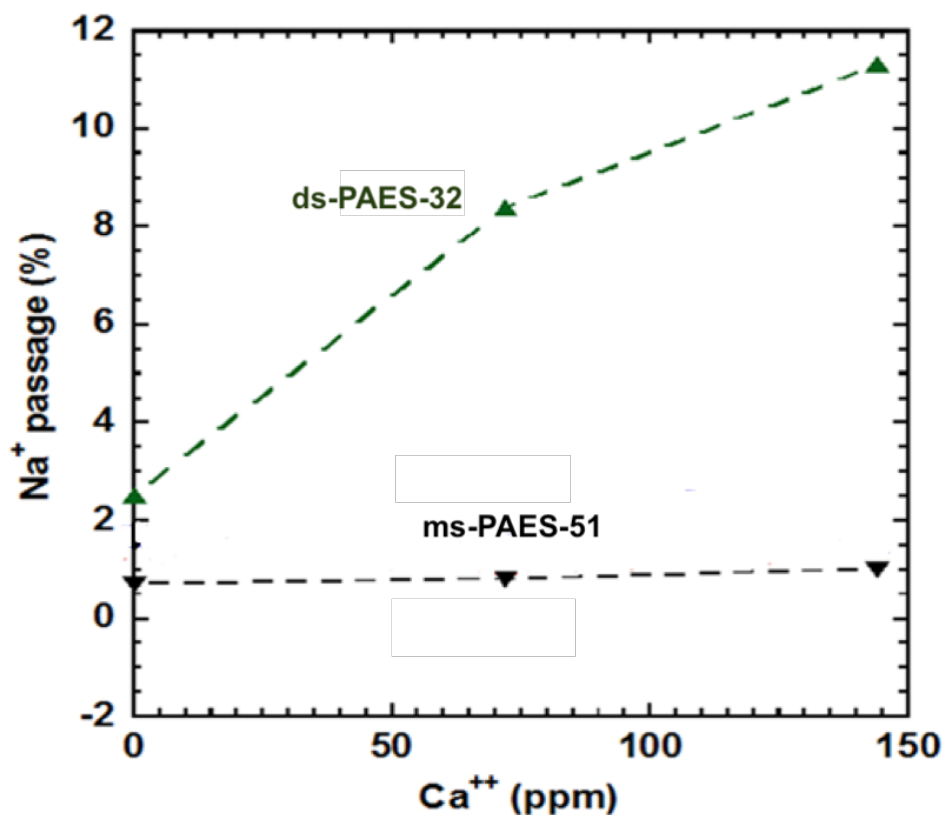


Figure 2.6. Comparison of *ms*-BPS-51 and *ds*-PAES-32 membranes Na^+ salt passage with mixed mono-divalent $\text{Na}^+/\text{Ca}^{2+}$ feed source at varying Ca^{2+} concentrations

and this is consistent with the research literature.²² The *ds*-PAES-32 membrane Na^+ passage = 2.51% at a Ca^{2+} concentration = 0 ppm, whereas the Na^+ passage = 11.5% at a Ca^{2+} concentration = 150 ppm. This divalent ion sensitivity can be attributed to reduction in Donnan exclusion where the divalent Ca^{2+} ion effectively neutralized the sulfonate fixed charged groups, and allowed for the substantial increase in monovalent Na^+ cation passage. However, the Na^+ passage with the *ms*-PAES-51 copolymer membrane was mostly unaffected by increasing the divalent Ca^{2+} concentration and remained at a steady-state Na^+ salt passage less than 1.0 %. It is hypothesized that this unexpected finding can be attributed to the increased spacing between sulfonate fixed charge groups along the polymer chain backbones.

2.5 Conclusions

The *ms*-DCDPS monomer was synthesized with a 55% yield by controlling the molar quantity of the electrophile to one per monomer and by limiting the isolation procedure to one recrystallization. HPLC-UV revealed completed isolation of the mono-sulfonated monomer from both non-sulfonated and di-sulfonated byproducts, and was used to determine the overall purity of the *ms*-DCDPS monomer with minor NaCl content. Sulfonated poly(arylene ether sulfone) copolymers were synthesized through direct polymerization of *ms*-DCDPS, DCDPS, and biphenol to afford high molecular weight polysulfones with varied sulfonate content depending on the ratio of sulfonated to non-sulfonated dihalide. The mono-sulfonated copolymers displayed excellent mechanical properties even when fully hydrated. The ability of each material to reject NaCl as were measured at 400 psi and 2000 ppm NaCl in the feedwater. The *ms*-PAES with 51% of the units mono-sulfonated had a high fixed charge concentration of 6.18, and also exhibited salt rejections in excess of 99%. Finally, the *ms*-PAES-51 copolymer salt rejection was mostly

unaffected by a mixed mono-divalent feed source with divalent Ca^{2+} concentrations up to 200 ppm.

Acknowledgements

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2.7 Supplementary Material

Table 2.S.1. NaCl concentration in *ms*-DCDPS by UV-Vis spectroscopy in comparison to HPLC with UV detection

1 st Recrystallization Analysis		
Compound	UV-VIS (wt %)	HPLC-UV (wt %)
<i>ms</i> -DCDPS	94.00	94.66
NaCl	6.00	5.34
R ²	0.982	0.999

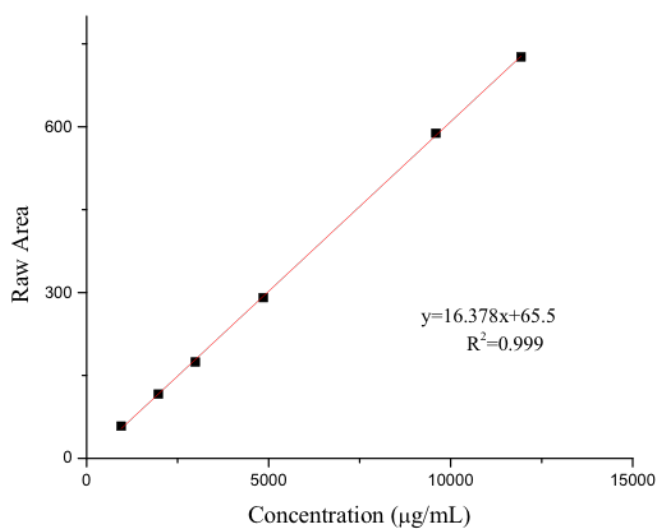


Figure 2.S.1 HPLC-UV Standard Calibration Curve of purified *ms*-DCDPS

Table 2.S.2. Molecular Weights of Sulfonated Poly(arylene ether sulfone)s

Polymer	M_n (kDa)	M_w (kDa)
High Molecular Wt.	87.5	127.5
ns-PAES	79.0	97.0
ds-PAES-22	56.4	97.0
ds-PAES-27	91.6	144.0
ds-PAES-32	32.2	51.4
ms-PAES-51	35.4	64.8
ms-PAES-61	47.1	93.3

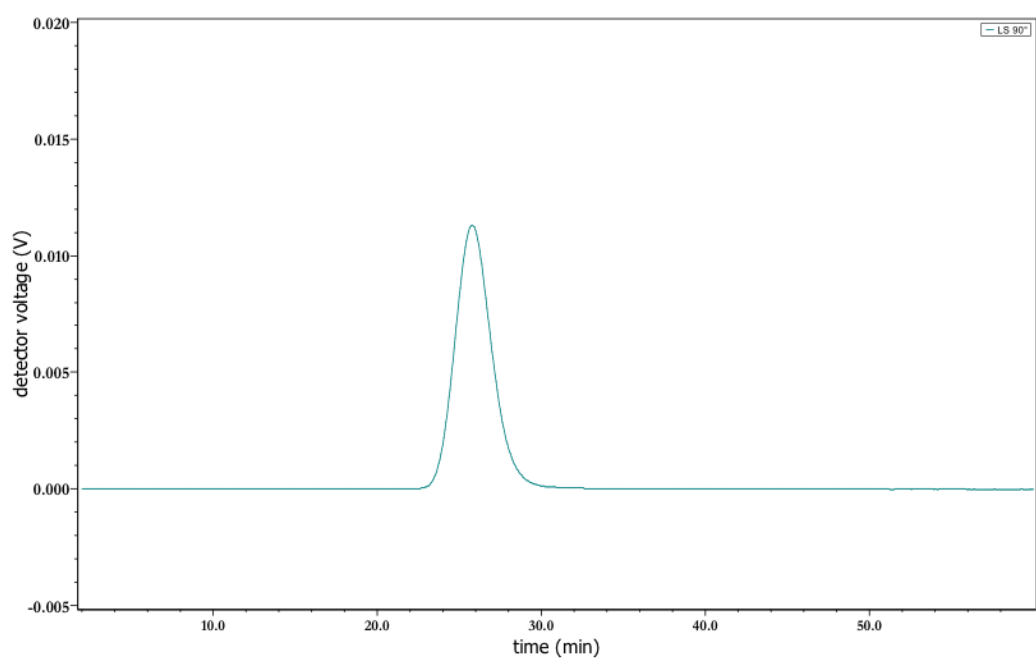


Figure 2.S.2 SEC light scattering chromatogram of sulfonated poly(arylene ether sulfone). 50% of the repeat units mono-sulfonated (high molecular weight)

CHAPTER 3: THERMAL AND UV FREE RADICAL CROSSLINKING OF SULFONATED POLY(ARYLENE ETHER SULFONE) TELECHELIC OLIGOMERS FOR POTENTIAL WATER DESALINATION MEMBRANE APPLICATIONS

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3.1 Abstract

In a one-pot reaction, a series of controlled molecular weight, phenol terminated, sulfonated poly(arylene ether sulfone) oligomers with varying degrees of sulfonation were synthesized by the direct polymerization of sodium 3-sulfonate-4,4'-dichlorodiphenylsulfone, 4,4'-dichlorodiphenyl-sulfone, and 4,4'-biphenol, and this was followed by functionalizing the phenol end groups with tetrafluorostyrene. Targeted molecular weight oligomers were obtained by controlling the stoichiometric quantities of the dihalide and biphenol monomers. ^1H NMR structural analysis confirmed the complete substitution of end groups with tetrafluorostyrene, and also confirmed that the targeted number average molecular weights of both 2,000 and 10,000 g/mol were achieved with either 50% sulfonation or 60% sulfonation of the repeat units. Size exclusion chromatography verified the molecular weights and distributions. Free-radical crosslinking of the sulfonated oligomers to form thin-films aided by an initiator were investigated by thermal and UV curing methods, without implementation of any additional cross-linking agents. Thermal curing revealed high degrees of crosslinking with gel fractions greater than 90% after only 20 minutes. UV-curing also achieved gel fractions greater than 87% after just 3 seconds of light exposure at a wavelength of 365 nm. Cross-flow testing of a crosslinked 50% sulfonated dense membrane consisting of the 10,000 g/mol oligomer, revealed salt rejection = $98.36 \pm 0.17\%$ with water permeability = $0.49 \pm 0.11 \times 10^{-6} \text{ cm}^2/\text{s}$.

3.2 Introduction

Sulfonated polysulfones can have excellent hydrated mechanical and transport properties suitable for reverse osmosis membranes provided the degree of sulfonation and the microstructure

are well controlled.¹⁻⁵ They can be synthesized either by incorporating sulfonated sulfone monomers or by post-sulfonation of preformed copolymers.⁶⁻¹³ The degree of sulfonation correlates with the hydrophilicity of the materials, which in turn controls the water uptake, salt rejection and water permeability. Using pre-sulfonated monomers, the degree of sulfonation can be precisely controlled by judicious choice of the ratio of mono- or di-sulfonated dichlorodiphenylsulfone relative to dichlorodiphenylsulfone.^{9,13} If post-sulfonation is implemented, then one relies on quantitative sulfonation of only the rings that are activated for electrophilic sulfonation. For example, if hydroquinone is incorporated along with bisphenol S and dichlorodiphenylsulfone, mild sulfonation parameters can be used to sulfonate only the hydroquinone rings since all of the other rings are deactivated against electrophilic sulfonation.¹⁰⁻¹² Random copolymer microstructures in all cases are dictated by the step-growth mechanism together with the fact that transesterification occurs throughout the nucleophilic aromatic substitution polymerization at the elevated temperatures that are employed.

State-of-the-art membranes for reverse osmosis are mostly aromatic crosslinked polyamides located at the top of a porous non-sulfonated polysulfone mechanical support. The aromatic polyamide separation layers are formed in an interfacial process as a highly crosslinked, ~100-200 nm thin film on the porous polysulfone. The transport properties of the polyamide class of membranes show excellent salt rejection and water permeability. However, the chlorine-containing disinfectants that are used in virtually all reverse osmosis processes degrade the polyamide membrane rather quickly.^{14,15} This requires that the water must be chlorinated prior to contacting the membrane, then the chlorine biocide must be removed. The water can then be purified by passing it through the membrane, then the biocide can again be added. It is established that aromatic sulfonated polysulfones are resistant to degradation by aqueous chlorine.^{4,16,17} For

example, chlorine tolerance was studied on a sulfonated polysulfone compared to a commercial polyamide thin film composite. Cross-flow filtration was utilized with a feed solution containing 2000 ppm of chlorine as NaOCl at pH 9.5. The NaCl rejection of the polyamide membrane decreased by >20% after only 10,000 ppm-hours (i.e., 20 hours), whereas the salt rejection of the sulfonated polysulfone membrane showed no change.¹⁶ Oxidation of the aromatic amide membranes by aqueous chlorine disinfectants proceeds via *N*-chlorination of the amide bond and then through an Orton rearrangement that results in chain scission.¹⁸⁻²² The chemically stable nature of the aromatic ether bonds in poly(arylene ether sulfone)s together with the lack of labile aliphatic C-H bonds improve stability against oxidative attack.

We have shown that crosslinking sulfonated poly(arylene ether sulfone)s with epoxy reagents by a step-growth mechanism to form films allows for better salt rejection at higher water permeabilities and increases the water-to-salt permeability selectivities.^{10,23} Sundell et al. prepared oligomers with 4,4'-disulfonate dichlorodiphenylsulfone, dichlorodiphenylsulfone and biphenol that were ~5,000 g/mole number average molecular weight and terminated on both ends with aromatic amine groups. The terminal amine groups were then crosslinked with a tetrafunctional epoxy reagent to form networks. In cross-flow filtration experiments, a crosslinked network with an ion exchange capacity of 1.48 meq/g showed a salt rejection of 96-97% with a water permeability of 0.36 L $\mu\text{m}/\text{m}^2$ h bar whereas an analogous linear membrane with an ion exchange capacity of 1.52 meq/g showed only 94% salt rejection with approximately equal water permeability. Roy Choudhury et al. synthesized aromatic amine terminated oligomers with ~5,000 and 10,000 g/mole molecular weights from dichlorodiphenylsulfone, bisphenol S and hydroquinone, then post-sulfonated those oligomers on the hydroquinone rings. Those oligomers were crosslinked with the same tetrafunctional epoxy reagent. At a given ion exchange capacity,

the crosslinked networks had lower maximum water uptakes relative to their linear counterparts. Moreover, a 10,000 g/mole epoxy network with an ion exchange capacity of 0.95 showed 98-99% salt rejection but with a higher water permeability of $\sim 0.2 \text{ L } \mu\text{m}^2 \text{ h bar}$ as compared to a linear copolymer with an ion exchange capacity of 0.88 meq/g that had approximately the same salt rejection but with a lower water permeability of $\sim 0.1 \text{ L } \mu\text{m}^2 \text{ h bar}$.

