The Synthesis of a MePEG-based Hydroxide Conducting Electrolyte and the Optimization of the MePEG-Tosylation Reaction

Andrew Ladner

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THE SYNTHESIS OF A MePEG-BASED HYDROXIDE CONDUCTING ELECTROLYTE AND THE OPTIMIZATION OF THE MePEG-TOSYLATION REACTION

by
Andrew Nicolas Ladner

A thesis submitted to the faculty of the University of Mississippi in partial fulfillment of the requirements of the Sally McDonnell Barksdale Honors College.

Oxford
May 2020

Approved by:

____________________________
Advisor: Dr. Jason Ritchie

____________________________
Reader: Dr. Jonah Jurss

____________________________
Reader: Dr. Walter Cleland
DEDICATION
To my family, who have pushed me to do my best and supported me throughout my entire life.
ACKNOWLEDGEMENTS

First, I would like to thank my parents, Steven and Carol Ladner. Without their continuing emotional support, I would not have been able to complete this project. They have helped me in every possible way throughout my four years at the University of Mississippi. I would also like to thank the Department of Chemistry and Biochemistry as a whole for giving me the tools and advice to succeed not only in my studies but in life as a whole. Thank you, Dr. Ritchie, for all of your guidance and patience. Your Chem 105 class is one of the key markers in my life that help me find a love and passion for chemistry, and your input as I completed this project has been invaluable. Lastly, I would like to thank the Sally McDonnell Barksdale Honors College for the innumerable opportunities they have granted me as well as their financial support which has allowed me to complete my thesis.
ABSTRACT

As society is becoming increasingly aware of the effects of climate change and the ever-looming threat of a fuel shortage, exploring green and renewable alternative energy production, such as fuel cells, is paramount. This project investigates the synthesis of a polyethylene glycol monomethyl ether (MePEGₙ) based polymer as well as the optimization of the MePEG Tosylation reaction. The MePEG explored contains seven polymerized ethoxy groups (MePEG₇). The MePEG₇ polymer was modified by substituting a positively-charged trimethylamine group in the place of the alcohol functional group at the end of the PEG chain. The reason for this substitution was to create a positive charge on the polymer electrolyte which could then potentially facilitate the movement of ions such as hydroxide ions. I have prepared the MePEG₇N(Me)₃⁺ Br⁻ product which would have been ion exchanged to the Hydroxide (OH⁻) form of the polymer. However, due to complications of COVID-19, the physical properties of the electrolyte, such as ionic conductivity and viscosity, will have to be completed in a future project to determine the viability of the synthesized material as an alkaline fuel cell (AFC) polymer electrolyte membrane.
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INTRODUCTION

In the 21st century, the planet will need to acknowledge and overcome the energy crisis that is present today. Not only are the effects of greenhouse gas emissions from the burning of fossil fuels letting itself be known in the form of climate change, but the finite reserves of fossil fuels are dwindling. The world could potentially deplete all oil and natural gas reserves in as little as 50 years. With oil and gas reserves depleted, an increase production in coal would be necessary, and, in turn, the known coal deposits could be depleted in as little as 150 years\(^1\). A shift to renewable energy, such as solar generated hydrogen-powered fuel cells, will be paramount in the century to come. It is also important that future energy systems shift away from emitting greenhouse gas emissions. Energy production is the main contributor to adding greenhouse gases into Earth’s atmosphere. Roughly 70% of all greenhouse gases derived from human activity come from energy production.

A fuel cell is an electrochemical device that can directly convert the chemical energy found in fuel into electrical energy. Fuel cells could potentially be an excellent alternative fuel source because of their clean environmentally-friendly productions as well as their simple reactions. Hydrogen is a potentially renewable energy source, and fuel cells are an efficient way to use hydrogen as a fuel. A fuel cell is composed of three distinct parts: an anode, a cathode, and electrolyte sandwiched in between the anode and cathode\(^2\). The most exploited reaction used in polymer electrolyte membrane fuel cells (PEMFC), also known as proton exchange membrane fuel cells, is as follows:

\[
\text{Equation 1:} \quad 2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (l) \quad \text{E}^0 = +1.23\text{V}
\]
Polymer Electrolyte Membrane Fuel Cells:

