ALKALINE DEGRADATION STUDIES OF ANION EXCHANGE POLYMERS
TO ENABLE NEW MEMBRANE DESIGNS

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by

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ABSTRACT

Current performance targets for anion-exchange membrane (AEM) fuel cells call for greater than 95% alkaline stability for 5000 hours at temperatures up to 120 °C. Using this target temperature of 120 °C, an incisive $^1$H NMR-based alkaline degradation method to identify the degradation products of $n$-alkyl spacer tetraalkylammonium cations in various AEM polymers and small molecule analogs. Herein, the degradation mechanisms and rates of benzyltrimethylammonium-, $n$-alkyl interstitial spacer- and $n$-alkyl terminal pendant-cations are studied on several architectures. These findings demonstrate that benzyltrimethylammonium- and $n$-alkyl terminal pendant cations are more labile than an $n$-alkyl interstitial spacer cation and conclude that Hofmann elimination is not the predominant mechanism of alkaline degradation. Additionally, the alkaline stability of an $n$-alkyl interstitial spacer cation is enhanced when combined with an $n$-alkyl terminal pendant. Interestingly, at 120 °C, an inverse trend was found in the overall alkaline stability of AEM poly(styrene) and AEM poly(phenylene oxide) samples than was previously shown at 80 °C. Successive small molecule studies suggest that at 120 °C, an anion-induced 1,4-elimination degradation mechanism may be activated on styrenic AEM polymers bearing an acidic α-hydrogen. In addition, an ATR-FTIR based method was developed to assess the alkaline stability of solid membranes and any added resistance to degradation that may be due to differential solubilities and phase separation.

To increase the stability of anion exchange membranes, Oshima magnesate–halogen exchange was demonstrated as a method for the synthesis of new anion exchange membranes that typically fail in the presence of organolithium or Grignard reagents alone. This new chemistry, applied to non-resinous polymers for the first time, proved effective for the $n$-akyl interstitial spacer functionalization of poly(phenylene oxide) and poly(styrene-$co$-ethylene-$co$-butylene-$co$-styrene) polymer backbones.
The comprehensive methodologies for the assessment of alkaline stability in AEMs as well as the new synthetic methodologies are intended as a guide toward robust AEM synthetic designs that approach current performance standards.


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I’d like to thank my neighbor Totoro.
Chapter 1

INTRODUCTION

Power Production and Storage

In recent years, there has been extensive research on the development of electrochemical devices fueled by renewables that have the ability to supply the energy demands of industrial, transportation and consumer applications. Devices powered by intermittent sources of energy such as solar, wind and hydropower aim to reduce dependencies on fossil fuels, but often require auxiliary platforms, such as fuel cells, to store chemical energy locally for continuous use.\textsuperscript{1}

![Figure 1-1: Representation of an AEMFC that utilizes a H\textsubscript{2} feed at the anode to generate water and electrical current. Electrons at the cathode reduce an O\textsubscript{2} feed to hydroxide anions that diffuse through the (polymer membrane) electrolyte.\textsuperscript{1} © Fuel Cell Markets, 2015.](image-url)
Fuel cells are galvanic devices that convert the free energy of chemical reactions to electrical energy. The most compelling renewable fuel source for fuel cells is hydrogen (H\textsubscript{2}) due to its high energy density and accessibility from water electrolysis. Alkaline exchange membrane fuel cells (AEMFCs) are designed to convert the chemical energy of H\textsubscript{2} directly into electrical current with high efficiency at low temperature.

AEMFCs operate using a hydroxide-based electrolyte solution whereby H\textsubscript{2} is oxidized on the anode with hydroxide anions to generate water and electrons. The electrons are then transferred through an external circuit (drain) to the cathode, where oxygen is reduced in the presence of water to generate regenerate hydroxide ions. These reactions at the electrodes are summarized with the following (SHE = standard hydrogen potential):

\begin{align*}
\text{Anode: } & \quad 2 \text{H}_2 + 4 \text{OH}^- \rightarrow 2 \text{H}_2\text{O}(l) + 4 \text{e}^- \quad E_{\text{ox}}^\circ = +0.83 \text{V}_{\text{SHE}} \\
\text{Cathode: } & \quad \text{O}_2 + 2 \text{H}_2\text{O}(l) + 4\text{e}^- \rightarrow 4 \text{OH}^- \quad E_{\text{red}}^\circ = +0.40 \text{V}_{\text{SHE}} \\
\text{Overall: } & \quad 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \quad E_{\text{tot}}^\circ = +1.23 \text{V}_{\text{SHE}}
\end{align*}

AEMFCs are the most efficient fuel cells that consume H\textsubscript{2}/O\textsubscript{2} feed stocks under alkaline conditions at temperatures below 200 °C. Specifically, the reaction kinetics and cell potential are greater than those possible under acidic conditions when compared to proton exchange membrane fuel cells (PEMFC). This high electrical efficiency and relatively non-corrosive high pH environment allows for the use non-precious metal catalysts (e.g., Ni and Ag) in the electrodes that reduce device capital costs over comparable PEMFCs that rely on Pd or Pt-based catalysts. AEMFCs also have some drawbacks, one of them being related to the use of the liquid basic electrolyte. The hydroxide-based electrolyte containing alkali metal cations is sensitive to the presence of carbon dioxide (CO\textsubscript{2}) impurities that tend to form precipitates near the electrodes and reduce performance. A major operating constraint is the requirement for low CO\textsubscript{2} concentrations.
in the feed oxidant stream that becomes particularly troublesome if air is substituted for purified
O$_2$. Despite this disadvantage, AEMFC research has primarily focused on improving the
efficiency and chemical stability of the polymer membrane in the presence of the hydrolytic
electrolyte. Polymer-based alkaline electrolytes have the advantage of not containing metal
cations and therefore, will not experience carbonate-based salt precipitation in the cell.

Fuel cell performance is influenced by many parameters including catalyst type,
operating temperature, pressure and relative humidity of the gas feed stocks, and flow rates.
However, the polymer-based AEM separator is undoubtedly one of the most important
contributors to fuel cell performance. The membrane must have: (i) mechanical stability in varied
states of hydration, (ii) chemical resistance to alkaline conditions at high temperature, (iii) low
fuel crossover through the membrane, (iv) negligible electronic conductivity, and (v) adequate
ionic conductivity ($\sim 10^{-3}$ S$\cdot$cm$^{-1}$) with minimal resistive losses. Of these desired properties, the
single most important consideration is resistance to alkaline conditions once a sufficient level of
conductivity has been reached. An AEM designed to address all of the parameters required for
AEMFC applications will undoubtedly fail in one or more categories if its intended chemical
structure does not persist under device operation.
The US Department of Energy (DOE) has outlined performance targets that serve as useful (and optimistic) goals to drive AEM development. Of the performance metrics outlined by the DOE in Table 1-1, performance targets for fuel cell durability (i.e., 2015, 5000 hours >80 °C) and lifetime degradation (i.e., 2015, 5%) under AEMFC operational conditions are the most difficult to satisfy due to the alkaline lability of AEM polymers and additional oxidative stress imposed by the operating fuel cell.

The continuous improvements in AEMs toward increasing performance and limiting the degradation of these materials in operating cells has the added benefit of reducing costs for eventual implementation in industries such as transportation (Table 1-2). Over the last decade, advances in fuel cell technology has allowed for reduced operational costs that are becoming increasingly competitive with fossil fuel-derived energy. Additionally, innovations in AEMs for
fuel cells may also be leveraged in other energy technologies such as redox flow and alkaline batteries.

Table 1-2: Projected Transportation Fuel Cell System Cost. © EERE, 2015.

**Synopsis of Research**

In a concerted effort to increase AEMFC performance, the fuel cell community has taken an interest in the examination of AEMs to understand the underlying reasons for alkaline instability. Measurements of alkaline stability have been assessed using a variety of techniques that include ion-exchange capacities, ionic conductivities, FT-IR and $^1$H NMR spectroscopies, that each have sought to quantify changes in chemical composition during accelerated degradation processes. With few exceptions, most methods that measure alkaline stability have not been standardized and have resulted in conflicting reports of stability. These variations in methods and other factors in assessment of AEM stability have made it difficult for the community to come to a consensus on the most promising directions for highly stable, highly conductive AEM backbones and cations.
The Literature Review section of this work (Chapter 2) examines methods for assessing polymer stability that includes several primary- and secondary-property measurement techniques to quantify alkaline degradation. With a focus on AEM polymers bearing tetraalkylammonium cations, the mechanisms of degradation for various polymer backbones and cations designs are discussed alongside with correlations to the influences of solvation and phase separation on alkaline stability. Since the aim of this body of work was to gain insight for the design of robust AEM architectures and the related chemistries that were necessary for accessibility, the current methods of post-polymer chemical modifications from commercial polymers are reviewed.

In Chapter 4, the alkaline stability at 80 °C of three classes of AEM polymers are presented using a simple methodology that provides quantitative $^1$H NMR spectroscopic data on dissolved polymer samples. The absolute degradation kinetics, backbone stability and observed degradation mechanisms are reported with recommendations for future synthetic designs.

Chapter 5 proposes a modified $^1$H NMR spectroscopic methodology at 120 °C under conditions similar to those conducted at 80 °C. Herein, the elevated temperatures are designed to induce failure modes for definitive alkaline stability correlations. Additionally, the absolute alkaline stabilities of benzyltrimethyl ammonium cations, and those containing an n-alkyl interstitial and/or n-alkyl terminal pendant spacer are reported with a definitive discussion of the contribution of each degradation mechanism.

The focus of Chapter 6 is on an alternative methodology that combines both $^1$H NMR and FT-IR spectroscopy to study the alkaline stability of fluorinated AEMs in both solution and the solid state.

Finally, Chapter 7 presents a completely new synthetic route to functionalize commercial AEM polymers alkaline-resistant n-alkyl interstitial and terminal pendant cations using unprecedented Oshima magnesate chemistry.
References:


Chapter 2

LITERATURE REVIEW

Introduction

Anion exchange membrane fuel cells are among the highest-performance fuel cells with operation temperatures below 200 °C that utilize H₂/O₂ feed stocks; merited by facile kinetics at the electrodes, and low-cost catalysis with non-precious metals. Despite these pros, the wide-scale implementation of AEMFCs is hindered by the modest thermochemical stability of the AEM polymers in the operational cell environment that fall considerably short of DOE performance targets. AEM performance failure in alkaline media is manifested by reduced function (i.e., ion conductivity) and deterioration of chemical and mechanical properties of the polymer backbone and/or cation. In addition, other factors such as temperature, solvation, and phase separation have been well-documented to influence overall alkaline stability of AEM polymers.

Prior strategies to improve AEM alkaline stability treated the chemical stability of the cationic headgroups separately from their respective polymer backbone. That is, research in this area suggested that once an alkali-resistant cationic headgroup was developed, it could be synthetically affixed to robust polymer backbone to form a durable AEM polymer. However, several studies over the last few years, including those reported in this body of work, indicate that there exists a stronger correlation between the cationic head groups and the polymer backbone than previously thought. For example, polysulfones are thermoplastic polymers known to be highly resistant to many harsh conditions including alkaline environments at elevated temperatures. However, if quaternary-ammonium functionalities are introduced, these cations increase polysulfone’s hydrophilicity and allow for closer approach of hydroxide ions into
electrophilic regions of the polymer backbone—inducing degradation.\textsuperscript{1} It is this hydrophobicity of unfuctionalized AEM polymer backbone candidates that affords alkaline resistance even though the bonds of the polymer may be susceptible to nucleophilic attack. Thus any evaluation of AEM polymer alkaline stability must consider both the cationic head group and polymer backbone architectures as a cooperative entity with properties unique to the given combination. Additionally, the stability of the components of the AEM must be assessed in such a way as to allow access of the hydroxide to the polymer and/or cation. For example, degradation experiments on both soluble species and membranes will give information on any steric barriers to degradation in the membrane phase.