A free radical crosslinking reaction using a photosensitive initiator together with UV light has the potential for very rapid curing times. The epoxy crosslinking reactions discussed above require several hours for cure, whereas photochemically initiated free radical reactions can often be accomplished within seconds. Thus, a major objective of the present work was to develop a free radical, light-induced, rapid cure that would produce networks with good mechanical properties, and preserving the stability in the presence of aqueous chlorine biocides that has been established for poly(arylene ether sulfone) membranes. Our work describes the use of oligomeric sulfonated polysulfones with reactive free radical functionality only on the termini of the chains in order to obtain good mechanical properties. Tetrafluorostyrene end groups are utilized for rapid free radical crosslinking reaction induced by light.

Tetrafluorostyrene crosslinkable groups have been studied previously but most of the work has been directed to crosslinking polymers with fluorinated backbones for electronic applications. Ding et al. reported highly fluorinated poly(arylene ether sulfone)s from $\sim 7,000 \text{ g/mole}$ oligomers with tetrafluorostyrene reactive end groups. They cured these polymers thermally over several hours with either dicumyl peroxide or benzoyl peroxide as the initiator at elevated temperatures.^{24,25} Fluorinated poly(arylene ether ketone) oligomers with tetrafluorostyrene end groups were also reported that were cured thermally with benzoyl peroxide as an initiator.²⁶ Poly(arylene ether ketone)s and poly(arylene ether sulfone)s with highly fluorinated backbones

and with pendent tetrafluorostyrene groups were prepared and crosslinked both thermally and with light in the presence of a photoacid generator at elevated temperatures.²⁷ Both the thermally cured and the light/photoacid generator-cured networks were evaluated for their potential for fabricating optical waveguides.^{27,28} Pitois et al. introduced fluorinated dendrimers by copolymerizing pentafluorostyrene with a series of comonomers at elevated temperatures.²⁹

This manuscript describes the synthesis and free radical curing of tetrafluorostyrene terminated oligomers. To our knowledge, this is the first report of end-functional sulfonated polysulfone oligomers or of a method for their rapid curing using UV light. The crosslinkable membranes could improve salt rejection from previously studied linear counterparts by increasing the overall fixed charge concentration. Tetrafluorostyrene end groups may permit retention of stability against aqueous chlorine disinfectants.

3.3 Experimental

Materials

4,4'-Biphenol was provided by Eastman Chemical Company, recrystallized from toluene/ethanol, and dried *in vacuo* at 120 °C for 48 h. 4,4'-Dichlorodiphenylsulfone (DCDPS) provided by Solvay Advanced Polymers was recrystallized from toluene, and dried *in vacuo* at 120 °C for 48 h. The sodium form of 3-monosulfonate-4,4'-dichlorodiphenylsulfone (*ms*-DCDPS) was synthesized by a previously reported procedure and recrystallized from water.¹³ 2,3,4,5,6-Pentafluorostyrene was purchased from Oakwood Products and used as received. Potassium carbonate was purchased from Sigma-Aldrich and dried *in vacuo* at 160 °C for 72 h immediately prior to use. Sodium chloride, ethanol, isopropanol, and toluene were purchased from Fisher Scientific and used as received. Reagent grade diethylene glycol (DEG) and 2,2'-azobis(2-

methylpropionitrile) (AIBN) were purchased from Sigma-Aldrich and used as received. 2,4,6-Trimethylbenzoyldiphenyl phosphine oxide (TPO) was purchased from TCI America and used as received. Anhydrous *N,N*-dimethylacetamide was purchased from Chem-Impex International and stored over 5 Å molecular sieves.

Characterization

Nuclear Magnetic Resonance Spectroscopy (NMR). ^1H and ^{19}F NMR spectra were acquired with an Agilent U4-DD2 400 MHz spectrometer operating at 400 MHz for ^1H spectra and 376 MHz for ^{19}F spectra. Chemical shifts are reported in ppm relative to an internal solvent resonance. All spectra were acquired with 10% (w/v) solutions in DMSO- d_6 .

Size Exclusion Chromatography (SEC). Molecular weight analyses are conducted using an Agilent 1260 Infinity system, which included an isocratic pump, autosampler, online degasser, and column oven equipped with 3 Agilent PL-gel 10-mm Mixed B-LS 300 x 7.5 mm columns (polystyrene/divinylbenzene) connected in series with a guard column. A multi-angle laser light scattering detector (DAWN-HELEOS II, Wyatt Technology Corp.), operating at a wavelength of 658 nm, and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corp.) provided online results. Both the columns and detectors were operated at 50 °C. The mobile phase was DMAc containing 0.1 M LiCl. The system was adjusted for delay and band broadening using a polystyrene standard ($M_n = 18.3$ kg/mol). ASTRA 6 software was implemented for data acquisition and analysis. Refractive indices were calculated online assuming 100% recovery.

UV-Visible Spectroscopy (UV-Vis). UV-Vis spectra were acquired with an Agilent Cary 100 Bio UV-Vis spectrophotometer. All measurements were conducted in a 1-cm path length

quartz cuvette at room temperature in methanol. All absorbance measurements were performed at a range from 300 to 400 nm with a concentration of 3×10^{-5} M.

Fourier-Transform Infrared Spectroscopy (FTIR). FTIR spectra were acquired with a Thermo Scientific Nicolet iS50 FTIR spectrometer and analyzed with SpectraGryph 1.2 spectroscopy software. *In situ* thermal crosslinking was conducted at 80 °C on NaCl salt plates and double bond loss was monitored at 935 cm^{-1} . UV crosslinking was determined by comparing the spectra of a non-UV irradiated versus a UV irradiated film. Double bond loss was monitored at 935 cm^{-1} .

Synthesis

Sulfonated Polysulfone Oligomer Terminated with Crosslinkable Tetrafluorostyrene Endgroups. A synthetic procedure for preparing a 10,000 g/mol number average molecular weight oligomer with 50% of the units sulfonated and with tetrafluorostyrene end groups is provided. DCDPS (38.43 mmol, 11.04 g), *ms*-DCDPS (38.43 mmol, 14.96 g), 4,4'-biphenol (80.55 mmol, 15.00 g), potassium carbonate (96.66 mmol, 13.35 g), dimethylacetamide (240 mL), and toluene (25 mL) were added to a 500-mL three neck round bottom flask equipped with a mechanical stirrer, Dean-Stark trap, condenser, and nitrogen inlet. The reaction vessel was immersed in an oil bath and heated to 150 °C to azeotropically dry the mixture for 4 h. The toluene was drained from the Dean-Stark trap and the oil bath temperature was increased to 180 °C for 48 h. The reaction was allowed to cool to room temperature, then pentafluorostyrene (72.44 mmol, 10 mL) was added to the reaction vessel, and the mixture was heated to 110 °C and maintained for 2 h. The reaction was diluted with dimethylacetamide (80 mL) and filtered hot to remove residual salts. The reaction mixture was precipitated in stirring isopropyl alcohol (2500 mL), resulting in a white polymer.

The polymer was filtered and added to stirring deionized water (3000 mL) at room temperature overnight to remove salts and residual DMAc. The polymer was isolated and dried in vacuo at 65 °C for 48 h to obtain an 87% yield.

Copolymers with number average molecular weights of 2,000 g/mol were synthesized in a similar manner by adjusting the ratio of the biphenol monomer relative to the dihalide monomers according to the Carrother's equation. Copolymers with 60% of the units sulfonated were prepared by adjusting the ratio of *ms*-DCDPS to DCDPS.

Film Casting and Crosslinking

Thermal Crosslinking. Polymer films for thermal curing were prepared by dissolving either the 2,000 or 10,000 g/mol oligomers (0.4 g) in DMAc (1 mL). AIBN (20 mg) was added to the solution containing the 2,000 g/mol oligomer and AIBN (8 mg) was added to the solution containing the 10,000 g/mol oligomer. The polymer solutions were sparged with nitrogen for 10 min at rt. The polymer solution was poured onto a preheated 4" x 4" glass plate at 80 °C in an oven purging with nitrogen. A doctor's blade set to a 50- μ m thickness was used to spread the polymer solution across the glass plate. Each film was crosslinked for 20 min at 80 °C. The film was submerged in DI water to delaminate it from the glass plate, then boiled in DI water for 2 h to remove residual DMAc. soaked in 2 M NaCl for 2 d to convert the salts to the sodium form, then soaked in DI water for 1 day (changing the water several times) to remove excess salts from the films. The films were stored in DI water.

UV Crosslinking. The oligomer (or blend of different molecular weight oligomers) (0.8 g) was dissolved in 8 mL of DMAc. The solution was filtered through a 0.45 μ m Teflon syringe filter. A stock solution of TPO was prepared by dissolving 20 mg of TPO in 1 mL of filtered DMAc.

The stock solution (0.2 mL) was added to the oligomer solution and stirred for ~30 min. A 5'' x 5'' glass plate was leveled on a heated block at 75 °C. The oligomer solution containing the TPO photoinitiator was poured onto the glass plate and heated at 75 °C for 2 h to concentrate the solution. The plate was immediately transferred to a Phoseon FireJet FJ800 UV curing chamber operating at a wavelength of 365 nm with a maximum intensity of 0.6 Watts and cured at ~65 °C at a distance of 7'' from the lamp and controlled with a FireJet FJ800 controller at 50% intensity for 3 s. The curing energy was ~430 mJ/cm². The film was dried overnight at 80 °C at ambient pressure, then for 24 hours at 80 °C under vacuum in a vacuum oven. The film was allowed to cool to rt, then delaminated from the plate by immersion in DI water. It was boiled in DI water for 2 h to remove residual solvent, soaked in 2 M NaCl for 2 d to convert the salts to the sodium form, then soaked in DI water for 1 day (changing the water several times) to remove excess salts from the films. The films were stored in DI water.

Characterization of Films

Gel-Fractions. Crosslinked films were dried *in vacuo* at 80 °C overnight. Dried films were analyzed by thermogravimetric analysis to determine residual solvent content as a weight percent. After drying, 0.1 - 0.3 g of polymer film was inserted into a 6-dram glass vial immersed in DMAc at rt for 24 h (stirring/heating provided similar results). The polymer gel was filtered and transferred to a pre-weighed 6-dram glass vial, which was dried *in vacuo* overnight at 110 °C. The vial/polymer was allowed to return to rt under vacuum and weighed. Once again, TGA was implemented to verify residual solvent content as a weight percent to accurately determine the gel fractions. Gel fractions were calculated by Equation 1 using 3 measurements for each film.

$$Gel\ Fraction\ (\%) = \frac{Final\ mass\ of\ extracted\ film}{initial\ mass\ of\ dried\ film} \times 100 \quad (1)$$

Water Uptake. The water uptakes of the membranes in their sodium salt form were determined gravimetrically. For water uptake measurements of the membranes in the sodium salt form, membranes in the K⁺ salt form were soaked in 2M NaCl solution for 2 days. These membranes were soaked in DI water to remove free NaCl from the membrane and then weighed. The water uptake of the membranes was calculated according to Equation 2, where mass dry and mass wet refer to the masses of the dry and the wet membranes, respectively.

$$Water\ Uptake\ (\%) = \frac{Mass_{wet} - Mass_{dry}}{Mass_{dry}} \times 100 \quad (2)$$

Ion Exchange Capacity (IEC). The IECs were determined by titrating the 2,000 and 10,000 g/mol oligomers (crosslinked networks provided inconsistent results). The oligomer films in their salt form were boiled in 1 M H₂SO₄ for 3 h to convert to the acidic form. The oligomers were boiled in DI water for 2 h and subsequently filtered and washed with DI water to remove residual H₂SO₄. The oligomers were dried under vacuum overnight at 120 °C. The dried oligomers were weighed and allowed to soak in aqueous 2 N NaCl for 48 h to convert the oligomers to their sodium salt form and release HCl. The solution was titrated with a standard 0.05 M NaOH solution. The theoretical IECs of the cured films were calculated by Equation 3, where IECs are reported in units of meq/g, V = volume of NaOH, N = the normality of NaOH, and M = mass of the dry oligomer.

$$IEC = \frac{V * N}{M} \times 1000. \quad (3)$$

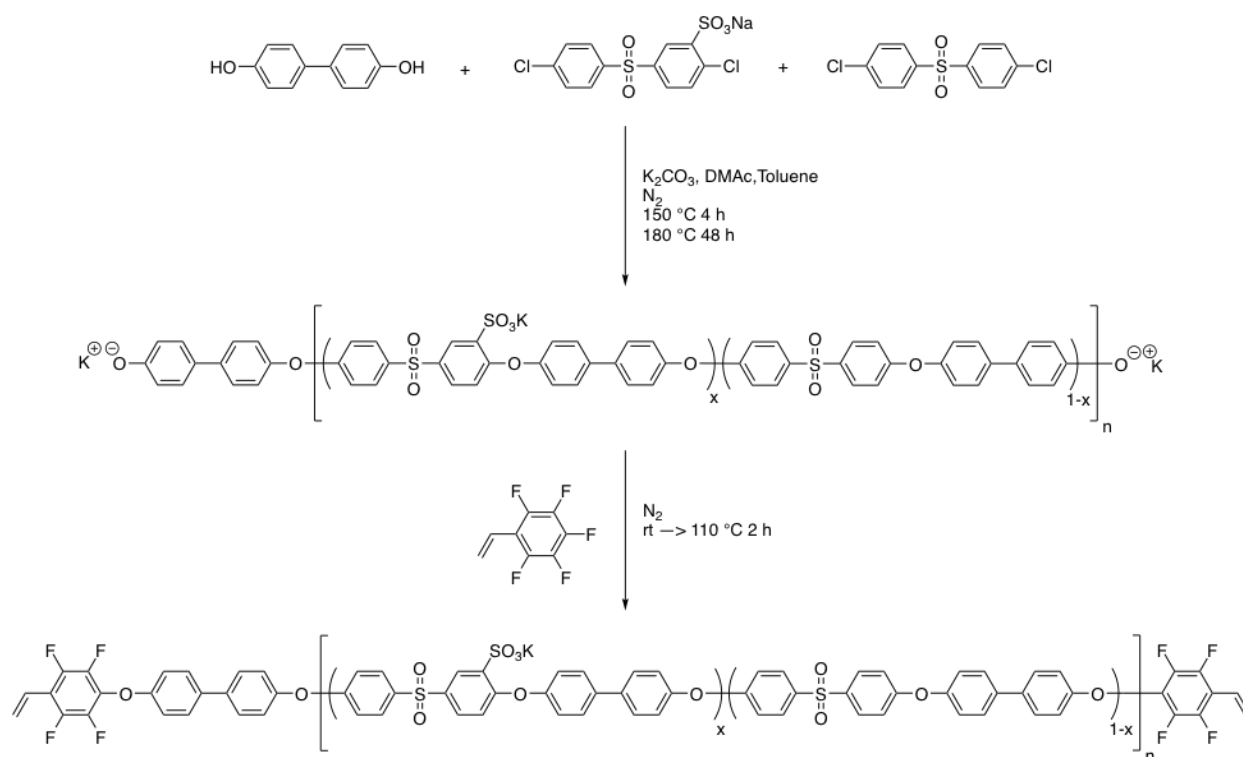
Transport Properties. Transport properties of the membranes were measured using a cross-flow filtration system. The concentration of the feed solution was 2000 ppm NaCl. The applied transmembrane pressure was 400 psi and the flowrate was 3.8 L/min (1 gpm). The feed solution temperature was maintained at 25 °C using a NesLab RTE 7 circulating bath (Thermo Electron Corporation, Waltham, MA). The pH of the solution was adjusted to approximately 7 using a sodium bicarbonate solution. The mass and conductivity of the permeate samples were measured to determine water permeability ($\text{L } \mu\text{m m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ or $\text{cm}^2 \text{ s}^{-1}$), salt permeability ($\text{cm}^2 \text{ s}^{-1}$), salt rejection (%), and water/NaCl selectivity.