PEMFCs use a proton conducting electrolyte, and are low temperature fuel cells (~100 °C) because water is required for conduction for the most popular electrolytes used in PEMFCs. Platinum-based catalysts are typically used in both electrodes of PEMFCs. With the current cost of platinum over twenty thousand dollars per kilogram, research is being carried out to find a cheaper catalyst for the PEMFC. Fuel cells are limited in their operating temperature by the need for hydration of the electrolyte membrane. For an alternative catalyst to be used, the efficiency of fuel cells at higher temperatures must be increased. The boiling point of water typically limits the efficiency of the electrolyte at higher temperatures due to the most popular electrolyte requiring water for conductivity. One way of increasing fuel cell efficiency at higher temperatures is to improve the electrolyte conductivity at lower concentrations of water.

In the PEMFC, hydrogen is brought to the anode via a gas stream, where the hydrogen is oxidized to produce both hydrogen ions as well as electrons (equation 2).

$$\text{Equation 2: } 2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^- \quad \text{E}^0 = 0 \text{ V}$$

The hydrogen ions created will move through the electrolyte in the direction of the cathode while the electrons will move through an external circuit toward the cathode. At the cathode, the hydrogen ions and the electrons will react with oxygen also being supplied through a gas stream. The oxygen is then reduced to form water. Pure hydrogen is needed to operate at maximum efficiency in the PEMFCs. PEMFCs are susceptible to carbon monoxide poisoning. Typical PEMFCs operate at around 80 °C. At this temperature, content as low as 10 ppm of CO results in a substantial loss in the efficiency of the fuel cell.

$$\text{Equation 3: } \text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad \text{E}^0 = +1.23\text{V}$$
Alkaline Fuel Cells:

Another type of fuel cell is the alkaline fuel cell (AFC). AFCs have a very efficient Oxygen Reduction Reaction (ORR) with platinum, but AFCs will only work properly if they are being supplied with pure Oxygen. This is an inconvenience, as other Fuel Cells, such as PEMFCs obtain oxygen from air. The AFC is sensitive to Carbon Dioxide in the air, because the electrolyte for AFCs is typically a concentrated KOH aqueous electrolyte, which typically consist of KOH in concentrations of 30 - 40% weight. If AFCs were to obtain oxygen from air, the carbon dioxide in the air would be absorbed by the strongly basic electrolyte, and eventually precipitate carbonate salts in the electrolyte. Thus, AFCs need to have a pure oxygen source. The advantage of AFCs over acidic fuel cells is the oxygen reduction reaction on a platinum.
electrocatalyst is much more efficient in an alkaline environment than that of an acidic environment. Both AFCs and PEMFCs suffer from poisoning of the platinum anode by carbon monoxide.

The AFC was one of the first fuel cells used in space. Although PEMFCs were used in the Gemini program, the AFC was used in the Apollo Program and the Space Shuttle Program. The requirement to use pure oxygen was not as much of a disadvantage in space, as the craft would already likely be carrying pure oxygen for life-support of the crew. The fuel cells were used for producing energy, cooling the Shuttle compartments, and producing water\(^4\).

In an AFC, both oxygen reduction and hydrogen oxidation involve the OH\(^-\) ion. The OH\(^-\) ions, formed through the reduction of oxygen at the cathode, move through the electrolyte media to the anode, where the OH\(^-\) ions recombine with hydrogen to form water. The half-reactions and overall reaction can be found below:

**Equations 4:**

**Cathode:** \( \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad E^0_{\text{red}} = +0.401 \text{ V} \)

**Anode:** \( 2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4e^- \quad E^0_{\text{red}} = -0.8277 \text{ V} \)

**Overall:** \( 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \quad E^0 = +1.229 \text{ V} \)
As stated previously, one of the most challenging aspects of the AFC is that it has to be supplied ultra-pure gases, lest it form carbonate precipitates. CO$_2$ found in the air interacts with the fuel cell according to the reaction below.