Assessments of the alkaline stability of AEMs are measured using various spectroscopic (e.g., \textsuperscript{1}H NMR, FTIR, MS) and secondary measurements (e.g., changes in IEC, conductivity, molecular weight) under accelerated degradation conditions. Methodologies to study the alkaline stability of AEMs are more commonly evaluated using secondary measurements as they provide data into the physical and performance properties that more appropriately correspond to desired AEMFC performance parameters. However, these secondary measurements fall short of providing insight into the chemical changes that result from alkaline degradation of the AEM polymer. Spectroscopic methods provide an understanding of stability data, degradation mechanisms of cations and polymer backbone, and their combined susceptibility to alkaline degradation in AEMFCs. Thus, spectroscopic analyses of a AEM polymer’s alkaline degradation provides a comprehension of chemical labilities that are invaluable for the redesign of more robust AEM polymer architectures and it is this comprehension that provides the motivation for the discovery of new synthetic chemistries.
Methods for Assessing Polymer Stability

Performance Failure (In-Device & Accelerated)

Generally, minimizing the thickness of AEMs improves fuel cell performance by decreasing membrane’s resistivity in the device. Reduced resistances in AEMs are pivotal to equivocate (slower) hydroxide transport in AEMFCs to faster proton conduction in PEMFCs. However, maintaining the mechanical integrity of thin membranes is difficult—especially those that are susceptible to alkaline degradation. Assessing AEM failure modes in real-world devices is a laborious and often costly process to assess over prolonged periods. Accelerated stress testing of AEMs in an ex-situ environment from an AEMFC and under harsh conditions increases sample throughput and reduces experimental times. Accelerated stress tests focus on activating the failure mode(s) of the polymer without confounding effects that would not be expected to occur in an AEMFC (e.g., secondary degradation from transition metals in electrodes, impure feed stocks, etc.). For example, an accelerated stress test designed to measure the chemical degradation of cationic headgroups under alkaline conditions should aim to: (i) induce a failure mode, (ii) identify the failure mode (i.e., degradation mechanism), and (iii) isolate the effects changing a single variable (e.g., temperature or alkali concentration). The problem with accelerated degradation testing is that non-representative failure modes can be activated giving results that do not apply to the material’s performance in the cell. This issue can be mitigated by carefully considering the failure modes that occur in the device and accelerated testing using different stressors.
Degradation tests with a corresponding real-world electrochemical cell performance test was conducted on a quaternary-ammonium functionalized-pol(sulfones) (QA-RADEL) and poly(phenylene oxide) (QA-PPO) membranes. HRSEM images of pristine membrane samples of QA-Radel exhibited a smooth surface with some hairline cracking while QA-PPO revealed a rougher surface with no cracking. Upon exposure to an aqueous 1 M KOH solution at 60 °C for 100 hours, a stark difference in the membrane surfaces was evident (Figure 2-2).
Following immersion, pits, cracks and holes appeared on both membrane surfaces on the surfaces of both membranes (Figure 2.2). The causes of these morphological changes were verified with a spectroscopic method and attributed to polymer backbone decomposition and hydrolysis of the cations.

Figure 2-2: HRSEM images of QA-PPO and QA-RADEL membrane samples exposed to 1 M KOH solution at 60°C for 100 h. Note: brightness and contrast have been adjusted equally by +35% for image clarity. © The Electrochemical Society 2014.

Figure 2-3: HRSEM of the morphological surface changes of a QA-Radel sample near the gasket line in a fuel cell after 50 cycles. Note: brightness and contrast have been adjusted equally by +35% for image clarity. © Springer Publishing 2011.
Similar degradation of membranes can occur in other types of electrochemical devices. A degradation test conducted on a QA-Radel membrane in a redox flow cell over 50 cycles revealed comparable results to the accelerated conditions in basic media. Figure 2-3 shows the morphological surface changes to QA-Radel near the fuel cell gasket line exhibited significant cracking.

A macroscopic examination of the cycled polysulfone membrane reveals compounding delamination within the active area of after 25 and 50 cycles (Figure 2-4).

**Accelerated Degradation Test Conditions**

The Department of Energy, US Fuel Cell Council and American Society for Testing and Materials have all proposed a set of standard conditions and operating procedures for evaluating the stability of PEMFC components, but to date, no such protocols exist for AEMFC components. This lack of standardization has led the research community to develop many independent accelerated degradation methods under wide-ranging conditions (i.e., duration,
temperature, solvent, alkali and alkali concentration, etc.) and evaluation techniques. Table 2-1 lists a summary of assorted accelerated degradation tests in the literature elucidating the variations in alkali concentration (e.g., 0.5–10 M), evaluation techniques (e.g., NMR, conductivity, and IEC) and duration (e.g., minutes to days). In addition, when combing through the literature, some trends become apparent: (i) typically only relative data on chemical stability is reported (as opposed to absolute), (ii) the methods require many steps that introduce reproducibility issues, and (iii) the methods tend ignore the stoichiometric relationship between the ion-conducting functional group and the concentration of the alkali.

These variations and other factors in measuring degradation, as meticulously discussed by Varcoe, in assessing the stability of AEMs using accelerated degradation protocols, have made it difficult for the fuel cell community to come to a consensus on the most promising directions for highly stable, highly conductive AEM backbones and cations.
Ion Exchange Capacity

Secondary measurements to assess alkaline stability under accelerated conditions such as the determination of ion-exchange capacity (IEC), that is, the number of functional ionic groups per unit mass of the polymer (millimolar equivalents per gram), has traditionally been employed as the standard technique of evaluating alkaline stability. IEC determinations are sensitive to the

Table 2-1: Literature Summary of the Alkaline Stabilities of Assorted AEMs. © American Chemical Society, 2014.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Polymer Backbone</th>
<th>Test Conditions</th>
<th>Stability Test Method</th>
<th>Stability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>polyacrylamide</td>
<td>3M NaOH, 65°C, 24h</td>
<td>conductivity</td>
<td>Not Stable</td>
<td>11,12</td>
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<tr>
<td></td>
<td>styrene</td>
<td>10M NaOH, 60°C, 120h</td>
<td>conductivity</td>
<td>Stable</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>styrene &amp; acrylonitrile</td>
<td>10M NaOH, 60°C, 72h</td>
<td>conductivity &amp; IEC</td>
<td>Stable</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>PMMA</td>
<td>1M NaOH, 80°C, 72h</td>
<td>NMR</td>
<td>Not Stable</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>2M KOH, 60°C, 13 days</td>
<td>IEC, NMR</td>
<td>Stable</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PPPO</td>
<td>2M KOH, 80°C, 7 days</td>
<td>IEC, conductivity</td>
<td>Not Stable</td>
<td>17</td>
</tr>
<tr>
<td>R = H, Me</td>
<td>styrene &amp; ETE</td>
<td>1M KOH, 60°C, 24h</td>
<td>conductivity, IEC, NMR</td>
<td>Not Stable</td>
<td>18</td>
</tr>
<tr>
<td>R = Me, iPr, Ph</td>
<td>none</td>
<td>1M KOH, 80°C, 108h</td>
<td>NMR</td>
<td>Stable</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>none</td>
<td>2M KOH in water, 80°C</td>
<td>NMR</td>
<td>t_{1/2} = 45 h</td>
<td>8,20-23</td>
</tr>
</tbody>
</table>

*R* groups represent the polymer backbone unless otherwise noted.
counterion form of the AEM polymer since they rely on back-titrations of the counterion (e.g., Mohr titrations), or the use of ion-selective electrodes to determine the ion concentration. In some cases, $^1$H NMR spectroscopy is used to determine IEC when the AEM contains an internal calibration standard for comparison to cation peak signals and, more importantly, when the polymer is soluble in available deuterated solvents. It is not unusual to observe significant variability in secondary and spectroscopic methods used to assess the IECs of AEM polymers. 

Figure 2-5 displays the measured IEC values of three AEM polymers after immersion in 1 M NaOH(aq) at 80 °C. Although the AEM polymers were reported to retain 80% of their conductivity, the reaction profile exhibited by all three samples is a common trend in the literature. A brief comparison between the decreasing rates of degradation at 0–100 hours, and 100–500 hours reveals contrasting kinetic rates. A change in kinetic rate is typically indicative of variable substrate concentration (i.e., the polymer or cation), changing mechanisms influenced by substrate or product concentrations, catalyst activation (e.g., changing initial hydration levels within the AEM), product inhibition and/or irreversible consumption of the alkali component. Although all of these extraneous variables can confound reports of alkaline stability, these methods have become the status quo to illustrate AEM polymer stability and little justification using chemical mechanisms is provided when these types of curves are observed.
Ionic Conductivity

Ion conduction, like IEC measurements, a secondary property of AEM polymers, has often been used to assess alkaline stability under accelerated degradation conditions. Measuring ionic conductivities in AEMs presents its own challenges stemming from counterion impurities and the ability of AEMs to quickly convert atmospheric CO$_2$ to carbonate ions (CO$_3^{2-}$) that differ in ion conductivities.

Figure 2-5: Measured IEC values of comb-shaped and poly(phenylene oxide) AEM polymers after immersion in 1 M NaOH$_{(aq)}$ at 80 °C. (square) PPO-DMHDA-20, (circle) PPO-DMHDA-40, (triangle) PPO-TMA-20. © The Royal Society of Chemistry, 2012.
Figure 2-6 depicts the hydroxide conductivity of fluorenyl-based AEMs under aqueous hydrolytic conditions at 80 °C for 100 h. Although hydrolysis of AEM cations and a resulting decrease in conductivity is the logical outcome of a degradation study, the AEMs display a progressive increase in conductivity throughout their immersion. The authors argue that the increase in conductivities arise from morphological changes in the AEMs that form better ionic channels, yet subsequent $^1$H NMR analysis of the samples revealed a 42–50% hydrolysis of the cations. An alternative hypothesis is that the sample is swelling greatly, thus increasing the water uptake of the sample, which can lead to greater ionic conductivity or that CO$_2$ is being purged from the system over the test duration resulting in a more pure hydroxide conductor which would manifest as an increase in conductivity.
$^1$H NMR Spectroscopy

Spectroscopic methods, such as $^1$H NMR have been used to quantify the alkaline stability of imidazolium-based AEMs over a broad range of humidities, temperatures, and alkaline concentrations (Figure 2-7).$^{12}$ The authors reported high chemical stability at 30 °C under low humidity conditions (30 °C) and saturated conditions (80 °C), but observed considerable degradation at temperatures above 25 °C and/or alkaline concentration greater than 1 M KOH.

Degradation of the imidazolium-based AEMs was suspected to occur via a ring-opening mechanism whereby imidazolium cation degrades to non-ionic formyl and imine functionalities. Examination of the rates of degradation in Table 2-2 at temperatures relevant to AEMFCs of 80 °C reveal significant chemical lability in even dilute 1 M KOH solutions. The authors argue their
AEMs are chemically stable under the low humidities that are desired to sustain long AEMFC lifetimes.

Table 2-2: Degree of Ring-Opening Degradation of Imidazole-based AEMs under Varied Conditions and Assessed by \(^1\)H NMR.\(^{12}\)

<table>
<thead>
<tr>
<th>(T (\degree C))</th>
<th>(\text{RH} (%) \text{ or KOH (M)})</th>
<th>(t (\text{h}))</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>RH = 10%-90%</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>30-80</td>
<td>RH = 90%</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>30-80</td>
<td>RH = 50%</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>30-80</td>
<td>RH = 10%</td>
<td>22</td>
<td>9.9</td>
</tr>
<tr>
<td>80</td>
<td>([\text{KOH}] = 0 \text{ M})</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>([\text{KOH}] = 0 \text{ M})</td>
<td>168</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>([\text{KOH}] = 1 \text{ M})</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td>80</td>
<td>([\text{KOH}] = 1 \text{ M})</td>
<td>168</td>
<td>38.3</td>
</tr>
<tr>
<td>25</td>
<td>([\text{KOH}] = 1 \text{ M})</td>
<td>24</td>
<td>3.8</td>
</tr>
<tr>
<td>25</td>
<td>([\text{KOH}] = 6 \text{ M})</td>
<td>24</td>
<td>41.9</td>
</tr>
<tr>
<td>25</td>
<td>([\text{KOH}] = 10 \text{ M})</td>
<td>24</td>
<td>49.7</td>
</tr>
</tbody>
</table>

The polymer backbone is a curious choice considering that PMMA backbones contain ester functionalities with known hydrolytic susceptibilities. Additionally, closer examination of the trend of samples degraded at 80 °C in 1 M KOH for 24 h and 168 h reveal non-linear polymer cation degradations of 18\% and 38.3\%, respectively, that is indicative of the consumption of KOH in the analysis.

While the use of \(^1\)H NMR in this study provides chemical insight into the degradation mechanisms of imidazolium-based AEMs, the method suffers from some faults apart from the apparent consumption of alkali in some cases. First, polymer samples exposed to various alkali concentrations were dried under vacuum at their respective time intervals without neutralization—this procedure has the effect of increasing the local concentration of degradation-inducing base. Secondly, the degradation values reported are relative as no internal standard was used for absolute comparisons. The use of a non-reactive internal standard not only yields
desirable absolute values but also removes the potential for side-reactions that affect the measurement of the peaks of interest.

**FT-IR Spectroscopy**

Infrared absorption spectral analyses for the determination of chemical stability has precedent in perfluorinated sulfonic acid PEMs, but very few spectral analyses have been conducted on AEMs. One of these limited IR spectroscopic studies conducted on a quaternary-ammonium-functionalized poly(phenylene oxide) (QA-PPO) investigated membrane alkaline stability. Absorption peaks corresponding to $C_4N^+$ vibrations and aryl ether asymmetric vibrations were identified at 918 cm$^{-1}$ and 1118 cm$^{-1}$ respectively. Normalization to a fixed point, aromatic C–C stretching at 1423 cm$^{-1}$, yielded quantifiable degradation rates based on FTIR absorptions for the polymer backbone and quaternary ammonium groups.