Tensile Testing of Fully Hydrated Films. The membranes were cut into dogbone samples with a gauge width of 3.18 mm and gauge length of 25 mm, Type V according to ASTM D638-14, using a Cricut Explore One™ stencil cutter. Four samples with uniform thickness of 60-70 μm from each membrane were tested. The thickness of the dogbones were measured at four points along the gauge length using a Mitutoyo digimatic micrometer model MDC-1^{re} SXF. A hydrated testing cell was secured onto the Instron to test samples under fully hydrated conditions. The wet samples were loaded into the cell of the Instron and the cell was filled with DI water. The samples were immersed in DI water for at least 24 h prior to testing and allowed to equilibrate in the Instron in the water for 3 min. Uniaxial load tests were performed using an Instron ElectroPuls E1000 testing machine equipped with a 250-N Dynacell load cell. The crosshead displacement rate was 10 mm/min and the initial grip separation was 25 mm. The hydrated stress-strain curves were smoothed using a 6-point moving average.

3.4 Results and Discussion

Synthesis and Characterization of Tetrafluorostyrene Endcapped Oligomers

Randomly sulfonated poly(arylene ether sulfone) oligomers were synthesized by direct polymerization of biphenol, *ms*-DCDPS, and DCDPS monomers by nucleophilic aromatic substitution polycondensation as shown in Scheme 1. Tetrafluorostyrene endcapped oligomers with controlled molecular weights were achieved in a two-step, but one-pot, sequence. The Carother's equation was implemented for step one to adjust the stoichiometric quantities where molecular weight of the oligomers was controlled with excess biphenol monomer. The reaction mixture was initially azeotropically dried with toluene to remove any water that could have hydrolyzed the aryl chlorides and thus adversely affect the polymerization. After polymerization, the reaction mixture was cooled to room temperature and a sample was taken to determine the molecular weight of the biphenol terminated oligomer by SEC. This was done to avoid having to conduct SEC on an oligomer with styrenic reactive end groups on it. After polymerization and lowering the temperature to room temperature, 2,3,4,5,6-pentafluorostyrene was injected into the reaction flask at a molar ratio of five equivalents with respect to phenolate end groups as shown in Scheme 1. The temperature was raised to 110°C and maintained for two hours, then the copolymer was isolated to achieve an overall yield of 87%. The end group reaction (step two) at the relatively low temperature of 110 °C was possible due to the very high reactivity of the pentafluorostyrene molecule towards nucleophilic aromatic substitution. This approach was desirable to avoid any thermal reaction of the styrenic double bond during the polymerization.



Scheme 3. 1. Polymerization of telechelic sulfonated poly(arylene ether sulfone) oligomers with tetrafluorostyrene end groups

^1H and ^{19}F NMR analysis confirmed the molecular structure and showed that the number average molecular weights corresponded with the targeted molecular weights (Figures 1 and 2 and Table 1). The integrals for the resonance of proton ‘h’ corresponding to the protons on the C-H bonds adjacent to the electron withdrawing sulfonate group were compared to the integrals from resonance ‘k’ that represents the protons on the carbons adjacent to the ether oxygens of the biphenyl moieties in both repeat unit structures (Figure 1). The approximately 1:8 ratio of the integrals in the spectrum in Figure 1 shows that ~50% of the repeat units contain a sulfonate ion as targeted. The phenol OH end group protons disappear as expected upon adding the pentafluorostyrene. The ^{19}F NMR spectra display the fluorine resonances of the pentafluorostyrene endcapper (Figure 2, bottom) and a tetrafluorostyrene endcapped 10,000 g/mol oligomer (Figure

2, top). The spectra suggest complete substitution at the *para* position of the pentafluorostyrene endcapping agent by the polymer phenolate end groups. The ^{19}F NMR spectrum of the telechelic tetrafluorostyrene terminated copolymer shows the complete disappearance of the *para* fluorine from the endcapper (peak ‘e’ in the bottom of Figure 2), and the appearance of only two resonances at -144 ppm corresponding to the fluorines *ortho* to the vinyl group and -156 ppm due to the fluorine substituents *meta* to the vinyl group with an integral ratio of 1:1 (Figure 2, top).²⁴

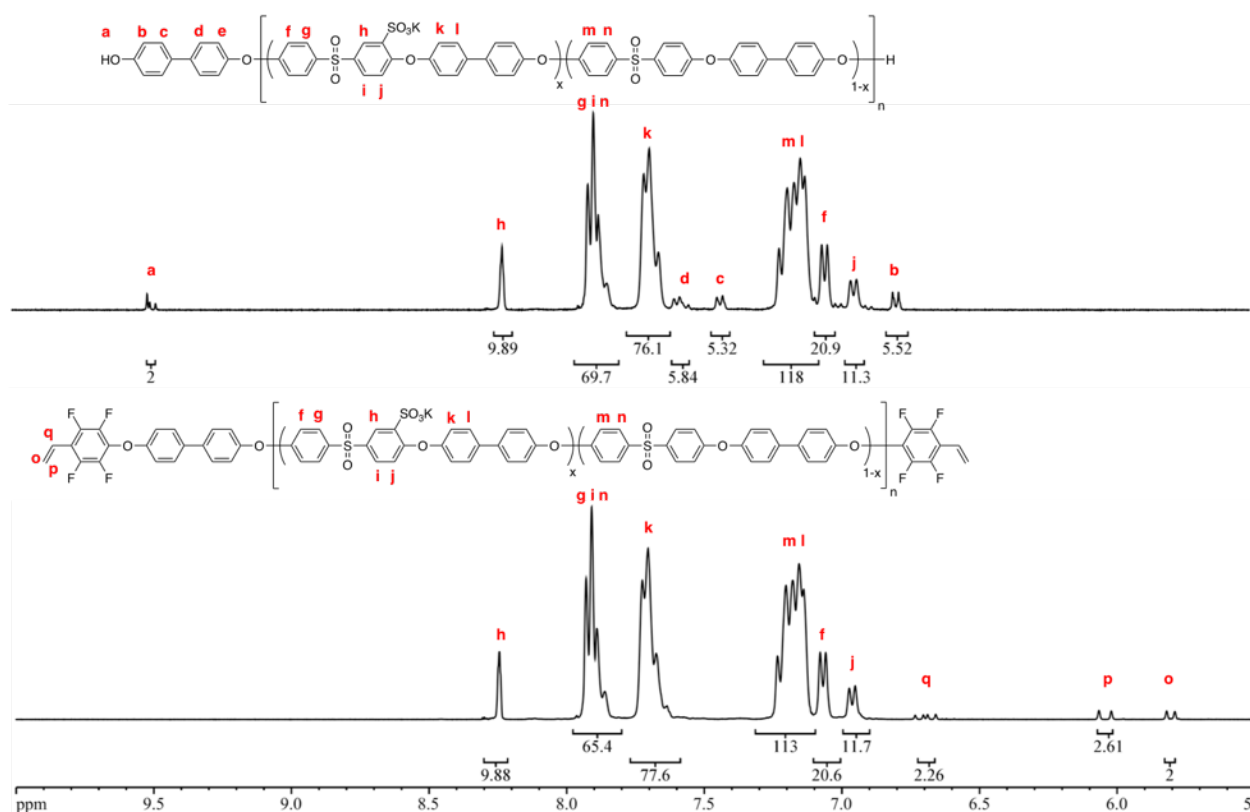


Figure 3. 1. ^1H NMR overlay of targeted 10,000 g/mol oligomers with 50% of the repeat units containing the monosulfonated *ms*-DCDPS. Resonance “e” is unassigned.

It was reasoned that the *para* and *ortho* positions relative to the vinyl group on the pentafluorostyrene should be the most active toward nucleophilic aromatic substitution since the vinyl group would be positioned to stabilize the Meisenheimer complex in the intermediate. The

low reaction temperature and excess pentafluorostyrene endcapping agent were utilized to avoid any di- or tri-substitution from potentially occurring. Other targeted molecular weight oligomers followed similar findings.

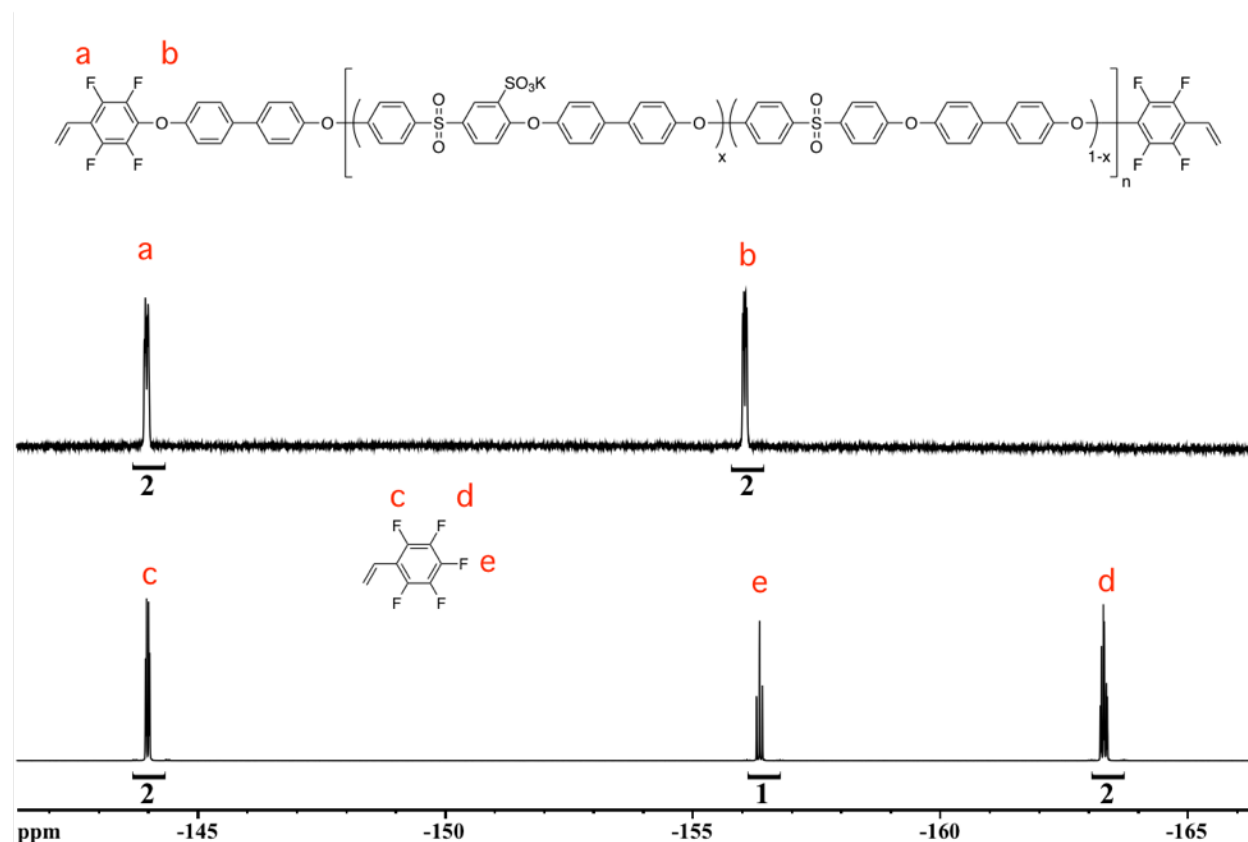


Figure 3. 2. ^{19}F NMR overlay of targeted 10,000 g/mol oligomers with 50% incorporation of *ms*-DCDPS repeat unit and pentafluorostyrene

SEC analyses were conducted with dry DMAc containing 0.1 M LiCl with absolute weight average molecular weights analyzed by light scattering at 50 °C (Figure 3 and Table 1). Precaution was taken when determining the molecular weights. The phenol endcapped oligomers were analyzed because it was believed that the tetrafluorostyrene endcap could possibly react in the columns under the SEC conditions, and damage the overall SEC system. The SEC traces of the targeted 2,000 and 10,000 g/mol oligomers with 50% incorporation of the repeat units containing

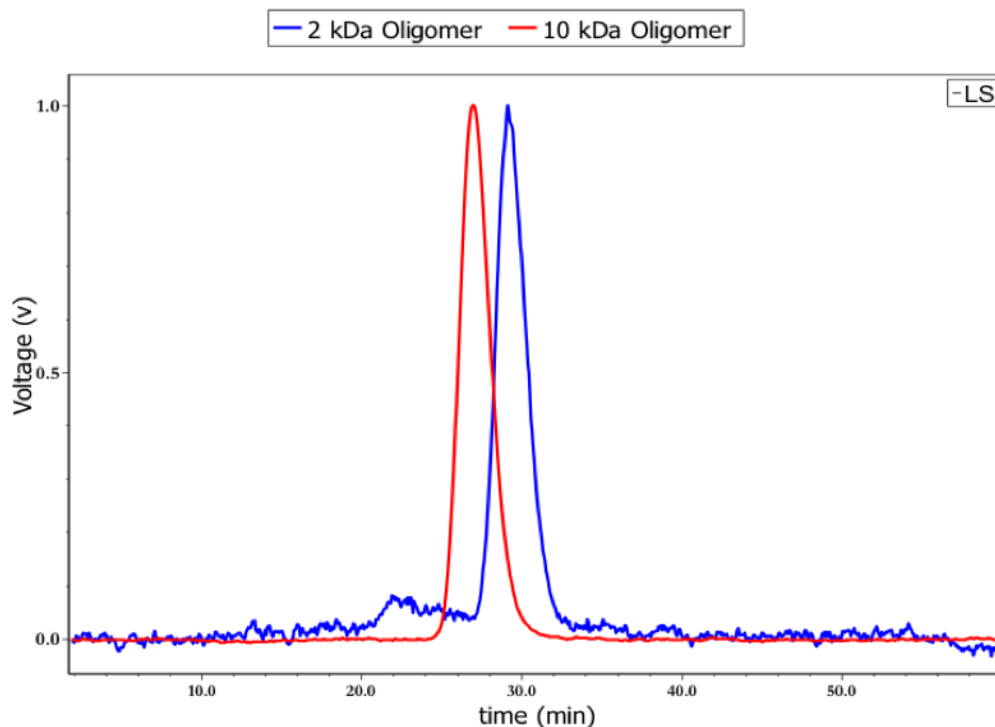


Figure 3. 3. SEC chromatograms of targeted 2,000 and 10,000 g/mol oligomers with 50% incorporation of *ms*-DCDPS repeat units and with biphenol endgroups

the *ms*-DCDPS unit display unimodal distributions and cyclic low molecular weight counterparts appear to be absent, as shown in Figure 3. The other targeted 2,000 and 10,000 g/mol oligomers with 60% incorporation of the *ms*-DCDPS repeat unit yielded similar results.