**Equation 7:** \[ \text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \]

Because this electrolyte is extremely basic, it will absorb carbon dioxide if present in the oxidizer stream that is introduced into the system which will eventually lead to precipitation of carbonate salts in the electrolyte. The precipitation of carbonates leads to a reduction of conductivity because there is an increasing presence of solid material in the conduction pathway.
To avoid the issue of precipitants forming, AFCs use pure oxygen which leads to a significant increase in cost. To increase the use of AFCs, the durability needs to increase. Our lab explores ways to increase the stability of the AFC by use of a polymer-based electrolyte.

Hydrogen Fuel Sources

Fuel cells have many inherent advantages over the current combustion-based energy systems in place, giving fuel cells potential to be the energy source of the future. One of the main advantages of a fuel cell is that they have the potential to reduce harmful emissions when compared to fossil-fuel combustion-based energy systems. The only products of a fuel cell or fuel cell stack when fueled by hydrogen are water, heat, and electricity. However, the reduction of harmful emissions depends on the production of the hydrogen fuel source.

Hydrogen can be produced from the steam-reformation of Methane (natural gas, equation 5). However, these processes are always contaminated with carbon monoxide (CO) because it is an intermediate of the first step in the process and is difficult to remove completely. The carbon monoxide “poisons” the electrocatalyst at the anode, by binding irreversibly to the electrode surface, and preventing any further electrochemical reactions from occurring at that site on the electrode surface.

When supplied with pure hydrogen (not reformation-based hydrogen), the durability and reliability of the fuel cell sees a substantial increase when compared to that of a fuel cell supplied with reformation-based hydrogen. The fact that the reliability and durability of the fuel cell increase as well as the fact that a reduction of harmful emissions takes place leads researchers to seek and develop new ways to acquire pure hydrogen based off of clean water electrolysis.
Equation 5: Steam Reformation of Methane, CH₄

Steam Reformation: \[ \text{CH}_4 (g) + \text{H}_2\text{O} (g) \rightarrow \text{CO} (g) + 3\text{H}_2 (g) \quad \Delta H = +206 \text{ kJ/mol} \]

Water-Gas Shift Reaction: \[ \text{CO} (g) + \text{H}_2\text{O} (g) \rightarrow \text{CO}_2 + \text{H}_2 (g) \quad \Delta H = -41 \text{ kJ/mol} \]

Overall: \[ \text{CH}_4 (g) + 2\text{H}_2\text{O} (g) \rightarrow \text{CO}_2 (g) + 4\text{H}_2(g) \quad \Delta H = +165 \text{ kJ/mol} \]

Fuel Cell Efficiency

Another advantage of fuel cells is that fuel cells inherently have a higher fuel efficiency when compared to that of combustion-based systems. Combustion-based systems’ energy efficiency is limited by the Carnot efficiency, given by the following equation:

Equation 8: \[ \eta_{\text{Carnot}} = (T_1 - T_e)/T_1 \]

Where \( T_1 \) is the absolute temperature at the engine inlet and \( T_e \) is the absolute temperature at the engine outlet. A fuel cell, however, is not limited by this equation because it does not undergo combustion oxidation, but instead a fuel cell undergoes isothermal oxidation. The maximum energy output of a fuel cell is bound by the chemical energy content of the fuel used which can be expressed by the following equation:

Equation 9: \[ \eta_{\text{rev}} = \Delta G_f/\Delta H_f \]

Where \( \Delta G_f \) is the change in Gibbs free energy of the reaction and \( \Delta H_f \) is the change in the enthalpy of formation. Part of the reason that fuel cells operate with higher efficiency than combustion-base systems is that a fuel cell stack undergoes less energy transformations when the final output is electricity. Losses of energy are associated with energy transformations; thus, the overall energy efficiency of a device generally decreases as the number of energy transformations increase. Figure 3 show the efficiency of fuel cells compared to other electricity
generating systems and **Figure 4** details the amount of energy transformations needed to generate electricity in different systems.