![Figure 2-8](image)

Figure 2-8. Normalized intensity of ether group (a) and QA group (b) in QA-PPO membrane at 60°C. © The Electrochemical Society, 2014.

In alkaline environments of 1–10 M KOH at an elevated temperature of 60 °C, QA-PPO showed negligible changes to the aryl ether asymmetric peaks—a result indicating the poly(phenylene oxide) backbone is resistant to alkaline hydrolysis (Figure 2-9a). The degradation
rates for the quaternary ammonium were significant for even 1 M KOH solutions at 60 °C (Figure 2-9b).

Degradation Mechanisms of Tetraalkylmmonium AEMs

![Diagram of degradation mechanisms](image)

Figure 2-9: Mechanisms of chemical degradation for a tetraalkylammonium small molecule under alkaline aqueous conditions. a A minor product of this substitution reaction results in 1-hexanol (not shown) as the dealkylation product. b A minor product of the Steven’s rearrangement results in the [2,3]-shift product (not shown).

Tetraalkylammonium cations have demonstrated appreciable alkaline stability, but are susceptible to several of chemical degradation pathways. These degradation mechanisms include substitutions (S_N2), eliminations (E2), Stevens or Sommelet—Hauser rearrangements and potentially, anion-induced 1,4-eliminations (Figure 2). Several studies on polymer-bound...
tetraalkylammonium cations have substantiated the occurrence of substitution and elimination reactions,\textsuperscript{19} but the contribution of Hofmann elimination remains a matter of discussion with little experimental evidence in AEM polymers. Stevens and Sommelet—Hauser rearrangements on benzyltrimethylammonium (BTMA or ambiguously, quaternaryammonium; QA) cations have been demonstrated under alkaline aqueous conditions\textsuperscript{20} and in silico,\textsuperscript{15,21} but have not been experimentally observed in AEM materials.\textsuperscript{18} A possible explanation for this result may involve side reactions in the presence of nucleophilic counterions.\textsuperscript{20} Finally, anion-induced 1,4-eliminations, a degradation mechanism seldom discussed in the context of AEM degradation, is fundamentally allowed when BTMA analogues (e.g., a tetraalkylammonium functionalized poly(styrene)) contain acidic $\alpha$-hydrogen(s) in ring-activating positions paired with a good leaving group.\textsuperscript{22} Unfortunately, the contribution of 1,4-eliminations\textsuperscript{7} cannot easily be discerned from benzyl substitutions under aqueous alkaline degradation conditions without sophisticated isotopic labeling studies and full analysis of the degradation product.

Factors Influencing Degradation

The susceptibility of AEM polymers to alkaline degradation is the result of the complicated relationship between the synthetic design of the polymer backbone and cation, their degree of solvation, and of any morphological features that allow for phase separation (Figure 2-10). No single study can yield insight into the individual contribution of each of these factors contributing to total degradation. To assert any conclusions on the cause of alkaline degradation, accelerated stress tests should be designed to induce and identify failure modes, and isolate the effects of a single change in the aforementioned variables.
AEM Polymer Backbone

There are very few systematic studies\textsuperscript{18} contrasting the stabilities of polymer backbones and their respective cations. Common polymer backbone architectures for AEMs have included poly(styrenes), poly(phenylene oxides), poly(arylene ether sulfones), poly(benzimidazoles), and poly(styrene-co-ethylene-co-butylene-co-styrenes) (Figure 2-10).

Figure 2-10: Interrelationship of factors contributing to alkaline degradation in AEMs.
For many years, poly(sulfone) backbones were used as the standard for functionalization to AEM materials. Decreases in performance and desired material properties as a result exposure to alkaline environments were often attributed specifically to cation degradation since poly(sulfone)s are characterized as chemically-resistant thermoplastics. An analysis by Arges using $^1$H NMR two-dimensional correlational spectroscopy (COSY) of benzyltrimethyl ammonium-functionalized poly(sulfones) revealed that in addition to cation hydrolysis, a peak signal corresponding to phenols and phenylpropane alcohol appeared (see annotation 9 in Figure 2-12).

Figure 2-11: Chemical structures of polymer backbones common to AEMs in fuel cell applications.
Figure 2-12: $^1$H NMR COSY spectrum of PSF-TMA\(^+\) exposed to 1 M KOH for 30 days at 60 °C. Signal "9" is known as degraded product 9 (phenylpropane alcohol). © The Electrochemical Society, 2013.\(^\text{23}\)

Figure 2-13: Mechanisms implicated for degradation of poly(sulfones) backbone in alkaline media: (A) hydroxide attack at quaternary carbon to generate phenylpropane alcohol, and (B) displacement by hydroxide of the aryl ethers to generate phenols. © The Electrochemical Society, 2013.\(^\text{23}\)
The implication of observing phenols and phenylpropane alcohol was that the poly(sulfones) backbone was hydrolyzing in alkaline solutions of 1 M NaOH and temperatures of 60 °C. The author’s suggested mechanism shown in Figure 2-13 describes a nucleophilic attack at the quaternary carbon (A) and displacement of the aryl ethers by hydroxide ions (B).

**AEM Cation Design**

The AEM performance and alkaline stability is a function of the chemical structure. AEM polymer-bound cations have included benzimidazolium,24 imidazolium,7 amino phosphonium,25 and sulfonium,26 but the most commonly studied cations are tetraalkylammonium salts due to their synthetic accessibility, inexpensive starting materials and verified practical membrane properties (Figure 2-14).

![Chemical structures of cations common to anion exchange membranes in fuel cell applications.](image)

Figure 2-14: Chemical structures of cations common to anion exchange membranes in fuel cell applications.
Specifically, benzyltrimethyl ammoniums (BTMA) have served as the default cation headgroup due to its synthetic accessibility on several commercial polymer backbones. The frequency to which AEMs functionalized with BTMA groups ought to suggest prolonged alkaline stability but studies in this area consistently report conflicting results. A couple systematic studies have compared BTMA to other cations and found BTMA to exhibit only modest alkaline stability for AEMFC applications. The overriding conclusion summarize alkaline stability with specific regard to the cation, is affect by a combination of steric, resonance and electronic effects.

Table 2-3 lists the half-lives of several tetraalkylammonium species in a 6 M NaOH solution at 160 °C.\textsuperscript{27} Compared to the half-life of tetramethyl ammonium (TMA) cation, small molecule analogs with a benzyl substituent (BTM, MBTM, NBTM) have a significantly lower half-life that is irrespective of the electron donating (MBTM) or withdrawing (NBTM) substituents. These observations suggest the benzyl group alone introduced the greatest chemical lability under alkaline conditions. Interestingly, the added steric of benzyltriethyl (BTE) ammonium is approximately an order of magnitude less persistent than BTM likely due to the compounded effects of Hofmann-type eliminations while alicyclic DMP is twenty-fold more persistent than BTM that is likely to an energetically disfavored conformation (i.e., syn-periplanar) for the occurrence of Hofmann eliminations.

The delocalization of charge on ammonium cations has been advocated in the literature to improve alkaline stability. Examples of charged-delocalized ammonium cation stabilities in 6 M NaOH at various temperatures are listed in Table 2-3 and include imidazoliums (TMI, MOI, BMI), a guanidinium (DTG) and a pyridinium (BP).
Compared to the half-life of the BTM ammonium cation (i.e., $t_{1/2} = 4.18$ h) which is presumably more labile due to the benzyl group under alkaline conditions, none of the aforementioned charged delocalized cations display half-lives long enough to measure even at reduced temperatures of 25 °C and 60 °C. Kreuer’s suggestion in this study is that charge

Table 2.3: Alkaline stability of various small molecule analogs at 160 °C in 6 M NaOH. © Wiley-VCH Verlag GmbH & Co., 2014.27

<table>
<thead>
<tr>
<th>Entry</th>
<th>QA</th>
<th>Abbreviation[8]</th>
<th>Half-life [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image" /> TMA</td>
<td>61.9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Image" /> MBTM</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Image" /> BTM</td>
<td>4.18</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Image" /> BTE</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Image" /> NBTM</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Image" /> MAABCO</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Image" /> BAABCO</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td><img src="image8.png" alt="Image" /> DMP</td>
<td>87.3</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td><img src="image9.png" alt="Image" /> BMP</td>
<td>7.3</td>
<td></td>
</tr>
</tbody>
</table>
delocalization alone is insufficient to increase alkaline stability in the absence of additional steric shielding.

Table 2-4: A comparison of the alkaline stability of various small molecule analogs elucidating resonance effects at 160 °C in 6 M NaOH. © Wiley-VCH Verlag GmbH & Co., 2014.27

<table>
<thead>
<tr>
<th>Entry</th>
<th>QA</th>
<th>Abbreviation(2)</th>
<th>Half-life (\text{[h]})</th>
<th>(T) (\text{[°C]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>BTM</td>
<td>4.18</td>
<td>160</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>PhTM</td>
<td>0.14</td>
<td>160</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>TMI</td>
<td>too short to measure</td>
<td>160</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>DTG</td>
<td>too short to measure</td>
<td>160</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5" alt="Chemical Structure" /></td>
<td>MOI</td>
<td>too short to measure</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6" alt="Chemical Structure" /></td>
<td>BMI</td>
<td>too short to measure</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7" alt="Chemical Structure" /></td>
<td>BP</td>
<td>too short to measure</td>
<td>25</td>
</tr>
</tbody>
</table>

A few studies have provided compelling evidence to support the benefits of steric shielding on the alkaline stability of ammonium cations. An early study by Tomoi28 on cross-linked poly(styrene) resins functionalized with various length n-alkyl interstitial spacers, that is, methylene groups (–CH\(_2\)–) separating the polymer backbone from the ammonium cation, revealed a trend whereby stability was gained with increased lengths of the interstitial spacer (Figure 2-14).
Under mildly alkaline (facilitated by hydroxide counterions) and hydrolytic aqueous conditions raging from 100–140 °C at 140 °C, benzyltrimethyl cations hydrolyzed to a remaining ratio of 1% after 30 days. Resin analogs with four- and six-carbon n-alkyl interstitial spacers exhibited a 20-fold and 39-fold increase in hydrolytic resistance under the same conditions, respectively (Figure 2-15).

Figure 2-14: Representation of poly(styrene) resins containing various length n-alkyl interstitial spacers. © John Wiley & Sons, 1997.

Figure 2-15: Thermal stability of alkyleneoxymethylene spacer-modified anion exchangers. Heat resistance test conditions: 100–140 °C; 30 days. © John Wiley & Sons, 1997.
Another study into the steric effects of alkyl chain substituents on ammonium groups was performed by Li\textsuperscript{29} on poly(phenylene oxide) backbones for AEMFC applications. Li functionalized terminal pendant n-alkyl spacers on ammonium groups affixed to the polymer backbone via a benzyl linkage. When compared to a benzyltrimethyl ammonium (BTMA\textsubscript{20}) cation functionalized PPO, these benzyldimethyl—n-alkyl terminal pendant cations consisting of methylene groups in six- (C\textsubscript{6}D\textsubscript{4}0), ten- (C\textsubscript{10}D\textsubscript{4}0), and sixteen-carbon (C\textsubscript{16}D\textsubscript{4}0) lengths exhibited greater alkaline stability in 1 M NaOH at 80 °C for 2000 hours. C\textsubscript{6}D\textsubscript{4}0 exhibited nearly three times the alkaline stability over BTMA\textsubscript{20} (Figure 2-16), while the presumed added sterics of C\textsubscript{10}D\textsubscript{4}0 and C\textsubscript{16}D\textsubscript{4}0 analogs were more labile than C\textsubscript{6}D\textsubscript{4}0—indicative of both a nominal and non-additive effect of increasing chain lengths.

![Figure 2-16](image_url)

**Figure 2-16:** The changing trend in (a) IEC values and (b) bicarbonate of comb-shaped CyD\textsubscript{x} and BTMA\textsubscript{x} membranes after immersion in 1 M NaOH solution at 80 °C. © Journal of the American Chemical Society, 2013.\textsuperscript{29}
Although the aforementioned studies affirm the added alkaline stability of n-alkyl substituents on ammonium cations, a recent polyethylene-based AEM with phosphonium cations suggests that peralkylation with sterically bulky carbocycles yields extraordinary resistance to alkaline conditions.

![Figure 2-17: Phosphonium cation designations and structures derived from computational models. © The American Chemical Society, 2012.](image)

The design of this phosphonium AEM was based on earlier work from Schwessinger\textsuperscript{30} whereby phosphonium cations substituted with i-propyl (Figure 2-17: 1f) groups and cyclohexyl groups (Figure 2-17: 1e) exhibited half-lives of 6 and 67 hours in 50% NaOH/chlorobenzene at 100 °C, respectively (Table 2-5).