The number average and weight average molecular weights are provided in Table 1. Number average molecular weights from ^1H NMR were calculated using the oligomers with tetrafluorostyrene endgroups where the proton resonance “o” (bottom of Figure 1) was assigned an integration value of 2 (2 end groups per oligomer) and all other integration values were established relative to that peak. It was noted that the phenol proton resonance “a” in the top spectrum of Figure 1 was too broad to be utilized quantitatively. Calculated number average molecular weights from the NMR spectra demonstrated that approximately the targeted values were achieved through polymerization and SEC number average molecular weights supported

those findings. Weight average molecular weights were obtained by light scattering analysis with SEC and are displayed in Table 3.1 Number average molecular weights by SEC were calculated using Wyatt Technology's Astra software. It is noted that some of the PDI values are lower than those expected for polycondensation ($PDI < 1.5$), and it is not clear why this is the case.

Table 3. 1. Molecular weight analyses for oligomers with targeted number average molecular weights of 2,000 and 10,000 g/mol and with 50% and 60% sulfonated repeat units

Polymer Targeted M_n	Monsulfonated Repeat Units (%)	^1H NMR	SEC	
		M_n^a (g/mol)	M_n^b (g/mol)	M_w^b (g/mol)
2,000	50.0	2,400	2,200	5,800
2,000	60.0	2,100	2,300	5,800
10,000	50.0	9,600	9,600	16,900
10,000	60.0	9,300	12,900	18,700

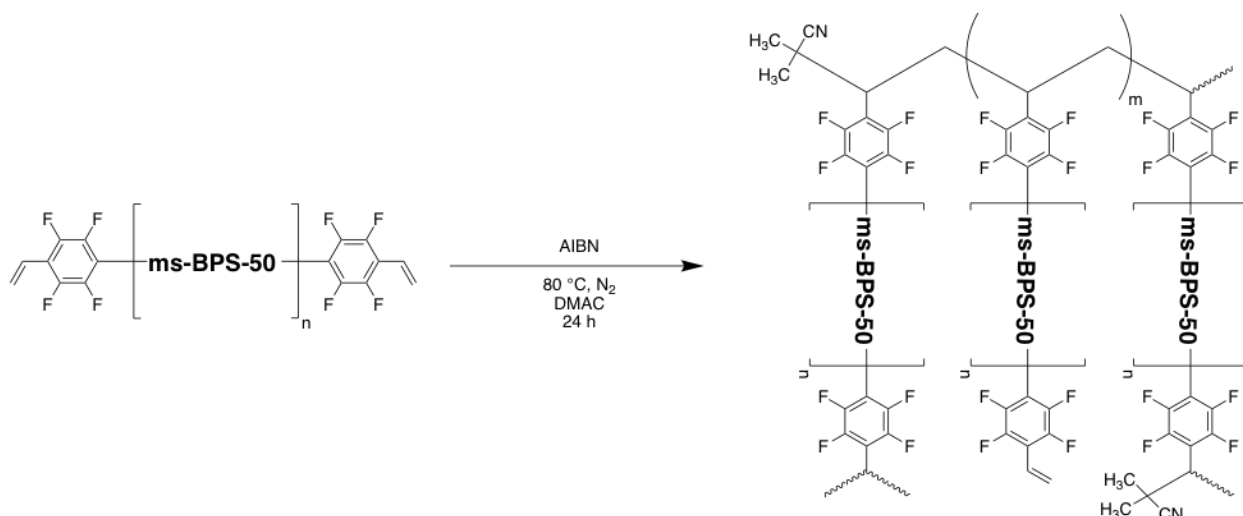
^aCalculated with tetrafluorostyrene endgroups as in the bottom spectrum of Figure 1

^bCalculated with biphenol endgroups as in the top spectrum of Figure 1

Thermal Crosslinking

Tetrafluorostyrene endcapped oligomers with controlled molecular weights were investigated to determine the optimal thermal crosslinking reaction conditions that would produce a highly crosslinked film. Oligomer concentration, initiator concentration, and thermal curing time were examined. A closed system was initially used to prevent solvent loss by curing solutions sealed in a vial, then the findings were applied to study fabrication of thin films.

The oligomer(s) and initiator (AIBN) were dissolved in DMAc in a glass vial. DMAc was chosen because both components dissolve in this organic solvent and AIBN is a commonly used thermal crosslinking initiator. The contents were then sealed with a rubber septum and sparged with nitrogen for 10 minutes to remove unwanted oxygen that could potentially influence the thermal crosslinking reaction. The vials with the reaction contents were heated at 80 °C for 24 hours. The temperature was chosen in large part due to the thermal degradation half-life of AIBN at 80 °C being ~one hour and it was believed that this might also avoid rapid solvent loss during film casting. The general reaction is shown in Scheme 2.



Scheme 3. 2. Thermal free radical crosslinking of tetrafluorostyrene functional oligomers

The thermal crosslinking reactions were characterized by measuring gel fractions of the resultant networks. Our goal was to attain a gel fraction greater than ~90% to achieve solvent resistant network films. The polymer concentration was evaluated over a range from 0.1 to 0.6 g/mL in solution while keeping the initiator concentration constant. Such conditions differ substantially from those normally employed for free radical polymerizations because the double

bond concentration is unusually low, due both to the amount of non-reactive solvent and also to the nature of the telechelic oligomers. The 2,000 and 10,000 kDa oligomers with 50% of the repeat units containing the *ms*-DCDPS repeat unit were crosslinked with 5 and 2 wt % of AIBN, respectively, based on the polymer weight. The gel fractions are shown in Figure 3 and Table 2.

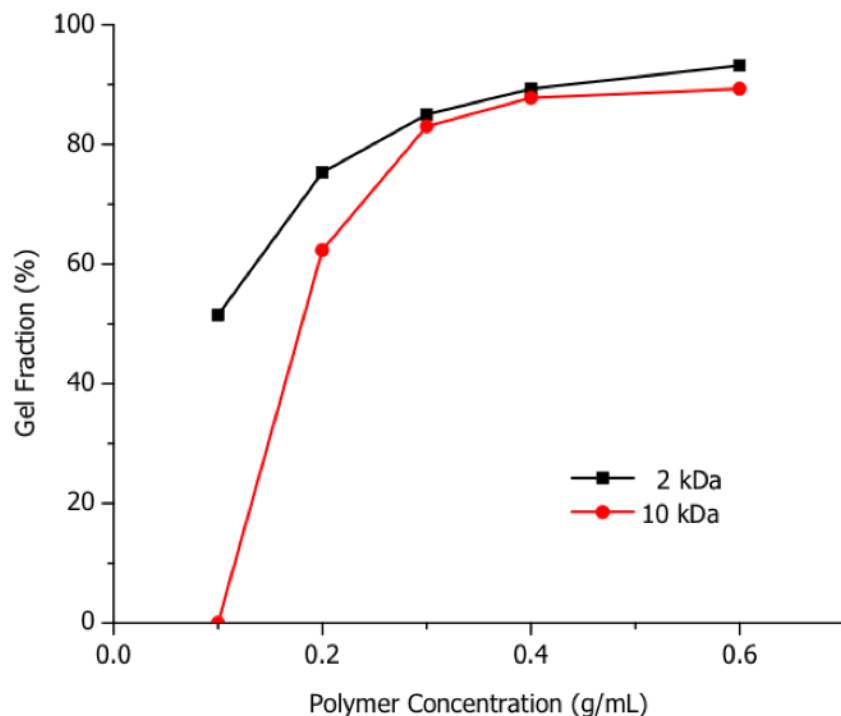


Figure 3. 4. Gel fractions vs. the amount of polymer dissolved in one mL of DMAc of networks prepared by thermally crosslinking telechelic 2,000 and 10,000 kDa oligomers endcapped with tetrafluorostyrene end groups. 50% of the repeat units in each polymer contained *ms*-DCDPS. “Mol. Eq.” refers to the equivalents of AIBN per styrenic double bond.

With a low polymer concentration of 0.1 g/mL, the 2,000 g/mol oligomer yielded a gel fraction of 51.5%, and attempts at crosslinking the 10,000 g/mol oligomer under these conditions did not produce any gel. At these low polymer concentrations combined with the high initiator concentrations employed, it is postulated that interchain propagation reactions are too slow relative to termination. Increasing the polymer concentration overcame this issue (see Figure 3). It was

found that a gel fraction greater than 89 % was achieved for both the 2,000 and 10,000 g/mol crosslinking systems at a polymer concentration of 0.6 g dissolved in one mL of DMAc. Figure 3 shows the crosslinking to plateau at this concentration. This is characteristic of a Trommsdorff effect where increases in viscosity of the system lead to slower diffusion and less termination.

Table 3. 2. Thermal curing effects of polymer concentration with respect to Gel Fraction (%) of both 2 and 10 kDa oligomers with 50% incorporation of *ms*-DCDPS repeat units

Amount of polymer dissolved in 1 mL DMAc (g)	2 kDa Gel Fraction (%)	10 kDa Gel Fraction (%)
0.1	51.5	0
0.2	75.3	62.3
0.3	85.0	83.0
0.4	89.3	87.8
0.6	93.2	89.3

The impact of initiator concentration was examined to determine whether the high concentration was generating too many free radicals that quenched the degree of crosslinking through termination of the propagating end groups, even at the higher polymer concentrations. The effect of initiator concentration was studied using the 10,000 g/mol oligomer at a polymer concentration of 0.4 g of polymer dissolved in one mL of DMAc over an initiator concentration range from 0 to 2 wt %. It was expected that the 2,000 g/mol oligomer would react similarly. The gel fractions with respect to initiator concentration are shown in Figure 4 and Table 3.

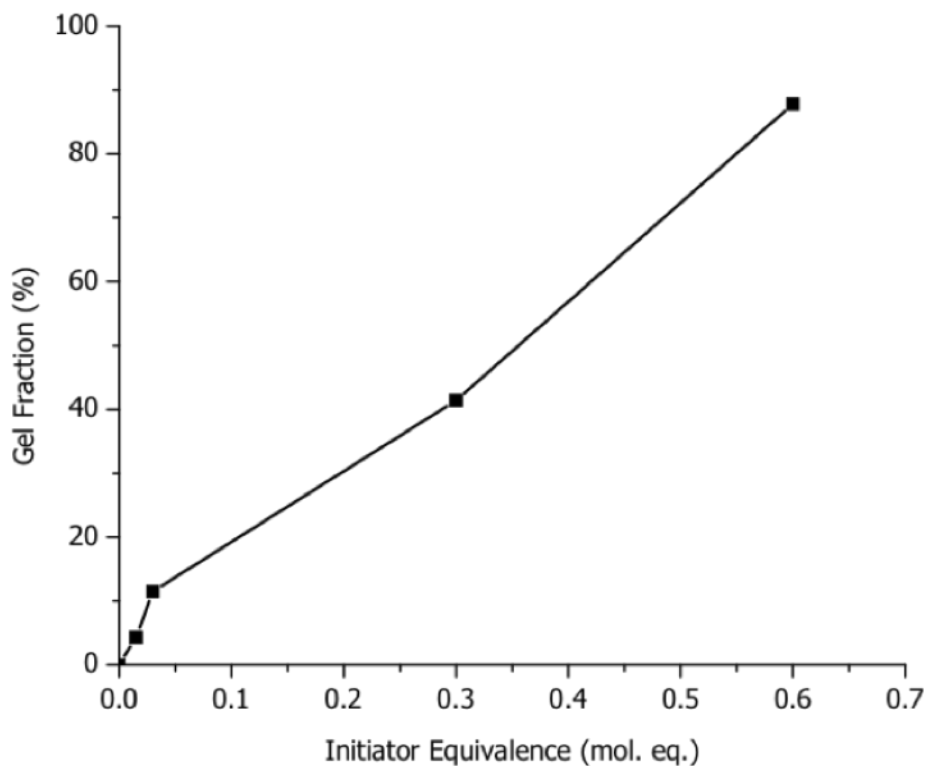


Figure 3. 5. Gel fractions upon thermal crosslinking as a function of initiator concentration using the 10 kDa oligomer with 50% incorporation of the *ms*-DCDPS repeat unit

No gel was observed with 0 wt % initiator, thus demonstrating that the fluorinated styrenic groups were relatively thermally stable. This was considered an attribute relative to the known lability of acrylate end groups because storage stability and the stability of the fluorinated styrenic double bonds during synthesis of the functional oligomers could be more easily handled. Figure 4 illustrates that the lower initiator concentrations did not result in significant gel fractions for the thermally cured 10,000 g/mol system, but the gel fraction reached as high as 87.8 % at 0.6 equivalents of AIBN relative to the number of double bonds over the 24 hour curing time. It is noteworthy that very few interchain reactions are needed for a 10,000 g/mole oligomer to reach a high molecular weight. The high concentration of initiator is characteristic of thermal crosslinking of telechelic oligomers without any addition of a small molecule crosslinking agent.^{30,31} Thus, both a high polymer concentration and a high initiator concentration are imperative for obtaining

sufficient gel fractions of sulfonated polysulfone oligomers endcapped with tetrafluorostyrene groups.

Table 3. 3. Thermal curing effects of initiator concentration with respect to gel fraction of a 10 kDa tetrafluorostyrene terminated oligomer containing 50% of *ms*-DCDPS repeat units

Initiator (wt. %)	Initiator (mol. eq.)	Gel Fraction (%)
0	0	0
0.05	0.015	4.3
0.1	0.03	11.5
1	0.3	41.4
2	0.6	87.8

In situ FT-IR analysis was employed to examine loss of the end group double bonds while thermally curing with AIBN at 80 °C. Two observable peaks associated with the double bonds were found at 935 cm⁻¹ and 973 cm⁻¹ (Figure 5). The 935 cm⁻¹ peak was used for monitoring double bond loss because the 973 cm⁻¹ peak was nearer to a large absorption peak at higher wavenumbers. A sample of the 2,000 g/mol oligomer at a polymer concentration of 0.4 g dissolved in one mL of DMAc that contained 5 wt% of AIBN (based on polymer weight) was thermally cured between two NaCl salt plates at 80 °C. The 2,000 g/mol oligomer was chosen rather than the 10,000 g/mol oligomer due to the higher concentration of styrenic double bonds. FT-IR spectra were recorded at 0, 10, 30, and 120 min as shown in Figure 5. The FT-IR spectra at 935 cm⁻¹ revealed the disappearance of 90 % of the double bonds after 10 minutes. This value was calculated by

integration and normalization with respect to the DMAc background noise. The peaks observed at 30 and 120 min did not show further double bond loss. It is reasoned that this behavior could be related to an increase in viscosity. Thermal crosslinking of the 2,000 g/mol system demonstrated that a fast curing rate was possible that resulted in high gel fractions.