![Figure 3: Efficiency vs Power Output of a variety of electricity generating systems](image)

**Figure 3**: Efficiency vs Power Output of a variety of electricity generating systems\(^2\)
Another advantage of fuel cells are their high modularity. Changing the number of fuel cells per stack or stacks per systems allows for the control of power output in any system that utilizes fuel cells. Fuel cells’ efficiency does not vary much with system size, unlike combustion-based systems. The high modularity of fuel cells means that larger and smaller fuel cell systems will have similar efficiencies, a feature that can potentially help facilitate future use of fuel cells in small-scale systems.
A fuel cell stack is a silent device due to its electrochemical nature. This can prove to be an advantage when power generation is needed for silent-operations. A fuel cell has very few dynamic parts so almost no vibrations are observed. The lack of dynamic parts also makes the design, manufacturing, assembly, and operations much simpler when compared to that of an engine. For instance, in a conventional four-door sedan, most of the noise produced comes from the engine. A car powered by a fuel cell stack could generate significantly less noise than that of the conventional sedan. The Honda FCX Fuel Cell vehicle, found in Figure 5, is available to be rented in select places around the world. Its specifications can be found in Table 1.

![Honda FCX Fuel Cell vehicle](image)

**Figure 5:** Honda FCX Fuel Cell vehicle

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>~280 miles</td>
</tr>
<tr>
<td>Power</td>
<td>100 kW (134 HP)</td>
</tr>
<tr>
<td>Top Speed</td>
<td>100 mph</td>
</tr>
<tr>
<td>0-60 mph</td>
<td>~9 seconds</td>
</tr>
<tr>
<td>H₂ Fuel Price</td>
<td>$3-5 per kilogram</td>
</tr>
<tr>
<td>Fuel Efficiency</td>
<td>68 miles/kilogram</td>
</tr>
</tbody>
</table>

**Table 1:** Specifications of the Honda FCS Fuel Cell vehicle

Fuel cells can be used for a wide variety of applications; they can be used from micro-fuel cells with less than 1 W of power output to multi-MW power generation plants. This can be
attributed to their high modularity and static nature. Fuel cells have the potential to replace batteries in electronics and auxiliary vehicular power. Fuel cells are highly integrable to most renewable power generation technologies.

Commercialization of Fuel Cells

Although fuel cells have been studied and rapidly developed over the past 20 years, they are still not ready to be at the widespread-commercialization stage yet due to many factors. The main challenges are detailed below.

As of now, the durability of fuel cells is a major hurdle for wide-spread fuel cell use. In its current form, the durability of fuel cells needs to be increased by about five times the current rate in order for fuel cells to be considered a long-term alternative energy source compared to the current power generation technologies. Contamination in fuel cells due to air pollutants and fuel impurities need to be addressed to help fix the fuel cell durability issue.

As stated above, another huge challenge facing fuel cells is the current hydrogen infrastructure. Over 96% of the world’s hydrogen is formed from hydrocarbon reformation processes. Producing hydrogen to be used in fuel cells from hydrocarbons found in fossil fuels, although better for the environment in many cases, is economically disadvantageous. The cost-per-kWh delivered from hydrogen generated from fossil fuel is higher than the cost-per-kWh if the fossil fuel was used directly. As stated before, a renewable-based hydrogen-facilitated economy that does not rely on fossil fuels must be developed to help favor the use of fuel cells. Hydrogen fuel storage is the second part of the hydrogen infrastructure problem. Hydrogen storage mechanism must provide higher energy density per mass and volume while maintaining a reasonable cost. New techniques must be developed to reduce the cost of hydrogen storage.
Another obstacle barring fuel cell use is the high cost. It is estimated that the cost-per-kW fuel cells generate must be decimated to become competitive against current energy production methods. Two reasons behind the cost of fuel cell operations are that fuel cells use platinum-based catalyst and the membrane fabrication techniques currently used are expensive.