Table 2-4: Half-lives of phosphonium cations in 50% NaOH/chlorobenzene at 100 °C. © European Chemical Society, 2006.\textsuperscript{30}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>$t_{1/2}$ [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bu$_4$P$^+$Cl$^-$</td>
<td>0.08/20°C\textsuperscript{[4]}</td>
</tr>
<tr>
<td>2</td>
<td>Ph$_3$As$^+$Cl$^-$</td>
<td>2/20°C\textsuperscript{[3]}</td>
</tr>
<tr>
<td>3</td>
<td>Ph$_3$PNPPPh$_3$$^+$Cl$^-$</td>
<td>1.1/20°C\textsuperscript{[3]}</td>
</tr>
<tr>
<td>4</td>
<td>Bu$_3$N$^+$Cl$^-$</td>
<td>0.33</td>
</tr>
<tr>
<td>5</td>
<td>1a-Cl</td>
<td>0.33</td>
</tr>
<tr>
<td>6</td>
<td>1b-Cl</td>
<td>0.9</td>
</tr>
<tr>
<td>7</td>
<td>1e-Cl</td>
<td>67</td>
</tr>
<tr>
<td>8</td>
<td>1f-Cl</td>
<td>6</td>
</tr>
</tbody>
</table>
When this small molecule phosphonium cation was compared to a benzyltrimethyl ammonium analog in 1 M NaOD/CD$_3$OD at 80 °C for 29 days, 1e exhibited negligible degradation compared to BTMA’s 66% degradation (Figure 2-18).  

Solvation

The degree of solvation of cations and hydroxide ions in solution profoundly affects the alkaline stability of AEM polymers and consequently, lifetimes in fuel cell applications. Generally, under low humidity conditions, less water is available for solvation of ions, and the reactivity of between cations and hydroxide ions is increased. PCM models$^{32}$ evaluating the free energy ($\Delta G^0$) and reaction barrier ($\Delta E^b$) for S$_N$2 displacements demonstrate the effect of water
and solvation with varying dielectric constants ($\varepsilon$) (Figure 2-19). Using the degradation of tetramethylammonium cations, the $\Delta G^0$ and $\Delta E^\#$ decreased with reduced dielectric constants. The solvation of hydroxide ions at low dielectric constants is said to be poor to the extent that for $\varepsilon < 10$, the reaction becomes instantaneous and limited only by diffusion.

![Figure 2-19](image)

**Figure 2-19**: Change in standard free energy ($\Delta G^0$) and activation energy barrier ($\Delta E^\#$) for the degradation of tetraalkylammonium as a function of the dielectric constant used in the PCM model. Note that a $\Delta E^\#$ value below zero (open red triangles) indicates a reaction without activation barriers and thus limited only by diffusion. © Journal of the American Chemical Society, 2008.32

It should be noted that while this pioneering computational study seeds insight into the effects of the dielectric medium on cation degradation, the authors conclude with the following:

“Our results indicate that tetraalkylammonium-based cations show reasonable stability in alkaline media. The chemical stability does not change dramatically with the modification of the alkyl group. The solvation of OH anions is very important for the stability of the headgroups. Membrane conditions that lead to poor solvation will lead to faster degradation of the cations.”
Phase Separation

One strategy to limit to decrease alkaline hydrolysis in AEM polymers has been to limit the exposure to hydroxide by limiting dimensional swelling upon hydration by designing AEM polymers architectures with phase separated morphologies. Studies by Arges\textsuperscript{18} have shown that quaternization of polysulfone-based AEMs and effectively placing the cation in close proximity to the polymer backbone (Figure 2-20a), changes the alkaline stability and hydrophobicity of the polysulfone backbone that unfuctionalized, is relatively hydrophobic. Elongating the distance between the cation and polymer backbone as shown with Tomoi’s resins\textsuperscript{28} (Figures 2-14, 2-20c), and/or introducing comb-like aliphatic chains such as Li’s n-alkyl terminal pendants\textsuperscript{29} (Figure 2-16, 2-20d) should in principle, lead to phase separation from the hydrophilic cation and consequently increase alkaline stability. Figure 2-20 summarizes several other general synthetic targets for inducing phase-separation: (i) copolymerization of quaternized and unquaternized blocks (Figure 2-20b), (ii) copolymerization, or cofunctionalization with benzyltrimethylammonium groups and aliphatic groups (Figure 2-20c), (iii) grafting ionic polymers onto a hydrophobic backbone (Figure 2-20f), and (iv) introducing alternative spacers between the polymer backbone and cation (Figure 2-20g). Although some of these synthetic strategies have been employed, these targets are limited by the few and/or or lengthy synthetic routes needed to introduce quaternary ammoniums cations.\textsuperscript{33}
AEM Synthetic Accessibility

Introduction

The design of new AEM polymers inherently involves a compromise between the properties of the membrane, such as the chemical and thermal stability, ion-exchange capacity (IEC), ion conductivity, mechanical properties, water uptake, and dimensional stability. The synthesis of AEM polymers is typically performed by: (i) polymerization of quaternary ammonium-functionalized monomers, (ii) polymerization of monomers containing reactive functional groups for post-polymer modification, or (iii) functionalization of a commercially available polymer. The preferred method is the latter choice as the functionalization of

Figure 2-20: Strategies for inducing phase separation in AEM polymers. The rectangles are representations of polymer backbones. © The Royal Society of Chemistry, 2014.
commercial polymers reduces concerns about costs, reproducibility in molecular weights, polydispersity, and purity.

Accessing a wide array of AEMs from commercial polymers is challenging given the selective reactivity of polymers, modest efficiencies of post-polymer modifications, and the limited known synthetic chemistries.

**Friedels—Craft Chloromethylation**

Functionalization of a commercial polymer usually involves a two-step process in which the polymer is chloromethylated$^{34}$ (Figure 2-21) using Friedels—Craft synthetic methodology for the activation of aromatic rings using a strong Lewis acid catalyst (e.g., ZnCl$_2$) in the presence of a reactive electrophile (e.g., chloromethylated methyl ether, CMME).

![Figure 2-21: Friedels—Craft alkylation of a poly(ether ether ketone) in the presence of a strong Lewis acid (ZnCl$_2$) and chloromethyl methyl ether (CMME) in 1,1,2,2-tetrachloroethane to generate the chloromethylated product. © Elsevier, 2011.](image)

Chloromethylation reactions are typically followed by amination reactions (more recently referred to as Menshutkin reactions)$^{35}$ (Figure 2-22), whereby a polymer-bound benzyl halide alkylates a tertiary amine to form a quaternary ammonium.
Radical bromination of benzylic groups using the Wohl—Ziegler reaction has been employed as a strategy to afford polymer-bound benzyl bromide functionalities for later amination (Figure 2-23). The Wohl—Ziegler reaction utilizes sub-stoichiometric 2,2’-azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO), a thermally-activated radical initiator, and N-bromosuccinimide (NBS) as an electrophilic source of bromine. Generally, temperatures above 40 °C are required induce homolytic cleavage of AIBN to generate two radical initiators that each perform a hydrogen abstraction to yield a polymer-bound benzyl radical. This radical then abstracts a bromine from NBS to yield the benzyl bromide and a succinimide radical that can propagate the reaction further in the absence of the AIBN activator. Careful temperature control is typically required as temperatures typically above 80 °C lead to aromatic bromination of the
polymer. The benzyl-brominated polymer product is then subjected to Menshutkin conditions to produce the quaternary ammonium functionality.

Figure 2-23: Wolf—Ziegler reaction of a poly(phenylene) in the presence of an electrophilic source of bromine, N-bromosuccinimide (NBS), and a radical initiator, benzoyl peroxide (BPO) to generate benzyl bromides for consequent amination. © The American Chemical Society, 2009. 36

**C-H Activation**

A recent method of functionalizing polymers for AEMFCs via C–H activation uses an iridium catalyst to generate an aryl boronate from a commercial poly(sulfone). 37 The resulting boronate is subjected to Suzuki-Miyaura cross-coupling conditions with an amine functionalized
aryl bromide to install benzylic tertiary amine pendants for subsequent alkylation to the quaternary ammonium.

Figure 2-24: C–H activation of a commercial poly(sulfone) toward a aryl borate substrate for a Suzuki—Miyaura cross-coupling reaction with a amine-functionalized aryl bromide for subsequent alkylation to a quaternary ammonium. © The American Chemical Society, 2014.
**Benzyl Lithiation**

Another approach that uses lithiation chemistry to functionalize a poly(phenylene oxides) has been reported to be successful contrary to other investigations across a number of labs. That is, lithium–halogen exchange reactions using benzyl-brominated polymers have invariably led to self cross-linked polymers. Jannash has reported this success with the treatment of commercial poly(phenylene oxide) with n-butyl lithium (pKb ~50) at −78 °C to facilitate the deprotonation of the benzyl group (pKa ~4.5) (Figure 2-25i). The subsequent addition of an electrophile, 1,6-dibromohexane, results in a bromohexyl-functionalized PPO (Figure 2-25ii) that is later treated with trimethylamine to the quaternary ammonium (Figure 2-25iii). A significant drawback of this scheme is that the synthesis is conducted under very dilute conditions to avoid crosslinking, which makes scale-up of this reaction sequence difficult.

![Figure 2-25: Benzyl functionalization of a commercial poly(sulfones) using benzyl Lithiation to install n-alkyl interstitial spacers. © The Royal Chemical Society.](image)

38
Summary

Overall, there are a number of promising approaches to the synthesis and study of anion exchange membranes, but there is currently no consensus in the field for how designs of new materials should progress. There is conflicting information on the stability of these compounds, although trends are beginning to emerge, and some of the proposed synthetic methods are not easily amenable to scale-up for device testing.
References


(12) Ye, Y.; Elabd, Y. A. Macromolecules 2011, 44, 8494.


(17) Nishimura, J.; Sano, H. Anion-Induced 1,4-Eliminations, 3rd ed.; Thieme Chemistry; Vol. 45, p 496.


Chapter 3

EXPERIMENTAL METHODS

$^1$H NMR DETERMINATION OF ALKALINE STABILITY OF AEMS FUNCTIONALIZED WITH BTMA CATIONS AT 80 °C

General Procedure for Measuring the Rates of QA Degradation Using $^1$H NMR

A 300 MHz spectrometer equipped with a variable temperature probe was heated to 80 °C, programmed to acquire 32 scans for each sample with a relaxation time of 5 s, and programmed to acquire acquisitions at intervals of 3600 s (1 h). $^1$H NMR spectra were acquired exactly 5 min after sample preparation. The time intervals reported indicate the average concentration of peak signals determined by the using the median acquisition time for each spectrum. Peak area deconvolution of the $^1$H NMR signals corresponding to the methyl groups of the quaternary-ammonium within the polymer and the methylenes of 1,4-dioxane (internal standard) were used to calculate the percentage of quaternary ammonium remaining.

Example Procedure for Sample Preparation

To a QA-PAES sample (19.6 mg) was added CD3OD (750 µL), and to the resulting suspension were sequentially added D2O (178.8 µL), and a 1.8 M solution of 1,4-dioxane (internal standard) in D2O (16.6 µL). The vial was capped and vortexed until the polymer was
completely dissolved (~60 s). To the resulting solution was added a 40% wt./v solution of KOD in D$_2$O (57.6 µL) and the vial was recapped and briefly vortexed (~5 s). A portion (600 µL) of the solution was transferred into a standard 5 mm NMR tube. The tube was capped and sealed with PTFE tape and inserted into the heated spectrometer immediately after preparation.

**Materials**

All reactions were performed in flame-dried glassware under positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids were transferred by syringe or canula. Organic solutions were concentrated by rotary evaporation (1–20 mmHg) at ambient temperature, unless otherwise noted. Radel® 5500NT (Solvay Specialty Polymers), poly(2,6-dimethyl-1,4-phenylene oxide styrene (Sigma—Aldrich), poly(styrene-co-chloromethylstyrene) (Sigma—Aldrich), and all other reagents were purchased commercially and were used as received unless otherwise noted. Thin-layer chromatography was carried out on Dynamic Adsorbents silica gel TLC (20 × 20 w/h, F-254, 250 µm). Deionized water was purified with a Millipore purification system (Milli–Q UV Plus).