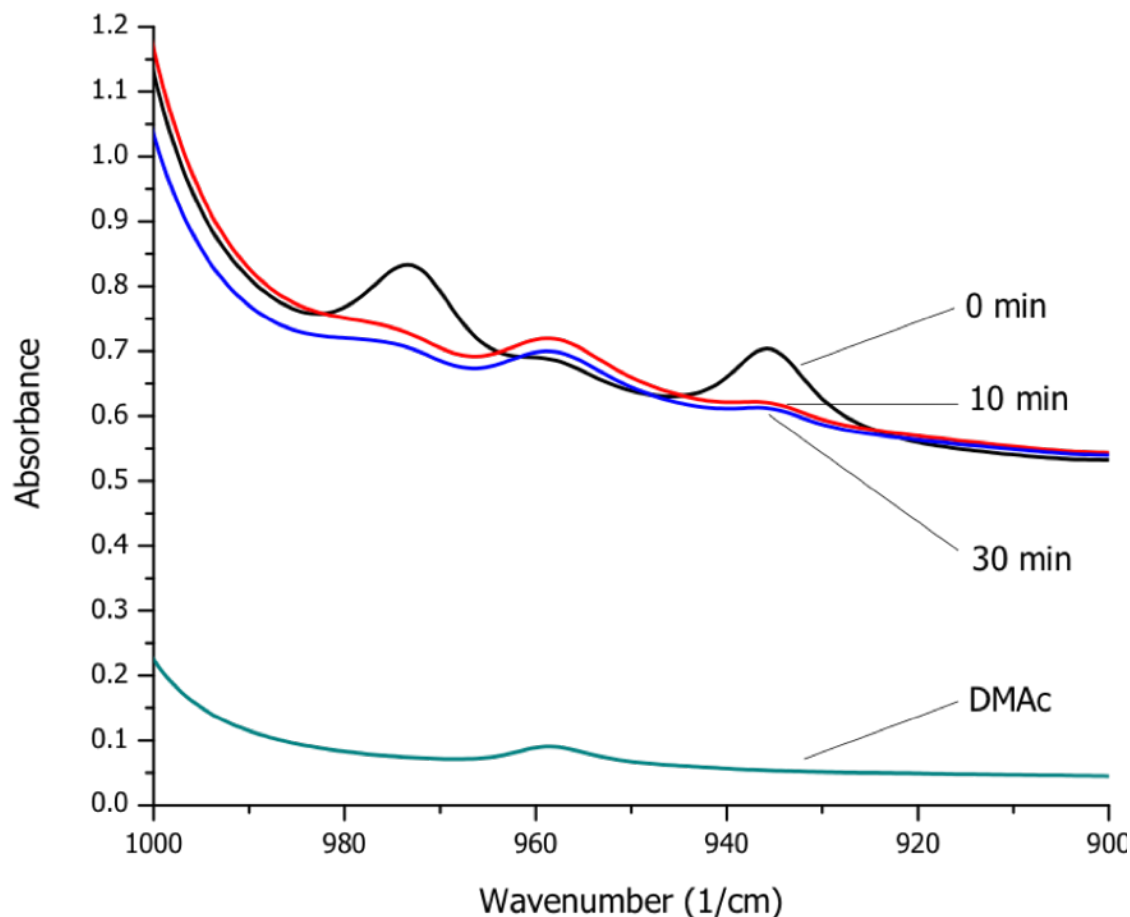


Figure 3. 6. Thermal free radical polymerization with crosslinking of a 2,000 g/mole oligomer with tetrafluorostyrene end groups as a function of time with *in-situ* FT-IR

The extent of crosslinking was further explored with the 2,000 g/mole oligomer at a polymer concentration of 0.4 g polymer in one mL of DMAc with an initiator concentration of 5 wt %. The gel fractions were measured at thermal curing times of 0, 5, 10, 20, 30, 120 minutes and

the findings are shown in Figure 6 and Table 5. The gel fraction was 79.3% after only five minutes and increased to 89.6% after ten minutes. The gel fraction plateaued at ~92% after 30 minutes of thermal curing and continued curing for 120 minutes resulted in similar results. This free radical thermal curing procedure shows that relatively fast crosslinking reaction kinetics are possible in comparison to previously explored epoxy crosslinking mechanisms.³²

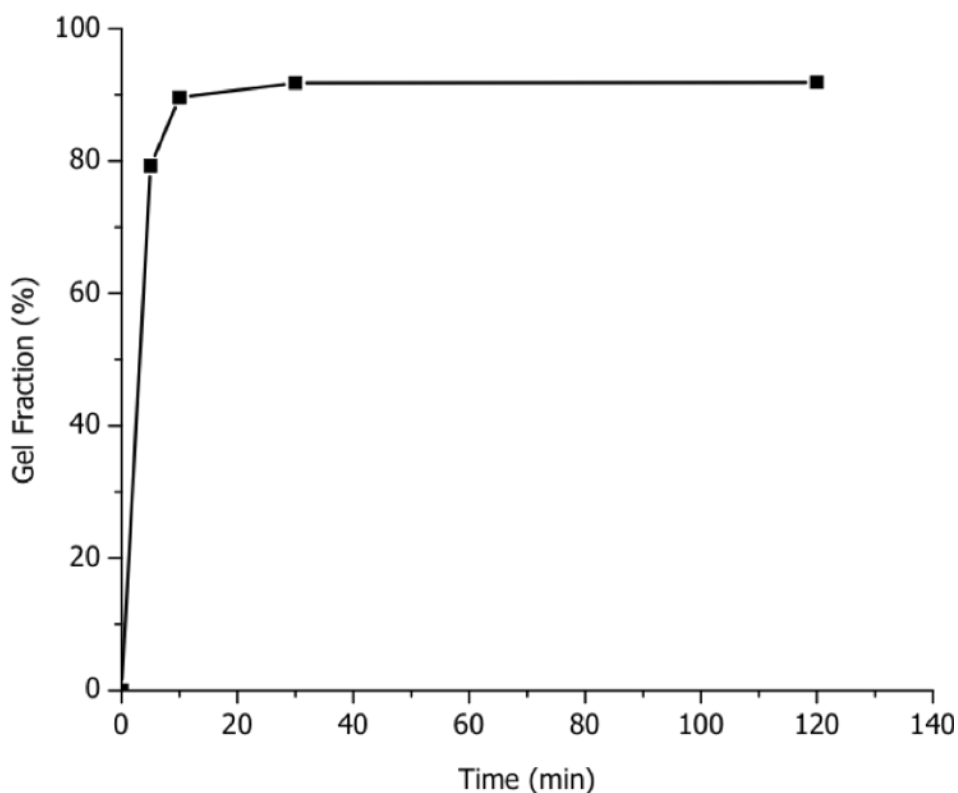


Figure 3. 7. Gel fractions vs. thermal curing time at 80°C of a 2,000 g/mol tetrafluorostyrene terminated oligomer that had 50% of the units containing *ms*-DCDPS

The high gel fraction and fast curing time yielded positive results so the reaction variables were explored for casting thin films. The 2,000 g/mol oligomer with 50% incorporation of the *ms*-DCDPS repeat unit was thermally crosslinked with a polymer concentration of 0.4 g of polymer in 1 mL of DMAc with 5 wt % of AIBN at 80 °C under nitrogen. A glass plate was preheated to 80 °C and the polymer/initiator solution was poured onto the glass plate. A doctor's blade was

used to spread the polymer solution across the glass plate, with the gap in the doctors' blade set at 50 μm thickness. The film was allowed to cure for 20 minutes. The crosslinked film produced by this method with the 2,000 g/mole oligomer was too brittle and ultimately broke apart. A similar procedure was used with the 10,000 g/mol oligomer with 50% incorporation of the *ms*-DCDPS repeat unit. The crosslinked film was found to be intact and displayed excellent mechanical properties after 20 minutes of thermal curing. The film was delaminated from the glass plate and a gel fraction was measured on the sample to estimate the extent of crosslinking. A 90% gel fraction was obtained that demonstrated a high degree of free radical thermal crosslinking.

Table 3. 4. Gel fractions as a function of thermal curing time at 80°C under nitrogen with a 2 kDa oligomer containing 50% incorporation of the *ms*-DCDPS repeat unit

Time (min)	Gel Fraction (%)
0	0
5	79.3
10	89.6
30	91.8
120	91.9

UV Crosslinking

Tetrafluorostyrene endcapped oligomers with controlled molecular weights (2,000 and 10,000 g/mol) were investigated to determine the optimum UV-crosslinking reaction conditions that would produce a highly crosslinked thin film. Initiator concentration, solvent type and amount,

and UV curing time and energy were examined to assess their potential influence on the degree of crosslinking. Gel fractions were measured to assess the extent of crosslinking.

The UV curing crosslinking reaction was conducted at 365 nm with TPO as the initiator. While TPO has a high absorbance at 365 nm, the sulfonated polysulfones have almost no absorbance. This high absorbance allows for the instantaneous generation of free radicals upon UV excitation of TPO and its degradation into free radicals.^{33,34} UV curing is advantageous with respect to thermal curing due to much faster curing times. The UV absorbance spectra of the 2,000 g/mol oligomer, pentafluorostyrene, DMAc, and diethylene glycol (DEG) were obtained as shown in Figure 7.

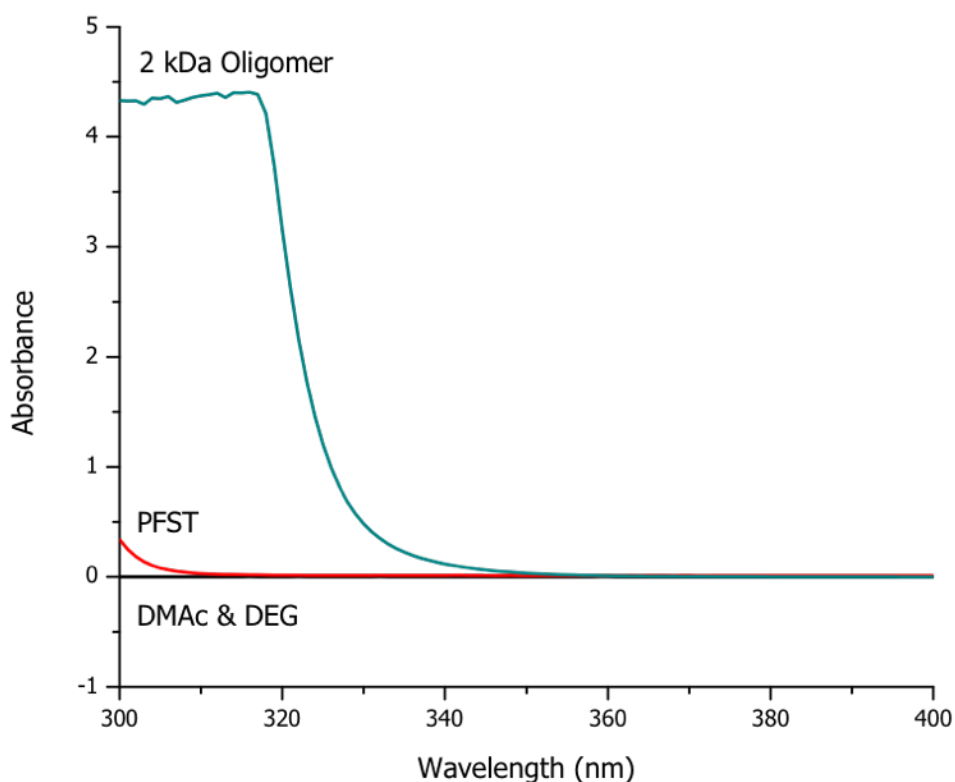
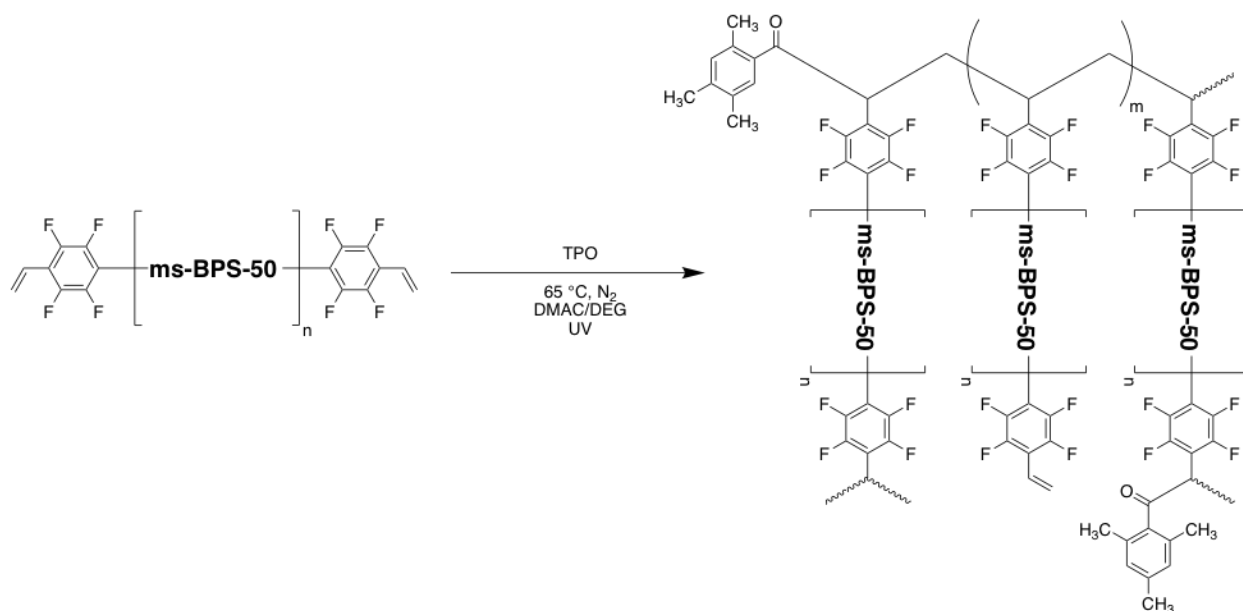


Figure 3. 8. UV spectra of the 2,000 g/mol oligomer containing 50% incorporation of *ms*-DCDPS repeat units, pentafluorostyrene (PFST), DMAc and DEG. Concentrations = 3×10^{-5} M

The sulfonated polysulfone oligomer, DMAc, and DEG lacked any absorbance at 365 nm. These findings potentially allow for UV curing of thin films with little to no inherent gradient caused by absorption of light by the components, which is ideal for the fabrication of membranes.

The oligomer and initiator (TPO) were dissolved in a solution of DMAc/DEG in varying ratios at a concentration of 0.4 g of polymer in one mL of solvent in a glass amber vial. The polymer solution was poured onto a glass plate and a doctor's blade was used to draw the solution across the glass surface at a 50 μm thickness. The glass plate and polymer were heated to 80 $^{\circ}\text{C}$ over a period of 20 minutes and then irradiated with UV light at 365 nm and 65 $^{\circ}\text{C}$. Gel fractions were measured to estimate the extent of UV crosslinking. Scheme 3 displays the overall reaction conditions. Initiator, solvent, temperature, curing energy, intensity, and time were investigated. No gel was observed after these solutions were irradiated at room temperature, whereas curing at 65 $^{\circ}\text{C}$ was relatively efficient.