One way to bring the cost of fuel cell operation and maintenance down is to develop a way for fuel cells to use catalysts that are not platinum-based. In order for this to happen, the electrolyte membrane must be able to operate at higher temperatures. The most popular electrolyte membranes used in fuel cells today have a high reliance on water for ion conduction. The reliance on water bars the fuel cell to operate at higher temperatures (>100 °C). The polymer we are synthesizing is made up of a polymer backbone with a covalently attached cationic group, which will assist in the movement of hydroxide ions in alkaline fuel cells. The polymer-based electrolyte must have a high degree of ionic conductivity to function as an electrolyte membrane in AFCs. As PEMFCs are more popular than AFCs, the study of AFCs are fairly new. In this project, we synthesize an MePEG-based, ion conducting electrolyte with plans to test its ion conducting and viscoelastic properties in the near future. A reaction in the synthesis of the MePEG-based ion conducting electrolyte was also optimized, and the conversion rate of the MePEG-Tosylation reaction was increased by 36%, which will also be covered in this project.
EXPERIMENTAL

Tosylation of MePEG7OH

The polymers used in this experiment were synthesized in the lab starting with a polyethylene glycol monomethyl ether (MW = 350 g/mol) backbone (The 350 MW MePEG has 7 repeating ethylene oxide units, and can be abbreviated: Me(PEG)7OH). Me(PEG)7OH can be seen below in Figure 6.

![Figure 6: General structure of the polyethylene glycol monomethyl ether backbone where n = 7 (350 g/mol)](image)

Tosylation of MePEG7OH (Scheme 1): This reaction was performed by using the procedure from Li, J., & Kao, W. J. (2003). 1.993 g of Me(PEG)7OH (0.00569 mol), 1.46 g of trimethylamine (0.0144 mol), and 2.724 g 4-toluenesulfonyl chloride (0.0143 mol tosyl chloride or TosCl) were originally combined in a 1:1:1 ratio (Note: pyridine was used in many trials in the place of trimethylamine). The MePEG7OH was first placed in a round bottom flask, followed by the trimethylamine and then tosyl chloride. A stir bar was placed in the round bottom flask, the flask was capped, and the reaction was allowed to stir for 8 hours. The reaction mixture was then separated using 30 mL of water and 30 mL of dichloromethane (CH2Cl2, DCM) in a separatory funnel. The less dense aqueous layer remained in the separatory funnel and was extracted with 30 mL of DCM twice more. The organic layer was collected and dried using anhydrous sodium sulfate (Na2SO4). The product was recovered by rotary evaporation. The NMR spectra obtained are as followed: NMR (1H, in CDCl3), δ 1.12 ppm (s), 1.37 ppm (t), 2.36 ppm (s), 2.45 ppm (s), 2.49 ppm (s), 3.38 ppm (s), 3.59 ppm (s), 3.65 ppm (m), 7.17 ppm (d), 7.34 ppm (d), 7.41 ppm (t), 7.79 ppm (t), 7.92 ppm (d): (NMR 13C, in CDCl3), δ 46.13 ppm,
59.04 ppm, 68.69 ppm, 68.69 ppm, 69.26 ppm, 70.52 ppm, 70.57 ppm, 70.61 ppm, 70.75 ppm, 71.94 ppm, 126.04 ppm, 127.06 ppm, 127.99 ppm, 128.83 ppm, 129.84 ppm, 130.25 ppm.

**Scheme 1:** Tosylation of Me(PEG)$_7$OH reaction

Bromination Reaction of Me(PEG)$_7$OH

The reaction can be seen below in **Scheme 2**. Me(PEG)$_7$OH (MW = 350 g/mol, 20.06 g, 0.057 mol) was added to a round bottom flask with a stir bar and combined with 30 mL of diethyl ether in an ice bath. 14.31 mL of a 2.07 M phosphorus tribromide (PBr$_3$) solution in DCM (0.0296 mol) were added dropwise by syringe to the stirred mixture of MePEGOH and diethyl ether. **Hazard warning:** PBr$_3$ is very reactive with water in the air forming HBr gas, thus we removed the PBr$_3$ solution from a storage flask under positive pressure of nitrogen. The first 10 minutes of the reaction was allowed to stir under nitrogen gas. After 10 minutes, the flow of nitrogen gas was turned off, and the round bottom flask was capped and allowed to stir for 8 hours. The reaction mixture was then extracted using 30 mL of water and 30 mL of dichloromethane (CH$_2$Cl$_2$, DCM) in a separatory funnel. The less dense aqueous layer remained in the separatory funnel and was extracted with 30 mL of DCM twice more. The organic layer was collected and dried using anhydrous sodium sulfate (Na$_2$SO$_4$). The product was recovered by rotary evaporation. NMR ($^{13}$C, in CDCl$_3$), δ 30.33 ppm, 59.05 ppm, 70.53 ppm, 70.55 ppm, 70.58 ppm, 70.60 ppm, 70.67 ppm, 71.22 ppm, 71.95 ppm, 72.58 ppm.
Synthesis of Me(PEG)$_7$-N(CH$_3$)$_3^+$ Br$^-$

