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# Modified Polysulfone Nanofiltration Membrane Synthesis for Hydraulic Fracturing Water Recycle

Blake Alexander Johnson  
*University of Arkansas, Fayetteville*

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Modified Polysulfone Nanofiltration Membrane Synthesis for Hydraulic Fracturing Water  
Recycle

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Master of Science in Chemical Engineering

By

Blake Johnson  
University of Arkansas  
Bachelor of Science in Chemical Engineering, 2014

December 2015  
University of Arkansas

This thesis is approved for recommendation to the Graduate Council.

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Professor Jamie Hestekin, Ph.D.  
Thesis Director

---

Professor Ranil Wickramasinghe, Ph.D.  
Committee Member

---

Professor Robert Beitle, Ph.D.  
Committee Member

## **Abstract**

The use of hydraulic fracturing has resulted in significant increases in the yield of oil and natural gas, as water pumped into wells at high pressure cracks the formations and releases the hydrocarbons that are locked in the rocks. This process has created large volumes of brackish water that is very difficult to process and is often disposed of into injection wells. Suspended solids and some dissolved solids are more readily removed, but the multivalent ions found in certain salts can precipitate in a well and complicate the reuse of flowback in future hydraulic fracturing operations.

Nanofiltration, a membrane separation technique, has the potential to remove these salts at a much lower cost than desalination techniques such as reverse osmosis. Secondary interactions, such as charge, can be added through functional groups to increase the rejection of the positive ions and allow for the reuse of flowback in operations where low quality water is acceptable.

To produce these membranes, polysulfone was reacted with trimethylchlorosilane and trimethylamine to produce a positively charged functional groups that would allow for selective rejection of ions. While the two-step reaction to produce these functional polymers was successful, the polymer created did not have the properties required to produce a membrane.

The positively charged polysulfone had functional groups that made it soluble in water, and membranes cast from this polymer readily swelled and deformed when exposed to most fluids, including water and air. While some characteristics of these membranes, such as pore diameter, were comparable to commercial membranes, the solubility characteristics made filtration testing impossible. However, while the final positively charged polymer was unusable, the functional precursor polymer was successfully synthesized and can be used with other methods to produce the positively charged polymers.

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## **1. Introduction:**

As the demand for energy in the form of oil and natural gas rises, the use of technologies that increase the yield of these hydrocarbons rises as well. Hydraulic fracturing is a widespread technology that relies on pressurized water to open and thereby increase the accessibility of oil and natural gas from wells.<sup>1</sup> Water mixed with additives to stabilize the fluid and hold open the fracture is pumped at high pressure into a drilled well. This cracks the formation and allows the hydrocarbons that are locked inside shale formations to be pumped out.

Hydraulic fracturing is highly water-intensive however, as each well requires upwards of 1 million gallons to fracture a vertical well, and 3-6 million gallons to fracture a horizontal well on average, though larger amounts can be necessary.<sup>2</sup> Only a small fraction of this water is recovered, and between 70-90% of the water used in a hydraulic fracturing operation is lost to the formations.<sup>2</sup> Only 10-30% of the water is recovered as flowback water, but this flowback is highly contaminated, both from the chemicals and additives put into the water in order to keep the formations open after fracturing, shown in Table 1, and from the compounds retained when the formation is opened, shown in Table 2.<sup>3</sup>

Table 1: Additives used in fracturing fluid, examples, and their primary purpose.<sup>3,4</sup>

Constituent	Composition (% by vol)	Example	Purpose	Often used
Water and sand	99.5	Sand suspension	“Proppant” sand grains hold microfractures open	Yes
Acid	0.123	Hydrochloric or muriatic acid	Dissolves minerals and initiates cracks in the rock	No
Friction reducer	0.088	Polyacrylamide or mineral oil	Minimizes friction between fluid and the pipe	Yes
Surfactant	0.085	Isopropanol	Increases the viscosity of the fracture fluid	No
Salt	0.06	Potassium chloride	Creates a brine carrier fluid	No
Scale inhibitor	0.043	Ethylene glycol	Controls precipitation and prevents scale deposits in pipes	Yes
pH-adjusting agent	0.011	Sodium or potassium carbonate	Maintains effectiveness of chemicals additives	No
Iron control	0.004	Citric acid	Prevents precipitation of metal oxides	No
Corrosion inhibitor	0.002	n,n-dimethyl formamide	Prevents pipe corrosion	No
Biocide	0.001	Glutaraldehyde, hydrogen sulfide	Minimizes growth of bacteria that produce corrosive, toxic or contaminating by-products	Yes

Table 2: Initial concentration range and concentration after 14 days of constituents of flowback water from shale gas formations.<sup>3,5,6</sup>

Constituent	Initial Concentration (mg/L)	Concentration at 14 days (mg/L)
Total dissolved solids	66,000-261,000	3,010-261,000
Total suspended solids	27-3,200	17-1,150
Hardness (as CaCO <sub>3</sub> )	9,100-55,000	630-95,000
Alkalinity (as CaCO <sub>3</sub> )	200-1,100	26.1-121
Chloride	32,000-148,000	1,670-181,000
Sulfate	ND-500	ND-89.3
Sodium	18,000-44,000	26,900-95,900
Calcium	3,000-31,000	204-14,800
Strontium	1,400-6,800	163-3,580
Barium	23,000-4,700	43.9-13,600
Bromide	720-1,600	15.8-1,600
Iron	25-55	13.8-242
Manganese	3-7	1.76-18.6
Oil and grease	10-260	4.6-103



The disposal of flowback water is a major environmental concern, as the total volume of flowback water recovered from hydraulic fracturing is sharply growing. The only current means of disposal is pumping the waste water into injection wells. Estimates show that between 2010 and 2011, disposal of water into injection wells in Ohio increased from 26 million gallons to 106 million gallons.<sup>7</sup> Disposing of flowback water in this way is cost inefficient and is a waste of a valuable resource. Dumping flowback water into a Class II Injection Well costs between \$1.50-\$2.00/barrel, and transporting that water to a well can cost up to \$4.00/barrel, depending on the proximity of the drilled well to a usable injection well.<sup>2</sup> These estimates combined with the volume of water injected into Ohio wells in 2011 results in a cost of over \$15 million to dispose of flowback water.

Other environmental concerns are present as well. Concerns have been raised on whether the use of injection wells to dispose of flowback water can cause groundwater contamination and reduce the supply of drinking water.<sup>8</sup> Geological surveys have also attributed disposal of water into injection wells to earthquakes, and more than a dozen of these earthquakes were reported in Ohio and linked to the injection of water into wells.<sup>7</sup>

Flowback from hydraulic fracturing cannot be reused for any purpose without first being filtered to remove the components present inside of the water. Various methods are available in order to remove the additives, dissolved solids, and suspended solids, which include coagulation, flocculation, and membrane filtration through ultrafiltration (UF) and nanofiltration (NF). However, these methods at present are not efficient in removing the salts present in flowback. Desalination is required in order to remove divalent salts, which can precipitate when exposed to sulfates and cause scaling in the well, preventing the formation from fracturing properly.<sup>2</sup>

This research paper was made to investigate a method of removing divalent salts from a salt water flowback solution using nanofiltration. A method was found in order to modify polysulfone polymer to give it a positive charge, which will allow for greater rejection of positively charged ions found in salt water. Methods to produce this modified polymer were investigated, and after characterization of the polymer, filtration tests were performed on ideal solutions and collected flowback samples.

## **2. Literature Review:**

### **2.1. Hydraulic Fracturing:**

Hydraulic fracturing is a process used to increase the recovery of oil and natural gas from drilled formations.<sup>9</sup> After an oil or gas well is drilled and cased, holes are shot into the casing at set intervals to reopen the casing and allow access to the formation.<sup>4</sup> Water is pumped into the well at high pressures of 480 to 680 bar to crack open the formation, increasing the flow of oil or gas from the undrilled portions of the well.<sup>10-12</sup> In order to hold the formations open, sand and chemical additives, listed in Table 1, are added to the water to aid in the fracturing and prevent the formation from closing after the water is withdrawn.<sup>1</sup>

For a hydraulic fracturing operation to successfully open a formation, large quantities of water are required, ranging from 2 million to 13 million gallons.<sup>13</sup> A portion of this water is lost to formation that was fractured, and the quantity returned to the surface is highly dependent on the shale type being drilled. The water that is recovered is highly contaminated and cannot be reused without treatment. A small percentage of recovered water, or flowback, is treated and recycled for other industrial applications, but 90% of the flowback is disposed of into injection wells.<sup>14</sup> On a national scale, the water required for hydraulic fracturing is small when compared to other technologies that use freshwater. While a well requires anywhere from 8,000 to 100,000 m<sup>3</sup> to perform a fracture, the water used for hydraulic fracturing is dwarfed by the cooling water requirements for thermoelectric power.<sup>13</sup> An estimated 40% of the national yearly freshwater withdrawal is used for cooling in thermoelectric power generation (278 billion m<sup>3</sup>), and 10% of this water is lost due to evaporation (27.8 billion m<sup>3</sup>). Over the last decade, hydraulic fracturing has required only 1% (300 million m<sup>3</sup>) of the water loss from evaporation to fracture 20,000 wells with an average water usage of 15,000 m<sup>3</sup> per well.

While this is a small percentage on a national scale, locally it causes water resource conflict in drought prone states, including Texas and Pennsylvania.<sup>9</sup> In the 2011 drought in Texas, supply of water for hydraulic fracturing nearly ceased, and natural gas companies attempted to buy their supply from farmers, creating a conflict for water usage to produce food. In the same year, Pennsylvania temporarily suspended 11 permits to natural gas companies to use water from the Susquehanna River Basin for use in hydraulic fracturing, due to the drought decreasing water levels in the basin. The ability to reuse flowback for hydraulic fracturing would have reduced pressure from freshwater sources in times of drought, and would have allowed for continued operations, albeit limited.

## **2.2. Shale Formation:**

Oil and natural gas is produced from shale formations that are rich in organic compounds such as hydrocarbons, namely oil and natural gas.<sup>15</sup> However, due to the non-porous nature of shale, the organic compounds locked in the formations cannot be removed without opening the formations. The widespread use of hydraulic fracturing drastically increased the drilling of shale for oil and natural gas, resulting in production of natural gas from shale increasing from 2% in 2000 to 23% in 2010, and an accessible yield increase from 58.3 billion m<sup>3</sup> to 13.8 trillion m<sup>3</sup>.<sup>11,15</sup> This increase in shale production has caused a surge in water usage for hydraulic fracturing, and as a result an increase in flowback produced.

The volume of water required to fracture a well, as well as the water recovered, is dependent on the shale play that the well is drilled to. Three of the main sources of natural gas shale—Marcellus Shale, Barnett Shale, and Haynesville Shale—have been investigated as to their water requirements to fracture a well, and the flowback recovered from the hydraulic fracturing, which are outlined in Table 3.<sup>14</sup>

Table 3: Water required fracturing a well and water recovered from three of the major natural gas shale formations.<sup>13,14</sup>

Shale Play	Production Contribution	Water Needed to Fracture	Water Recovered	TDS (mg/L)
Marcellus	29%	5.6 million gallons	25%	180,000
Haynesville	23%	5.6 million gallons	34%	110,000
Barnett	17%	4.0 million gallons	35%	60,000

As well as the water requirements, the amount of total dissolved solids (TDS) in flowback is highly dependent on the shale type being fractured. The concentration of TDS can range from near seawater levels of 25,000 mg/L, such as flowback found in Fayetteville Shale, to 180,000 mg/L found in Marcellus Shale.<sup>13</sup> This large variation, as well as the high TDS concentrations found in some shale, makes treatment of flowback difficult.

### **2.3. Flowback:**

While the disposal of flowback is now heavily regulated by the EPA, improper disposal of flowback led to several environmental hazards before regulations were put in place.<sup>16</sup> Before 2010, several sites of flowback disposal lead to environmental contamination, and both ground water and drinking water were polluted with flowback contaminants.<sup>17</sup> After regulations were put in place in 2010, several EPA investigations in Pennsylvania and Texas revealed that tap water was polluted with benzene, a known carcinogen, and flammable concentrations of methane.<sup>16,17</sup>

Currently, flowback is pumped into Class II injection disposal wells as the main method of disposal.<sup>18</sup> This method of disposal requires little to no treatment and results in a very low risk of contamination if proper methods are used.<sup>5</sup> This method is also very wasteful, as the water that is injected can no longer be recycled or reused. It's estimated that 106 million gallons of flowback was disposed of into Ohio injection wells in 2011 alone.<sup>7</sup> For dry regions such as Texas and

California, this water is a precious resource and being able to reuse it would alleviate some pressure of currently scarce water resources.

Unfortunately, due to the high levels of contamination in flowback, reuse of this water is impossible without treatment. Water that is recovered from hydraulic fracturing operations is contaminated with hydrocarbons, organic compounds, and salts as outlined in Table 2,<sup>3,5,6</sup> as well as toxicant-producing microbes.<sup>1,19</sup> While it is not economically feasible to remove enough contaminants to produce drinkable or dischargeable water, it can be treated to a degree and reused in another hydraulic fracturing operation.<sup>3</sup>

Many of these contaminants, including the hydrocarbons and organics, can be removed with conventional and developed treatment methods such as microfiltration, ultrafiltration, and chemicals.<sup>20</sup> Additionally, salts at lower concentrations could be economically removed through reverse osmosis.<sup>21</sup>

However, the salt concentrations that are typically present cannot be removed economically through reverse osmosis.<sup>22</sup> To reuse this water for further hydraulic fracturing, multivalent salts, such as calcium, must be removed, as they can precipitate much more readily than sodium and cause scaling and blockages in wells, reducing flow through pipes and reducing the opening of formations.<sup>2,11</sup>

#### **2.4. Membrane Filtration:**

Membrane separations are processes that use a membrane film in order to filter out different species from a liquid solution.<sup>23</sup> The species that are separated with membranes are determined by the pore diameter, membrane thickness, and the materials that the membrane is made of.

Typical membrane separations include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, with forward osmosis becoming more widespread. Microfiltration and ultrafiltration are

able to remove suspended and dissolved solids from a solution, while nanofiltration, reverse osmosis and forward osmosis are able to filter ions and nanoparticles from liquids.<sup>24,25</sup> Non-membrane methods of filtering salt water are available, but a comparison will be made between reverse osmosis, forward osmosis, and nanofiltration.

#### **2.4.1. Reverse Osmosis:**

Reverse osmosis is a high pressure membrane separation technique that uses pressure and a concentration gradient to remove, or reject, salt ions from a salt water solution.<sup>24</sup> Reverse osmosis membranes use their web-like structure to filter water, forcing water molecules to navigate the fibrous layers and preventing dissolved solids and salts from passing through, or permeating, the membrane.<sup>26</sup> The rejection of salt through reverse osmosis is dependent on the pressure applied to the feed and the salt concentration.<sup>27</sup>

A significant drawback of reverse osmosis is fouling—the buildup of dissolved and suspended solids in the membrane—hindering the flux of water.<sup>28</sup> This fouling can be reduced through pretreatment with microfiltration and ultrafiltration to remove suspended solids. However, these processes are not suited for removing dissolved solids, and fouling can still occur due to the high salt concentrations.

To reduce fouling, reverse osmosis membranes can also be treated with polymers to prevent the buildup of suspended solids. Several research groups have coated commercial reverse osmosis membranes with polydopamine to make the surface hydrophilic and remove surface charges, reducing the tendency for suspended solids to attach to the membrane.<sup>29</sup> These methods helped to reduce the fouling of membranes with minimal effect on the water flux or salt rejection as compared to the manufacturer specifications. However, this study did not perform an economic

analysis on the filtration, and it is unknown if the process was economically viable based on the data presented.

The methods of combined filtration have been tested for the filtration of flowback using a coupled ultrafiltration and reverse osmosis system. A pilot study conducted compared two systems with ultrafiltration coupled with reverse osmosis, one using commercial membranes and the other using a polydopamine and PEG coating on both the ultrafiltration and reverse osmosis membranes.<sup>2</sup> Fouling of the reverse osmosis membrane was significantly reduced in both systems, and salt rejection was increased in the system with the polydopamine coating. The uncoated membranes reduced calcium concentrations from 3,790 mg/L to 59 mg/L (98.5% rejection) and coated membranes reduced concentrations from 3,790 mg/L to 2 mg/L (99.9% rejection). However, this study did not conduct an economic analysis, so it is unknown if this process was economical. This study also tested the minimum concentration of calcium seen in flowback (near 3,000 mg/L), as opposed to using a value closer to the maximum 30,000 mg/L, resulting in a low osmotic pressure of 2,500 kPa (25 bar). An economic analysis using this osmotic pressure would not be representative of a real-world flowback filtration.

Another drawback is that, while filtration through reverse osmosis would desalinate the water and remove the multivalent ions, the pressure required to filter the salts to a low concentration is too great to be commercially viable. This is due to the high concentration of monovalent ions that are present in the solution, which increases the osmotic pressure to filter the ions.<sup>3</sup> Reverse osmosis membranes require a pressure of 15-25 bar to filter brackish water, which has a salt concentration of 1000-5000 ppm, but the required pressure increases to 40-80 bar to filter seawater at a concentration of 35,000 ppm.<sup>23</sup> The amount of salt present in flowback water can be up to 44,000 ppm sodium and 31,000 ppm calcium.<sup>3</sup>



Although limited on flowback treatment through reverse osmosis have been published, efforts have been made to use reverse osmosis to treat flowback water that show it can be an economic process.<sup>30</sup> The pilot unit tested in a previous study was able to filter flowback water at a cost of \$1.25/barrel, considerably lower than the transportation and disposal cost which averages \$6/barrel, estimated to be a net savings of \$253,000/well. However, this study used low concentrations of total dissolved solids, 55,000 mg/L for a blend of flowback and produced water, where an average well would have a considerably higher concentration of total dissolved solids, ranging from 66,000 to 261,000 mg/L.<sup>3</sup> For these applications, other processes are more reasonable, such as forward osmosis.<sup>31</sup>

#### **2.4.2. Forward Osmosis**

Forward osmosis is a membrane separation technique that, unlike pressure-driven processes such as reverse osmosis and nanofiltration, relies on the principle of direct osmosis to facilitate transport across a membrane.<sup>25</sup> Direct osmosis is the drive for the TDS concentration on each side of a membrane to equalize by transporting water across the membrane to dilute the higher concentration side.<sup>31,32</sup>

A typical forward osmosis relies only on the osmotic pressure difference, defined by the difference in concentration of the feed and draw solution, to facilitate transport across a semipermeable membrane that is similar to that of a reverse osmosis membrane.<sup>33</sup> This poses several problems for forward osmosis filtration.