**Instrumentation**

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded at 25 °C. Proton chemical shifts are expressed in parts per million (ppm, δ scale), and are referenced to tetramethylsilane ((CH$_3$)$_4$Si, 0.00 ppm) or to residual protium in the solvent (CHCl$_3$, 7.27 ppm; CD$_2$OD, 1.73 ppm; CD$_3$SOCD$_2$H, 2.50 ppm. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), integration, and coupling constant (J) in hertz.
Synthesis Procedures

Chloromethylated poly(arylene ether sulfone) (I) To a round-bottom flask was added Radel® 5500 NT (10 g, 25 mmol, 1 equiv.) and 1,1,2,2-tetrachloroethane (300 mL). The suspension was stirred for 2 h at 60 °C until the polymer was completely dissolved. The solution was cooled to 25 °C and fitted with an addition funnel. To the addition funnel was added a solution of zinc chloride (3.3 g, 50 mmol, 2 equiv.) dissolved in chloromethyl methyl ether (85 mL, 1.05 M, 40 equiv.) and slowly added to the flask over ~20 min. (Note: Chloromethyl methyl ether is a carcinogen and should be handled with care). The addition funnel was removed and the
flask fitted to an oil bubbler. (Note: The gaseous byproduct of the reaction upon heating is extremely corrosive to standard manifold tubing and difficult to condense. Therefore we recommend the reaction flask be vented into a separate oil bubbler in a well-vented fume hood to avoid damage to the manifold and reduce the risk of inhalation.) The resulting solution was heated to 60 °C for 4 h and cooled to 25 °C. The product mixture was precipitated into methanol (750 mL) at room temperature and collected as white fibers. The fibrous product was dissolved in dichloromethane (150 mL) and reprecipitated into methanol (2 × 750 mL). The product was collected and dried under reduced pressure (0.1 torr) to afford 1 as white fibrous strands. IR (cm⁻¹): 3067, 2360, 1583, 1480, 1320, 1294, 1236, 1148, 1105, 1073, 1010. ¹H NMR (CDCl₃): δ 7.90–7.94 (m), 7.72 (br s), 7.53–7.61 (m), 7.02–7.14 (m), 4.65 (br s). ¹³C NMR (CDCl₃): δ 161.7, 161.5, 161.4, 154.8, 152.7, 152.5, 137.5, 137.0, 136.4, 136.3, 136.1, 135.6, 130.1, 130.0, 129.9, 129.8, 128.8, 128.7, 120.8, 120.6, 118.0, 117.9, 40.5.

Benzyltrimethylammonium poly(arylene ether sulfone) chloride (QA-Radel). To a round-bottom flask was added 1 (2.0 g) and N,N-dimethylacetamide (10 mL) and an aqueous solution of trimethylamine (~45 wt. %, 10 mL). The flask was sealed and was stirred for 24 h at 25 °C. Excess trimethylamine was removed by bubbling nitrogen gas through the product mixture for 3 h at 25 °C. The product mixture was precipitated into isopropanol (250 mL) at room temperature and collected as tan fibers. The fibrous product was filtered and washed with isopropanol (2 × 200 mL). The product was collected and dried under reduced pressure (0.1 torr) at 35 °C to afford QA-PAES as tan fibrous strands. IR (cm⁻¹): 2037, 1654, 1582, 1582, 1480, 1412, 1219, 1236, 1169, 1147, 1105, 1071, 1009. ¹H NMR ((CH₃)₂SO): δ 8.31 (br, s), 8.15 (br, s), 7.77–8.07 (m), 7.20–7.37 (m), 4.77 (br, d, J = 14.0), 3.22 (br, d, J = 6.3). ¹³C NMR ((CH₃)₂SO): δ 161.4, 161.0, 159.8, 154.6, 154.3, 136.3, 136.1, 135.7, 135.2, 134.9, 134.0, 133.6, 130.5, 129.9, 129.8, 128.6, 128.4, 120.6, 120.5, 120.3, 120.0, 119.1, 118.0, 52.3.
Brominated poly(phenylene oxide) (2) To a round-bottom flask was added poly(2,6-dimethyl-1,4-phenylene oxide) (15 g, 125 mmol) and chlorobenzene (120 mL, 1.04 M) until the polymer was completely dissolved. To the flask was added N-bromosuccinimide (11.1 g, 62.5 mmol) and 2,2’-azobis-isobutyronitrile (0.63 g, 3.75 mmol). The flask was fitted with a reflux condenser and heated to 125 °C for 3h. The product mixture was cooled to 25 °C and slowly poured into a flask of stirring ethanol (~1 L) at room temperature to precipitate the product residue. The product residue was filtered and washed with ethanol (2 × 200 mL). The product residue was collected and dissolved in chloroform (150 mL) and then reprecipitated in ethanol (~1 L). The product was collected and dried under reduced pressure (0.1 torr) for 12 h to afford 2 as a yellow powder. $^1$H NMR (CDCl$_3$): δ 6.63–6.70 (m), 6.46–6.51 (m), 4.33 (s), 2.08 (s). The $^1$H NMR data are in agreement with literature values.

Benzyltrimethylammonium poly(phenylene oxide) (QA-PPO). To a round-bottom flask was added 2 (2.0 g) and N,N-dimethylacetamide (10 mL) and an aqueous solution of trimethylamine (~45 wt. %, 10 mL). The flask was sealed and was stirred for 24 h at 25 °C. Excess trimethylamine was removed by bubbling nitrogen gas through the product mixture for 3 h at 25 °C. The product mixture was poured into a recrystallization dish and the solvent removed in a vacuum (~1 torr) oven at 35 °C. The resulting brittle film was removed to afford QA-PPO as brown translucent crystals. IR (cm$^{-1}$): 3391, 2919, 1602, 1463, 1380, 1302, 1182,
1018. $^1$H NMR ((CH$_3$)$_2$SO): $\delta$ 6.89–7.08 (m), 6.52 (br s), 4.44 (br s), 3.40 (br s), 3.11 (br s), 2.04 (br s). $^{13}$C NMR ((CH$_3$)$_2$SO): $\delta$ 154.1, 145.0, 132.3, 132.1, 114.9, 114.4, 52.3, 16.3.

Poly(styrene-co-benzyltrimethylammoniumstyrene) (QA-Styrene). To a round-bottom flask was added poly(styrene-co-chloromethylstyrene) (2.0 g), tetrahydrofuran (10 mL), and an aqueous solution of trimethylamine (45 wt. %, 10 mL). The flask was sealed and was stirred for 24 h at 25 °C. The excess trimethylamine was removed by bubbling nitrogen gas through the product mixture for 3 h at 25 °C. The product mixture was then concentrated under reduced pressure (0.1 torr) at 25 °C for 24 h to afford QA-Styrene as a white translucent film. IR (cm$^{-1}$): 3373, 3024, 2922, 1614, 1511, 1488, 1451, 1425, 1320, 1021. $^1$H NMR (CD$_3$OD): $\delta$ 6.56–7.20 (m), 4.56 (br s), 3.05 (br s), 1.0–2.5 (m). $^{13}$C NMR (CD$_3$OD): $\delta$ 133.8, 129.3, 126.8, 69.9, 53.0, 41.8.

Figure 3-4: Synthesis of QA-Styrene.

Poly(styrene-co-benzyltrimethylammoniumstyrene) (QA-Styrene). To a round-bottom flask was added poly(styrene-co-chloromethylstyrene) (2.0 g), tetrahydrofuran (10 mL), and an aqueous solution of trimethylamine (45 wt. %, 10 mL). The flask was sealed and was stirred for 24 h at 25 °C. The excess trimethylamine was removed by bubbling nitrogen gas through the product mixture for 3 h at 25 °C. The product mixture was then concentrated under reduced pressure (0.1 torr) at 25 °C for 24 h to afford QA-Styrene as a white translucent film. IR (cm$^{-1}$): 3373, 3024, 2922, 1614, 1511, 1488, 1451, 1425, 1320, 1220, 1021. $^1$H NMR (CD$_3$OD): $\delta$ 6.56–7.20 (m), 4.56 (br s), 3.05 (br s), 1.0–2.5 (m). $^{13}$C NMR (CD$_3$OD): $\delta$ 133.8, 129.3, 126.8, 69.9, 53.0, 41.8.

Figure 3-5: Synthesis of pMeBTMA.
p-Methylbenzyltrimethylammonium bromide (pMeBTMA). To a round-bottom flask was added 4-methylbenzylbromide (1.0 g, 5.4 mmol, 1 equiv.) and tetrahydrofuran (5 mL). The flask was cooled to 0 °C and an aqueous solution of trimethylamine (~45 wt. %, 5 mL) was added. The flask was warmed to 25 °C and was stirred for 12 h. The excess trimethylamine was removed by bubbling nitrogen gas through the product mixture for 3 h at 25 °C. The product mixture was then concentrated under reduced pressure (0.1 torr) at 25 °C for 24 h to afford pMeBTMA as a white powder. IR (cm⁻¹): 3477, 3419, 3005, 2968, 2359, 1615, 1485, 1459, 1413, 1394, 1225, 1209, 1075, 1047, 1013. ¹H NMR (CD₃OD): δ 7.53 (d, 2H, J = 8.1 Hz), 7.34 (d, 2H, J = 7.7 Hz), 4.64 (s, 2H), 3.14–3.17 (s, 9H), 2.39 (s, 3H). ¹³C NMR (CD₃OD): δ 142.2, 133.9, 130.8, 126.1, 70.0, 53.1, 21.3.

**Modeling of a Small Molecule Analogue for QA-PAES to Rationalize Degradation**

![Figure 3-6: (Left) Structure of small molecule analog for the modeling of QA-PAES conformation. (Right) Semi-empirical (PM3) minimized structure of a small molecule analogue for QA-PAES. The double-headed arrows indicate the distance between the nitrogen of the quaternary-ammonium and the oxygens of the sulfone. The modeling of structures was conducted with Spartan Student 5.0.0.](image)

A small molecule analogue for QA-PAES (Figure S9) with an analogous arrangement of functional groups was modeled to rationalize the increased degradation observed in the presence
of KOD at 80 °C. An energy-minimized (PM3) model of the small molecule reveals the structure adopts a conformation that places the quaternary nitrogen and the electron-rich oxygens of the sulfones in close proximity. In this conformation, the $\sigma^*$ of the CH2–N(CH3)3 bond is partially exposed and susceptible to nucleophilic attack. If the barrier to rotation of the Ph–CH2 sigma bond is increased as a result of this close association between the quaternary nitrogen and the oxygens of the sulfone, the $\sigma^*$ of the CH2–N(CH3)3 bond may be more susceptible to interactions with nucleophiles.\textsuperscript{2} We believe this rationale explains the observed increase rates of degradation in QA-PAES over the un-sulfonated variant, QA-PPO.

\section*{1H NMR DETERMINATION OF ALKALINE STABILITY OF TETRAALKYLAMMONIUM CATIONS AT 120 °C}

\textbf{Materials}

All reactions were performed in flame-dried glassware under positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids were transferred by syringe or canula. Organic solutions were concentrated by rotary evaporation (1–20 mmHg) at ambient temperature, unless otherwise noted. Poly(2,6-dimethyl-1,4-phenylene oxide) (Sigma—Aldrich), poly(styrene-co-chloromethylstyrene) (Sigma—Aldrich), benzyltrimethylammonium chloride (Sigma—Aldrich) and all other reagents were purchased commercially and were used as received unless otherwise noted. Thin-layer chromatography was carried out on Dynamic Adsorbents silica gel TLC (20 × 20 w/h, F-254, 250 μm). Deionized water was purified with a Millipore purification system (Milli–Q UV Plus). High temperature NMR samples were prepares in Wilmad quick pressure valve tubes (5 mm, heavy wall, 300 MHz or better).
Instrumentation

Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded at 25 °C. Proton chemical shifts are expressed in parts per million (ppm, $\delta$ scale), and are referenced to tetramethylsilane (($\text{CH}_3$)$_4\text{Si}$, 0.00 ppm) or to residual protium in the solvent (CHCl$_3$, 7.27 ppm; CD$_2$HOD, 3.31 ppm; CD$_3$SOCD$_2$H, 2.50 ppm. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), integration, and coupling constant ($J$) in hertz.

General Procedure for Sample Preparation and Data Acquisition.