Scheme 3. 3. Overall reaction for UV curing of tetrafluorostyrene endcapped oligomers

The initiator concentration relative to the polymer concentration was varied to determine the relationships among TPO concentration and gel fractions. Curing reactions of the 10,000 g/mole oligomer with 50% of the repeat units containing *ms*-DCDPS were investigated with the solutions containing 100% DMAc and with a 50/50 v/v mixture of DMAc and DEG. All curing reactions were conducted with a curing energy of 57,850 mJ/cm² over 300 seconds at 65 °C. The results are shown in Figure 8 and Table 6. TPO concentrations between 0.1-1 wt % revealed a plateau region of 75.6 to 79.0% gel fractions for the 50/50 v/v DMAc/DEG solvent system, with a severe drop at higher concentrations of TPO. This decrease in the extent of crosslinking at higher concentrations of initiator is attributed to an increase in termination relative to propagation. Both systems suggested that ~1 wt % of TPO relative to polymer was an efficient initiator concentration.

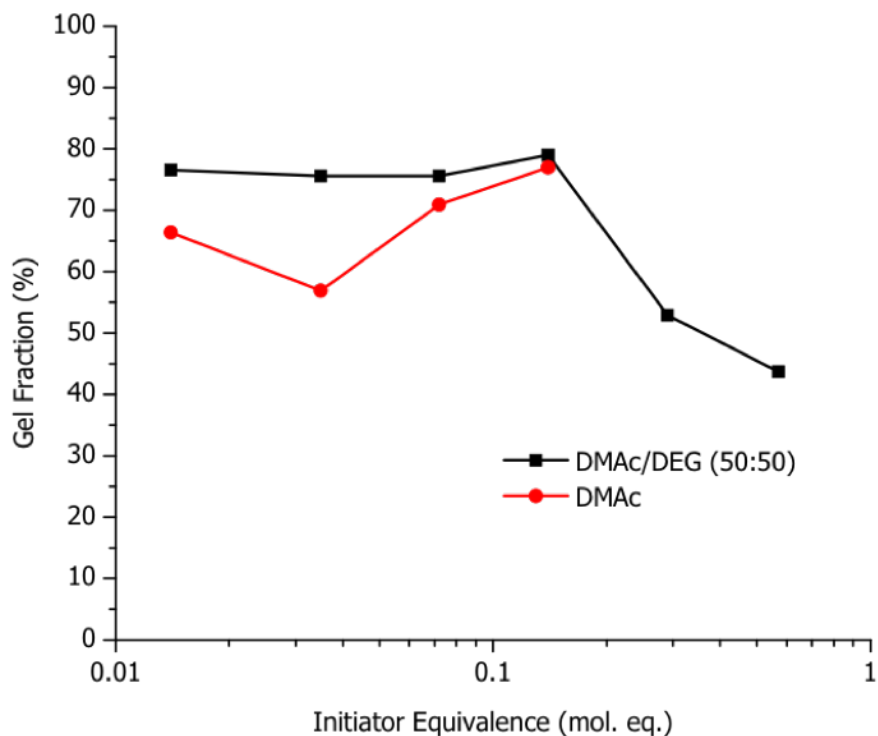


Figure 3. 9. Effects of TPO concentration on crosslinking a 10,000 g/mol oligomer with 50% of the repeat units containing the *ms*-DCDPS

The effect of adding diethylene glycol into the DMAc solvent is complicated by the fact that the solvent partially volatilizes during the heating step where the solutions (on the glass plates) are heated over 20 minutes to increase the temperature from room temperature to the curing temperature of 65°C. Thus, it is recommended that further investigation of the effects of the initial solvent mixtures be conducted with the objective of optimizing these reactions in membrane formation studies.

Table 3. 5. Gel fractions vs. TPO initiator concentration during curing of a 10,000 g/mole oligomer with 50% incorporation of repeat units containing *ms*-DCDPS

Initiator (wt % relative to polymer)	Initiator (mol. eq.)	Gel Fraction DMAc/DEG (%)	Gel Fraction DMAc (%)
0.1	0.014	76.6	66.4
0.25	0.035	75.6	56.9
0.5	0.072	75.6	70.9
1.0	0.14	79.0	77.0
2.0	0.29	52.9	/
4.0	0.57	43.7	/

The extent of crosslinking at lower energies and lower curing times was explored with the 10,000 g/mol oligomer (50% incorporation of *ms*-DCDPS repeat unit) at a polymer concentration of 0.4 g dissolved in one mL of solvent with a TPO initiator concentration of 1 wt % using 50/50 v/v DMAc/DEG solvent. The gel fractions were measured after curing for 3, 30, 60, 150, and 300 seconds at 100% intensity of the UV lamps. The findings are shown in Figure 9 and Table 7. It should be noted that no gel was observed after 20 minutes of heating the material before UV curing, and thus, no thermally induced crosslinking was observed. The gel fraction was found to be 62.2%

after one second (curing energy = 148 mJ/cm²), and increased to 81.1% after 3 seconds (curing energy = 517 mJ/cm²). The gel fraction plateaued at 79.0-81.8% after the 3 seconds as shown at 30, 60, 150, and 300 seconds of UV curing times. Thus, it was concluded that the UV free radical curing process could be conducted relatively quickly.

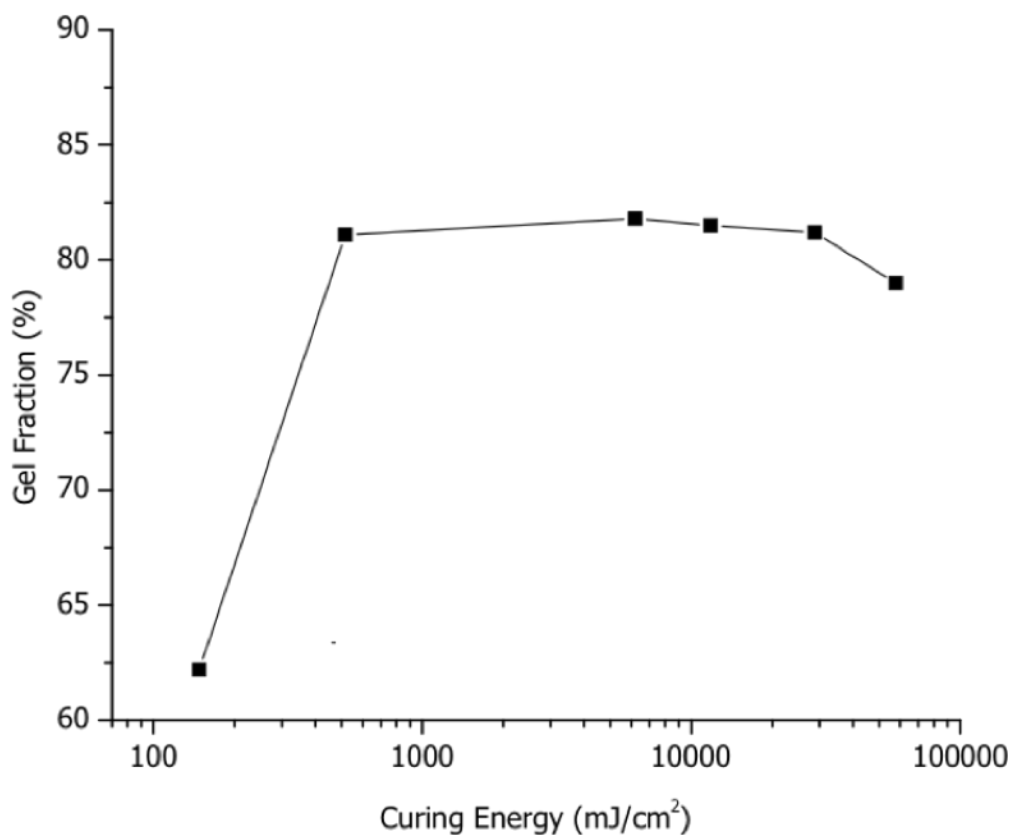


Figure 3. 10. Gel fractions after curing a tetrafluorostyrene endcapped 10,000 g/mole oligomer with UV light at 365 nm and 65°C as a function of curing energy

Table 3. 6 Gel fractions after curing a tetrafluorostyrene endcapped 10,000 g/mol oligomer with 50% of the repeat units containing *ms*-DCDPS with varying curing energies

Time (s)	Curing Energy (mJ/cm ²)	Gel Fraction (%)
1	148	62.2
3	517	81.1
30	6,176	81.8
60	11,818	81.5
150	28,786	81.2
300	57,569	79.0

Initial results demonstrated that a 1 wt % initiator concentration based on polymer mass and ~500 mJ/cm² of curing energy produced a gel fraction of ~ 80%. Earlier findings of the optimal initiator concentration were conducted at 300 seconds with a curing energy of 57,850 mJ/cm². It is reasoned that such an overexposure could potentially degrade or create adverse effects with regards to the degree of crosslinking of the polymer film. Thus, gel fractions were also measured after curing for short times with lower initiator concentrations. TPO concentrations of 0.1, 0.25, 0.5, and 1.0 wt % (50:50 DMAc/DEG) were exposed to a low cure energy of 517 mJ/cm² over 3 seconds. The results are shown in Figure 10 and Table 8. At initiator concentrations of 0.1, 0.25, and 0.5 wt %, lower gel fractions between 66.5 to 70.2% were observed. These were significantly lower than the 81.8% gel fraction achieved with 1 wt % of initiator.

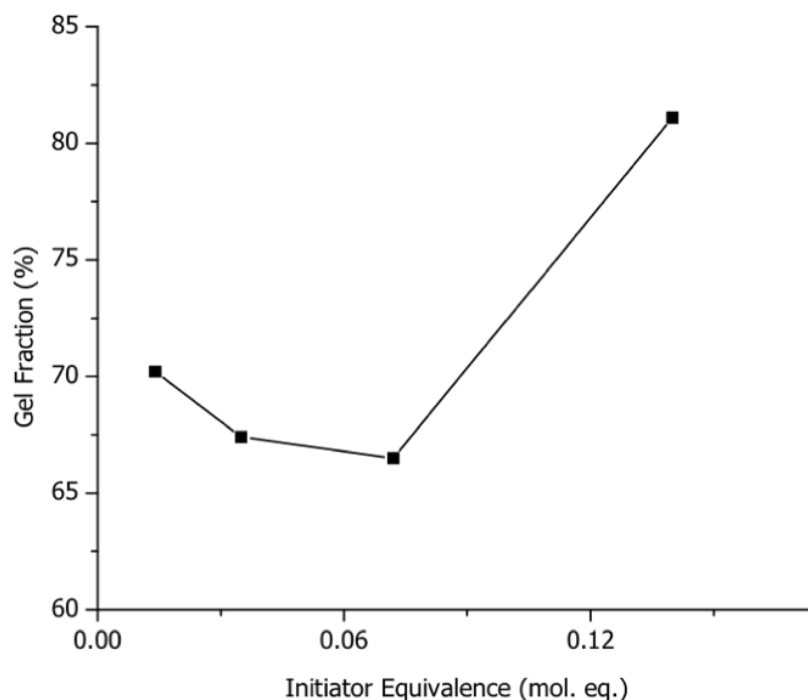


Figure 3. 11. UV curing with varying TPO initiator concentration at low curing energies of the 10,000 g/mol tetrafluorostyrene oligomer with 50% incorporation of *ms*-DCDPS repeat unit

Table 3. 7. UV curing with varying initiator concentration at low curing energy exposure of the 10,000 g/mol oligomer with 50% incorporation of *ms*-DCDPS repeat unit

Initiator (wt %)	Initiator (mol. eq.)	Gel Fraction (%)
0.1	0.014	70.2
0.25	0.035	67.4
0.5	0.072	66.5
1.0	0.14	81.8

Preliminary findings demonstrated that the highest degree of UV crosslinking for the 10,000 g/mol oligomer occurred at 65°C with 1 wt % of TPO initiator relative to the mass of polymer at a curing energy of 517 mJ/cm² over three seconds to afford a gel fraction of 81.8%.

The 50/50 v/v DMAc/DEG solvent system produced a higher gel fraction compared to using 100% DMAc. A reaction was also tried with the tetrafluorostyrene endcapped 10,000 g/mole oligomer dissolved in DMAc/DEG with a 90/10 v/v ratio. The oligomer was UV-cured at varying intensities (curing energy) over 3 seconds with 1 wt % TPO. The results are shown in both Figure 11 and Table 9. Lower gel fractions of 62 and 75% were reached with lower curing energies of 98 and 276 mJ/cm², respectively. However, a higher gel fraction of 85.0% resulted after curing with an energy of 437 mJ/cm² and an astonishing 91.7% gel fraction was achieved with a curing energy of 517 mJ/cm². The results with the 90:10 ratio of DMAc/DEG suggest that the solvent system plays an important role and that it warrants further investigation.

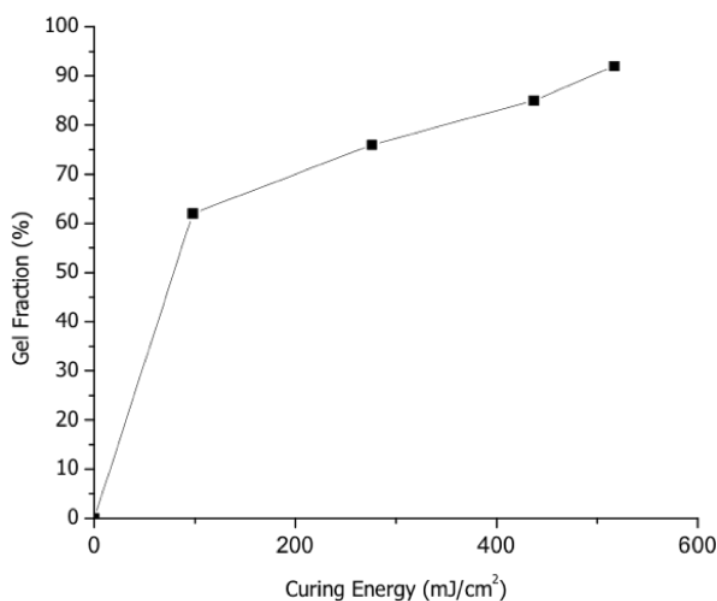


Figure 3. 12. Gel fractions of networks prepared with a 10,000 g/mole oligomer with 50% incorporation of *ms*-DCDPS repeat units in DMAc/DEG (90/10 v/v) as a function of curing energy

UV curing of the 2,000 g/mole oligomer with incorporation of *ms*-DCDPS in 50 % of the repeat units produced brittle membranes, similar to the results that were obtained after free radical

thermal curing. However blends of small and large molecular weight oligomers have been shown to possess robust mechanical properties.³⁵ Therefore a blend of the 2,000 g/mol and 10,000 g/mol oligomers was UV cured at a mass ratio of (1:3) with 0.5 wt % initiator in DMAc/DEG (90:10) as shown in Table 10. A gel fraction of 87.0% was measured. It should be noted that the highly crosslinked networks derived from both the 10,000 g/mole oligomer and also the 1:3 blend remained as intact films after the gel fraction experiment.