While forward osmosis is not an energy intensive process when compared to pressure filtration techniques, it results in a low transport of water across a membrane.<sup>34</sup> This is due to the fact that the draw solution needs to have a considerably higher osmotic pressure than the feed solution. This can be achieved in two ways: the osmotic pressure of the draw solution can be increased by

adding salt or dissolved solids, or the feed solution can be diluted to decrease the concentration of solids.<sup>35</sup> This as well carries the disadvantage that the draw solution has to be treated to remove the salt added to facilitate the transport of water.<sup>25</sup>

To compensate for this disadvantage, the draw solution can be composed of an easily removable salt solution, such as volatile solvents or perceptible salts.<sup>36</sup> When the volatile solvent, such as sulfur dioxide, is added to the draw solution, the osmotic pressure can be increased past the osmotic pressure of the feed solution. Once the osmotic pressure difference nears zero, the draw solution can be mildly heated to separate the volatile solvent by returning it to a gas state. Afterwards, the volatile solvent can be re-added to the upstream draw solution to continue transport across the membrane.

This process can also be conducted by using precipitable salts, such as aluminum sulfate.<sup>36</sup> In this process, the salt is mixed into the draw solution to increase the osmotic pressure. After the dilution is carried out, the draw solution is treated with a precipitating agent complimentary to the precipitable salt. This process can require considerable treatment though, as any leftover precipitating agent must be removed as well.

For low-salinity operations where the removal of water to purify the feed solution is the desired outcome, or to purify the water for environmental ejection, sodium chloride solutions are often used as the draw solution.<sup>37,38</sup> Potassium chloride has also shown to be an effective draw for these purposes, as it is more easily removed than sodium chloride.<sup>39</sup> However, studies testing these draw solutions have used feed solutions with TDS less than 7,000 mg/L and have the goal of removing oil and acids as opposed to ions.<sup>39,40</sup> For the purposes of removing salt from flowback, this process is not ideal.

For high-salinity operations, including the treatment of flowback, a volatile solution of ammonia and carbon dioxide creates an ideal draw solution.<sup>36,37,41,42</sup> By mixing water with soluble ammonium bicarbonate, a high-salinity solution is created with a high osmotic efficiency, meaning that small concentrations are required to increase the osmotic pressure.<sup>37</sup> The osmotic efficiency allows for high water recovery; a 1.5 M solution can produce an osmotic pressure of 50 bar, which can recover 50% of water from seawater, and a 3 M solution will produce 100 bar of osmotic pressure for a 75% water recovery.<sup>36</sup> Once the draw is diluted, the solution only needs to be heated to 60°C to convert the ammonium bicarbonate to ammonia and carbon dioxide, allowing it to evaporate from solution and be recycled in the draw upstream.<sup>36</sup> By treating water using this solution, a water recovery of 60% can be obtained while reducing the TDS from 70,000 mg/L to dischargeable levels of less than 500 mg/L.<sup>37,41</sup> The process to remove the ammonia and carbon dioxide is energy efficient as well, requiring 275 kWh<sub>th</sub>/m<sup>3</sup> to heat the water to 60°C, which is 57% less energy than would be required to evaporate the water for filtration.<sup>41</sup>

An efficient means of heating the draw solution is using the heat from flared gas.<sup>43</sup> By utilizing the waste heat from flaring, the required energy input can be greatly reduced, allowing for an efficient separation or allowing the use of higher ammonium bicarbonate solutions to increase water recovery.

One of the advantages of forward osmosis over reverse osmosis is the reduction in membrane fouling. In a reverse osmosis system, the applied pressure drives the suspended and dissolved solids into the membrane, whereas in forward osmosis systems the water alone is drawn towards the membrane, resulting in minimal interaction of the dissolved and suspended solids with the membrane.<sup>28,32</sup>

Hybrid reverse osmosis and forward osmosis systems, known as pressure-assisted forward osmosis, have been tested to treat flowback water.<sup>34</sup> In this system, a forward osmosis system is combined with a low to medium pressure pump to increase the flux across the membrane. The addition of pressure to the transport mechanism reduces the required osmotic pressure difference at the drawback of increased energy costs. The unit tested increased the water flux by 22% after a pressure of 10 bar was applied, and reduced the total dissolved solid concentration to 200 mg/L.

#### **2.4.3. Ultrafiltration:**

Ultrafiltration is a membrane separation technique that uses size-exclusion to filter materials from a liquid solution.<sup>23</sup> Ultrafiltration membranes require a low pressure, 1-10 bar, to perform a separation, making them an effective means of removing dissolved and suspended solids from a solution.

Ultrafiltration membranes have pores that range from 1-100 nm to filter materials such as suspended solids and microsolute. While the pore diameter of these membranes can reach close to 1 nm, the species separated must have a considerably lower molecular weight, at least ten times smaller, than the species being retained.<sup>23</sup> This makes the membranes ideal for the removal of chemical additives and solids present in flowback, but not reasonable for the removal of calcium from sodium, which have a much narrower difference in molecular weight.

#### **2.4.4. Nanofiltration:**

Nanofiltration is a membrane separation process that lies between ultrafiltration and reverse osmosis in its separation abilities.<sup>44,45</sup> It is a salt separation technique that relies on an open network structure to separate the ions, as opposed to the homogeneous structure of reverse osmosis.

The pore diameter distribution of nanofiltration membranes is typically less than 2 nm, which is considerably smaller than the pore diameters of ultrafiltration membranes.<sup>23</sup> While the reduction in pore diameter allows for the separation of smaller particles and ions, nanofiltration membranes use surface properties such as the presence of charged groups to increase separation of ions and compounds with different characteristics.<sup>46,47</sup>

For applications in desalination, nanofiltration membranes have the ability to selectively filter different ions in a salt solution, resulting in a higher rejection of multivalent ions than monovalent ions in a salt water solution.<sup>48</sup> This separation of multivalent salts attracted interest towards use in frack water filtration to remove precipitable ions for flowback reuse.

While reverse osmosis can potentially conduct a complete separation, nanofiltration can instead be used in order to carry out the filtration at a considerable lower osmotic pressure, as the membrane will be removing the multivalent ions and a smaller fraction of the monovalent ions.<sup>49</sup> This selectivity reduces the pressure required to filter seawater from the 40-80 bar required for reverse osmosis to 10-25 bar.<sup>23</sup> While this separation can't produce drinking water, as a large concentration of monovalent ions will still be present, the reduction of multivalent ions is large enough that salt water can be filtered and reused for other applications, including hydraulic fracturing.

Commercial nanofiltration membranes, unfortunately, are not suited for the high rejection of multivalent ions necessary for flowback reuse. As shown in research conducted by Haley Cleous, commercial membranes, namely NF3A and others produced by Sepro Membranes, could selectively reject divalent calcium ions to 69.8% while only rejecting 4% of monovalent sodium ions with 16,000 mg/L of calcium in solution. However, this separation was inadequate, and the

commercial membranes could not achieve a 90% rejection and reduce the calcium concentration to below 2,000 mg/L, the concentration required for reuse in hydraulic fracturing.

Titration testing of these membranes showed that most of the membranes contained a negligible charge, and others contained small charges. The quantifiable charges detected on these membranes were predominantly negative charges, which corresponds with previous observations that most commercial membranes are either uncharged or negatively charged.<sup>48</sup>

Uncharged membranes rely on sieving based on pore diameter to filter ions and particles, but the lack of charge and, by extension, the exclusion of Donnan (electrical) effects reduced the effectiveness of the separation of charged ions.<sup>45,50</sup>

Nanofiltration membranes can conduct a separation using both sieving and Donnan effects, allowing for more selective separations than those based on molecular weight. A novel membrane with an added positive charge could be used in order to achieve the desired selective rejection of multivalent positively charged ions. The positively charged membrane would have an increased repulsion of positive ions based on the strength of the charge due to the Donnan exclusion mechanism, the separation resulting from electrostatic interactions of similarly charged membranes and ions.<sup>51</sup> This increased repulsion would allow for the desired rejection of multivalent ions, as divalent and multivalent positively charged ions would receive a stronger repulsion to the membrane than the weaker-charged monovalent ions.

Producing a positive charge on a nanofiltration membrane can be performed through several mechanisms: addition of functional groups, adsorption of ions in the membrane structure, and adsorption of charged molecules.<sup>52</sup> Of interest to this research project was the production of a permanent positive charge on a membrane through the addition of functional groups. This method, unlike adsorption of ions or charged molecules, results in a stable charge that will not be

reduced over time, resulting in a longer-lasting membrane functionality. To produce these charged membranes, the polymer polysulfone was selected for modification by the additional of functional groups.

### **2.5. Polysulfone:**

While commonly used to create ultrafiltration membranes, polysulfone is a widely used polymer for membrane synthesis. Polysulfone is an ideal membrane polymer due to its glass transition temperature of 185-195°C, high pH resistance for both acids and alkalis, and thermal stability, being resistant to hydrolysis in both hot water and steam.<sup>53,54</sup> Membranes produced with polysulfone are highly durable due to the high mechanical properties, including tensile strength and tensile impact, compared to other amorphous thermoplastics.<sup>53</sup> Of interest for the production of novel polymers, polysulfone has the ability to be reacted to produce a variety of functional groups. These reactions include chloromethylation, sulfonation, metalation, and quaternization.<sup>55,56</sup>

The primary reaction of interest to this study is the chloromethylation of polysulfone to add functional chloromethyl groups to the polysulfone monomer, shown in **Error! Reference source not found..** The chloromethylation of polysulfone has been researched considerably for its applicability as a precursor for a wide variety of processes, including functional membranes, coatings, and selectively permeable films.<sup>57</sup> Chloromethylated polysulfone possesses a high chemical stability and retains the physical properties of polysulfone, making it an ideal modified polymer.<sup>57,58</sup>

However, many studies have reported varied procedures and conflicting results, and it is necessary to determine the correct operating procedure and conditions to produce the best polymer.

This chloromethyl group can be reacted with other compounds through a substitution nucleophilic ( $S_N2$ ) reaction, the replacement of chlorine with a strong nucleophile, to form more specific functional groups. Reacting the polymer with trimethylamine, the selected nucleophile, produces a functional group with a positive charge, allowing for higher rejection of positively charged groups.



### **3. Experimental Methods and Procedure:**

The goal of this study is to separate multivalent ions from a salt water frack water solution, while retaining monovalent ions. This was accomplished by producing a polysulfone polymer that held a charge than could increase the selectivity of ions based on their charge. The modification was conducted by performing a chloromethylation reaction on polysulfone polymer, using paraformaldehyde and trimethylchlorosilane as the chloromethylating agent and stannic chloride as the catalyst. Amination of the chloromethylated polysulfone used trimethylamine as the amination agent to produce the charge.

#### **3.1. Polymer Synthesis:**

##### **3.1.1. Chloromethylation of Polysulfone:**

Chloromethylation of polysulfone was carried out as described in previous research.<sup>47,55,59,60</sup> In the initial runs, 13 g polysulfone was mixed with 141 mL of chloroform in a three-neck round-bottom flask to allow for the use of a condenser, a nitrogen inlet, and an inlet for reagents. The flask was heated to 40°C using an oil bath with a temperature control probe.<sup>47</sup> The side necks of the flask were capped with septums and the central neck was coupled with a condenser capped with a septum, shown in Figure 1. Nitrogen was fed into the system through the condenser to remove water and air from the flask, and the solution was stirred for 24 hours with a Teflon-coated stir bar.

When the polysulfone was in solution, paraformaldehyde and trimethylchlorosilane were added in a 1:3:3 molar ratio to the polysulfone for excess reactants, with 0.18 mol/g of the catalyst stannic chloride, shown in Figure 2. Before the trimethylchlorosilane was added, the system was



Figure 1: Apparatus used for polymer modification.

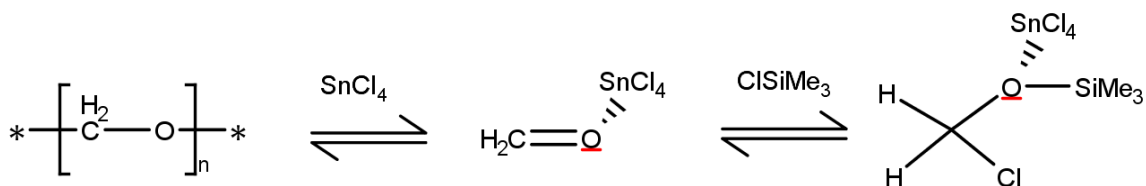


Figure 2: Reactant formation from catalyst, trimethylchlorosilane, and paraformaldehyde.

flushed with nitrogen for five minutes, then the trimethylchlorosilane was added dropwise to the solution, as shown in Figure 3.<sup>55</sup> The flask was then heated to 50°C and mixed with the stir bar for 5 hours. When the reaction came to completion, the solution was poured into methanol to precipitate the chloromethylated polysulfone and separate the remaining reactants. Once the methanol was drained off, the precipitated product was rinsed in methanol and dried in a vacuum overnight, as opposed to an oven to prevent introducing methanol to an ignition source.<sup>54</sup>

After several unsuccessful attempts to modify the polymer, it was found that polysulfone will crosslink if mixed in concentrations greater than 5% mass to volume of polymer and solvent, and

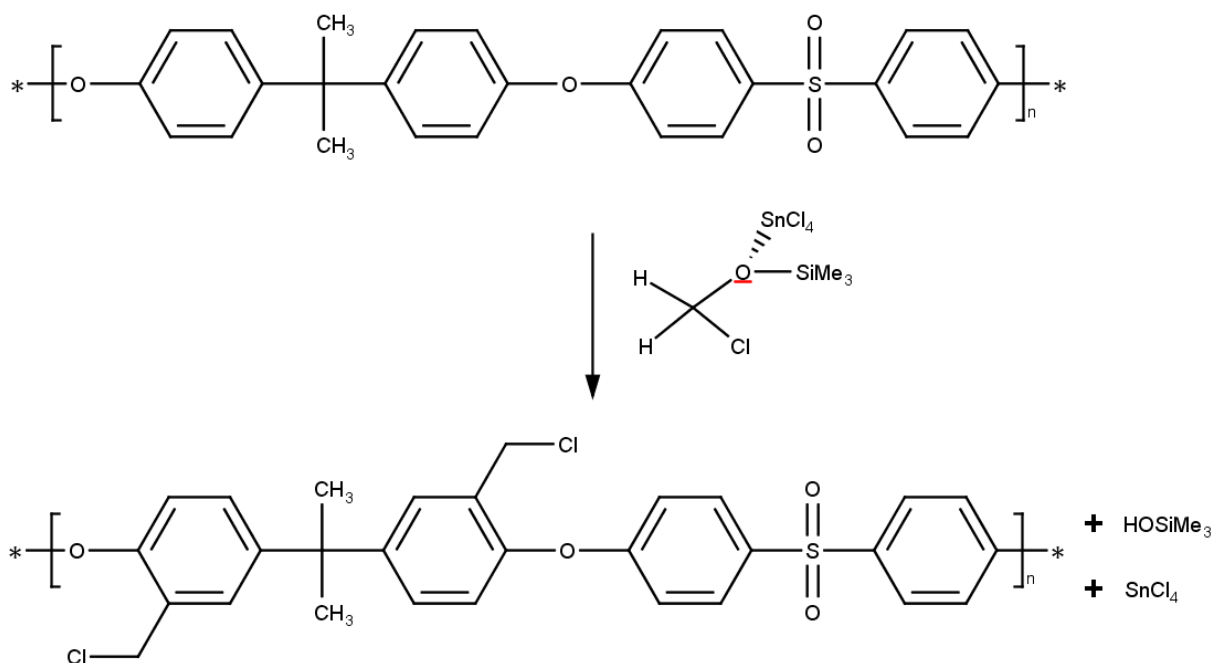


Figure 3: Reaction of polysulfone to chloromethylated polysulfone.

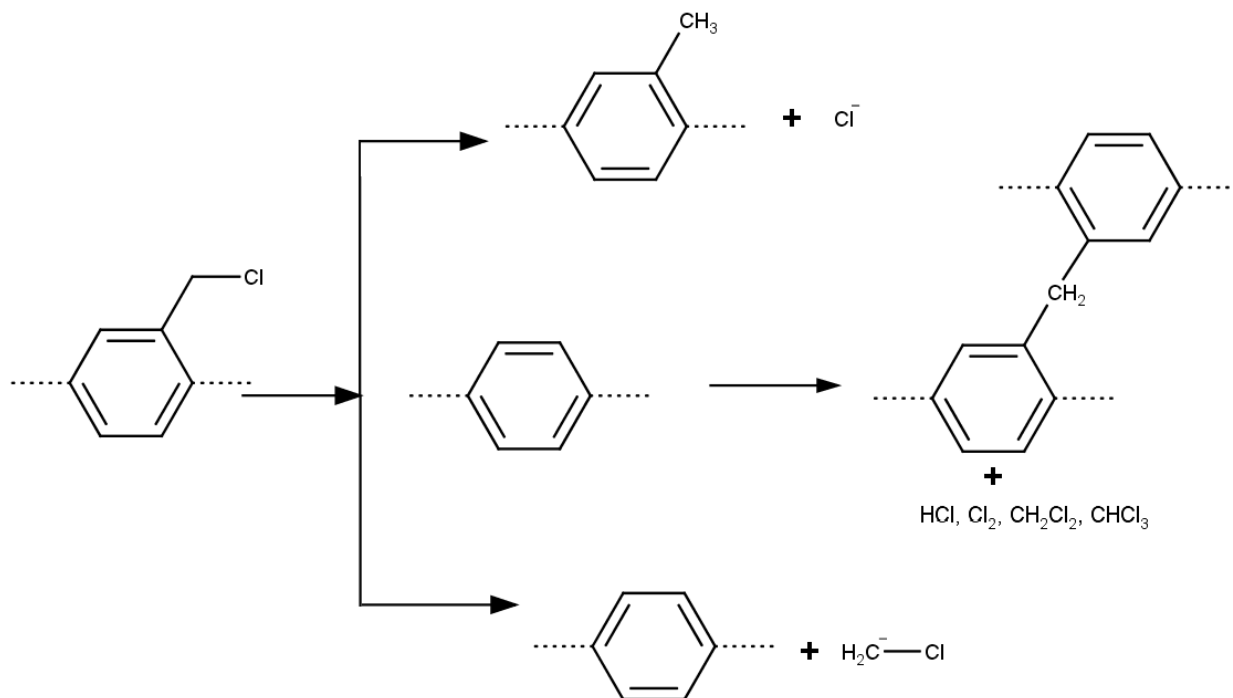


Figure 4: Crosslinking mechanism.

further reactions were carried out in a less than 2% solution with chloroform to prevent this reaction, shown in Figure 4.<sup>59</sup> Additionally, the 1:3:3 molar ratio of polysulfone to paraformaldehyde and trimethylchlorosilane was too low for the reactants to bind at high concentrations. Further reactions used a ratio of 1:10:10<sup>55</sup> to allow the polymer to react, and the ratio of polysulfone to stannic chloride catalyst was changed to 10:1,<sup>61</sup> as described in previous research. To further increase the substitution of the reaction, the reaction temperature was also increased to 60°C<sup>62</sup> and the reaction time was increased to 120 hours.<sup>57</sup>

Initial tests following this procedure used a half batch of 7.44 g of polysulfone, while further tests used the full described batch of 14.88 g of polysulfone.<sup>61</sup> This increase in reactants resulted in an increase in required reaction time, and tests were run for 240 hours to maximize substitution, described as the percent substitution.