To a QA–PS sample (# mg) was added CD$_3$OD (750 µL), D$_2$O (178.8 µL) and a 1.8 M solution of 1,4-dioxane (internal standard) in D$_2$O (# µL). The vial was capped and vortexed until the polymer was completely dissolved (~60 s). To the resulting solution was added a 40% wt/v solution of NaOD in D$_2$O (# µL), and the vial was recapped and briefly vortexed (~5 s). The solution was transferred into a medium-wall NMR tube (300 MHz, 5 mm, 7 in., max. pressure 150 psi) and fitted with a PTFE pressure. The sample tube was inserted into a 300 MHz NMR spectrometer equipped with a variable-temperature probe preheated to 60 °C. The sample was allowed to equilibrate (~5 min) and the spectrometer programmed to acquire an initial spectrum with 48 scans and a relaxation time of 5 s. Upon completion of the acquisition, the sample NMR tube was removed from the spectrometer and inserted into a solid-state aluminum heating block preheated to 120 °C (see SI for specifications). After each consecutive hour, the sample tube was removed from the heating block, agitated by inversion (2 ×) and inserted into the spectrometer for additional acquisitions using identical parameters to the initial spectrum.
Synthesis Procedures

\[ \text{pMeBTMA} \]

To a round-bottom flask was added 4-methylbenzylbromide (1.0 g, 5.4 mmol, 1 equiv.) and tetrahydrofuran (5 mL). The flask was cooled to 0 °C and an aqueous solution of trimethylamine (~45 wt. %, 5 mL) was added. The flask was warmed to 25 °C and was stirred for 12 h. The excess trimethylamine was removed by bubbling nitrogen gas through the product mixture for 3 h at 25 °C. The product mixture was then concentrated under reduced pressure (0.1 torr) at 25 °C for 24 h to afford pMeBTMA as a white powder. \(^1\)H NMR (CD\(_3\)OD):
\[ \delta 7.53 (d, 2H, J = 8.1 \text{ Hz}), 7.34 (d, 2H, J = 7.7 \text{ Hz}), 4.64 (s, 2H), 3.14–3.17 (s, 9H), 2.39 (s, 3H). \]

\[ \text{pMeBQA6} \]

Figure 3-7: Structure representation of pMeBTMA

\[ \text{pMeBQA6} \]

Figure 3-8: Structure representation of pMeBQA6
**pMeBQA6.** To a round-bottom flask equipped with a stir bar was added 4-methylbenzylbromide (1.0 equiv., 1.35 mmol, 250 mg), N,N-dimethylhexylamine (1.0 equiv., 1.35 mmol, 0.45 mL) and THF (1.35 mL). The flask was sealed and stirred for 24 h at 25 °C. The residual solvent was evaporated from the crude product mixture under reduced pressure followed by the addition of ethyl acetate (10 mL) and the organics were washed with 0.1 M HCl (2 × 10 mL). The organics were washed with deionized water (2 × 10 mL) and the organics collected and dried over sodium sulfate and evaporated under reduced. The product residue was then further dried under reduced pressure (0.1 torr) at 25 °C for 24 h to afford the chloride salt of pMeBQA6 as a clear viscous liquid. $^1$H NMR (CD$_3$OD): δ 7.43 (d, 2H, $J = 10.8$), 7.34 (d, 2H, $J = 7.2$), 4.50 (s, 2H), 3.28 (m, 2H), 3.02 (s, 6H), 2.41 (s, 3H), 1.86 (m, 2H), 1.40 (m, 6H), 0.93 (t, 3H, $J = 7.2$).

![Figure 3-9](attachment:structure_representation.png)

**BTMA-PS.** To a round-bottom flask was added poly(styrene-co-chloromethylstyrene) (2.0 g), tetrahydrofuran (10 mL), and an aqueous solution of trimethylamine (~45 wt. %, 10 mL). The flask was sealed and was stirred for 24 h at 25 °C. The excess trimethylamine was removed by bubbling nitrogen gas through the product mixture for 3 h at 25 °C. The product mixture was then concentrated under reduced pressure (0.1 torr) at 25 °C for 24 h to afford the chloride salt of BTMA-PS as a white translucent film. $^1$H NMR (CD$_3$OD): δ 6.56–7.20 (m), 4.56 (br s), 3.05 (br s), 1.0–2.5 (m).
BTMA-PPO. To a round-bottom flask was added poly(2,6-dimethyl-1,4-phenylene oxide) (15 g, 125 mmol) and chlorobenzene (120 mL, 1.04 M) until the polymer was completely dissolved. To the flask was added N-bromosuccinimide (11.1 g, 62.5 mmol) and 2,2’-azobis-isobutyronitrile (0.63 g, 3.75 mmol). The flask was fitted with a reflux condenser and heated to 125 °C for 3h. The product mixture was cooled to 25 °C and slowly poured into a flask of stirring ethanol (~1 L) at room temperature to precipitate the product residue. The product residue was filtered and washed with ethanol (2 x 200 mL). The product residue was collected and dissolved in chloroform (150 mL) and then reprecipitated in ethanol (~1 L). The product was collected and dried under reduced pressure (0.1 torr) for 12 h to afford a yellow powder.

To a round-bottom flask was added the aforementioned yellow powder precursor (2.0 g) and N,N-dimethylacetamide (10 mL) and an aqueous solution of trimethylamine (~45 wt. %, 10 mL). The flask was sealed and was stirred for 24 h at 25 °C. Excess trimethylamine was removed by bubbling nitrogen gas through the product mixture for 3 h at 25 °C. The product mixture was poured into a recrystallization dish and the solvent removed in a vacuum (~1 torr) oven at 35 °C. The resulting brittle film was removed to afford BTMA-PPO as yellow powder. $^1$H NMR (CDCl$_3$): δ 6.63–6.70 (m), 6.46–6.51 (m), 4.33 (s), 2.08 (s).
To a round bottom flask equipped with a stir bar was added poly(styrene-co-chloromethylstyrene) (1.0 equiv., 14.2 mmol, 2.0 g), dimethylacetamide (20 mL), deionized water (4 mL), and N,N-dimethylhexylamine (2.5 equiv., 35.5 mmol, 6.1 mL). The flask was sealed and stirred for 24 h at 25 °C. To the product mixture was added diethyl ether (40 mL) and the organics washed with 0.1 M HCl (3 × 40 mL). The organics were then washed with deionized water (2 × 20 mL) and the organics collected and dried over sodium sulfate and evaporated under reduced pressure (0.1 torr) at 25 °C for 24 h to afford the chloride salt of QA6-PPO as a tacky yellow crystalline solid. $^1$H NMR (DMSO-d$_6$): δ 6.50–6.97 (bm, 2H), 4.36 (bs, 2H), 3.17 (bm, 2H), 2.96 (bs, 6H), 2.02 (bm, 2H), 1.62 (bm, 2H), 1.21 (bm, 6H), 0.80 (bs, 3H).

Figure 3-11: Structure representation of QA6-PPO.

QA6-PPO. Figure 3-11: Structure representation of QA6-PPO. To a round bottom flask equipped with a stir bar was added poly(styrene-co-chloromethylstyrene) (1.0 equiv., 14.2 mmol, 2.0 g), dimethylacetamide (20 mL), deionized water (4 mL), and N,N-dimethylhexylamine (2.5 equiv., 35.5 mmol, 6.1 mL). The flask was sealed and stirred for 24 h at 25 °C. To the product mixture was added diethyl ether (40 mL) and the organics washed with 0.1 M HCl (3 × 40 mL). The organics were then washed with deionized water (2 × 20 mL) and the organics collected and dried over sodium sulfate and evaporated under reduced pressure (0.1 torr) at 25 °C for 24 h to afford the chloride salt of QA6-PPO as a tacky yellow crystalline solid. $^1$H NMR (DMSO-d$_6$): δ 6.50–6.97 (bm, 2H), 4.36 (bs, 2H), 3.17 (bm, 2H), 2.96 (bs, 6H), 2.02 (bm, 2H), 1.62 (bm, 2H), 1.21 (bm, 6H), 0.80 (bs, 3H).

Figure 3-12: Structure representation of ArPrHxDMA.

Figure 3-12: Structure representation of ArPrHxDMA.
**ArPrHxDMA.** To a round bottom flask equipped with a magnetic stir bar was added 1-bromo-3-phenylpropane (1.0 equiv., 13.2 mmol, 2.0 mL), tetrahydrofuran (10 mL), and N,N-dimethylhexylamine (3.0 equiv., 39.4 mmol, 6.85 mL). The flask was sealed and stirred for 24 h at 25 °C. The residual solvent was evaporated from the crude product mixture under reduced pressure followed by the addition of ethyl acetate (10 mL) and the organics were washed with 0.1 M HCl (2 × 10 mL). The organics were washed with deionized water (2 × 10 mL) and the organics collected and dried over sodium sulfate and evaporated under reduced. The product residue was then further dried under reduced pressure (0.1 torr) at 25 °C for 24 h to afford the chloride salt of ArPrHxDMA as white foam. \(^1\)H NMR (CD\(_3\)OD:D\(_2\)O (3:1)): \(\delta 7.27–7.31\) (m, 5H), 3.05 (s, 6H), 2.71 (m, 2H), 2.06 (m, 2H), 1.64 (m, 2H), 1.34 (m, 6H), 0.93 (t, 3H).

![QA6-PS](image)

**Figure 3-13:** Structure representation of QA6-PS.

**QA6-PS.** To a round-bottom flask was added poly(styrene-co-chloromethylstyrene) (2.0 g), dimethylacetamide (20 mL), deionized water (4 mL), and N,N-dimethylhexylamine (5.0 equiv., 71 mmol, 12.3 mL). The flask was sealed and was stirred for 24 h at 25 °C. To the product mixture was added diethyl ether (40 mL) and the organics washed with 0.1 M HCl (3 × 40 mL). The organics were then washed with deionized water (2 × 20 mL) and the organics collected and dried over sodium sulfate and evaporated under reduced. The product residue was then further dried under reduced pressure (0.1 torr) at 25 °C for 24 h to afford the chloride salt of QA6-PS as a white foam. \(^1\)H NMR (CD\(_3\)OD:D\(_2\)O (3:1)): \(\delta 6.47–7.22\) (bm, 4H), 4.53 (bs, 2H), 3.26 (bm, 2H),
2.86 (bs, 6H), 1.76 (bm, 2H), 1.27 (bm, 6H), 0.85 (bm, 3H).

**ArPrTMA**. To a round bottom flask equipped with a magnetic stir bar was added 1-bromo-3-phenylpropane (1.0 equiv., 13.2 mmol, 2.0 mL), tetrahydrofuran (10 mL). The flask was cooled to 0 °C and an aqueous solution of trimethylamine (~45 wt. %, 5 mL) was added. The flask was warmed to 25 °C and was stirred for 24 h. The excess trimethylamine was removed by bubbling nitrogen gas through the product mixture for 3 h at 25 °C. The product mixture was then concentrated under reduced pressure (0.1 torr) at 25 °C for 24 h to afford **ArPrTMA** as a white foam. $^1$H NMR (CD$_3$OD:D$_2$O (3:1)): $\delta$ 7.24–7.35 (m, 5H), 3.36 (m, 2H), 3.15 (s, 9H), 2.78 (m, 2H), 2.18 (m, 2H).

**References**


1H NMR DETERMINATION OF ALKALINE STABILITY OF AEMS FUNCTIONALIZED WITH BTMA CATIONS AT 80 °C

The main parts of this chapter were published as, Quantitative 1H NMR Analysis of the Chemical Stabilities of Anion Exchange Polymers for Fuel Cell Applications, ACS Macro Lett, 2013, 2 (1), 49–52.

The alkaline stability of three classes of anion exchange membranes that are leading candidates for applications in platinum-free fuel cells were compared. A methodology is presented for the study of chemical stability of anion-exchange polymers in alkaline media that provides clear and quantitative 1H NMR spectroscopic data of dissolved polymers containing benzyltrimethylammonium functionalities. Recent studies have investigated the stabilities of benzimidazolium- and alkylimidazolium-bearing polymers using periodic 1H NMR sampling. These studies included varying alkaline concentrations, external heating sources, excessive processing, and contained no internal standard for absolute measurements. Key aspects of the time-resolved 1H NMR methods presented include in situ heating and sampling within the spectrometer, fixed stoichiometric relationships between the benzyltrimethylammonium functionalities of each polymer and KOD, and the incorporation of an internal standard for the absolute measurement of the polymer degradation. In addition, this method permits the identification of the degradation products to find the underlying cause of chemical lability. Our results demonstrate that a styrene-based polymer containing benzyltrimethylammonium
functional groups is remarkably stable when exposed to 20 equivalents per cation of KOD at 80 °C with a half life ($t_{1/2}$) of 2887 h. Under these standard conditions, functionalized poly(phenylene oxide) and poly(arylene ether sulfone) copolymers both bearing benzyltrimethylammonium functionalities were found to degrade with a half lives of 57.8 h and 2.7 h, respectively.

**Introduction**

Anion-exchange membranes (AEMs) have attracted interest for their operation in platinum-free fuel cells and electrolyzers that feature carbon-free supports, increased tolerances to CO$_2$ impurities in gaseous feeds, and conductivities that rival proton exchange membranes. However, the use of AEMs in a wide range of devices has been limited due to the polymers’ poor stability in the highly alkaline environment required for fuel cells that necessitates generation of hydroxide anions and transport through the solid polymer membrane. Recent studies have determined the chemical stabilities of AEMs using measurements of ion-exchange capacities, ionic conductivities, FT-Raman and $^1$H NMR spectroscopy that sought to address the change in chemical composition of materials during degradation processes. FT-Raman studies of AEM degradation are typically conducted on films with varying levels of humidity but only provide relative data of chemical stability due to varying absorption coefficients of specific functional groups among different polymers. Current $^1$H NMR methods investigate benzimidazolium and imidazolium-bearing polymers but lack an internal standard for absolute measurements, use external heating sources, involve multiple steps (i.e., exposure to alkali, evaporation of the solvent, and characterization), and ignore the stoichiometric relationship between the ion-conducting functional group and the concentration of the alkali. These variations in methods and other factors in measuring degradation, as meticulously discussed by Varcoe, in assessing the
stability of AEMs have made it difficult for the community to come to a consensus on the most promising directions for highly-stable, highly-conductive AEMs.