The reaction can be seen below in Scheme 3. Me(PEG)$_7$Br MW = 412.904 g/mol (1.53g, 0.00371 mol) was added to a round bottom flask with a stir bar. Then 33% trimethylamine in ethanol (TMA, 5.41 mL, 0.00750 mol) was added to the flask dropwise with stirring in an ice bath. The round bottom flask was immediately capped with a plastic pop-off cap in case of unintended pressure generation, and the reaction was allowed to stir for 8 hours. It is important to cap the round bottom flask immediately after placing both reactants in the flask as trimethylamine is a gas at room temperature and will eventually escape from the flask if not capped which could potentially cause the reaction to not go to completion. The reaction mixture was extracted using 30 mL of water and 30 mL of dichloromethane (CH$_2$Cl$_2$, DCM) in a separatory funnel. The less dense aqueous layer remained in the separatory funnel and was extracted with 30 mL of DCM twice more. The organic layer was collected and dried using anhydrous sodium sulfate (Na$_2$SO$_4$). The product was recovered by rotary evaporation. The NMR spectrum obtained is as followed: NMR ($^{13}$C, in CDCl$_3$), $\delta$ 59.04 ppm, 61.73 ppm, 70.34 ppm, 70.52 ppm, 70.58 ppm, 71.94 ppm, 72.56 ppm, 77.25 ppm.
Scheme 3: Synthesis of Me(PEG)$_7$N(CH$_3$)$_3^+$ Br$^-$
RESULTS AND DISCUSSION

Optimization of the MePEG Tosylation Reaction

Figure 7: $^1$H NMR Spectrum of Me(PEG)$_7$OH
**Figure 8:** $^1$H NMR Spectrum of Me(PEG)$_7$-tosylate following Scheme 1 in a 1:1:1 ratio of reactants

As the conversion rate was only 48.5% from reactants to products, a number of trials detailed in Table 2 in order to obtain a higher conversion rate.
<table>
<thead>
<tr>
<th>Ratio ((\text{Me(PEG)}_7\text{OH}:\text{TosCl}:\text{Pyridine}))</th>
<th>Condition</th>
<th>Length</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1:1</td>
<td>Room Temperature: stirring</td>
<td>8 hours</td>
<td>48.5% Conversion</td>
</tr>
<tr>
<td>1:2:3</td>
<td>Heated at 53 °C: stirring</td>
<td>4 hours</td>
<td>50% Conversion</td>
</tr>
<tr>
<td>1:2:3</td>
<td>53 degrees Celsius under Reflux</td>
<td>4 hours</td>
<td>53% Conversion</td>
</tr>
<tr>
<td>1:1.5:2</td>
<td>Room Temperature: stirring: 1 mL Chloroform added for each mL of (Me(PEG)_7OH</td>
<td>8 hours</td>
<td>63% Conversion</td>
</tr>
<tr>
<td>1:2:1</td>
<td>Room Temperature: stirring</td>
<td>8 hours</td>
<td>65.5% Conversion</td>
</tr>
<tr>
<td>1:2:1</td>
<td>Dissolved (Me(PEG)_7OH in pyridine in an ice bath: reaction allowed to run in ice bath</td>
<td>8 hours</td>
<td>70% Conversion</td>
</tr>
<tr>
<td>1:2.5:2.5*</td>
<td>1 mL of DCM per gram of Me(PEG)_7OH: stirred reaction under nitrogen</td>
<td>8 hours</td>
<td>84.5% Conversion</td>
</tr>
</tbody>
</table>