### 3.1.2. Amination of Chloromethylated Polysulfone:

Chloromethylated polysulfone was then mixed with 1-methyl-2-pyrrolidinone in a 30% by mass polysulfone concentration and stirred for 10 hours. The solution was then poured onto a paper backing and sheered using a casting knife to a thickness of 200  $\mu\text{m}$ .<sup>47</sup> The membrane was left in open air for 30 seconds, then submerged in a cold water bath at 5°C for phase inversion to allow for a smaller pore diameter.<sup>63</sup> To aminate the chloromethylated polysulfone, the solidified membrane was submerged in 28% trimethylamine for 6 hours, as shown in Figure 5. The trimethylamine was drained, and after rinsing the membrane with DI water, the membrane was submerged in 2 M hydrochloric acid for 1 hour. This process was repeated several times with polysulfone that, as later discovered, was not successfully reacted, and no amination was observed.

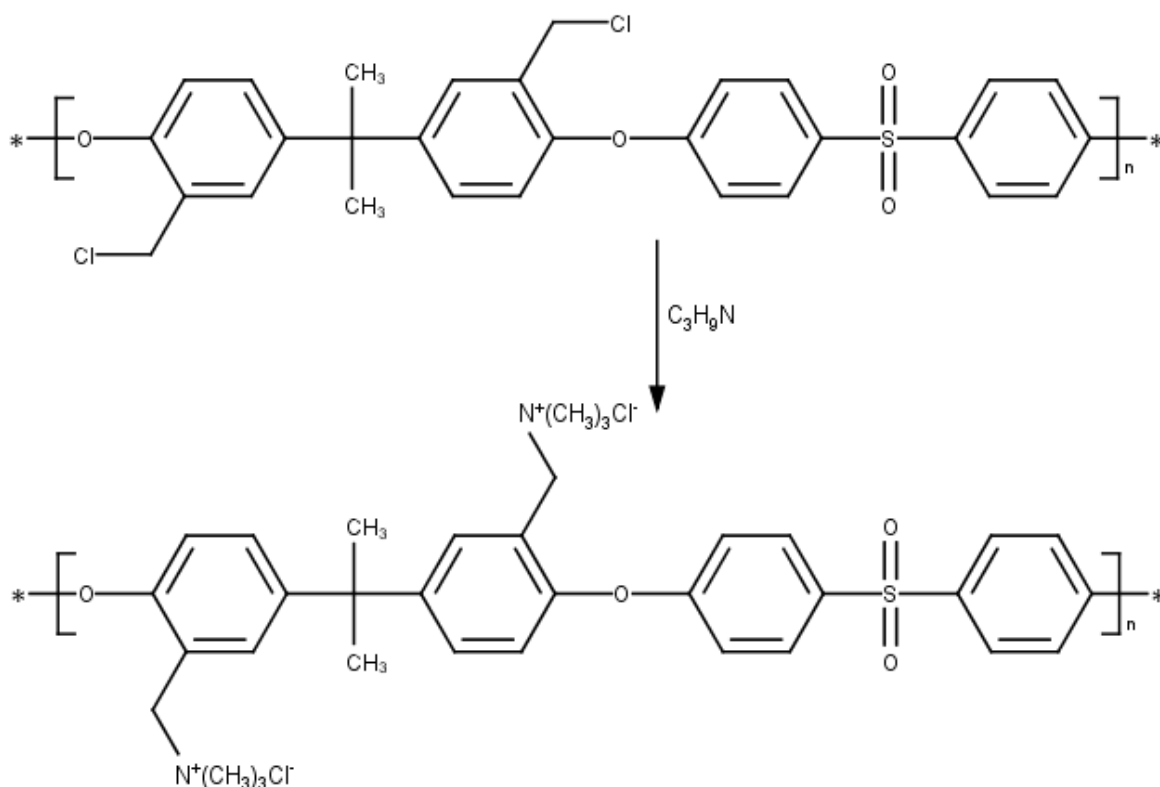


Figure 5: Reaction of chloromethylated polysulfone to quaternary ammonium polysulfone.

During early testing with properly modified polysulfone, it was found that the reaction with trimethylamine caused the membrane to swell. The resulting dried membrane was unusable due to the thinness of the membrane and the cracked features. As a result, a new method was used to introduce trimethylamine into the polysulfone while in solution with 1-methyl-2-pyrrolidinone.<sup>58</sup> Polysulfone in 30% solution was mixed with trimethylamine in a 2:1 mole ratio of substituted chloromethyl groups and stirred for 15 hours at 60°C. The polymer initially phase inverted at the surface, producing a white film, but re-entered solution after heating and mixing. Other methods were explored to use trimethylamine to aminate the polysulfone, such as bubbling trimethylamine vapor into the solution.<sup>64</sup> However, due to the hazards of trimethylamine and the lack of adequate lab space and equipment, the aqueous solution of trimethylamine was favored to aminate the polymer. After amination, the membrane was cast using the previous method to 200  $\mu\text{m}$ .<sup>47</sup>

The membranes cast from the quaternary ammonia polysulfone, the aminated polysulfone produced in this reaction, did not phase invert however, and a spongy gel was formed on the paper backing once the DI water was introduced. Further research found that quaternary ammonia polysulfone is prone to swelling, and requires cross-linking in order to improve the membrane stability.<sup>65</sup>

### **3.2. Phase Inversion of Quaternary Ammonia Polysulfone:**

To crosslink the membranes, quaternary ammonia polysulfone first had to be cast and phase inverted. Most methods that were tested involved a liquid phase inversion, though most research had suggested using gas phase inversion.<sup>58</sup> Gas phase inversion methods involving oven heating or vacuum phase inversion were not tested, as a safe means of containing the n-methyl-2-pyrrolidone vapor was not available.<sup>66,67</sup> Initially, calculations using the Hansen Solubility

Parameters were used to determine a suitable non-solvent for the phase inversion.<sup>68,69</sup> However, the methods used to calculate solubility are not suited for amines, and incorrect behavior was predicted for most solutes, including a determination that the polymer would be insoluble in water.<sup>68,70</sup>

Trial and error was used to determine a proper non-solvent for the phase inversion.<sup>67</sup>

Hydrocarbons and alcohol—hexane, acetone, methanol, ethanol, isopropanol, and 1-butanol—were used to immerse the polymer and attempt phase inversion. Several of these chains had a minor leaching effect on the n-methyl-2-pyrrolidone, but most resulted in either swelling of the polymer or no interaction. Following suggestions from several members of the chemistry department, including Dr. Matthew McIntosh and Dr. Tammy Rehtin, mixtures of salt water were successfully used to perform a phase inversion. 5 M, 3 M, and 1 M sodium chloride solutions were prepared with deionized water, with the 5 M and 3 M solutions resulting in a complete, slow phase inversion and the 1 M solution performing a partial phase inversion. While the membranes could be phase inverted using 3 M or 5 M salt water, their stability in air, DI water, or other solvents did not improve. Consequently, the cast membranes had to be stored in 3-5 M water to prevent the membranes from deforming.

### **3.3. Crosslinking:**

To stabilize the quaternary ammonia polysulfone membranes, a glutaraldehyde solution, diluted to 2% in DI water, was used to crosslink the amine groups.<sup>71</sup> The phase inverted quaternary ammonia polysulfone membranes were immersed in the glutaraldehyde solution and left for a minimum of 2 hours, although most were left overnight to ensure a complete reaction.<sup>71</sup> After crosslinking, the membranes were washed with DI water.

The crosslinking procedure was not entirely successful. The crosslinked quaternary ammonia polysulfone membranes were stable in water and did not swell. However, their stability in air and solvents did not improve. Crosslinked membranes left in air did not expand like the non-crosslinked membranes, but they did become dry and cracked, and as such were unusable. As well, the crosslinked membranes were not stable in alcohols, resulting in swelling in isopropanol, and complete dissolving in ethanol and methanol.

Additionally, the crosslinking failed altogether with highly substituted chloromethylated polysulfone, unlike initial tests with 57% substituted chloromethylated polysulfone. Upon immersing membrane formed with 88% substituted chloromethylated polysulfone, the membrane quickly began to swell. Within 30 minutes the membrane formed a gel like those seen with the attempted phase inversions of quaternary ammonia polysulfone.

Other crosslinking would have been attempted with lower percent substituted polysulfone to determine the characteristics at different substitution stages, but a lack of produced polymer of sufficient quality prevented this test.

#### **3.4. Polymer Mixing:**

In an attempt to improve the stability of the polymer, chloromethylated polysulfone was mixed with unmodified polysulfone to artificially reduce the degree of substitution. Polysulfone from the 57% substituted batch was mixed in equal amounts with unmodified polysulfone in *n*-methyl-2-pyrrolidone. The modified and unmodified mixed homogeneously in the solution, and amination with 28% trimethylamine in water was performed as previously described. However, the water present in the trimethylamine solution caused the unmodified polysulfone to phase invert and precipitate to the bottom of the flask. The precipitated polysulfone did not re-enter



solution after heating and mixing, resulting in a thinner solution of quaternary ammonia polysulfone as opposed to a mixture of polysulfone and quaternary ammonia polysulfone.

### 3.5. Filtration

Testing of commercial membranes was conducted by Haley Cleous and Long Tran using a SEPA CF II cell produced by GE Osmonics, shown in Figure 6. The unit was operating under tangential flow. Feed water was pumped into the cell using a water pump while the cell was held closed under pneumatic pressure. On the same side of the membrane, a retentate outlet allows for rejected water to be removed from the cell. Using a valve with a pressure gauge, the unit was pressurized by closing the valve and reducing the retentate flow. The applied pressure was then



Figure 6: SEPA CF II cell used for nanofiltration.

able to overcome the osmotic pressure and forced water and ions to cross the membrane as permeate.

Solutions tested in this unit included a 50,000 mg/L sodium chloride solution, a 16,000 mg/L calcium chloride solution, and a mixture of sodium chloride and calcium chloride. The unit was operated at 250, 400, 600, 700, and 800 psig to model the sodium and calcium rejection from the tested solutions at different operating pressures. The permeate from these tests was collected and tested for conductivity to determine the ion concentrations of sodium and calcium.

### **3.6. Evaporimetry:**

In order to determine the average pore diameter of the membranes, a technique called evaporimetry was used.<sup>72</sup> In this setup, shown in Figure 7, a high precision scale was

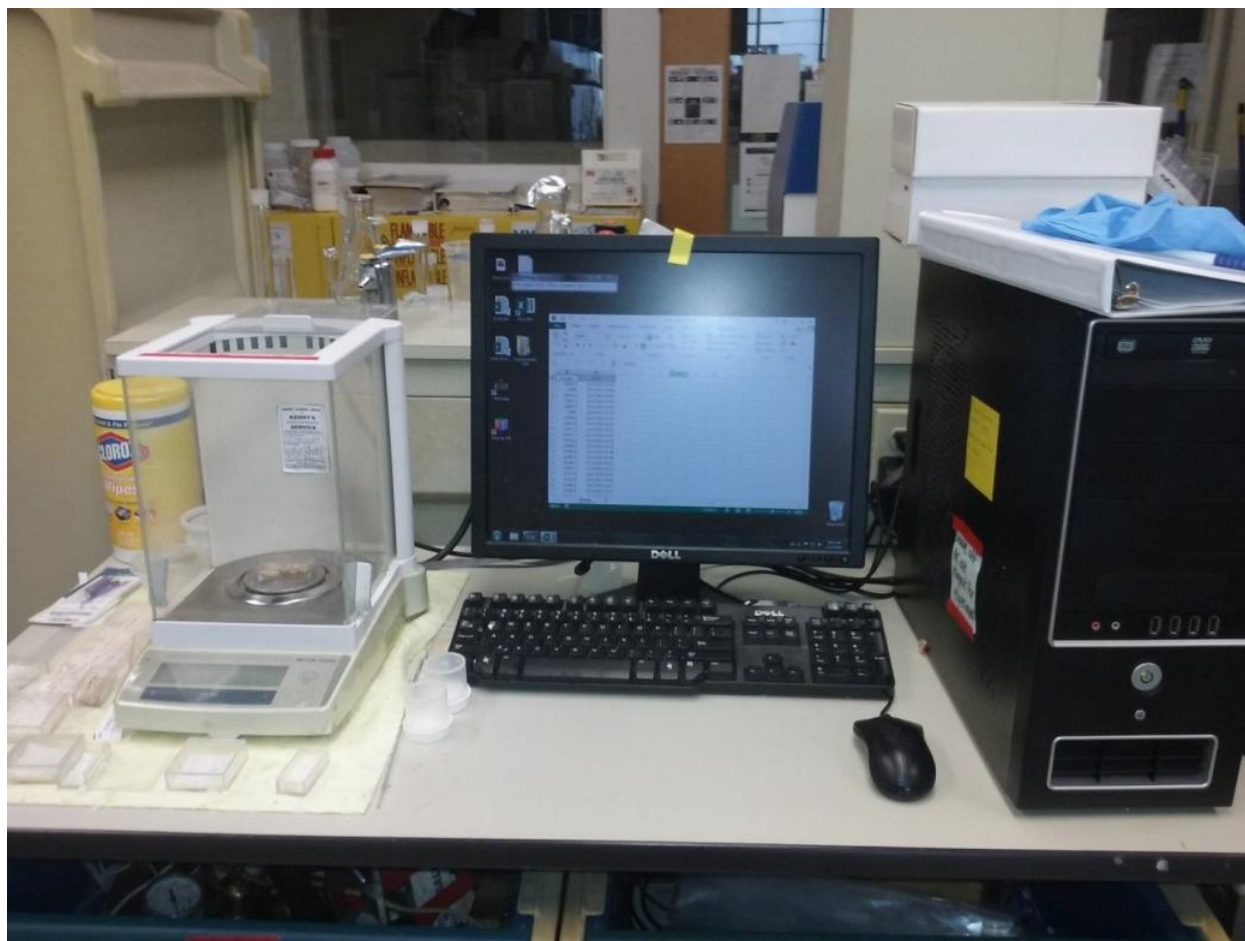


Figure 7: Evaporimetry setup used for pore size determination.

connected to a computer with data logging software.<sup>73</sup> A small, circular piece of a membrane was cut and placed in the lid of a cylindrical container. Isopropanol was poured into the container and the lid was secured then set upside down so the isopropanol could permeate the pores and saturate the membrane. After two hours, the isopropanol was poured off and a new cylinder, with the bottom cut off, was placed on the lid in order to secure the membrane to the vessel. A small volume of isopropanol, enough to cover the membrane surface, approximately 2 mL, was placed on the membrane via the open bottom of the vessel. The vessel was then placed on the scale and the data logging program was initiated, recording the mass of the sample every 30 seconds.

By collecting the mass of the sample every 30 seconds, the evaporation rate of the isopropanol could be measured over time. Using Irvin Langmuir's Equation, the vapor pressure,  $P_v$ , can be calculated from the evaporation rate:

$$W = (P_v - P_p) \sqrt{\frac{m}{2\pi RT}} \quad (1)$$

where  $W$  is the evaporation rate of isopropanol in g/min. This holds true as the isopropanol evaporated from the membrane surface, as it is nearly constant and equivalent to literature values. The instantaneous vapor pressure can be obtained this way from the change in evaporation rate as the isopropanol evaporates from the pores of the membrane. After calculating the vapor pressure, the Kelvin Equation can be used to determine the radius of the pores<sup>74</sup>; this method has been validated to a diameter of 2 nm.<sup>75</sup>

$$\ln \frac{P'}{P} = - \frac{2\sigma V}{RT r \cos\theta} \quad (2)$$

where  $P'$  is the instantaneous vapor pressure and  $P$  is the vapor pressure at standard conditions. Solving for the radius and substituting the instantaneous and standard vapor pressure for the

instantaneous and standard evaporation rate respectively, the equation can be solved for the radius:

$$r = - \frac{2\sigma V}{RT \cos\theta \ln \frac{W'}{W}} \quad (3)$$

Using a programmed excel file, the evaporation rate at each point can be calculated from the recorded mass and the calculated pore diameter at each data point from the evaporation rate.<sup>73</sup> By averaging the pore diameter values obtained in the period that isopropanol is evaporating from the pore structure and not the surface, the average pore diameter of the membrane can be obtained.

When performing this procedure with the crosslinked quaternary ammonia polysulfone membranes, a substitute evaporation liquid had to be used, as the membrane was soluble in the isopropanol that was previously used. Instead, DI water was used by soaking the membrane, as done previously, and placing a small volume, approximately 1 mL, on the membrane. As water has a higher vapor pressure than isopropanol, the evaporation rate was slower, and the procedure was carried out over a three day period, as opposed to overnight. To allow for easier data management, data points in groups of four were averaged out to produce a similar quantity of data points to the isopropanol experiments.

### **3.7. Titration**

Due to the fact that stable quaternary ammonia polysulfone membranes could not be reliably formed, titration testing could not be conducted as planned. Titration testing with complete membranes would have been performed as described in previous research.<sup>52</sup>

Comparisons would be made between three membranes: standard polysulfone as a control, chloromethylated polysulfone, and quaternary ammonia polysulfone. To determine the negative charge, a 3x3 cm piece of each membrane would be washed then immersed in 50 mL of a 0.1 M

NaCl solution to allow sodium to replace the original counter-ions. After being immersed for at least 15 minutes, the determined adequate time for complete counter-ion replacement, the membranes would be immersed in 50 mL of a 0.01 M MgCl solution to allow the sodium ions to enter solution. The membranes would be immersed in this solution for at least 15 minutes as well. This solution was tested with atomic absorption spectroscopy determine the sodium concentration. This procedure was performed to determine the positive charge by replacing NaCl with NaF and MgCl with Na<sub>2</sub>SO<sub>4</sub>. This allowed for fluorine to replace the original counter ions and the concentration of fluorine was determined using a conductivity meter.