To date, few researchers\textsuperscript{9a,9b} have employed a standardized methodology to determine the rate of degradation in AEMs that include a coherent \textit{stoichiometric relationship} between the concentration of alkali and the concentration of ion-conducting functional groups within the polymer. The established mechanisms of degradation in quaternary ammonium (QA)-based AEMs occur as a result of hydrolysis in aqueous alkaline solutions.\textsuperscript{11} Establishing this \textit{stoichiometric relationship} is essential to accurately measure and describe the stabilities of these polymers—thereby establishing a precedent for describing the stability of QA AEMs in the field.

This \textit{chapter} describes a simple methodology and provides clear $^1$H NMR spectroscopic data to quantitatively study the stability and degradation pathways of dissolved AEMs under standardized conditions. Four benzyltrimethylammonium-functionalized compounds consisting of a model small molecule, pMeBTMA, and three polymers, QA-PAES, QA-PPO, and QA-Styrene (Figure 4-1). These polymers represent three major AEM candidates based on widely accessible polymer backbones. This new methodology should guide others to easily and accurately determine the stability of dissolved AEMs for meaningful comparisons.
H NMR Degradation of AEMs Under Alkaline Conditions

Since quaternary-ammonium functionalities are susceptible to degradation under alkaline conditions, the stabilities of AEMs with potassium deuteroxide (KOD) were investigated at elevated temperatures to provide an accelerated assessment of the stability of these molecules. One initial challenge was finding a suitable deutorated solvent system to dissolve the selected QA AEM, the alkali (KOD), an internal standard, and the resulting products of degradation. After considering a number of single- and mixed-solvent systems, we determined a 3:1 CD$_3$OD–D$_2$O mixed-solvent system was suitable to solvate the components throughout the duration of the experiment. The samples consisted of the selected AEM (30 mM, based on repeat unit) in 3:1 CD$_3$OD–D$_2$O with an excess of KOD (0.6 M, 20 equiv.) and 1,4-dioxane (internal standard). The resulting sample solutions were transferred to a standard NMR tube and heated in-situ at 80 °C within the spectrometer. Under these conditions, quaternary ammonium decomposition was measured by the deconvoluted peak area of the methyl groups of the QA (i.e., N(CH$_3$)$_3$) relative
to 1,4-dioxane in the \(^1\)H NMR spectrum. Figure 4-2 reveals a stacked overlay of QA-PAES spectra taken over 779 min (12.9 h) in ~64 min intervals. The signal corresponding to the methyl groups of the benzyltrimethylammonium and the covalently-bonded benzylic methylene (i.e., CH\(_2\)) decrease in agreement against the fixed internal standard concentration. Additionally, the \(^1\)H NMR spectrum revealed two products of degradation: a benzylmethyl ether (i.e., CH\(_2\)OCH\(_3\); 3.17 ppm, see Chapter 3) and a benzyldimethylamine (i.e., N(CH\(_3\))\(_2\), 2.19 ppm, see Chapter 3). The benzylmethyl ether and benzyldimethylamine functionalities were believed to arise from the dealkylation of a benzyltrimethylammonium moiety followed by the substitution of methoxide (i.e., CH\(_3\)O\(^–\)) generated at a separate QA site. These results are consistent with the reported pathways of degradation for QA-based AEMs.\(^{11}\)

Figure 4-2: Stacked overlay of \(^1\)H NMR spectra of QA-PAES in CD\(_3\)OD–D\(_2\)O (3:1), 1,4-dioxane (internal standard), KOD (20 equiv.), from 7–779 min in ~64 min intervals at 80 °C; (a) overlay of the aliphatic region, (b) overlay of benzylic methylene decaying, (c) overlay of 1,4-dioxane (internal standard), (d) overlay showing decay of QA over the course of the study and the evolution of a benzylmethyl ether product (i.e., CH\(_2\)OCH\(_3\)). Note: \(^1\)H NMR signal movement in aqueous solutions is a commonly observed phenomena.\(^{14}\)
Quantitative Analysis of QA-AEM Degradation by $^1$H NMR.

The stabilities of 30 mM solutions of QA-PAES, QA-PPO, QA-Styrene, and pMeBTMA dissolved in 3:1 CD$_3$OD–D$_2$O at 80 °C in the presence of 20 equivalents of KOD (0.6 M) were evaluated. Hydrolysis of QA head-groups is accelerated under basic conditions but is equally possible in the absence of highly alkaline conditions, thus a control experiment under the exact same conditions, but in the absence of KOD was performed. In all cases with KOD, the decomposition of the polymers was observed by solely monitoring the disappearance of the QA (i.e., N'(CH$_3$)$_3$) peak in the $^1$H NMR spectrum relative to a fixed internal standard, 1,4-dioxane (Figure 3a). Under these conditions, pMeBTMA, showed virtually no signs of degradation in the presence of KOD (i.e., 99.5% ± 0.9% remaining QA) with a negligible rate of hydrolysis in the absence of KOD (i.e., 99.8% ± 0.6% remaining QA) after 779 min, as shown in Figure 4-3a. Similarly, QA-Styrene showed comparable stability to pMeBTMA (i.e., 95.2% ± 1.1% remaining QA) in the presence of KOD and had minimal hydrolysis (i.e., 98.0% ± 0.8% remaining QA) in the absence of KOD. QA-PPO showed considerable hydrolysis with only 84.2% ± 0.9% of the QA remaining after 779 min in the presence of KOD and 96.6 ± 0.9% of the QA remaining in the absence of KOD. Finally, QA-PAES showed significant degradation in the presence of KOD with only 9.9% ± 0.3% of the QA remaining after 779 minutes and equally significant hydrolysis in absence of KOD with only 87.3% ± 2.8% of the QA remaining.
The rates of degradation were determined from the linear regression plot of the natural log of polymer concentration versus time using a pseudo first-order approximation (Figure 4-3b). The concentration of base (i.e., 20 equivalents) with respect to the quaternary-ammonium group on the degraded species is in significant excess to assume a constant base concentration and pseudo first-order kinetics. Table 4-1 summarizes the $^1$H NMR-determined experimental kinetic rates of degradation for our selected QA-AEMs in 3:1 CD$_3$OD–D$_2$O with 20 equiv. KOD at 80 °C. As expected, pMeBTMA, QA-Styrene, and QA-PPO, show the greatest stability with half-lives of 2887, 231, and 57.8 h, respectively.

Table 4-1: $^1$H NMR experimental rates and half-lives of selected QA AEMs in 3:1 CD$_3$OD–D$_2$O with 20 equiv. KOD at 80 °C.
The small molecule, \textbf{pMeBTMA}, and \textbf{QA-Styrene} show considerable stability with \textbf{pMeBTMA} displaying higher half-life stability by an order of magnitude. However, styrene-based ion-containing membranes generally have poor mechanical properties, especially when hydrated. Thus, strategies to reinforce the mechanical properties of functionalized styrene-based AEMs are required.\textsuperscript{15}

The data for QA-PAES did not fit a constant first-order rate expression. The initial rate of degradation (primary) was significantly greater than the rate after 328 min (secondary). Further analysis revealed that assigning two separate first-order rates resulted in agreement with the primary half-life of 2.7 h and the secondary half-life of 5.5 h. The change in rate is believed to be due to a change in the solubility\textsuperscript{16} of QA-PAES resulting from the degradation of the solubilizing polar QA salts to the more hydrophobic moieties: benzyl alcohols, dimethylamines, and methyl ethers.

<table>
<thead>
<tr>
<th></th>
<th>(k) (m(^{-1}))</th>
<th>(t_{1/2}) (h)</th>
<th>QA remaining at (t_{79\text{\scriptsize{h}}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QA-PAES:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>primary</td>
<td>4.3</td>
<td>2.7</td>
<td>–</td>
</tr>
<tr>
<td>secondary</td>
<td>2.1</td>
<td>5.5</td>
<td>9.9 (\pm) 0.1</td>
</tr>
<tr>
<td>QA-PPO</td>
<td>0.2</td>
<td>57.8</td>
<td>84.2 (\pm) 0.9</td>
</tr>
<tr>
<td>QA-Styrene</td>
<td>0.05</td>
<td>231</td>
<td>95.2 (\pm) 1.1</td>
</tr>
<tr>
<td>pMeBTMA</td>
<td>0.004</td>
<td>2887</td>
<td>99.5 (\pm) 0.6</td>
</tr>
</tbody>
</table>
Comparing the kinetic rates of degradation and half-lives of the samples, we have concluded the stability of the sulfone-containing \textbf{QA-PAES} as greatly reduced compared its poly(phenylene oxide) analogue, \textbf{QA-PPO}. To explain the differences in the stability of \textbf{QA-PAES}, we reason that the electron-withdrawing sulfone exerts a long-range inductive effect, thereby reducing the electron density of the benzyl carbon. It has been previously noted that poly(sulfone) backbones are not stable under basic conditions,\textsuperscript{17} but in the present study we directly assess the stability of the quaternary ammonium cation and not scission of the backbone chain. Thus there appears to be an influence by the backbone type on the stability of the quaternary-ammonium. In \textbf{QA-PAES}, the inductive effect of the sulfone moiety may increase electrophilic character of the benzylic methylene, increasing its susceptibility of nucleophilic attack.\textsuperscript{11c} Additional information to explain the reduced stability of \textbf{QA-PAES} using steric arguments with molecular modeling of a small molecule analog is offered in Chapter 3.

\textbf{CONCLUSIONS}

This chapter demonstrates a spectroscopic method to systematically measure AEM stability under controlled and reproducible test conditions. Thereby consistently affording knowledge the cationic quaternary-ammonium stabilities. The results indicate the para-substituted styrenic AEM, \textbf{QA-Styrene}, offers a significant increase in stability over quaternary ammonium functionalized poly(phenylene oxide), \textbf{QA-PPO}, and the ortho-substituted poly(arylene ether sulfone), \textbf{QA-PAES}. The \textbf{QA-PAES} showed surprisingly low stability and calls into question the suitability of benzyltrimethyl quaternary ammonium cations on poly(sulfone) backbones for long-lived devices. The standardized approach presented here offers a powerful method to compare AEM stabilities and identify the products of degradation, while also identifying the underlying cause of degradation. Using this systematic investigation will
help build a consistent and uniform database of knowledge that can be applied in the search for new, stable AEMs. While this study primarily focused on benzyltrimethylammonium groups, the method could be extended to other AEMs that contain ionic groups such as imidazolium, guanidinium, and phosphonium moieties.
REFERENCES:


12. With respect to the QA functionalities in the polymer.

13. An inert and water-miscible organic solvent with a boiling point of 101.1 °C.


18. Long range inductance.

Chapter 5

1H NMR DETERMINATION OF ALKALINE STABILITY OF TETRAALKYLAMMONIUM CATIONS AT 120 °C

This chapter has been prepared for publication as: “N-Alkyl Interstitial Spacers and Terminal Pendants Influence on the Alkaline Stability of Tetraalkylammonium Cations for Anion Exchange Membrane Fuel Cells,” to be submitted.

Current performance targets for anion-exchange membrane (AEM) fuel cells call for greater than 95% alkaline stability for 5000 hours at temperatures up to 120 °C. Using this target temperature of 120 °C, an incisive 1H NMR-based alkaline degradation method to identify the degradation products of n-alkyl spacer tetraalkylammonium cations in various AEM polymers and small molecule analogs. Herein, the degradation mechanisms and rates of benzyltrimethylammonium-, n-alkyl interstitial spacer- and n-alkyl terminal pendant-cations are compared on several architectures. The findings demonstrate that benzyltrimethylammonium- and n-alkyl terminal pendant cations are more labile than an n-alkyl interstitial spacer cation and conclude that Hofmann elimination is not the predominant mechanism of alkaline degradation. Additionally, it was found that the alkaline stability of an n-alkyl interstitial spacer cation is enhanced when combined with an n-alkyl terminal pendant. Interestingly, at 120 °C, an inverse trend in the overall alkaline stability of AEM poly(styrene) and AEM poly(phenylene oxide) samples than was previously shown at 80 °C. Successive small molecule studies suggest that at 120 °C, an anion-induced 1,4-elimination degradation mechanism may be activated on styrenic AEM polymers bearing an acidic α-hydrogen. These findings are intended as a guide toward robust AEM synthetic designs that approach current performance targets.
Introduction

The global demand for energy is projected to rise 1.8% YOY until 2020 with an expected fossil fuel contribution of only 0.8% YOY.\(^1\) This discrepancy between demand and fossil fuel shortcomings has fueled the development of alternative energy technologies that (i) utilize renewable materials, (ii) employ renewable energy schemes, and (iii) regeneration-schemes bearing low environment impact. A leading solution, fuel cell devices, utilizes renewable feedstocks for the electrochemical conversion of renewable fuels to electrical energy and energy storage. Anion exchange membrane fuel cells (AEMFC) have been proposed as viable alternatives to proton exchange membrane fuel cells (PEMFCs)\(^2\)-\(^4\) arising from their use of platinum-free electrodes,\(^5\)-\(^7\) and as electrolyzers\(^8\) that feature precious-metal-free catalysts.\(^9\)-\(^11\) Reducing production costs using non-precious metal catalysts is the primary motivator for adopting AEM-based devices. Other benefits increased tolerances to CO\(^12\) or NH\(_3\)\(^13\) impurities in the fuel which can extend their applications significantly over PEM-based devices.