*Triethylamine (TEA, N(CH\text{2CH}_3)_3) used as base in place of pyridine

**Table 2: Selected trials of deviation from Scheme 1**

The result of this reaction was the conversion of the alcohol group (MePEG-OH) to a tosyl group (MePEG\text{_7OSO}_2\text{C}_6\text{H}_4\text{CH}_3). The tosylate-group is a great leaving group that has now been bonded to the backbone of the polymer backbone. The polymer can now undergo nucleophilic substitution to bond many different nucleophilic substitutes that we may prefer in future experiments. The initial trial with the reactants in a 1:1:1 ratio only had a 48.5% conversion from reactants to products, which was supported through the NMR spectra integral ratios obtained in the experiment. Through the many tests conducted, a condition was obtained that produced a 84.5% conversion rate from reactants to products, producing a 36% higher conversion rate in the final experiment.

This reaction does not produce the desired product without complications, however. Separation of the starting TosCl from the product MePEG-SO\text{2C}_6\text{H}_4\text{CH}_3 proved to be difficult.
Given that this reaction would, in practice, be one of the starting reactions this lab would undergo on several different projects in order to attach a good leaving group to the polymer backbone, our lab wanted to optimize this reaction so that it would be simple, cheap, and time-efficient. The TosCl could not be separated from the product MePEG-SO$_2$C$_6$H$_4$CH$_3$ by employing the use of a separatory funnel. When the reaction mixture was ran on a thin-layer chromatography (TLC), it showed promising signs of separation through the use of silica-gel column chromatography. However, given that the reaction did not produce a 95+% conversion of reactants to products and that separation of the starting material from the product proved to be difficult, our lab decided to instead explore the use of PBr$_3$ to bond a leaving group to the polymer backbone in hopes that it would create less complications.

**Optimization of the MePEG$_7$OH Bromination Reaction with PBr$_3$**

A $^{13}$C NMR spectrum was obtained for both the starting Me(PEG)$_7$OH (Figure 9) and the product Me(PEG)$_7$Br (Figure 10).
Figure 9: $^{13}$C spectrum for Me(PEG)$_7$OH
Comparing Figure 9 and Figure 10, a new peak appeared at 30.33 ppm. This peak is assigned to the carbon of the polymer backbone that is now bonded to bromine. Also, peak at 61.64 ppm in Figure 9, which is assigned to the same carbon of the polymer backbone that was once bonded to hydroxide, is no longer seen in Figure 10, confirming that this reaction has essentially gone to completion.
Synthesis of Me(PEG)$_7$-N(CH$_3$)$_3$$^+$ Br$^-$

Comparing Figure 9 and Figure 11, we see the peak at 30.33 ppm in Figure 9, which was assigned to the carbon bonded to the bromine, shift in Figure 11 to 61.71 ppm. This shift is indicative of the change in environment from the carbon atom being bonded to a bromine to the same carbon atom now bonded to N(CH$_3$)$_3$. We can successfully say that this reaction has gone to completion.
As stated above, we wish to explore the use of PBr$_3$ as a reagent to convert the alcohol to a halide group. PBr$_3$ is widely known and employed to do such a task, but our lab has never attempted to use it until this experiment. Because PBr$_3$ naturally reacts with the water found in the air, it was first dissolved in DCM. The PBr$_3$ solution was exclusively handle with a syringe when the solution was under a positive pressure created by nitrogen to make sure water vapor found in the air did not leak into the flask. From the NMR spectra gathered, the conversion of the reaction from Me(PEG)$_7$OH to Me(PEG)$_7$Br was essentially 100% conversion. Although extra safety precautions must be followed to use this reaction in favor of the tosylation reaction, our lab concluded that the advantages of the use of PBr$_3$ outweigh the disadvantages, and we will continue to use this reaction in the future. The second step of the reaction found in Scheme 3 posed no complications, and we have deduced from the $^{13}$C NMR spectra that the reaction essentially went to 100% completion.

Ion Exchange Reactions (planned)

Due to logistical complication imposed by the threat of COVID-19, this project unfortunately has been left incomplete. Future experimentation must be required to complete the synthesis of the MePEG-based hydroxide conducting electrolyte.