## 4. Results and Analysis:

### 4.1. Economics

To determine if nanofiltration would be a competitive technology compared to reverse osmosis, economic analyses were made to compare the disposal costs through deep well injection with the treatment costs through reverse osmosis and conventional nanofiltration. Due to the fact that stable positively charged membranes could not be formed, an economic analysis was not performed with filtration measurements for the novel membranes, as the rejection of calcium and sodium could not be determined.

Disposal of flowback into injection wells can cost up to \$6/barrel, where between \$1.50-\$2.00/barrel is required to inject the water and up to \$4/barrel are required for transportation. For a treatment technology to be economical, the cost per barrel to filter the flowback must be lower than the disposal cost, and units should be mobile to minimize the cost of transportation.<sup>2</sup>

Reverse osmosis is not competitive when compared to these costs. Small scale reverse osmosis plants can desalinate pretreated brackish water at a cost of \$4.28/barrel, but the calcium and sodium concentrations are much lower in brackish water than in flowback.<sup>76</sup> As such, the cost to filter flowback with a comparable reverse osmosis unit would be significantly more as the TDS concentration increases from 3,800 mg/L to up to 66,000 mg/L.<sup>3</sup> Conversely, the cost to treat flowback using nanofiltration can be as low as \$1.31/barrel due to the significant decrease in the required osmotic pressure.<sup>76</sup>

Calculations for the treatment costs through reverse osmosis and nanofiltration were performed by Haley Cleous using the Van't Hoff Equation to calculate the osmotic pressure to filter real world flowback solutions and determining the water recovered for each solution:<sup>77</sup>

$$\Delta\pi = iCRT \quad (4)$$

By calculating the water recovered, the cost to dispose the water that could not be filtered can be determined. The theoretical percentage of water recovered assumed 99.9% rejection of Ca and Na in RO systems and 67% rejection of Ca and 5% rejection of Na in NF systems.

Table 4: Theoretical water recoveries of collected flowback.

Na and Ca Concentration (mg/L)	RO – 1,500 psi	RO – 3,000 psi	NF – 700 psi	NF – 1,500 psi
66,000 (TX)	0%	25%	86%	88%
51,100 (OK)	0%	42%	90%	92%
26,900 (ND)	35%	70%	86%	90%
17,313 (UT)	55%	80%	97%	98%

As reverse osmosis systems require a large osmotic pressure to filter flowback, the system cannot recover water from high-salinity flowback (66,000 mg/L) unless higher-than-standard operating pressures are used. At standard operating pressure, only 55% of the water can be recovered in low salinity flowback (17,313 mg/L), resulting in a considerable amount of flowback (45% of the original flowback) that must still be disposed of through conventional methods.

Nanofiltration allows for a significantly greater quantity of water to be recovered through the reduction of the osmotic pressure. At standard operating pressures, nanofiltration can recover 97% of water in low salinity flowback and up to 86% in high-salinity flowback. This considerably reduces the total cost of disposal and results in a more economical approach to filtration. The significant decrease in required energy to perform the desalination, the substantial increase in the water recovered, and the near ideal salinity composition of recovered water led to the investigation of functional nanofiltration membranes.<sup>77</sup>

However, these water recovery values can be expected to be less for highly selective positively charged membranes, as the increased rejection of calcium will increase the required osmotic pressure. Considering this factor, the percent of recovered water will still be substantially higher

than reverse osmosis filtration, and treatment costs would only be minimally increased by the higher operating pressure.

#### 4.2. Filtration:

Filtration of commercial membranes was conducted by Haley Cleous and Long Tran to determine the ion rejection of calcium and sodium in nanofiltration.<sup>77,78</sup> Five commercial membranes produced by Sepro were tested at operating pressures ranging from 250-800 psi in solutions containing 50,000 mg/L of sodium and 16,000 mg/L of calcium. The results of the mixture of sodium chloride and calcium chloride are shown in Figure 8 and Figure 9. These concentrations match the measured calcium chloride and sodium chloride found in Texas flowback.

In ideal solutions containing only calcium chloride at measured concentrations, NF3A and NF3.1A outperformed the other commercial membranes. At pressures above 600 psig, NF3A

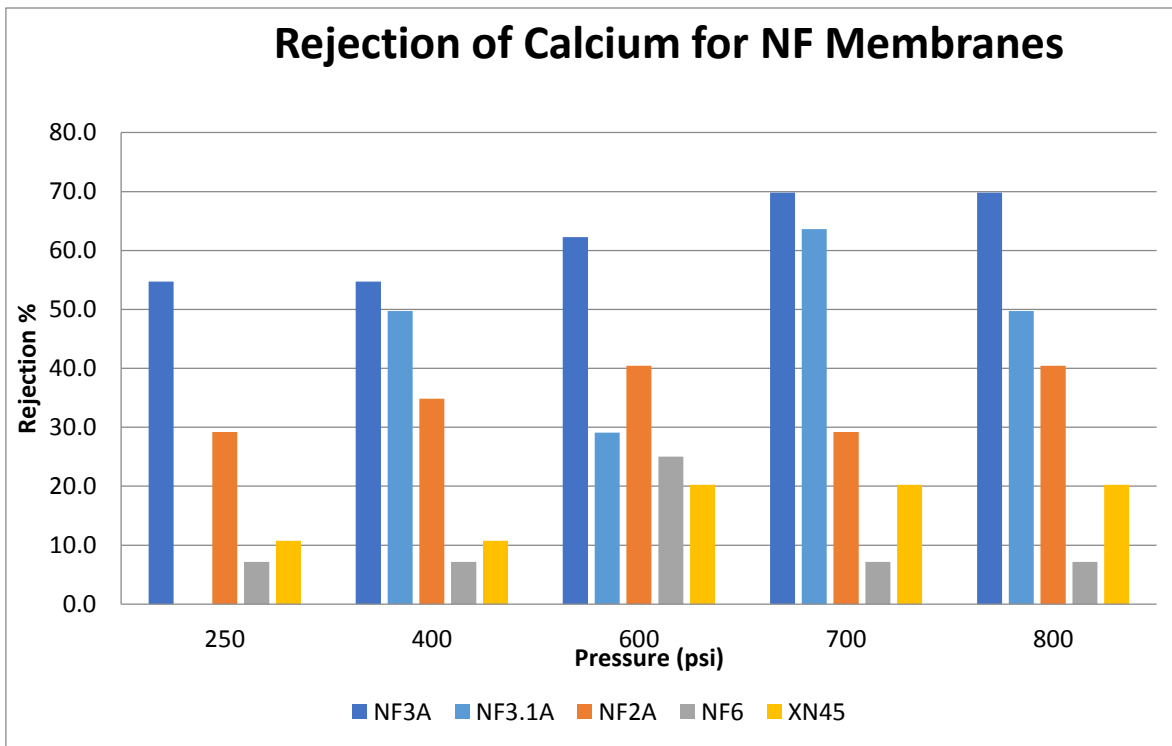


Figure 8: Rejection of calcium in filtration using commercial nanofiltration membranes.<sup>78</sup> This graph was produced by Long Tran.



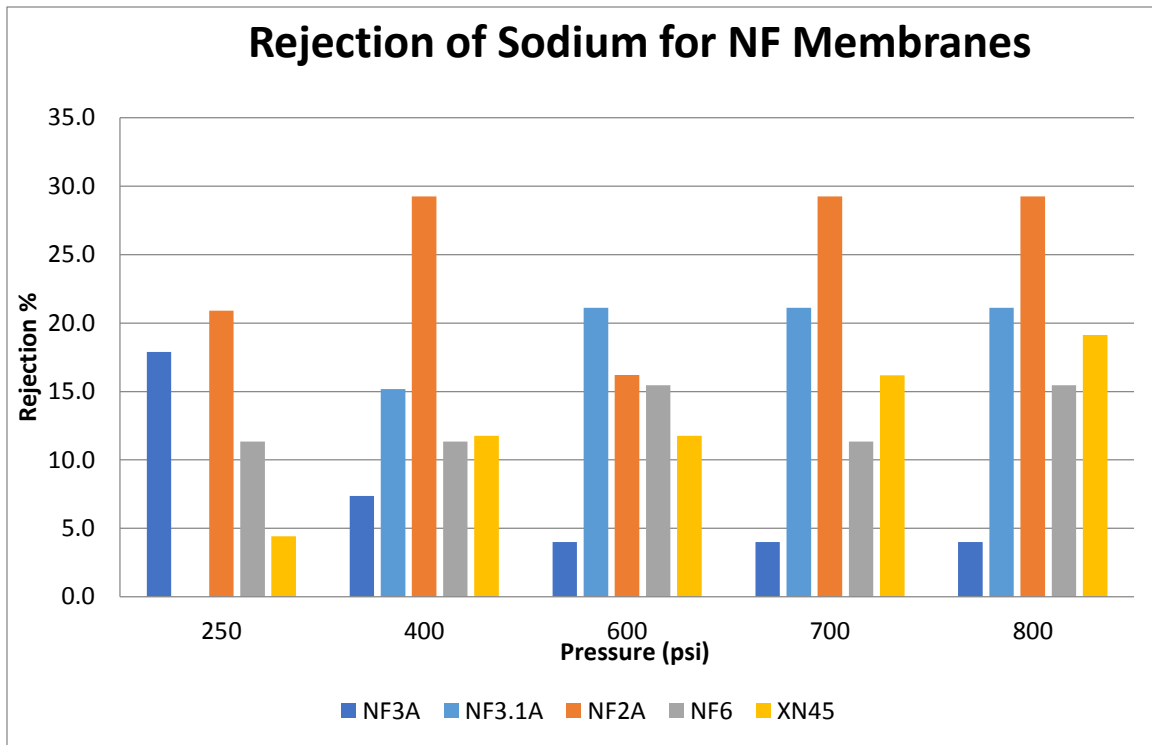


Figure 9: Rejection of sodium in filtration using commercial nanofiltration membranes.<sup>78</sup> This graph was produced by Long Tran.

rejected between 84% and 91% of calcium in the solution, and NF3.1A rejected between 94% and 95.5%. Of these two membranes, NF3A had far superior performance in real world solutions. NF3A showed the highest rejection of calcium: 69.8% at both 700 and 800 psig. This membrane also resulted in the lowest rejection of sodium at 4% at 600, 700, and 800 psig. NF3.1A only rejected 53.6% and 49.7% of calcium at 700 and 800 psig respectively, and rejected as much as 25% sodium at 700 psig, resulting in a far lower separation than NF3A. As previously stated, the 69.8% rejection of calcium was inadequate to reduce the calcium concentration required for flowback reuse. To reduce the concentration to below 2,000 mg/L, new membranes were required that had a greater rejection of calcium.

Due to the instability of the quaternary ammonia polysulfone membranes in water, filtration testing could not be conducted with the custom membranes created in this experiment. In

addition, limitations with the phase inversion apparatus meant that membranes of an adequate size could not be produced to conduct filtration testing with the reverse osmosis apparatus present in the lab. Modifications were made to a dead-end flow unit to allow for tangential flow filtration. Filtration testing would have been conducted using the modified Millipore Filtration Unit shown in Appendix 8.2.

### **4.3. Characterization:**

#### **4.3.1. Evaporimetry**

For pore diameter characterization, a technique known as evaporimetry was used to correlate the evaporation of isopropanol from membrane pores to the pore diameter. Extensive tests were run to determine the pore size distribution of polysulfone and commercial membranes, both in this study and in research conducted by Haley Cleous. Unfortunately, the lack of refinements in the procedure for performing evaporimetry resulted in potentially inaccurate, although consistent, data. The initial procedure did not include soaking the membrane in isopropanol before the experiment began. As a result, isopropanol began soaking into the membrane as the evaporimetry was being conducted, and the standard evaporation rate was not consistent. Additionally, the membrane was not fully saturated when the surface isopropanol evaporated, and the pore diameters obtained instantaneous evaporation rates that were not representative of the actual pore diameters. The issues created through the improper procedure are shown in Figure 18 in Appendix 8.3. The procedure was altered so that membranes would be soaked for several hours before evaporimetry was conducted. Short soaking times of 2-4 hours resulted in curves that were improved but still incorrect, so a modification to an overnight soak was used, and proper results were obtained using this soak time.

Another issue that arose when obtaining evapoporometry results was a miscalculation in the membrane thickness when conducting the phase inversion. Initial membranes were cast to a thickness of 200  $\mu\text{m}$ , as described in previous research.<sup>47</sup> However, the thickness of the paper backing was not taken into account, and the cast membranes only had a polymer thickness of 48  $\mu\text{m}$ , with the backing making up 152  $\mu\text{m}$  of the membrane thickness, producing plots like those of Figure 17 in Appendix 8.3. These membranes had an average pore diameter of 57 nm—much too low for nanofiltration. After these results were obtained, the casting thickness was increased to include the thickness of the backing, which corrected the results showing large pore diameters. Accounting for procedural changes in both evapoporometry and membrane casting, the new membranes produced results more similar to that of commercial membranes, although with a larger pore diameter and wider pores size distribution.

Testing of commercial membranes with Haley Cleous showed that the tested membranes had large concentrations of pores below 2 nm, ranging from 41% to 69% of the pores.<sup>77</sup> Of the membranes, NF2A had the highest concentration of 2 nm or less pores at 68.9%, followed by NF3A with 63.4%, shown in Figure 21 and Figure 22 respectively in Appendix 8.3. While NF2A had the highest concentration of 2 nm and smaller pores, this membrane also had a considerable concentration—roughly 9%—of 6 nm pores.

Table 5: Comparison between percent of pores below 2 nm and rejection of calcium and sodium at 700 psig.

Membrane	% of Pores below 2 nm	Rejection of Na (700 psig)	Rejection of Ca (700 psig)
NF2A	68.9%	29.2%	29.2%
NF3A	63.4%	4.0%	69.8%
NF3.1A	44.5%	21.1%	63.6%
NF6	41.1%	11.3%	7.10%
XN45	43.2%	16.2%	20.2%

While NF2A had the highest concentration of small pores, it performed very poorly in filtration testing, rejecting only 29.2% of calcium and the same percentage of sodium, neither of which are desirable permeate concentrations for reuse. The best performing membrane, NF3A, had a similar concentration of small pores, and a significantly improved selective rejection of sodium and calcium. In opposition to NF2A, NF3A had a very small pore diameter distribution and almost no notable concentrations of pores above 2.5 nm, shown in Figure Figure 23: Pore size distribution of NF3.1A. in Appendix 8.3. NF3.1A, which has a much smaller concentration of 2 nm or smaller pores at 44.5%, had a rejection of sodium near that of NF2A but a rejection of calcium just below NF3A. Similarly to the NF2A membrane, NF3.1A had a high concentration of 6-8 nm pores; this range accounted for nearly 25% of the pores. Even consideration to the undesirable pore characteristics of NF3.1A, this membrane had a greater selectivity and higher calcium while having a larger pore diameter distribution and percentage of small pores than NF2A. It could be correlated that a reduction in pore diameter distribution and average pore diameter may not be the most efficient method to increase the selective rejection of calcium over sodium. This led to the increased desire to explore positive charge as a means to further the separation.

Early-cast membranes did not produce a desirable pore diameter distribution when compared to that of commercial membranes. The standard polysulfone membranes measured an average pore diameter of 16 nm, closer to that of an ultrafiltration membrane, which can be seen in Figure 19 of Appendix 8.3. The pore diameter is especially poor when compared to the commercial membranes tested by Haley Cleous, which had a high percentage of 1 and 2 nm pores. It is possible to improve this however by optimizing the casting process.

After chloromethylation, amination, and crosslinking, new polysulfone membranes were tested with evaporimetry using DI water, due to the isopropanol causing the membranes to swell. These membranes produced a much more promising curve, shown in Figure 20 in Appendix 8.3. The measured average pore diameter for these membranes was 6 nm, much closer to that of the commercial membranes tested. This could have been a result of the slow phase inversion in the salt water bath. Unfortunately, the pore diameter distribution was large in comparison to commercial membranes, which had a very small concentration of large pores above 4 nm. Figure 24 in Appendix 8.3 shows that there is a moderate concentration of 1.5-3.5 nm pores, but there are also higher concentrations of larger pore diameters ranging from 5-14 nm nearly equal to that of small pores. This is likely an issue caused by the phase inversion process used in the experiment; improved equipment to allow for consistent shearing and faster phase inversion could produce higher quality membranes with a narrower pore diameter distribution. While decreasing the pore diameter to lower values than those of commercial membranes would potentially increase the separation, this is difficult due to the limitations of the apparatus being used. Applying a secondary means of separation such as positive charge would have a stronger effect in increasing the separation. The methods involved in producing positive charges in a membrane are more feasible as well, due to the equipment and facilities made available by Dr. McIntosh and Brian Walker in the chemistry department.

#### **4.3.2. Titration**

To determine the charge of commercial membranes, titration was performed by Haley Cleous to quantify the positive or negative charge of the membranes.<sup>77</sup> The titration tests showed that the tested commercial membranes had a small charge density. These membranes each contained a positive charge between 2.72 to 3.11 milli-equivalents (the number of functional groups) per

square meter. While these equivalents are greater than those tested for other membranes, the exact charge density could not be determined.<sup>52</sup> The atomic absorption tests performed to determine the presence of negative charges on the membranes were inconclusive, as the ion concentrations obtained from the titration were too low to quantify using the standards available. As such, a comparison between the equivalent positive and negative charges could not be made, and the net charge could not be determined.

Regardless of how many negatively charged groups were present, a stronger equivalent positive charge is likely required to produce the net positive charge desired for the selective separation. Membranes tested with similar equivalents per square meter were predominantly negatively charged or had a small net positive charge.<sup>52</sup> Increasing the charge density will produce a membrane with the desired separation characteristics.