Table 3. 8. Gel fractions after UV curing of a 10,000 g/mole oligomer containing *ms*-DCDPS in 50% of the repeat units in DMAc/DEG (90/10 v/v)

Curing Energy (mJ/cm ²)	Gel Fraction (%)
0	0
98	62.0
276	76.0
437	85.0
517	91.7

Table 3. 9. UV curing a 10,000 g/mol and a blend of 2000 and 10,000 g/mole oligomers containing *ms*-DCDPS in 50% in DMAc/DEG (90/10 v/v) results in efficient curing at low curing energies

Polymer	Initiator (wt. %)	Initiator (mol. eq.)	Curing Energy (mJ/cm ²)	Gel Fraction (%)
2 + 10 kDa (1:3 wt/wt)	0.5	0.035	437	87
10 kDa	1.0	0.14	517	92

The theoretical IECs of the crosslinked membranes were calculated from the known IECs of the oligomers with little to no impact from the small amount of initiator, and blended IECs were determined by averaging the ratio between the 2,000 and 10,000 g/mol oligomers. Unsurprisingly, water uptake for the UV crosslinked membranes strongly correlated to ion exchange capacities, where water uptake increased with increasing IEC values (Table 3.10). McGrath *et al.* also confirmed a similar result when determining water absorbance with epoxy di-sulfonated PAES containing varying IECs.²³ For example, 10,000 g/mol crosslinked membranes with 50% and 60% sulfonation displayed water uptakes of 14% and 17% respectively, whereas linear counterparts yielded water uptakes of 16% and 20%. Crosslinking afforded lower water absorbance by reducing dimensional swelling. Crosslinked film blends of 2,000 g/mol and 10,000 g/mol (1:3) oligomers with 50 and 60% sulfonation of the repeat units showed lower water uptakes than the corresponding 10,000 g/mol crosslinked films. The crosslinked oligomer blends likely have a higher crosslink density that created the lower water absorbance by reducing the available free volume.

RO membranes are subjected to high pressures and these membranes require high mechanical stability in order to withstand failure or compaction. The mechanical properties of UV-crosslinked membranes were determined by tensile testing and compared to high molecular weight linear counterparts (Table 3.10). Both linear and crosslinked sulfonated PAES membranes exhibit a polymeric glassy state under fully hydrated conditions. The 50% and 60% sulfonated crosslinked fully hydrated films showed good average elastic moduli with values exceeding 600 MPa with reasonable average yield stresses greater than 23.0 MPa. The mechanical properties of the crosslinked membranes appear slightly lower than the linear membranes and the difference is

likely attributed to incomplete formation of a crosslinked network, with gel fractions between 85-92%. One would expect higher elastic moduli with increased crosslinking.

Table 3. 10. Directly polymerized sulfonated poly(arylene ether sulfone) (PAES) ion exchange capacity (IEC), water uptake (WU), and hydrated mechanical properties. *ms*-PAES-xx are the linear sulfonated PAES containing the mono-sulfonated monomer (*ms*-DCDPS), and *xl-ms*-PAES-xx are the crosslinked sulfonated PAES containing the mono-sulfonated monomer (*ms*-DCDPS). xx denotes the mol. percentage of mono-sulfonated monomer incorporated in the oligomer.

Membrane Name	Average IEC* (meq/g)	Average WU (%)	Average Elastic Modulus (MPa)	Average Yield Stress (MPa)
ms-PAES-51	1.16**	16±1.0	816±53	21.8±0.9
ms-PAES-61	1.36**	22±1.5	762±56	23.0±2.3
xl-ms-PAES-50-10K	1.03*	14±1.2	699±89	29.6±2.4
xl-ms-PAES-60-10K	1.23*	19±0.5	634±92	23.1±2.1
xl-ms-PAES-50-2/10K	0.99*	11±1.7	621±65	28.1±2.1
xl-ms-PAES-60-2/10K	1.16*	17±2.1	680±120	26.8±1.4

*IEC values based on the targeted degree of sulfonation

**Determined by titration

Figure 3.13. displays the stress vs strain curves for linear and crosslinked membranes. The 50% and 60% sulfonated crosslinked membranes demonstrated elongations at break in excess of 50%, while the linear copolymers showed strains greater than 140%. After reaching the yield point, both the linear copolymers and the 60% crosslinked membranes displayed stress-induced strain hardening.

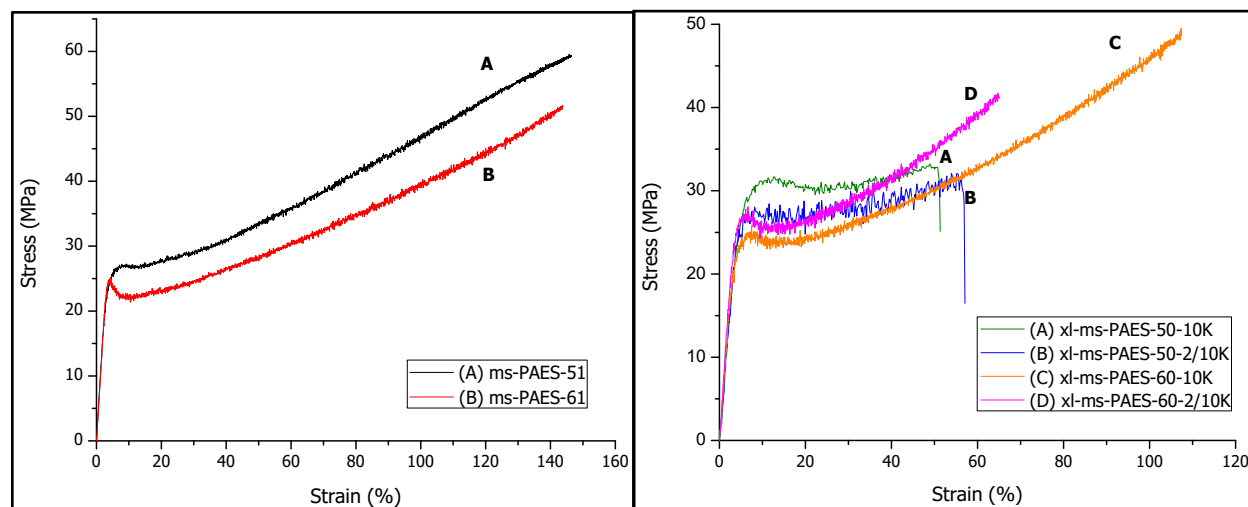


Figure 3. 13. Hydrated uniaxial mechanical properties of linear high molecular weight mono-sulfonated PAES (ms-PAES-xx) and crosslinked mono-sulfonated oligomers (xl-ms-PAES-xx). xx denotes the mol. percentage of mono-sulfonated repeat unit, and 2/10K is a 25:75 (w/w) blend of both 2 and 10 KDa oligomers

Water transport properties of the crosslinked membranes with 50% sulfonate incorporation were compared with linear membranes (Table 3.11). The crosslinked 10,000 g/mol oligomer membrane with an IEC = 1.03 yielded an average NaCl rejection of 98.36% and a water permeability of $0.49 \times 10^{-6} \text{ cm}^2/\text{sec}$, whereas the linear membrane with 51% sulfonate incorporation and a measured IEC of 1.16, displayed slightly higher NaCl rejection of 99.25% and a water permeability of $0.57 \times 10^{-6} \text{ cm}^2/\text{sec}$. The crosslinked membrane yielded a lower water permeability than the linear membrane and this difference can be attributed to a difference in IEC and water uptake, where the crosslinks reduced dimensional swelling. The crosslinked film also demonstrated a lower salt rejection then its linear counterpart, where differing casting conditions likely played a significant role. Future research must be performed in order to understand the water/salt transport differences between crosslinked and linear membranes.

Table 3. 11. Water transport and salt rejection properties of crosslinked oligomers and linear polymers. ms-PAES-xx is the linear sulfonated PAES containing the mono-sulfonated monomer

(*ms*-DCDPS), and *xl-ms*-PAES-*xx* is the crosslinked sulfonated PAES containing the mono-sulfonated monomer (*ms*-DCDPS). *xx* denotes the mol. percentage of mono-sulfonated monomer incorporated in the oligomer.

Polymer	IEC (meq/g)	NaCl Rejection (%)	Water Permeability (cm ² /s)
<i>xl-ms</i> -PAES-50-10K	1.03 [*]	98.36 ± 0.17	(0.49 ± 0.11) x 10 ⁻⁶
<i>ms</i> -PAES-51	1.16 ^{**}	99.25 ± 0.14	(0.57 ± 0.02) x 10 ⁻⁶
<i>ms</i> -PAES-61	1.36 ^{**}	98.65 ± 0.63	(2.09 ± 0.26) x 10 ⁻⁶

^{*}IEC values based on the targeted degree of sulfonation

^{**}Determined by titration

3.5 Conclusions

Mono-sulfonated poly(arylene ether sulfone) oligomers with targeted molecular weights were synthesized by direct polymerization followed by endgroup functionalization with tetrafluorostyrenic endgroups in a one-pot reaction. ¹H NMR verified the oligomer structures with complete endgroup functionalization and size exclusion chromatography confirmed that the targeted molecular weights were achieved. Thermal and UV-curing reaction conditions were optimized to afford highly crosslinked networks with fast curing rates. Solvent extraction of membranes with either single or blended oligomers displayed high gel fractions greater than 87%. Crosslinked membranes had lower water uptakes than their linear counterparts, and tensile tests of fully hydrated films established that the crosslinked membranes were mechanically robust. Initial transport properties of the 50% sulfonated crosslinked membrane with the 10,000 g/mol oligomer displayed high salt rejection and similar water permeability of the 51% sulfonated linear

membrane. Future research will study UV crosslinked membranes with higher degrees of sulfonation with varying crosslink density in order to increase water permeability while maintaining high salt rejection. The fabrication of thin-film composites should also be explored and could provide an alternative to currently employed commercial polyamide thin-film composites.

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Chapter 4: Conclusions and Suggested Future Work

4.1. Conclusions

Sulfonated poly(arylene ether sulfone)s have been thoroughly investigated as a potential alternative to commercially employed aromatic polyamide thin-film composite reverse osmosis membranes. Sulfonated PAES demonstrate several advantages with comparison to polyamide TFCs, including: chlorine resistance, smooth surface, and operability over a wide pH-range.^{1,2} However, sulfonated poly(arylene ether sulfone) membrane performance suffers when introduced to divalent cations, especially calcium. NaCl salt rejection decreases as calcium ion concentration increases in the feed source. Calcium cations bind with the sulfonate fixed charge groups allowing for the passage of monovalent ions. Allegrezza showed this drawback using post-sulfonated Udel® based membranes and Funk *et. al.* also found this characteristic working with directly polymerized di-sulfonated PAES (Figure 4.1).^{3,4}

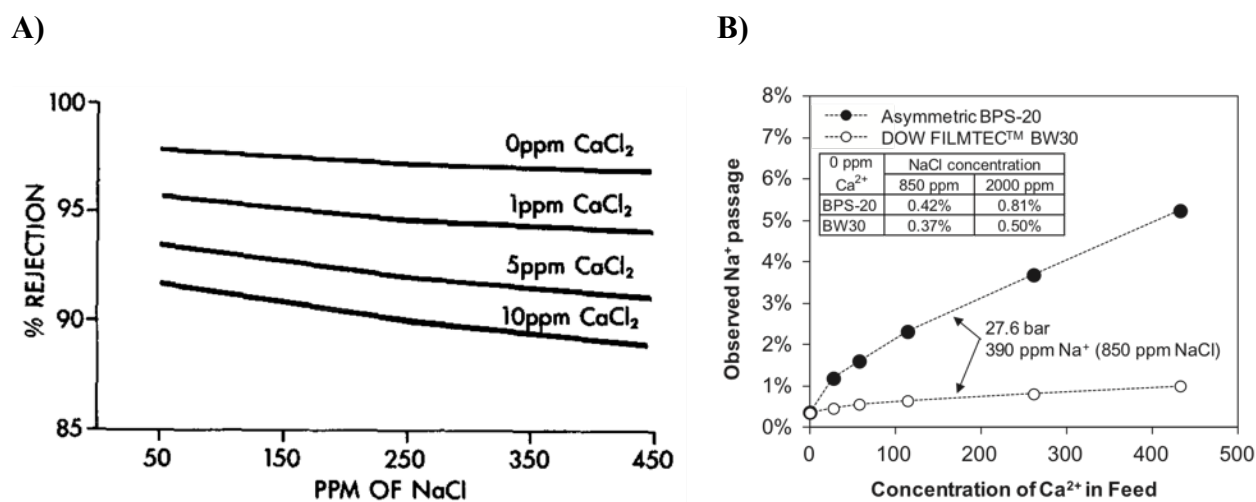


Figure 4. 1. Effects of NaCl salt rejection with Ca^{2+} concentration in feed source. (A) Sulfonated Udel® at 400 PSI (B) Di-sulfonated poly(arylene ether sulfone) and polyamide TFC. Used with permission from Elsevier^{3,4}

Therefore, considerable research has been performed to alter the chemistry and morphology of sulfonated poly(arylene ether sulfone)s in order to prevent reduction of salt rejection due to exposure to divalent cations membrane, as well as developing asymmetric RO membranes for increase water flux.

The research presented in this dissertation addresses some issues commonly associated with sulfonated poly(arylene ether sulfone)s. First, a mono-sulfonated dichlorodiphenylsulfone monomer was synthesized and characterized for purity. A series of linear, statistical mono-sulfonated poly(arylene ether sulfone)s copolymers as synthesized by direct polymerization of ms-DCDPS, DCDPS, and biphenol to yield high molecular weight polymers with varying degrees of mono-sulfonation incorporation. The copolymers were shown to have tremendously lower water uptake values at higher IEC values than their linear di-sulfonated counterpart polymers with similar IECs. Dense membranes made from the mono-sulfonated copolymers displayed high NaCl salt rejections (greater than 99%), and most of these membranes did not suffer decreased salt rejection when calcium cations at various concentrations were introduced in the feed source. The increased distance between sulfonate ions along the polymer backbone contributed to the higher fixed charge concentrations which improved Donnan exclusion, and prevented divalent cation membrane sensitivity.

Mono-sulfonated oligomers with crosslinkable end groups were studied to increase the fixed charge concentration in membranes. Statistical telechelic oligomers were synthesized by the direct polymerization of ms-DCDPS, DCDPS, and excess biphenol. Phenolate end groups were functionalized with pentafluorostyrene, creating 2,2',3,3'-tetrafluoro-4-vinylphenyl end groups. Highly crosslinked membranes were formed without any additional crosslinking agents by either

thermal or UV free radical crosslinking mechanisms. Both methods afforded gel fractions greater than 90%, with high double bond conversion. UV-crosslinking demonstrated fast curing times (~3 seconds) with high salt rejections (>97%) depending on the degree of sulfonation and blending of oligomers with different molecular weights. Although the salt rejections of the crosslinked materials appear to be lower than their linear counterparts, it is believed that this difference was possibly caused by the membrane casting procedure. More research must be performed to understand the potential of these crosslinked membranes.

4.2. Suggested Future Work

Commercial polyamide thin-film composite RO membranes exhibit both high salt rejection and high water flux, and these characteristics can be attributed to a high degree of crosslinking, carboxylate groups, and membrane fabrication.⁵ Sulfonated poly(arylene ether sulfone)s for potential reverse osmosis applications should display similar water/salt transport properties. In order to be a potential commercial alternative, sulfonated poly(arylene sulfone)s must meet the following criteria: limited water uptake, high ion-exchange capacity, divalent cation insensitivity, high chemical resistance, good mechanical properties, reproducibility, fast/easy membrane fabrication, and economically to manufacture and use.