The next stepped planned for this experiment is to conduct an ion exchange of the MePEG$_7$-trimethylamine$^+$ bromide$^-$ (Me(PEG)$_7$-$N$(CH$_3$)$_3^+$ Br$^-$) to MePEG$_7$-trimethylamine$^+$ hydroxide$^-$. This process would be done by using an anion exchange resin column. To exchange the negatively-charged counter-ion bromide, a strongly basic exchange column will be used. The column will be filled with 160 mL of Amberlite IRA-400 chloride-form, strongly basic ion exchange resin. The column will then be rinsed with nanopure water and charged with 150 mL
of 4.0 M solution of sodium hydroxide (NaOH). Then the column will be rinsed with nanopure water until the pH is around 8.0. The Me(PEG)$_7$-N(CH$_3$)$_3^+$ Br$^-$ obtained would slowly run through the column in a solution of water, then rinsed with nanopure water until the pH of the effluent is back to around 8.0. This would ensure that all of the Me(PEG)$_7$-N(CH$_3$)$_3^+$ OH$^-$ product would be completely eluted.

Once the solution obtained was rotary evaporated with ethanol, the effectiveness of the ion-exchange would have to be assessed through a titration. Methanesulfonic acid would be the acid used to titrate a small amount of the Me(PEG)$_7$-N(CH$_3$)$_3^+$ OH$^-$. The Me(PEG)$_7$-N(CH$_3$)$_3^+$ OH$^-$ will be titrated to an equivalence point at pH 7.00 because this is a strong acid-strong base titration. If the total number of moles used for the methansulfonic acid to reach the equivalence point equals the total number of moles used for the Me(PEG)$_7$-N(CH$_3$)$_3^+$ OH$^-$, we can say with that our target molecule has been synthesized. Conductivity and viscosity measurements would be conducted on the newly synthesized hydroxide conducting electrolyte.

Ionic Conductivity Measurements (planned)

Once the Me(PEG)$_7$-N(CH$_3$)$_3^+$ OH$^-$ product was prepared by ion exchange, we planned to measure the ionic conductivity of this material using AC-impedance spectroscopy. Conductivity is measured in Siemens/cm and is the ability of a material to allow ions to diffuse through it. The AC-impedance spectroscopy applies an alternating-current potential through the sample which measures the real and imaginary components of impedance through the sample. The resistance is the real component of impedance that is manifested from the opposition of a current under a voltage, and the imaginary component of impedance is derived from the capacitances that arise from electrical contact with the electrolyte material as well as the double layer.
capacitance formed at the electrode. A Nyquist plot can be used to graphically show the data (Figure 12).

Figure 12: Typical Nyquist plot for conductivity where $R_{AB}$ is the measured bulk resistance. Figure adapted from Reference.7

A system with no Faradaic current will typically form in the shape of a half circle at high frequencies. The x-axis is the real component of impedance, and the y axis is the imaginary component of impedance that is representative of the capacitance of the sample. By taking the reciprocal value of the diameter and dividing by an experimentally determine geometric factor for the electrode (determined by the calibration with low conductivity standards), the ionic conductivity can be obtained.
CONCLUSION

In this thesis, we have optimized the MePEG-tosylation reaction as well as synthesized Me(PEG)$_7$-$N$(CH$_3$)$_3^+$ Br$^-$ in order to produce the Me(PEG)$_7$-$N$(CH$_3$)$_3^+$ OH$^-$ electrolyte in a future experiment using anion-exchange chromatography. We also found that the optimal ratios of the starting products for the MePEG tosylation are 1:2.5:2.5 (Me(PEG)$_7$OH:TosCl:TEA) with 1 mL of DCM (solvent) per gram of Me(PEG)$_7$OH. The reaction was allowed to stir for 8 hours under the presence of nitrogen gas. These conditions led to 84.5\% of the reactant to be converting to the product, an increase of 36\% conversion from the ratio of 1:1:1 (Me(PEG)$_7$OH:TosCl:Pyridine) previously used.
REFERENCES


3 Ritchie, Jason. Effects of Polymer Structure on Ion Transport in an Anhydrous Proton-Conducting Electrolyte