#### **4.3.3. Proton Nuclear Magnetic Resonance:**

Due to the fact that the product was a modified version of polysulfone, analytical techniques were required to quantify the polymer and determine the completion of the reaction. Proton nuclear magnetic resonance (H-NMR) was used to characterize the unreacted polysulfone, chloromethylated polysulfone, and quaternary ammonia polysulfone. Most literature for reacting polysulfone to a functional polymer used this chloromethylation reaction, as the functional polymer is highly reactive and produces distinct H-NMR plots.<sup>47,58,60</sup> Chloromethylated polysulfone can be easily formed into a membrane, and can be reacted with a strong nucleophile to produce specific functional groups, namely a positively charge formed from a quaternary ammonia functional group. The high concentration of positive charge formed from this polymer could drastically increase the selective rejection of multivalent positively charged ions over

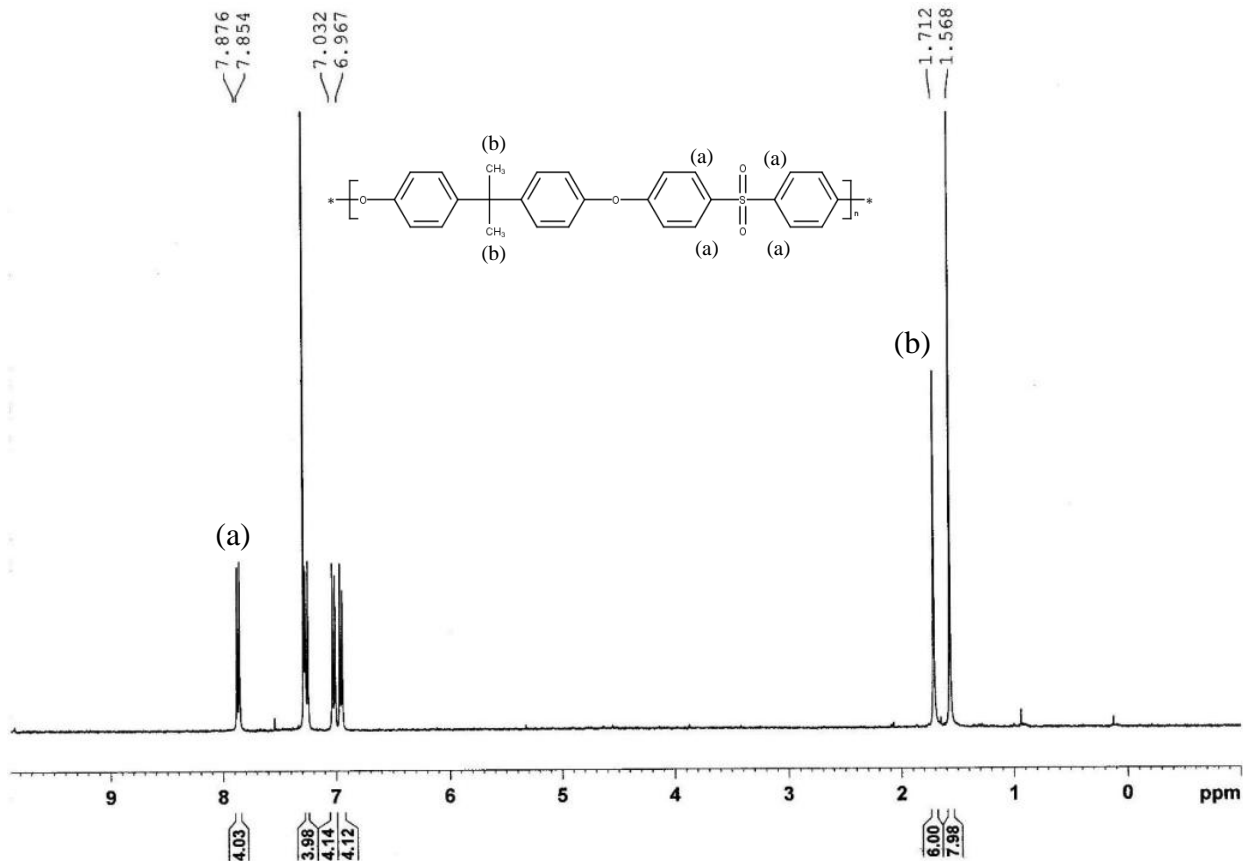


Figure 10: NMR results of polysulfone polymer.

monovalent positively charged ions. This would allow for the collected flowback from hydraulic fracturing operations to be reused in future hydraulic fracturing.

Samples for H-NMR characterization were taken by collecting polysulfone in chloroform solution and quenching the sample in methanol to precipitate the polysulfone. The methanol and chloroform were removed, and the sample was dried in a vacuum to remove the remaining solvent. In some runs, not all solvent could be removed before H-NMR was run, resulting in large peaks at 7.4 and 1.5. The solid polymer was mixed with deuterated chloroform (CDCl<sub>3</sub>) to prevent interference.

Standard polysulfone produced H-NMR data as predicted by previous research, with the addition of methanol and chloroform curves shown in Figure 10. The peak marked as (a) correspond to

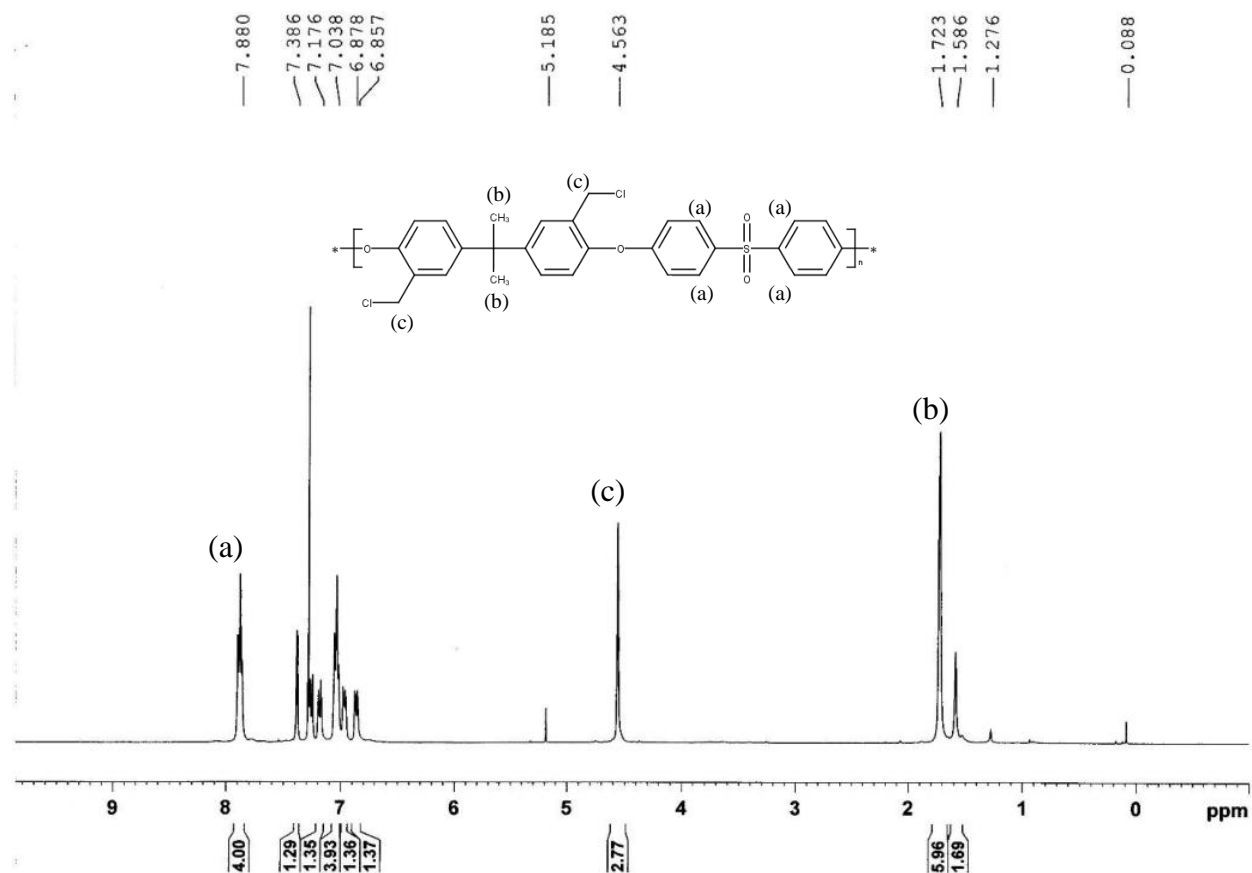


Figure 11: NMR results of chloromethylated polysulfone after procedure changes.

the four hydrogen atoms adjacent to the sulfone group, and peak (b) corresponds to the six hydrogen atoms present in the two methyl groups. The integration of the peaks was performed by correcting the value of the area at peak (a) to 4, allowing for the number of hydrogens present at the characteristic peaks to be quantified.

Chloromethylated polysulfone was analyzed at different reaction times and batch sizes to determine the optimum conditions for maximum substitution. H-NMR results revealed that the chloromethylation of polysulfone was dependent on the polysulfone batch size and the reaction time of the chloromethylation reactions. The half batch that initially provided successful results was collected at 72 hours and immediately tested in H-NMR, showing a substitution of 26%. The subsequent test was allowed to run for 96 hours and yielded a substitution of 69%, shown in



Figure 11. When the batch size was increased to match the procedure used, a reaction time of 120 hours only produced a substitution of 58%. The final run that was conducted was allowed to react for 240 hours, and H-NMR revealed a substitution of 88% shown in Figure 13 in Appendix 8.3. Comparisons of experimental results and literature substitutions under the same reactant ratio and solvent concentration are listed in Table 6.

Table 6: Comparison of batch size, reaction temperature, and reaction time to degree of substitution.

Batch Size (g of PS)	Reaction Temp (C)	Reaction Time (hours)	Substitution
0.5 <sup>55,59,60,79</sup>	50	72	79%
5 <sup>58</sup>	55	48	50%
14.88 <sup>62</sup>	60-70	72	75%
7.44	60	96	69%
14.88	60	120	58%
14.88	60	240	88%

H-NMR was also performed on quaternary ammonia polysulfone produced from the 69% substituted chloromethylated polysulfone shown in Figure 14 in Appendix 8.3. The spectra showed two peaks where the quaternary ammonia was thought to be, so the exact completion of the reaction could not be determined. However, both peaks had integrated values close to that of the expected substitution, so it was concluded that the amination was reacted to near completion.

#### 4.3.4. Fourier Transform Infrared Spectroscopy:

Another analytical technique used to quantify the polysulfone was Fourier Transform Infrared Spectroscopy (FTIR). However, the results obtained through FTIR were ultimately inconclusive. While the characteristic peaks of modified polysulfone could be found in FTIR tests, neither the characteristic peaks of the chloromethyl group nor the quaternary ammonia group had peaks with the same magnitude described in any articles.<sup>47,58</sup> In select FTIR results these peaks were discernable and had a small magnitude (the peak present at 751 cm<sup>-1</sup> in Figure 16 in Appendix 8.3). However, given the magnitude of H-NMR peaks of the same polymer batch, the FTIR peak

magnitude did not indicate the degree of reaction actually present in the polymer. There were also inconsistencies between FTIR peak magnitudes of the membranes, even between the same polymer chains, and subsequent tests of different membrane pieces showed either different peak magnitudes or complete shifts in the spectrum. These differences in peak magnitude could have been the result of inconsistent or uneven spreading of reacted polymer in the membrane, resulting in sections of membranes having higher concentrations of chloromethyl groups than others. Spectrum shifts could have been the result of surface deformities resulting in more open space being analyzed. This led to a high degree of variability between tests and difficulty in comparing results between different polymer batches, examples of which are shown in Figure 15 and Figure 16 in Appendix 8.3. As a result, FTIR was not used in the determination of the polymer functional groups.

#### **4.3.5. Scanning Electron Microscopy:**

To determine the surface characteristics of the membranes produced, scanning electron microscopy (SEM) was required to observe the characteristics, irregularities and defects of the membranes. SEM analysis of unmodified polysulfone membranes revealed a flat surface where several types of irregularities could be seen, including protrusions, creases (shown in Figure 12), and foreign grain structures. Due to the limited resolution of SEM images, pore diameter analysis couldn't be performed using this technique, as the pores were determined to be in the nanometer scale through evapoporometry. Pores could be seen, however, as numerous black spots that covered the surface.

No SEM analyses were performed on the quaternary ammonia polysulfone membranes, due to the difficulty of producing stable membranes. Membranes were required to be dehydrated before scanning, and the quaternary ammonia polysulfone membranes had to remain wetted with salt

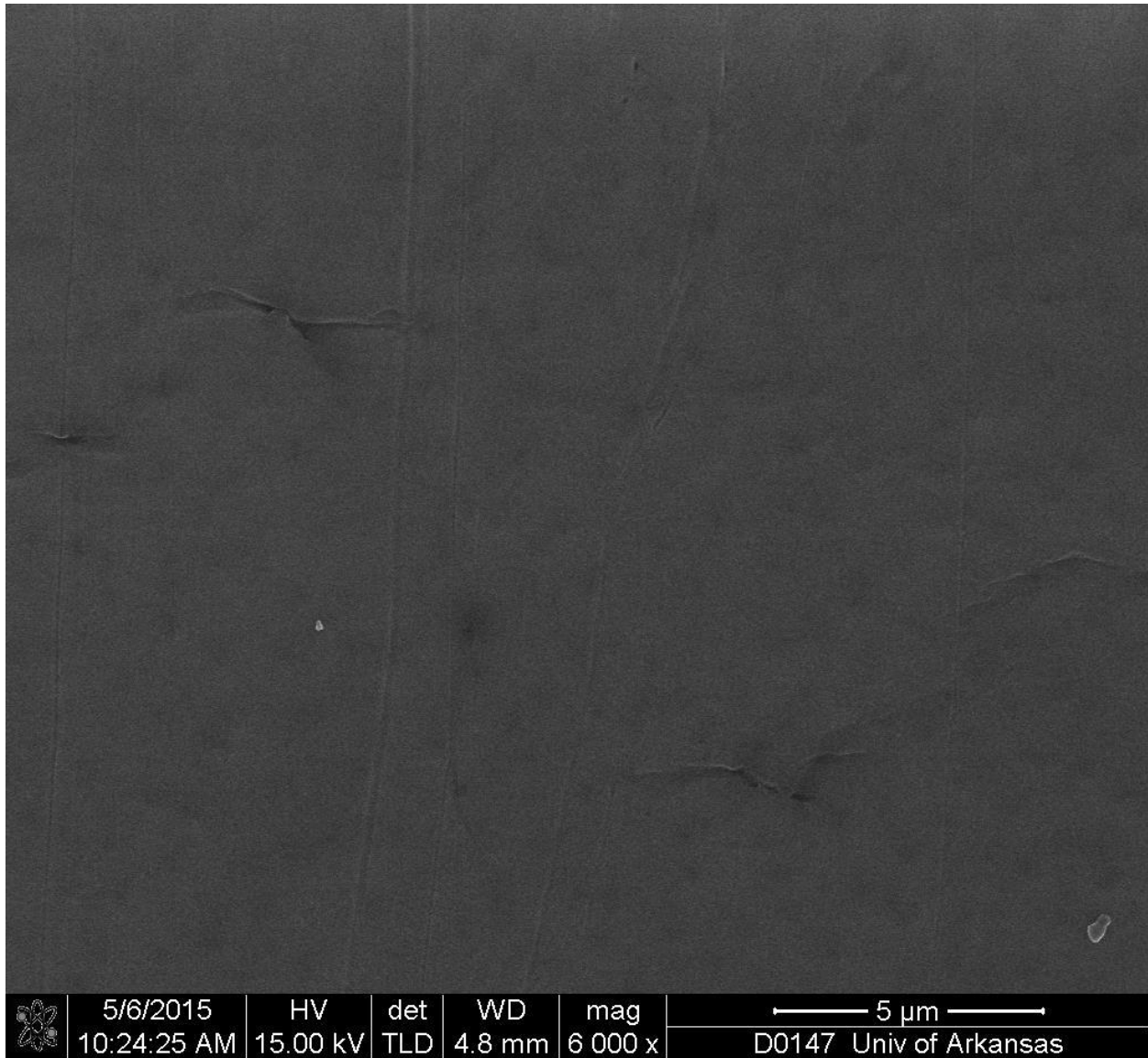


Figure 12: SEM surface image of an unmodified polysulfone membrane.

water, otherwise they would deform. As a result, membranes prepared for SEM analysis became deformed and unusable for analysis when testing was attempted, and SEM could not be performed on stable membranes due to the fact that they were not fully dried. Environmental SEM—a related SEM technique—could have been used on these membranes, but the decreased contrast would have decreased the quality of the images to the point that pores could not be resolved.

## 5. Conclusions:

The method of producing chloromethylated polysulfone was tested and optimized. Experiments using methods of several previous research projects produced unreacted and potentially crosslinked polymers.<sup>47,58</sup> A low concentration of polysulfone—less than 2% of polysulfone in chloroform solvent—and a high ratio of reactants to polymer—10:1—are required to successfully produce chloromethylated polysulfone.<sup>55,62</sup> The required reaction times were also significantly longer than those mentioned in previous research, which ranged from 5 to 120 hours. Batches reacted for 120 hours only produced one functional group on each monomer, and 240 hours was required to approach two functional groups per monomer.

Amination with trimethylamine was successful, but did not produce desired qualities in membranes. The solubility of quaternary ammonia polysulfone in water caused severe swelling with surface modification, and inhibited phase inversion with bulk modification. Phase-inverted membranes were still soluble in water, most organic compounds, and low molarity salt solutions. It is possible that the presence of high concentrations of functional groups prevented proper crosslinking, and other aminating procedures should be pursued.

Crosslinking with glutaraldehyde was only successful with specific polymer batches, and only improved the solubility in water. Polymer batches substituted to 58% were successfully crosslinked, but were still soluble in organic compounds and quickly deformed when left in open air. At higher degrees of substitution, the polymer was not successfully crosslinked at the concentrations used, and the membrane swelled in the glutaraldehyde solution. Either a higher concentration of glutaraldehyde should be used or a lower degree of substitution of chloromethylated polysulfone should be used for amination and subsequent crosslinking.

The membranes produced were of much lower quality than commercial membranes, with many of them having defects, including rippling on the polymer, non-uniform thickness from one side of the membrane to another, and large holes where air bubbles formed could have prevented polymer coating. Polysulfone membranes had a considerably wider pore diameter distribution than commercial nanofiltration membranes, and quaternary ammonia membranes had nearly triple the average pore diameter, although this could potentially be negligible effect on separations when the separation effect of surface charge is accounted for.

Due to the large quantities of hazardous chemicals used in the chloromethylation reaction, as well as the reaction times required for adequate substitution, the chloromethylation of polysulfone does not seem to be a safe process for industrial applications. The standard operating procedure used a maximum chloroform volume of 750 mL to produce a batch of polysulfone with a final mass of roughly 18 g. Scaling up this process from the initial 100 mL batch size led to a use of 42.5 mL of trimethylchlorosilane and 0.39 g of stannic chloride to complete the reaction. The hazardous nature of trimethylchlorosilane makes storing large quantities of the material unsafe, as both the liquid and vapor phases are highly flammable and can cause skin corrosion and eye damage. The use of large quantities of chloroform—a known carcinogen—is also troubling, as large quantities are needed to make a small batch of polymer, and the output of product cannot be increased without sacrificing the quality of the polysulfone. To produce industrial quantities of chloromethylated polysulfone, several liters of chloroform may be required to make a few hundred grams of polymer. Additionally, the long reaction time required creates an unsafe environment, as these compounds must be mixed near the boiling point of chloroform for periods over ten days for a complete reaction, and periods near a week for a 50% degree of substitution.