The research in this dissertation has shown that the spacing of the sulfonate groups along the polymer chains prevents divalent cation sensitivity and also decreases water uptake which increases the fixed charge concentration. Therefore considerable emphasis should be placed on synthesizing new sulfonated monomers for direct polymerization of PAES by utilizing activated monomers for post-sulfonating PAES. One could also try incorporating other types of fixed charge groups, such as carboxylates or phosphonates that may be unaffected by divalent cation sensitivity.

Finally, I propose that future poly(arylene ether sulfone) membranes for reverse osmosis membranes should be designed as UV-curable asymmetric thin-film composites. Crosslinking would lower water uptake and asymmetric membranes by phase inversion could increase water flux without compromising salt rejection.

Recently, Riffle *e. al.* showed that post-sulfonated hydroquinone and biphenol based PAES linear copolymers did not display any compromise in NaCl salt rejection in the presence of calcium cations in the feed source (Figure 4.2). The authors hypothesize that the spacing between sulfonated hydroquinone repeat units and the non-planar sulfonated biphenol-rings prevented the binding of calcium cations by prohibiting chelation with the sulfonate groups. With this in mind,

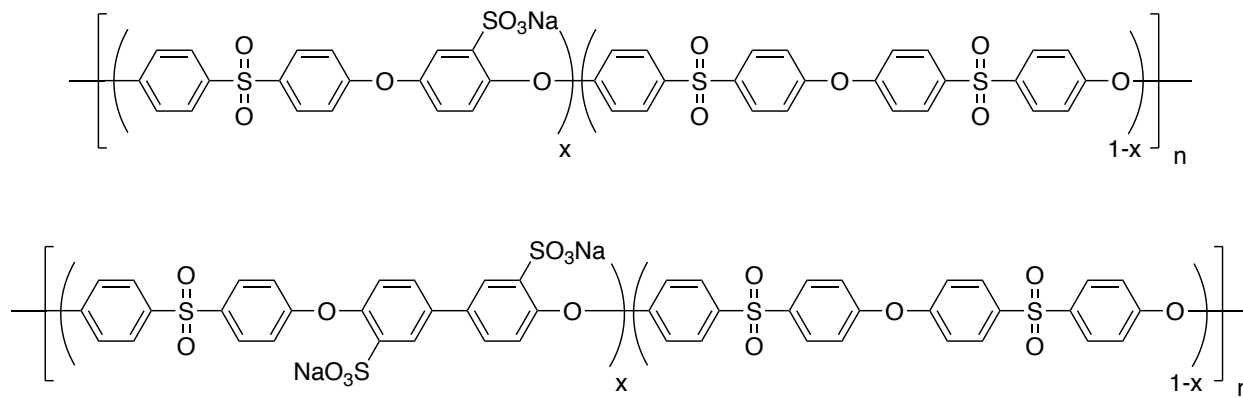
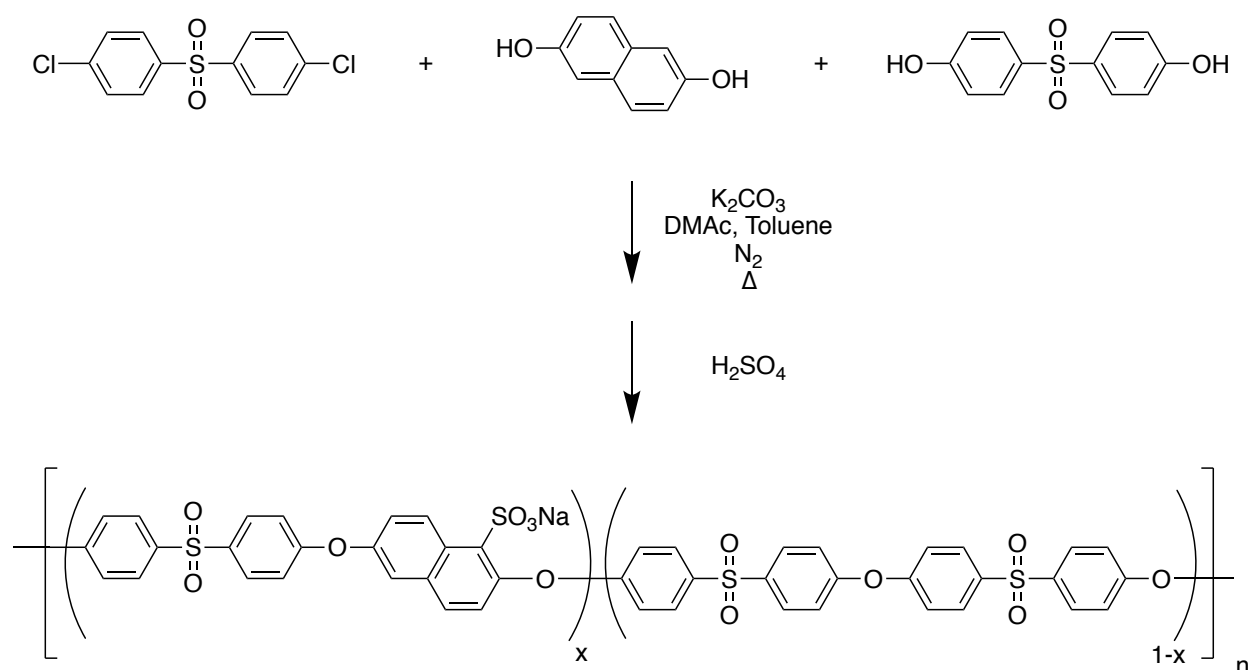


Figure 4. 2. Post-sulfonated hydroquinone and biphenol based poly(arylene ether sulfone)s

I think it would be very interesting to synthesize a series of linear poly(arylene ether sulfone)s by incorporating 2,6-dihydroxy naphthalene into the backbone and then post-sulfonate (Scheme 4.1). Sulfonation would most-likely occur at only one of the naphthalene-rings under mild reaction conditions because the 1st ring sulfonation would deactivate the other ring through aromatic electron withdrawal and stop further electrophilic aromatic substitution. The degree of sulfonation

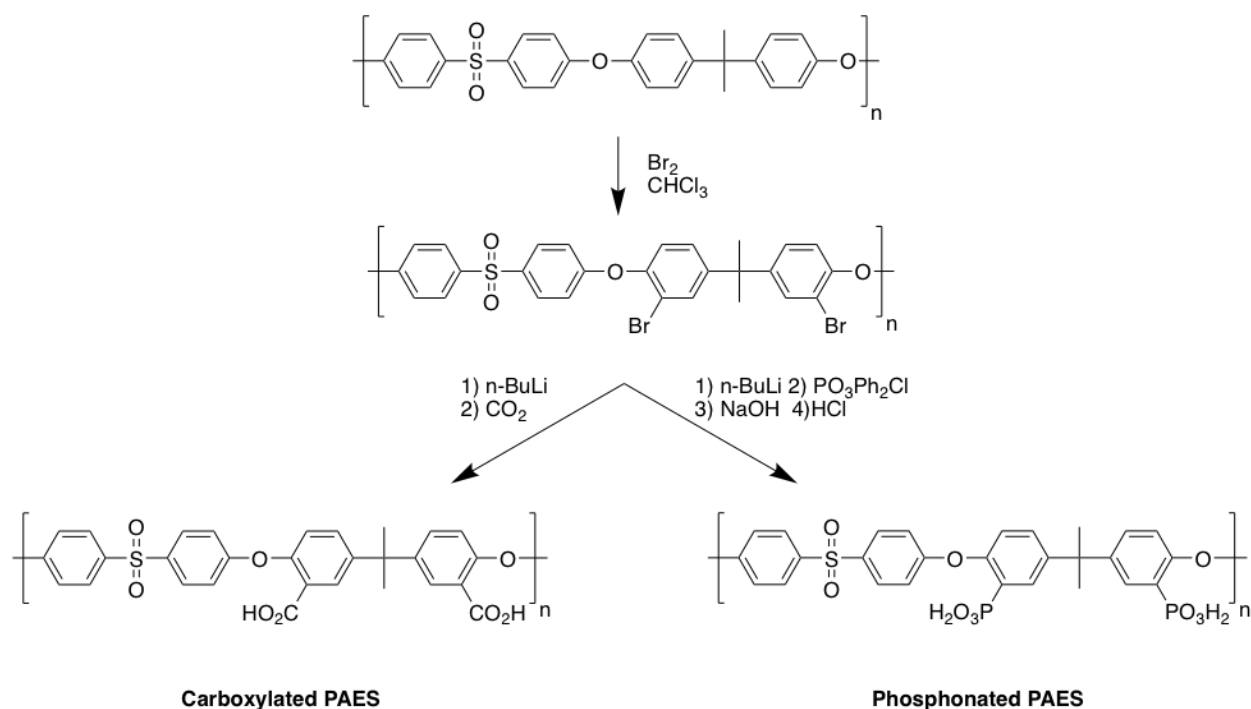
could be controlled by using deactivated monomers like bisphenol-S within the repeat unit that are not prone to post-sulfonation. If preliminary findings of these linear high molecular weight polymers showed positive RO water transport and salt rejections, I would explore additional research and synthesis of sulfonated oligomers with UV-crosslinking capability. Molecular weights could be controlled by offsetting excess bisphenol-S or by end-capping with m-aminophenol functionalized endgroups and converting to UV-crosslinkable groups.



Scheme 4. 1. Polymerization and post-sulfonation of dihydroxynaphthalene based poly(arylene ether sulfone)

Post-carboxylated and post-phosphonated poly(arylene ether sulfone)s have been thoroughly studied in recent years, but research was primarily limited to fuel cell applications.^{6,7} Scheme 4.2 shows two common routes for functionalizing poly(arylene ether sulfone)s with either carboxylate or phosphonate groups.^{8,9} First, both processes involve the bromination of activated

phenyl rings by electrophilic aromatic substitution. Next, the bromo groups are lithiated by *n*-butyl lithium, and finally converted to either carboxylic acid or phosphonic acid groups. The degree of carboxylation/phosphonation can be controlled by incorporating more deactivated monomers within the polymer chains. A series of linear polymers could be examined for RO properties and then UV-crosslinkable oligomers created if initial findings are positive. As mentioned before, target molecular weights can be achieved through utilizing excess deactivated monomers or *m*-aminophenol for endcapping groups, followed by the introduction of UV-curable endgroups.



Scheme 4. 2. Carboxylated and phosphonated poly(arylene ether sulfone)s

Much like PAES post-functionalization methods, functionalized monomers have also been heavily studied for mostly fuel cell applications, and many of these monomers could potentially be studied for reverse osmosis applications. Functionalized monomers allow for better

control/distribution and reproducibility for the direct polymerization of statistical, functionalized poly(arylene ether sulfone)s. Although several functionalized monomers have been synthesized, I list below in Figure 4.3 the monomers I believe to be potentially noteworthy for further reverse osmosis research. The sulfonated naphthalene monomer can be synthesized by an electrophilic aromatic substitution reaction between 2,6-dihydroxynaphthalene and sulfuric acid. Yan *et. al.* has reported a similar synthesis strategy for sulfonated difluoro-triphenylphosphine oxide.¹⁰ Carboxylated phenolphthalein can be synthesized by the reduction of phenolphthalein using zinc and sodium hydroxide.^{7,11} These monomers can be used to develop a series of linear directly polymerized poly(arylene ether sulfone)s with varying degrees of hydrophilicity for typical reverse osmosis properties. Finally, further synthesis and fabrication of UV-curable oligomers can be investigated.

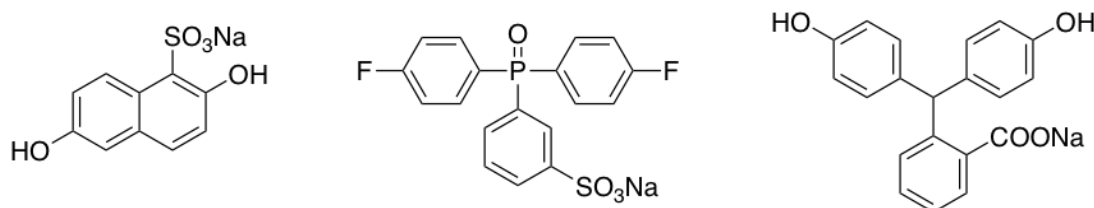


Figure 4. 3. Sulfonated and carboxylated monomers for potential reverse osmosis applications

As reported in this dissertation, highly-crosslinked sulfonated poly(arylene ether sulfone)s can be achieved through UV-curing without the aid of photo-crosslinkable agents. However, it might be worthwhile to explore how crosslinking agents might permit improved water/salt transport properties by increasing crosslinking density or explore the effects of crosslinker hydrophobicity. Finally, asymmetric UV-curable membranes could be formed through a phase

separation process by following a procedure similar to that as described by Yagci *et al.* (Figure 4.4).^{12,13}

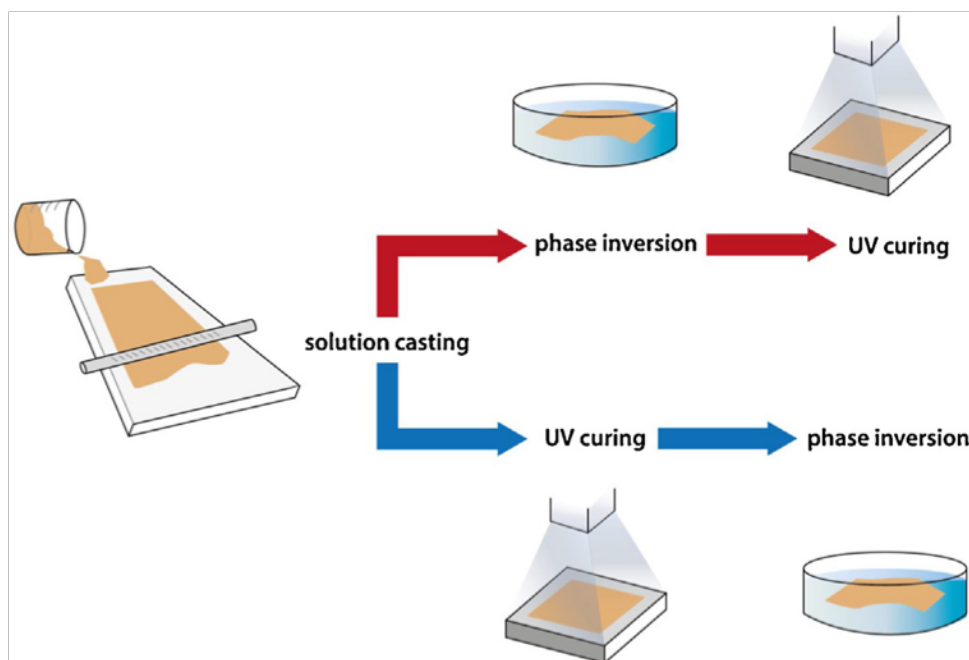


Figure 4. 4. General diagram of two methods for creating asymmetric crosslinked membranes. Used with permission from Elsevier¹³

4.3. References

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