## 6. Future Work:

In light of the quaternary ammonia polysulfone membranes being unstable in water, a new aminating agent is necessary if a water insoluble membrane is to be produced. Amines related to trimethylamine should be explored with caution. Ethylamine, dimethylamine, and methylamine are classified as highly hazardous by OSHA, and as such will require a meticulous standard operating procedure (SOP) like that for trimethylchlorosilane in Appendix 8.1. If these are used, then new equipment will be required and—as per OSHA regulations—undergraduates will not be allowed to work with the procedure.

Both diethylamine and triethylamine are potential aminating agents that could be explored. Diethylamine is less flammable than trimethylamine, although the compound has a higher health and reactivity risk. Triethylamine was suggested by the chemistry department as a safer alternative to trimethylamine. However, it was noted that steric hindrance will severely increase the required time for the  $S_N2$  reaction due to the longer ethyl chains. This will both slow down research and create an additional safety hazard by having a hazardous chemical in the fume hood for long periods of time, well exceeding 24 hours.

Recommendations from faculty in the chemistry department and used in several articles are pyridine compounds.<sup>55</sup> Pyridine is a heterocyclic organic molecule with a similar structure to benzene with one methine group replaced with nitrogen. Of particular interest is 4,4'-bipyridine. This compound is composed of two pyridine molecules bound together at the fourth methine on each chain, leaving the nitrogen atoms at opposing ends of the compound. This compound is particularly promising due to the ability to crosslink without the use of secondary compounds such as glutaraldehyde.<sup>80</sup> Additionally, aminated polysulfone that is crosslinked with 4,4'-bipyridine contains two positive charges, one on each tertiary amine, increasing charge density.

These two effects could lead to a more stable membrane with a greater rejection of positively charged ions.

Alternatively, 4-phenylpyridine has been recommended. The structure of this pyridine is identical to that of 4,4'-bipyridine, but with only one nitrogen group.

Optimization of the chloromethylation reaction should be investigated as well. Limited reactions were run to focus efforts on optimizing the amination of the chloromethylated polysulfone.

Additional tests should be run to plot the substitution of the chloromethyl functional group over time. This can be performed by taking a sample of the reaction solution every 12 to 24 hours and analyzing it through H-NMR. Plotting this data with several repetitions would allow for the creation a model for predicting the time required to reach a desired substitution.

To determine if the behavior of quaternary ammonia polysulfone is determined by the substitution of amine groups to the polysulfone chain, additional tests should be run to aminate low degree of substitution polymer—less than 50% chloromethylated polysulfone. It is possible that the high grouping of positively charged amine groups or electrostatic interactions with the methyl groups caused the quaternary ammonia polysulfone to become unstable in water. A reduced concentration of these groups could result in a more stable membrane. If stable membranes can be produced this way, filtration testing should be conducted with different degrees of substitution to determine the required charge density to perform the calcium filtration.

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## **8. Appendix:**

### **8.1. Standard Operating Procedure: Trimethylchlorosilane:**

Safe handling and disposal of trimethylchlorosilane (C<sub>3</sub>H<sub>9</sub>ClSi, CAS No: 75-77-4)

This material is toxic and can be harmful if inhaled, ingested, or absorbed through the skin. Trimethylchlorosilane must be kept moisture free at all times. Hydrochloric gas can form when exposed to moisture, and in contact with metal surfaces can generate flammable and/or explosive hydrogen gas. May cause irreversible effects on the eye and severe skin irritation. Trimethylchlorosilane is toxic but the main hazard is its extreme flammability, having a flash point of -28oC (-18.4oF) – closed cup.



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Department: CHEG

Date when SOP was submitted: 10-15-14

Date when SOP was approved by the lab supervisor: 10-15-14

Principal Investigator: Jamie A. Hestekin, Ph.D.

Internal Laboratory Safety Coordinator/Lab Manager: Jamie Hestekin, Ph.D.

Laboratory Phone: 479-575-6721

Office Phone: 479-575-3492

Emergency Contact: Jamie Hestekin, Ph.D. 479-575-3492

Location(s) covered by this SOP: CHEM 305

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**Classification of the substance or mixture:**

GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)

Flammable liquids (Category 2), H225

Acute toxicity, Dermal (Category 4), H312

Acute toxicity, Oral (Category 3), H301

Skin corrosion (Category 1A), H314

Acute toxicity, Inhalation (Category 3), H331

Serious eye damage (Category 1), H318

**Hazard Statement(s)**

H225 Highly flammable liquid and vapour.

H301 + H331 Toxic if swallowed or if inhaled

H312 Harmful in contact with skin.

H314 Causes severe skin burns and eye damage.

**Precautionary statement(s)**

P210 Keep away from heat/sparks/open flames/hot surfaces. - No smoking.  
P233 Keep container tightly closed.  
P240 Ground/bond container and receiving equipment.  
P241 Use explosion-proof electrical/ventilating/lighting/equipment.  
P242 Use only non-sparking tools.  
P243 Take precautionary measures against static discharge.  
P261 Avoid breathing dust/fume/gas/mist/vapours/spray.  
P264 Wash skin thoroughly after handling.  
P270 Do not eat, drink or smoke when using this product.  
P271 Use only outdoors or in a well-ventilated area.  
P280 Wear protective gloves/protective clothing/eye protection/face protection.  
P301 + P310 If swallowed: immediately call a poison center or doctor/physician.  
P301 + P330 + P331 If swallowed: rinse mouth. Do not induce vomiting.  
P303 + P361 + P353 If on skin (or hair): remove/take off immediately all contaminated clothing. Rinse skin with water/shower.  
P304 + P340 If inhaled: remove victim to fresh air and keep at rest in a position comfortable for breathing.  
P305 + P351 + P338 If in eyes: rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.  
P310 Immediately call a poison center or doctor/physician.  
P322 Specific measures (see supplemental first aid instructions on this label).  
P363 Wash contaminated clothing before reuse.  
P370 + P378 In case of fire: use dry sand, dry chemical or alcohol-resistant foam for extinction.  
P403 + P233 Store in a well-ventilated place. Keep container tightly closed.  
P403 + P235 Store in a well-ventilated place. Keep cool.  
P405 Store locked up.  
P501 Dispose of contents/container to an approved waste disposal plant.

**Hazards not otherwise classified (HNOC) or not covered by GHS**

Reacts violently with water. Corrosive to the respiratory tract.

Keep away from food, drink and animal feeding stuffs. Wear suitable protective clothing. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible). This material and/or its container must be disposed of as hazardous waste. Avoid release to the environment. Refer to special instruction/Safety data sheets.

**Typical Permissible Exposure Limit (PEL):** No occupational exposure limits have been established for trimethylchlorosilane.

**Toxicity Data:** LD50 Oral, Rat < 214 mg/kg  
LD50 Inhalation, Rat – 1 h – 19 mg/L  
LD50 Dermal – Rabbit – 1.527 mg/kg



## **Exposure Symptoms**

Symptoms of trimethylchlorosilane exposure are listed below. Individuals may not have all symptoms:

- Behavioral: Altered sleep time (including change in righting reflex).
- Diarrhea Nutritional and Gross Metabolic: Weight loss or decreased weight gain.

**Storage:** Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage. Never allow product to get in contact with water during storage. Store under inert gas.

**Safe Disposal:** Have a chemical hazard glass bottle labeled “Trimethylchlorosilane and Hydrochloric Acid” along with the words “Hazardous Waste” ready before starting procedures involving trimethylchlorosilane.

## **Personal protective equipment (PPE) must be worn while handling trimethylchlorosilane.**

**Do not** proceed without any one of these PPE:

1. Safety goggles or glasses.
2. Heavy-Duty gloves such as those sold under the name “SilverShield” should be used to handle n-methyl-2-pyrrolidone. Nitrile gloves may be used to handle other chemicals. Use proper glove removal technique (without touching glove’s outer surface).
3. A working fume hood.

## **Precautions**

Be careful with potential secondary transfer, i.e., gloves to hands, lab coat to hands, etc. remove and dispose of gloves into solid waste container immediately after handling trimethylchlorosilane. Keep gloves in hood temporarily in order to allow any spillage to react and dissipate. Wash hands immediately after handling the product and before taking a break. Do not wear lab coat outside of the laboratory.

## **Training**

Special Note: Trimethylchlorosilane is very dangerous. You especially want to avoid:

1. Getting it on you
2. Getting it in you
3. Breathing hydrochloric gas, which evolves from trimethylchlorosilane that is exposed to moisture in the air when the trimethylchlorosilane is not handled with care.

All Dr. Hestekin’s (graduate students, postdoctoral associates, and program associates) are required to study the Material Safety Data Sheets and this SOP. They will be trained by Dr. Hestekin on the proper storage, use, and disposal of all chemicals used in this procedure.

## **Notifications**

The supervisor, Dr. Jamie Hestekin, must be notified the day before the procedure is to take place. In addition, all personnel located in the laboratory must be notified.

One other highly trained person, such as the supervisor, must be present while handling stock solutions of trimethylchlorosilane.

## **Hazardous Waste**

Request Hazardous Waste Pickup by logging in to the following website <http://ehs.uark.edu/Login.aspx>. Indicate “Trimethylchlorosilane” in the “Special Handling” box on the online form.

## **If any liquid is spilled outside the hood**

- Evacuate lab and post DO NOT ENTER on doors  
Avoid breathing vapors. Respirator protection required upon reentry (located in CHEG Safety Officer room 2223)
- Notify EH&S (phone: 479-575-5448 during work hours or 479-575-2222 after work hours). Emergency contact numbers are posted on the lab door.
- Notify lab personnel and neighbors of the accident.
- Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided. Use personal protective equipment (goggles, face shield, impervious gloves [such as “SilverShield”], and fire retardant antistatic clothing).

## **Post Exposure Plan**

### **General advice**

Consult a physician. Show safety data sheet to the doctor in attendance. Move out of dangerous area.

### **If inhaled**

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

### **In case of skin contact**

Take off contaminated clothing and shoes immediately. Wash off with soap and plenty of water. Take victim immediately to hospital. Consult a physician.

### **In case of eye contact**

Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician. Continue rinsing eyes during transport to hospital.

**If swallowed**

Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician

**Dr. Jamie Hestekin's Lab Protocol for Use of Trimethylchlorosilane for Membrane Modification**

Dr. Jamie Hestekin, Principal Investigator and Supervisor of the Membrane Lab at the Department of Chemical Engineering and secretary for the North American Membrane Society, is a well-published Chemical Engineer whose expertise are in the area of charged separations and extractions. He is asking the Toxic Substance Committee of the University of Arkansas to approve the conduct of these experiments for a two-year period (Oct. 15, 2014 to Oct. 15, 2016). Trimethylchlorosilane is required for the formation of positively charged nanofiltration membranes in which other chloromethylating agents cannot provide the desired characteristics. His lab has adapted a research protocol for the use of Trimethylchlorosilane for the chloromethylation of polymers, which has been proven to be the safest and most effective method for the formation of positive charges in membrane formation. 1-5 All Dr. Hestekin's lab personnel (graduate students, postdoctoral associates, and program associates) are required to study the Material Safety Data Sheets and are trained by Dr. Hestekin on the proper storage, use, disposal, and emergency protocols of this chemical. The membrane modification protocol adapted in Dr. Hestekin's Lab will require 216-336 hours, as described below:

**PROTOCOL FOR USE**

**Initial reactions were conducted in a total volume of less than 100 mL. Later these reactions were scaled up to 250 mL, 335 mL, then the literature value of 750 mL.**

**A typical reaction is as follows:**

Perform all steps in a fume hood

1. Preparation of chloromethylated polysulfone [CMPS]
  - a. Mix 14.88 g (33.6 mmol) of polysulfone [PS] in 750 mL of chloroform in a 3 neck 2 L round bottom flask
    - i. Cap both side necks with septums
    - ii. Cap the central neck with a condenser with a nitrogen inlet at the top and an outlet to the back of the hood. Feed cooling water into the condenser
  - b. Stir with a Teflon coated stir bar for 24 hours at 40°C with an oil bath
  - c. Turn off heating element and allow to cool
  - d. Remove septum from one neck and add 10 g (336 mmol) of paraformaldehyde to the PS chloroform mixture
  - e. Recap with a septum. Allow nitrogen to displace any air in system
  - f. Use a syringe to add 0.39 mL (3.36 mmol) of stannic chloride through the septum
  - g. Allow paraformaldehyde to dissolve for 1 hour before continuing

- h. Use a syringe to add 42.5 mL (336 mmol) of trimethylchlorosilane through the septum
- i. Stir with a Teflon coated stir bar for 120-240 hours at  $60\pm 20^{\circ}\text{C}$  with a heating mantle or oil bath while observing and maintaining temperature
  - j. Reaction time will depend on desired chloromethyl substitution. 120 hours will yield just above 50% substitution (1 chloromethyl group on every monomer). 240 hours will yield 88% substitution (1 chloromethyl group on every monomer, and an additional chloromethyl group on 76% of the monomers)
- k. Let the mixture cool to room temperature
- l. Pour mixture into 1.5 L of methanol to precipitate CMPS in a 3 L glass basin while stirring with a stir bar
- m. Filter precipitate and wash with additional methanol
  - i. Dispose of methanol mixture into hazardous waste container labeled Chloroform, Methanol, Trimethylchlorosilane, Tin Chloride, and Paraformaldehyde
- n. Dry CMPS under nitrogen for 24 hours

**Quaternary ammonia polysulfone membranes were produced as follows. This procedure produced low quality membranes and is not recommended.**

1. Preparation of quaternary ammonia polysulfone [QAPS] membranes
  - a. Mix 10 g of CMPS in 32.43 mL of 1-methyl-2-pyrrolidinone [NMP] in a 125 mL Erlenmeyer flask
  - b. Stir with a Teflon coated stir bar for 10 hours
  - c. Add 28% trimethylamine in a 3:2 mole ratio with chloromethyl groups, as detected through NMR
  - d. Continue stirring and heat to  $60^{\circ}\text{C}$  for 15 hours
  - e. Using a polyester non-woven fabric, cast polymer to backing
  - f. Level polymer using a casting knife to 200  $\mu\text{m}$  thick
  - g. Keep in open air for 30 seconds
  - h. Immerse in 5 M sodium chloride dissolved in DI water at  $5\pm 20^{\circ}\text{C}$
  - i. Allow membrane to phase invert for 2 hours
    - i. Dispose of DI water into hazardous waste
  - j. Rinse with DI water
  - k. Store in 5 M sodium chloride dissolved in DI water

#### References:

1. Wang, J., Wang, J., Wang, H., & Zhang, S. (2013). Preparation and characterization of positively charged composite nanofiltration membranes by coating poly(ether ether ketone) containing quaternary ammonium groups on polysulfone ultrafiltration membranes. *Journal of Applied Polymer Science*, 127(3), 1601-1608.

2. Avram, E., Butuc, E., Luca, C., & Druta, I. (1997). Polymers with pendant functional group. III. polysulfones containing viologen group. *Journal of Macromolecular Science, Part A*, 34(9), 1701-1714.
3. Avram, E. (2001). Polymers with pendent functional groups. vi. a comparative study on the chloromethylation of linear polystyrene and polysulfone with paraformaldehyde/me3sicl. *Polymer-Plastics Technology and Engineering*, 40(3), 275-281.
4. Dong, H., Xu, Y., Yi, Z., & Shi, J. (2009). Modification of polysulfone membranes via surface-initiated atom transfer radical polymerization. *Applied Surface Science*, 255(21), 8860-8866.
5. Pantamas, N., Khonkeng, C., Krachodnok, S., & Chaisena, A. (2012). Ecofriendly and simplified synthetic route for polysulfone-based solid-state alkaline electrolyte membrane. *American Journal of Applied Sciences*, 9(10), 1577.

**I have read and understand the above standard operating procedure and realize that trimethylchlorosilane is extremely dangerous. I agree to follow the protocol as described above.**

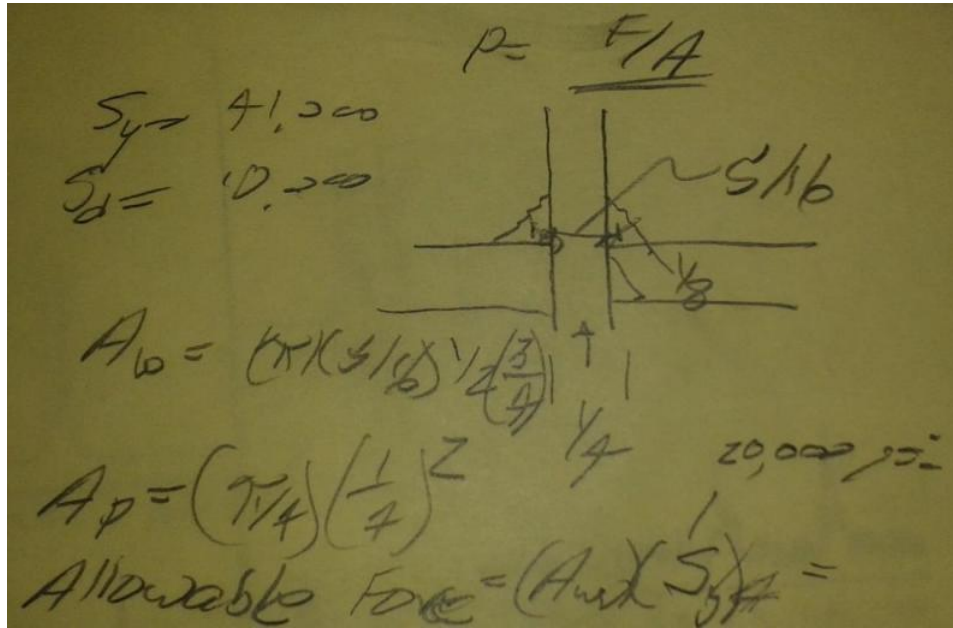
Printed Name \_\_\_\_\_

Signature \_\_\_\_\_ Date signed \_\_\_\_/\_\_\_\_/\_\_\_\_

## **8.2. Risk Assessment: Modified Millipore Filtration Unit:**

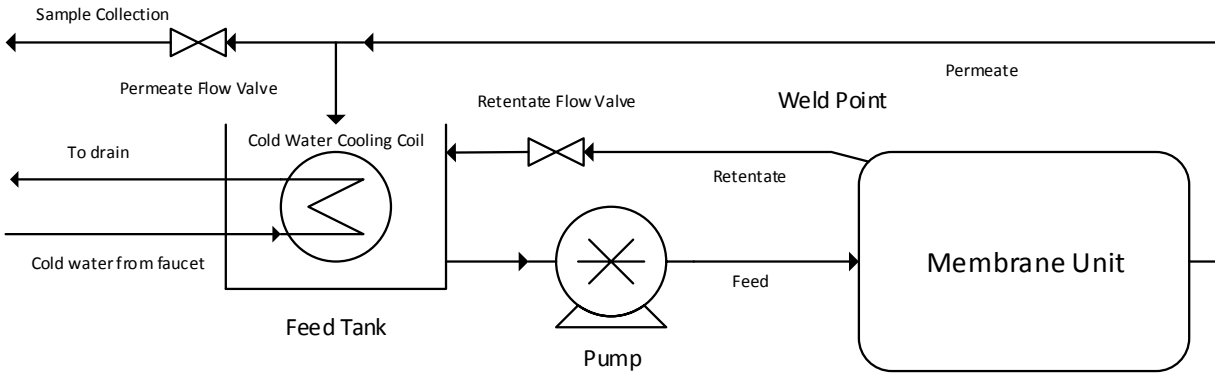
### Risk Assessment: Tangential Flow Filtration Unit

The unit will perform a small-scale nanofiltration process. A salt water mixture will be pumped into the filtration unit where a nanofiltration membrane will filter the salts through a tangential flow process. A retentate outlet has been welded to the unit to allow for tangential flow, which is the most likely point of failure of the unit. The weld has been determined to hold a maximum pressure of 42,700 psig with a safety factor of 4, with the assumption that the weld is defect free. Actual maximum pressure may be lower.



Component	Safety Issue	Remedy
Water	None	
Sodium chloride	Corrosion	Check unit for rust or deterioration and clean regularly.
Calcium chloride	Corrosion	Check unit for rust or deterioration and clean regularly.
Electrical	Shock/water contact	Shut down pump and dry the area. Check unit for leaks.
Weld point	Break	Shut down pump and depressurize unit.

Operating Condition: 0-450 psig	All components rated to 1000 psig or greater
---------------------------------	--



Component	Pressure Rating
Membrane unit	10,000 psig
Weld point	41,700 psig
Retentate flow valve	1,000 psig
Stainless steel tubing	2,000 psig

**Start Up:**

1. Add water and salt to feed tank and mix until salt is dissolved.
2. Connect pump to inlet of membrane unit, and outlet hoses to retentate and permeate outlets. Check that retentate flow valve is fully open.
3. Insert coil in feed tank. Connect inlet hose to faucet and place outlet hose at drain. Begin feeding cold water.
4. Plug in the pump into the wall socket.
5. Turn on the pump to flow water into the membrane.

**Operation:**

1. Close retentate flow valve to pressurize the system and increase permeate flow rate.



2. Increase pressure until desired permeate flow is reached.
3. Collect permeate sample at selected intervals.

**Shut down:**

1. Fully open retentate flow valve.
2. Shut off pump
3. Unplug pump from wall socket.
4. Turn off cooling water flow.
5. Allow water in system to drain.
6. Disassemble unit, clean with DI water and dry.

**Emergency:**

In the event of a leak, shut off pump and unplug it from the wall. Clean spilled water and check for leaks in the unit.

If the weld point should fail, shut down the pump and open the retentate flow valve to depressurize the unit.

### 8.3. Data:

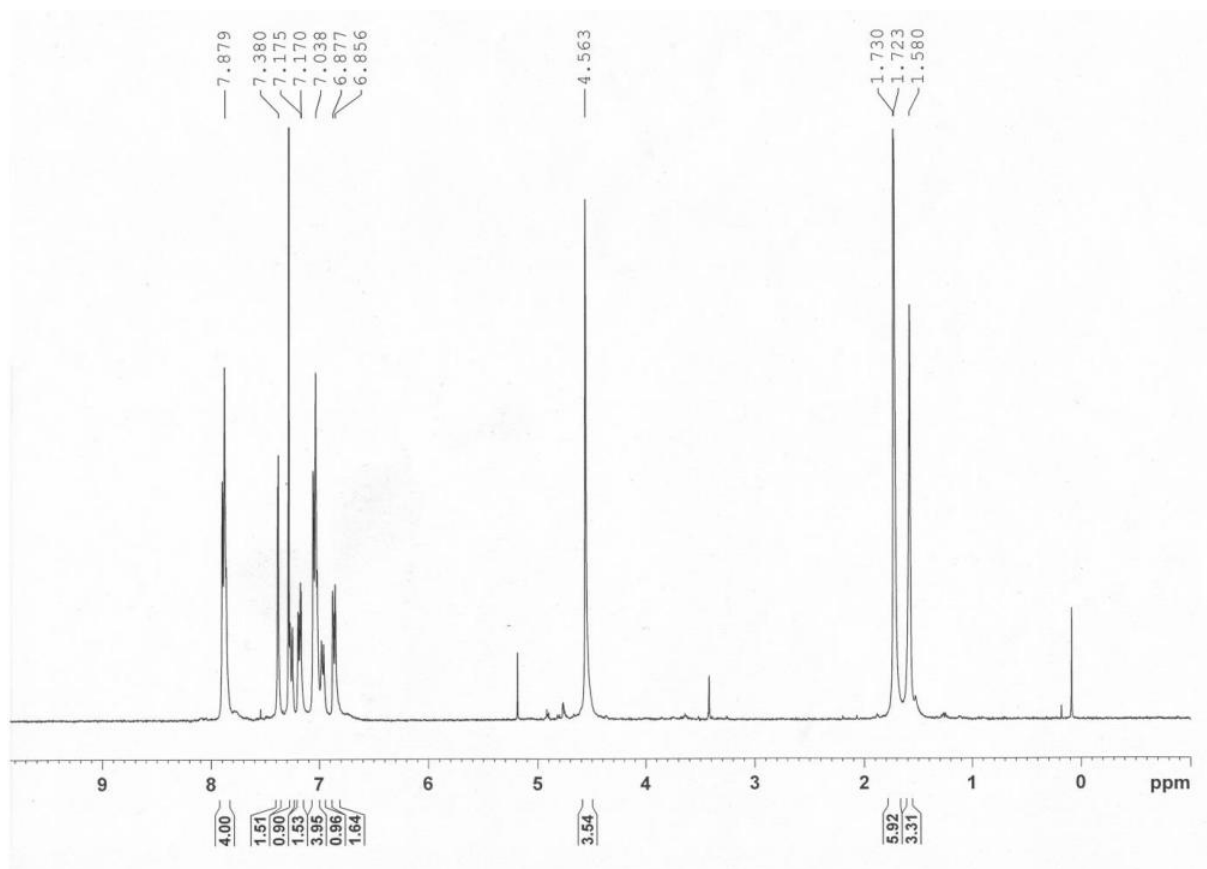


Figure 13: H-NMR of 88% chloromethylated polysulfone.

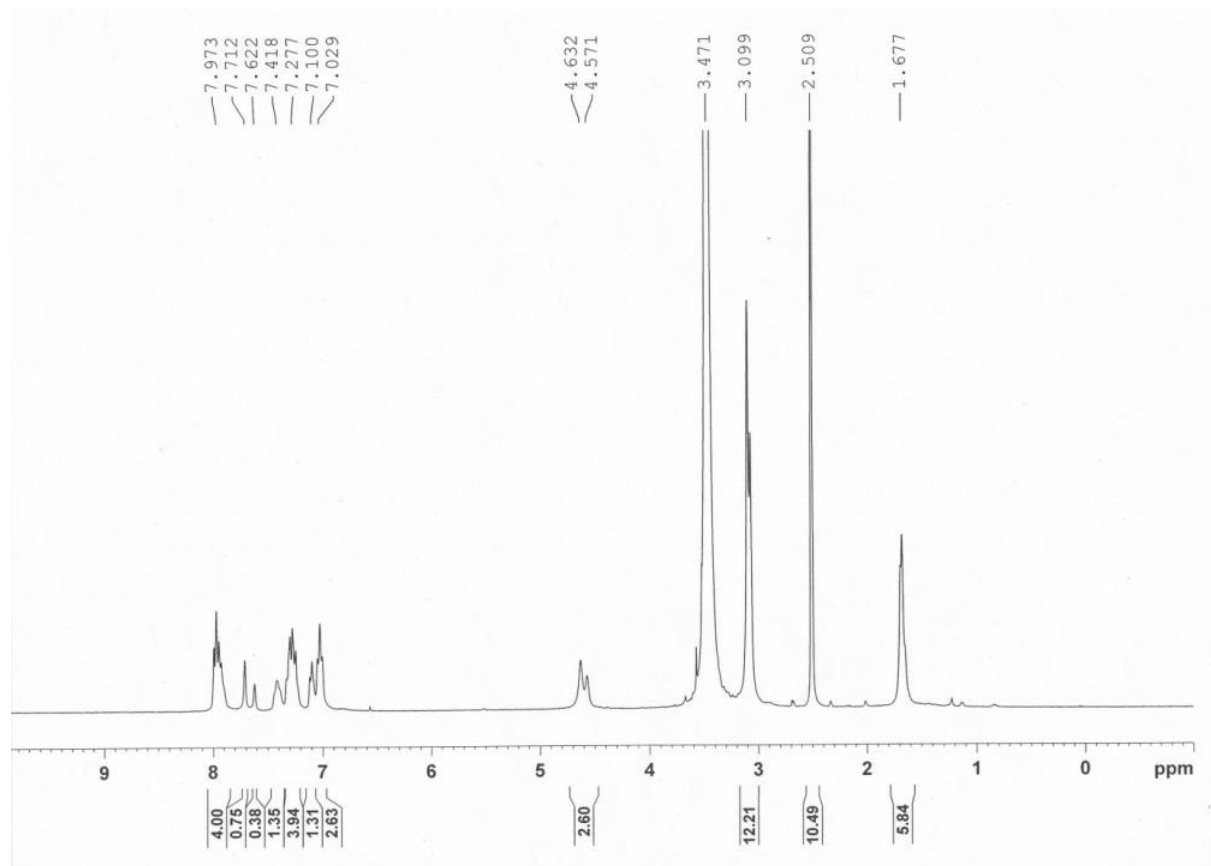


Figure 14:  $^1\text{H-NMR}$  of quaternary ammonia polysulfone produced from 69% chloromethylated polysulfone.

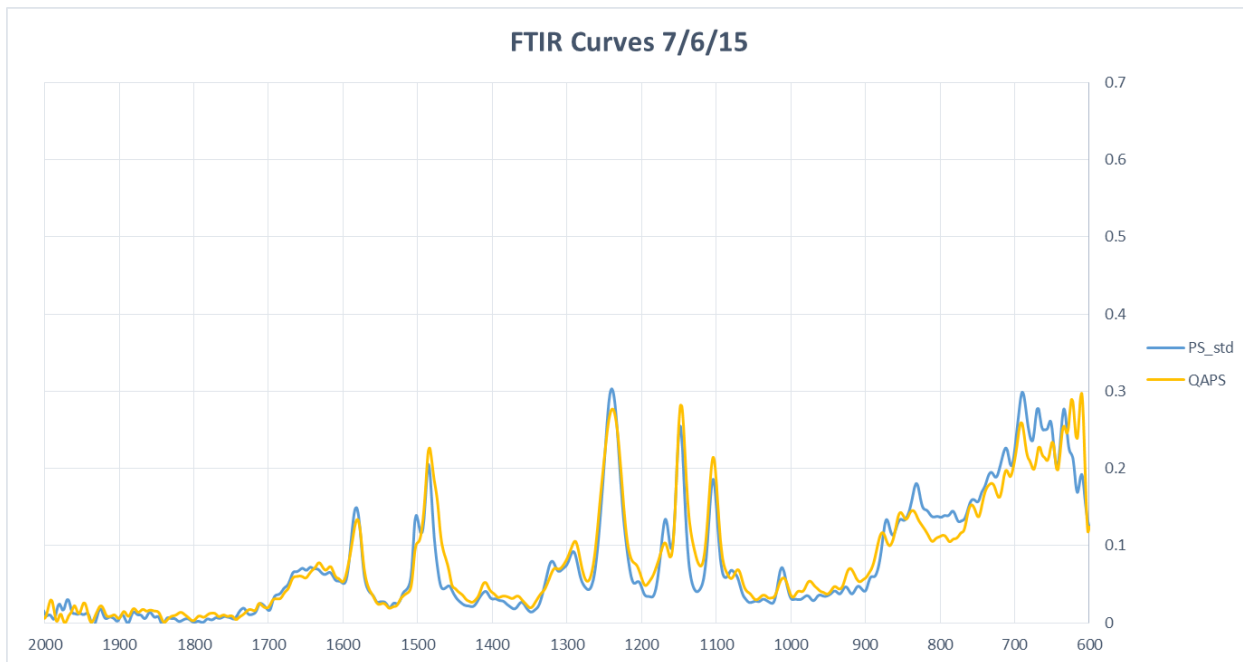


Figure 15: FTIR curves from standard polysulfone and quaternary ammonia polysulfone.

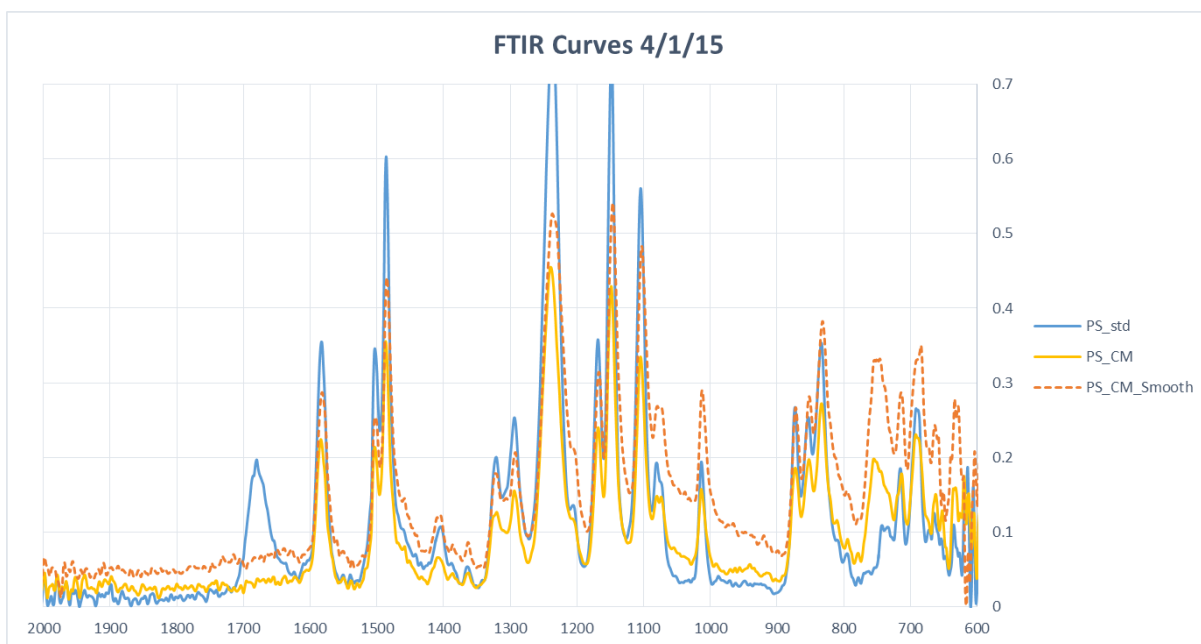


Figure 16: FTIR curves from standard polysulfone and an early batch of chloromethylated polysulfone.

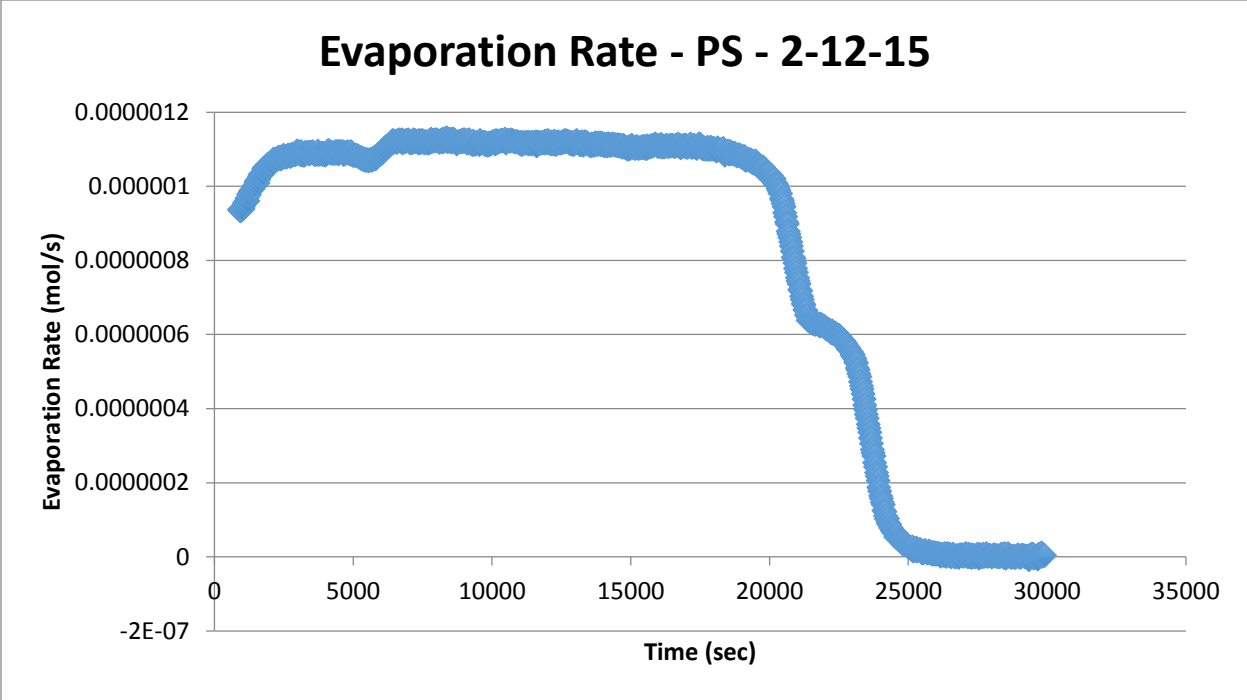


Figure 17: Evapoporometry results of thin polysulfone membrane.

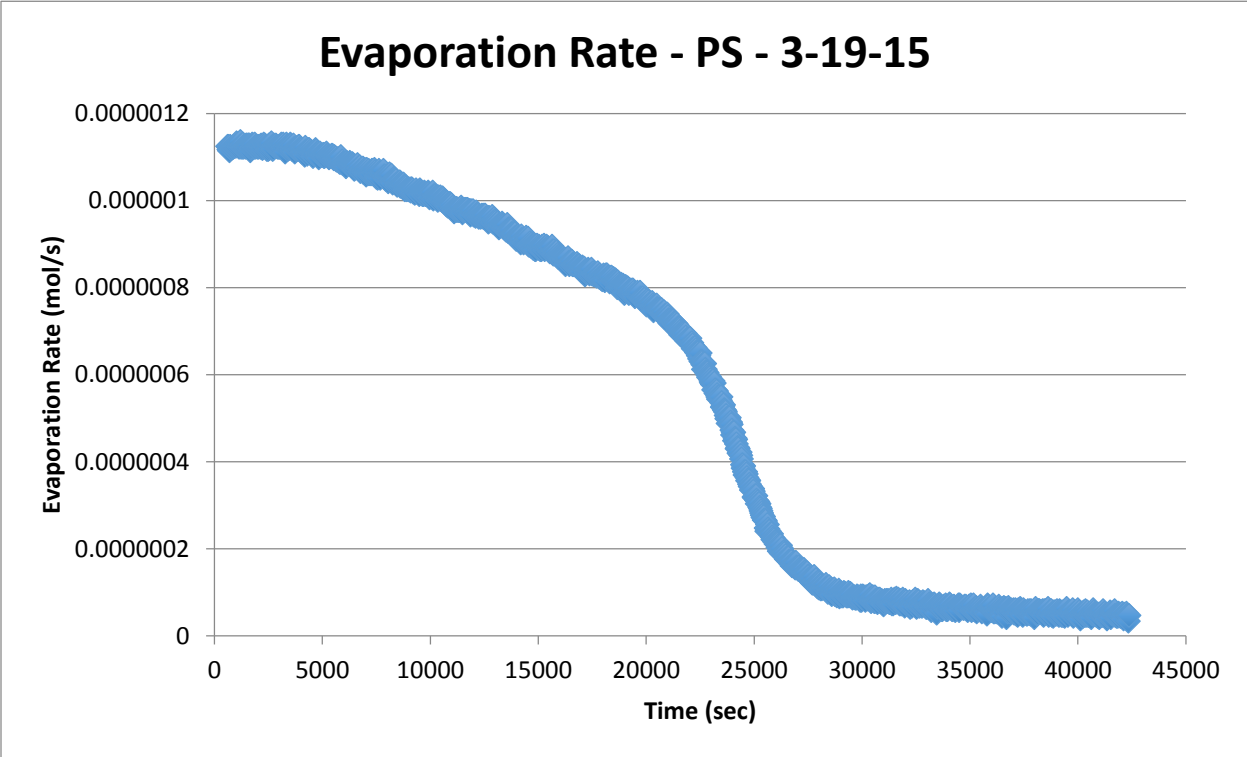


Figure 18: Evapoporometry results of think polysulfone membrane with improper procedure.

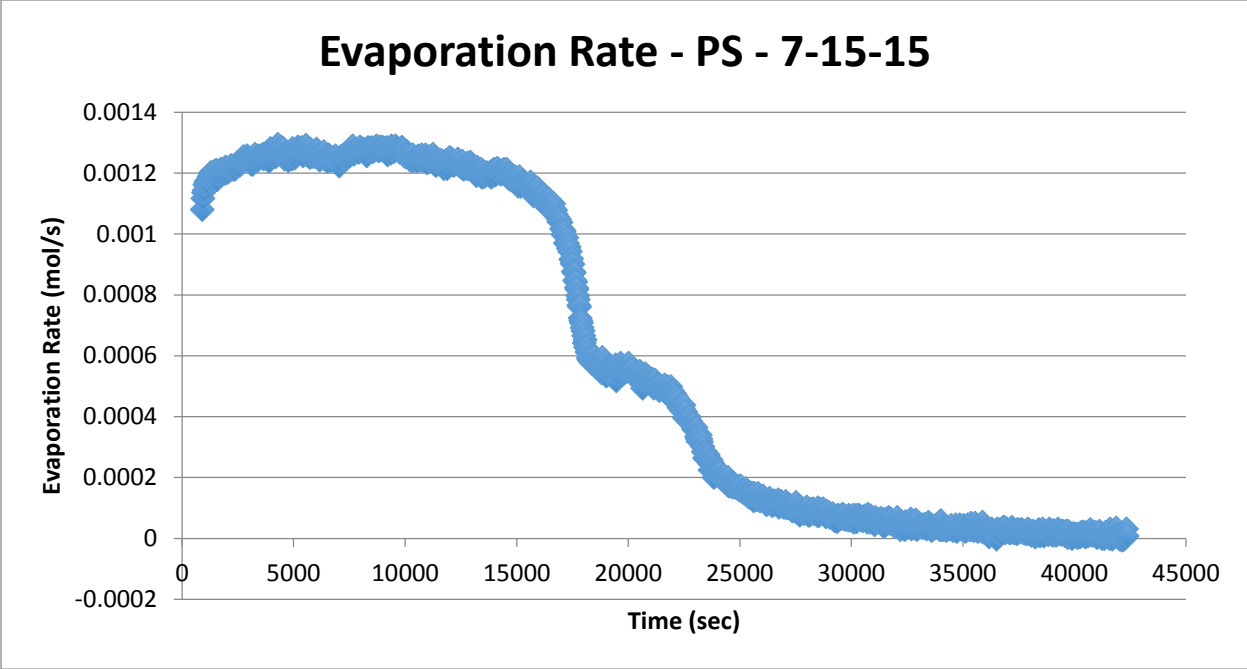


Figure 19: Evapoporometry results of standard polysulfone at full thickness after proper procedural changes.

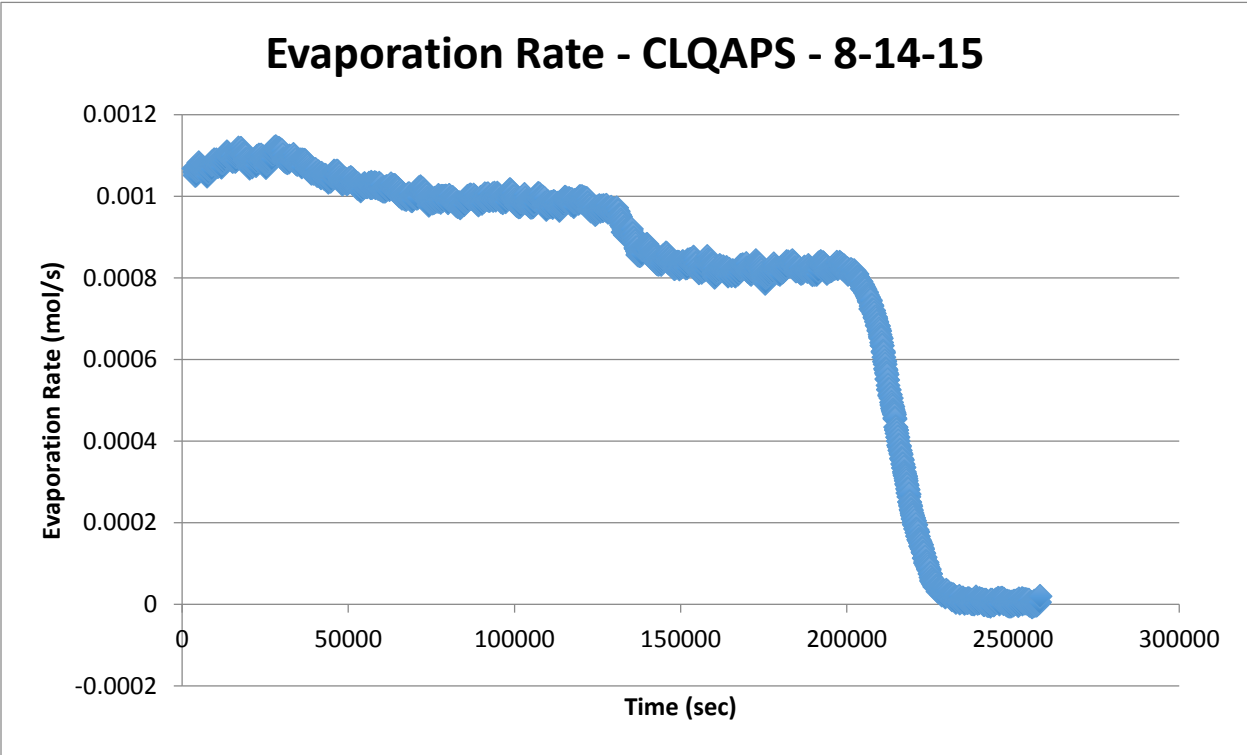


Figure 20: Evapoporometry results of crosslinked quaternary ammonia polysulfone.

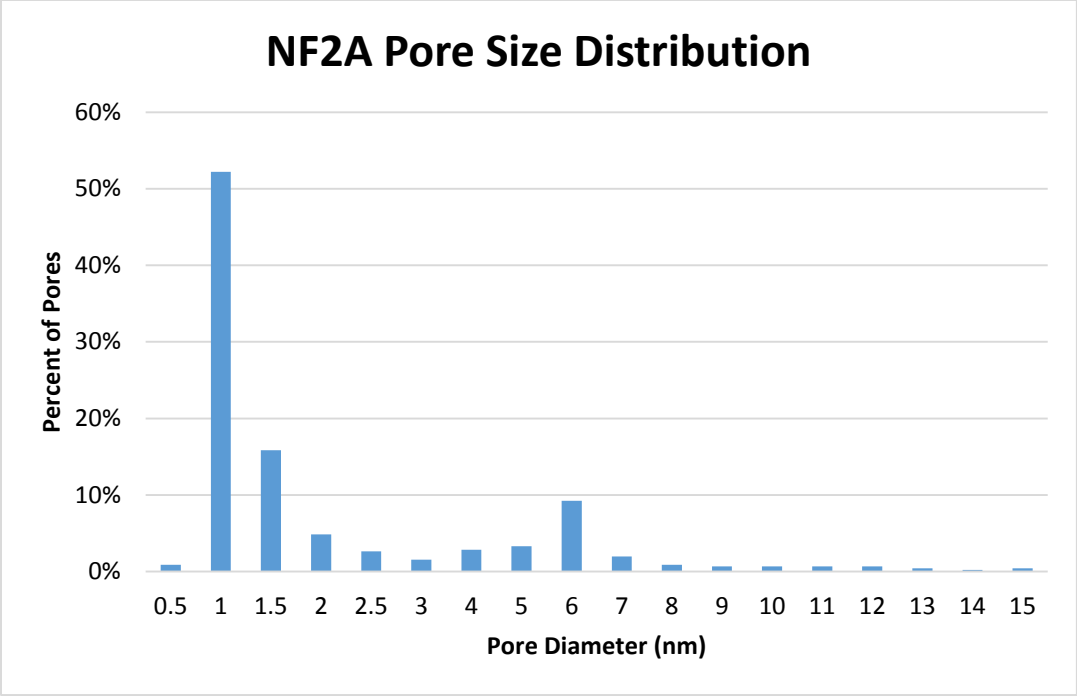


Figure 21: Pore size distribution of NF2A.

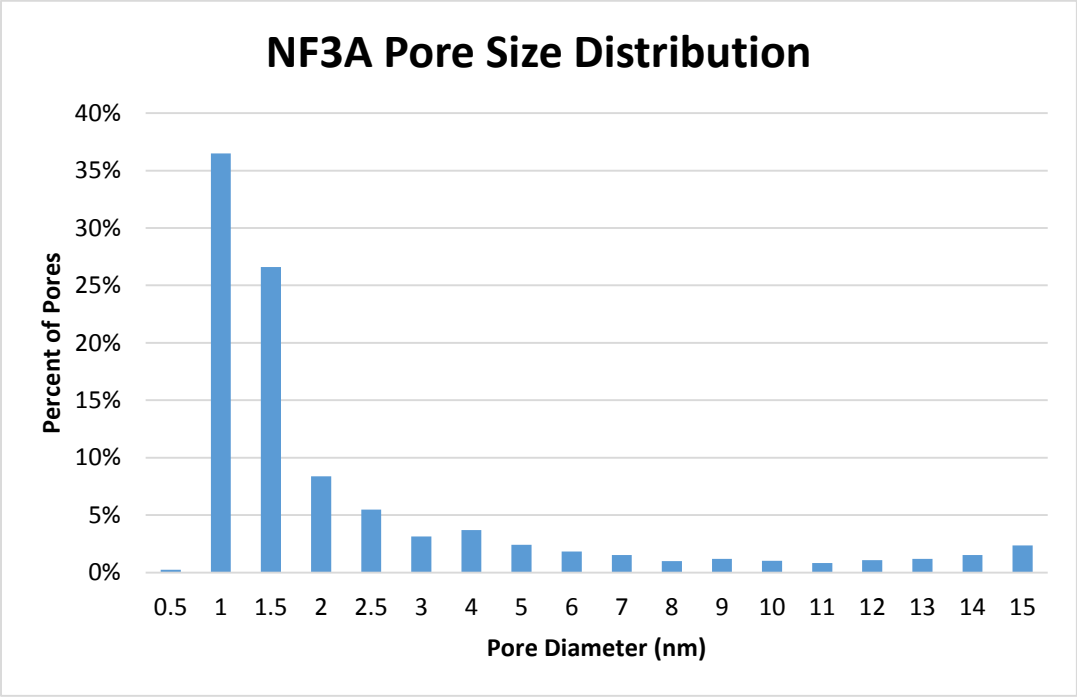


Figure 22: Pore size distribution of NF3A.

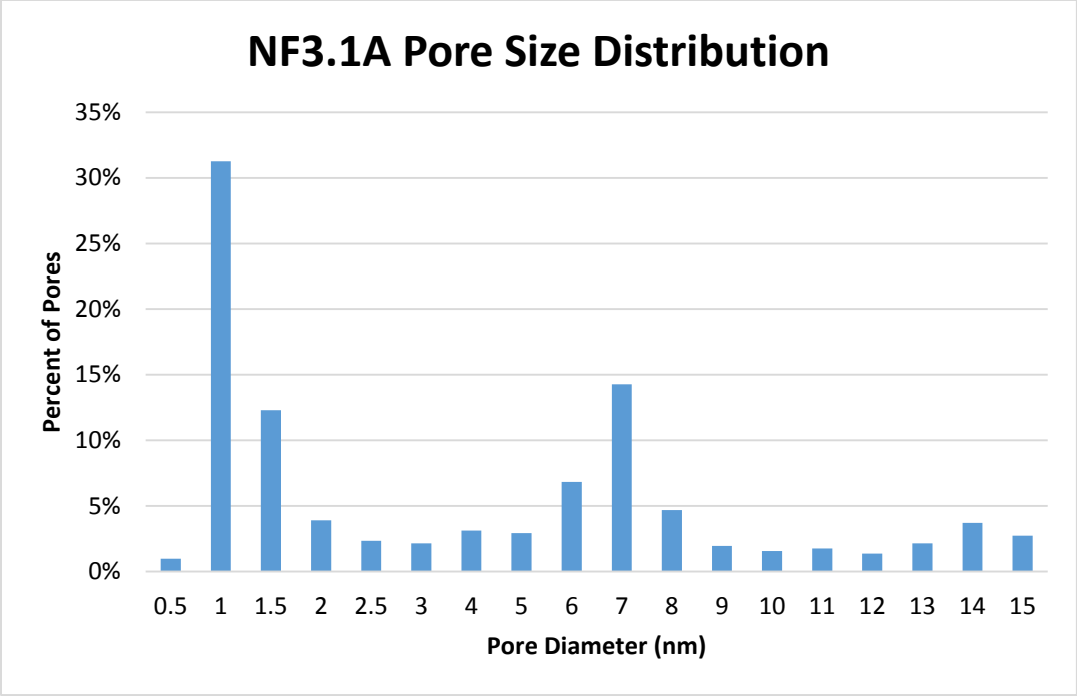


Figure 23: Pore size distribution of NF3.1A.

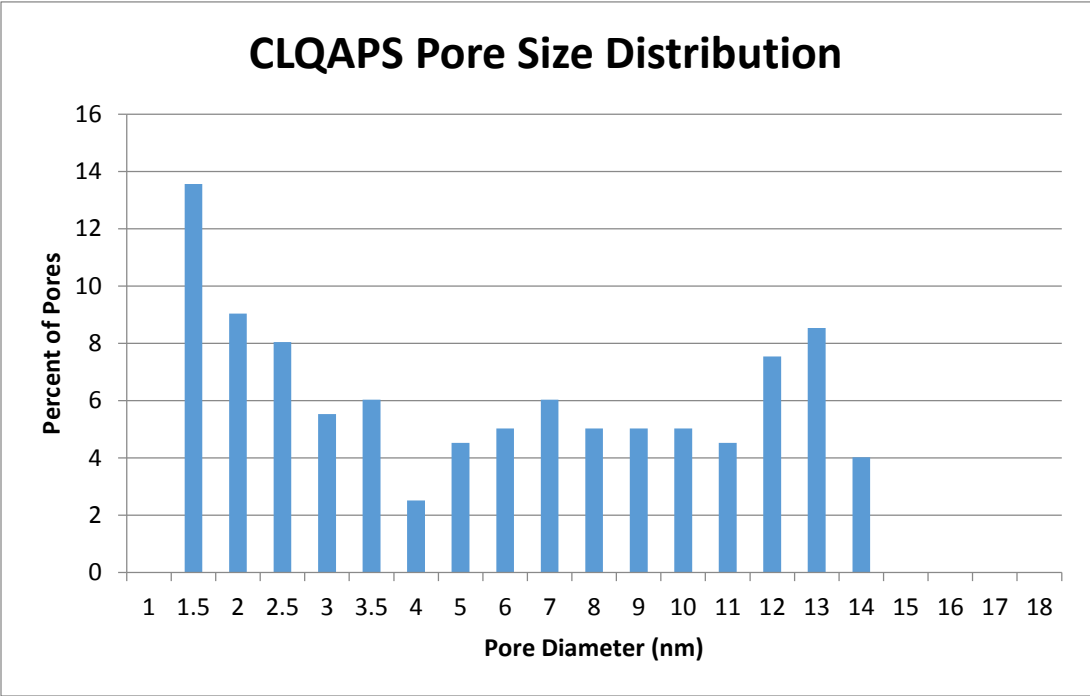


Figure 24: Pore size distribution of crosslinked quaternary ammonia polysulfone membrane.