Preliminary AEMs exhibited low efficiencies as measured by reduced polarization performance, but newer AEM fuel cell devices have improved conductivities that rival PEMs.\(^14\),\(^15\) One challenging drawback to the widespread adoption of AEMs in fuel cell devices is due to the AEM polymers’ limited stability in the required alkaline electrochemical environment that facilitates the transport of hydroxide anions through the solid polymer membrane. Since there is a linear correlation between increased device temperature and AEM conductivity, high temperature (i.e., > 100 °C) alkaline stability is the current challenge for developing AEM fuel cell devices capable of achieving performance standards such as the Department of Energy’s 2015 performance targets calling for greater than 95% alkaline stability for 5000 hours at temperature up to 120 °C.\(^16\)
AEM polymer-bound cations have included benzimidazolium, imidazolium, amino phosphonium and sulfonium, but the most commonly studied cations are tetraalkylammonium (TAA) salts due to their synthetic accessibility, commercially-available synthetic components, and verified practical membrane properties. TAA cations have demonstrated appreciable alkaline stability, but they remain susceptible to a variety of chemical degradation pathways.

Figure 5-1: Chemical degradation reaction mechanisms for a TAA small molecule under alkaline aqueous conditions (i). A minor product of this substitution reaction results in 1-hexanol (not shown) as the dealkylation product. A minor product of the Steven’s rearrangement results in the [2,3]-shift product (not shown). Anion-induced 1,4-eliminations (f) arise from the presence of an acidic hydrogen paired with a good leaving group (e.g., TAA cation) in the highlighted configuration to generate a transient 1,4-quinodimethane intermediate that hydrolyses under aqueous conditions.
These degradation mechanisms include substitutions (S_N2),\textsuperscript{21} eliminations (E2),\textsuperscript{22} Stevens or Sommelet—Hauser rearrangements\textsuperscript{22} and potentially, anion-induced 1,4-eliminations\textsuperscript{23} (Figure 5-1).
Several studies\textsuperscript{26,27} on polymer-bound TAA cations have substantiated the occurrence of substitution reactions,\textsuperscript{28} but the contribution of Hofmann eliminations remains a matter of discussion with little experimental evidence in AEM polymers. Stevens and Sommelet—Hauser rearrangements on benzyltrimethylammonium (BTMA) cations have been demonstrated under alkaline aqueous conditions\textsuperscript{29} and \textit{in silico},\textsuperscript{25,30} but have not been experimentally observed in AEM materials.\textsuperscript{26} A possible explanation for this result may involve side reactions in the presence of nucleophilic counterions.\textsuperscript{29} Finally, anion-induced 1,4-eliminations, a degradation mechanism (seldom discussed in the context of AEM degradation) is fundamentally allowed when BTMA analogues (e.g., a TAA functionalized polystyrene) contain an acidic hydrogen in ring-activated positions that is electronically paired with a leaving group (Figure 5-1f).\textsuperscript{31} Unfortunately, the contribution of 1,4-eliminations cannot easily be discerned from benzyl substitutions under aqueous alkaline degradation conditions without sophisticated isotopic labeling studies and an involved analysis of the degradation products.\textsuperscript{32}

A recent review by Kreuer \textit{claimed that base stable} [TAA cations] \textit{are abundant, but so far, many results have not been verified by independent studies}.\textsuperscript{33} In addition, Kreuer surmised that the steric shielding of cations with (alkyl) spacers offers the most promising approach to increase alkaline stability, which is likely the result of increasing hydrophobicity or steric hindrance around the cationic center.\textsuperscript{34} Indeed these claims of enhanced alkaline stability have been corroborated in AEM polymers with the implementation of: (i) \textit{interstitial} \textit{n}-alkyl spacers between the polymer backbone and nitrogen of the TAA,\textsuperscript{35,36} (ii) \textit{terminal} \textit{n}-alkyl pendants from the nitrogen of the TAA,\textsuperscript{37} and (iii) crosslinking spacers adjoining TAA groups from two congruent polymer backbones.\textsuperscript{38,39}

Given the synthetic challenges of simple and effective post-polymerization chemical modifications to incorporate \textit{interstitial} \textit{n}-alkyl spacers, most attempts towards increased stability of TAA-based AEM polymers feature crosslinking strategies with diamines or functionalization
with terminal n-alkyl spacers. Diamine crosslinking and functionalization with n-alkyl terminal spacers, while sterically shielding, generally introduce β-hydrogen(s) that can undergo Hofmann elimination. Interestingly, the specific contribution of Hofmann elimination to polymer-bound TAA cations, contrary to many claims, has not been directly substantiated or compared to the relative contributions of other possible degradation mechanisms. Therefore, incisive chemical methods that quantitatively assess and identify the reaction products of AEM degradation are required for the non-serendipitous design of robust AEM polymers.

Prior work has: (i) highlighted the utility of small molecule analogs for AEM polymer degradation, (ii) demonstrated a spectroscopic method to systematically measure AEM alkaline stability under controlled and reproducible test conditions, and (iii) substantiated the contribution of polymer backbones on alkaline stability. Furthermore, an emphasis was placed on the importance of ranking alkaline stability under harsh conditions where degradation is clearly observed. The given suggestion was that degradation could not be readily assessed unless there is significant reaction or conversion of the polymer or small molecule. AEM studies often claim good stability at low temperatures (e.g., 60 °C) while reporting poor device stability. This contradiction identifies a clear disconnect between membrane and device studies. To consolidate these issues, follow-up studies have focused on methods that are specifically designed to induce the degradation of both the polymer backbone and TAA cation architecture in order to identify leads for advanced synthetic designs. One such way to readily induce alkaline degradation is to raise temperatures in excess of 80 °C towards TAA cation or polymer backbone failure. A second approach, lowering the dielectric constant of the solvent medium, appears to be critical in observing functional group degradation in a reasonable time period.

Herein, a strategy employing high temperatures (120 °C) within a low dielectric solvent medium (i.e., 3:1 CD$_3$OD–D$_2$O) is employed to compare relative alkaline stability and operative degradation mechanisms in BTMA- and TAA-cations by $^1$H NMR. Three BTMA-functionalized
compounds consisting of pMeBTMA, BTMA-PS, and BTMA-PPO (Figure 2) were evaluated. Additionally we examined compounds containing $n$-alkyl terminal spacers of variable length: pMeBQA6, QA6-PS, and QA6-PPO. Finally, we studied small molecule analogues, ArPrTMA, that contains an n-alkyl interstitial spacer and ArPrHxDMA that contains both $n$-alkyl interstitial and terminal spacers. The approach presented offers chemical structure–alkaline stability insight in to the contribution of polymer backbones and the effect of $n$-alkyl spacers on TAA cations to overall alkaline stability.

Figure 5-2: Chemical structures of TAA small molecule AEM analogs and polymers studied.

**Results and Conclusions**

The products resulting from the degradation of TAA cations are extensive but were simplified by considering only the degradation products that were most likely to occur. For
instance, the absence of β-hydrogens for trimethylbenzylammoniums samples analyzed precludes Hofmann eliminations (E2).

Likewise, the presence of an interstitial spacer, limits the possibility of Sommelet–Hauser and Stevens rearrangements in ArPrHxDMA—although the exact distribution of degradation mechanisms remains inconclusive.

Equally important is the inability to distinguish between anion-induced 1,4-eliminations (in all samples excluding PPO where this mechanism is not possible) and benzyl substitution. For this reason, the shared products of these degradation pathways were strictly treated as substitution (S_N_2_Bn or S_N_2_NMe) at the benzyl position. Interestingly, the formations of ylides, that is, any decay of spectral peaks without corresponding products of degradation was not specifically detected and any uncategorized peak decay was characterized as non-specific (N-S) degradation. Additionally, in selected experiments precipitation and/or turbidity resulted during the heating process. In such instances, an analysis was conducted only on spectra wherein the sample was known to be soluble.

Aiding in the interpretation of our results were small molecule ^1^H NMR reference standards under analogous alkaline degradation solution conditions. These standards consisted of commercially-available or synthesized small molecule analogs of the major degradation products. However in some cases, ^1^H NMR discerned only one byproduct of a specific degradation pathway. In these instances, where peaks overlapped, the discernable mechanism-specific product was used for the determination of the operative mechanism.
Figure 5.3: Rates of degradation and offset $^1$H NMR spectral overlays of pMeBTMA and pMeBQA6 as 30 mM solutions in CD$_3$OD–D$_2$O (3:1), 1,4–dioxane (int. std.), and NaOD (20 equiv., 0.6 M) from 0–3 h shown in hourly intervals at 120 °C.
Influence of Terminal N-Alkyl Pendants on Benzyl-Linked Cations

The incorporation of terminal n-alkyl pendants in TAA have been identified as a facile route to achieve alkaline stability in cast AEMs. In solution studies on small molecules and polymers, we observed that pendant n-alkyl chains decreased the stability of benzylidimethyl n-alkyl ammonium groups compared to BTMA analogs. Shown in Figure 5-3a is the contribution of each degradation mechanism to the overall degradation of the TAA of pMeBTMA and pMeBQA6 in a solution of 3:1 CD$_3$OD–D$_2$O with 20 equivalents of NaOD at 120 °C. The progressive summation of degradation indicates that benzyl substitution ($S_{N2_Bn}$) is the operative mechanism in both samples followed by dealkylation ($S_{N2_{NMe}}$) to a lesser extent. Interestingly, the presence of Hofmann elimination (E2) in pMeBQA6 is nearly insignificant (t = 3 h, 4.0%). Degradation determinations were principally assessed using the aliphatic $^1$H NMR regions displaying the characteristic products of degradation consisting of trimethylamine, p-methyl-N,N-dimethylbenzylamine, and p-methylbenzyl alcohol for pMeBTMA (Figure 5-3b) and N,N-dimethylhexylamine, and p-methyl-N-methyl-N-hexylbenzylamine for pMeBQA6 (Figure 5-3c). The occurrence of Hofmann elimination was determined by the unsaturated protium of 1-hexene (not shown).
The comparison between pMeBTMA and pMeBQA6 was designed to approximate the degradation kinetics and product distribution of their respective poly(styrene) macromolecules. The resulting relative degradation between pMeBTMA and pMeBQA6 were contrary to the added stability reported by Li in poly(phenylene oxides) samples.\textsuperscript{43} pMeBTMA displayed greater stability with a 38.6\% loss of its absolute TAA concentration compared to a 55.7\% loss for pMeBQA6 at 3 h (Figure 5-3a) with both samples experiencing similar degradation from benzyl substitution (\(S_{\text{N2Bn}}\)) and dealkylation (\(S_{\text{N2NMe}}\)). Furthermore, the degradation product distributions for pMeBTMA indicated by \(H_f\) (2.25–2.33 ppm) and \(H_g\) (2.11–2.25 ppm) (Figure 5-3b), does not suggest the increase in degradation of pMeBQA6 results from Hofmann elimination. Figure 5-3d shows the kinetic profiles of pMeBTMA and pMeBQA6 with half-lives of 267 min and 151 min, respectively, a significantly reduction over our prior work conducted at 80 °C.

Consistent with the results of pMeBTMA and pMeBQA6 small molecule analogs, our poly(styrene) sample, QA6-PS, experienced a higher loss of its TAA functionality over BTMA-PS, albeit at a much higher rate of 92\% after 3 h at 120 °C, respectively (Figure 5-4a).
Poly(phenylene oxide)-based samples were surprisingly more resistant to alkaline degradation; **BTMA-PPO** lost 66.9% of its TAA groups after 3 hours while **QA6-PPO** was observed to precipitate from solution at 3 h, but yielded a 2 h degradation of 62.9%. Interestingly, the increased stability of **BTMA-PPO** over **BTMA-PS** with respective half lives of 120 min and 56.8 min distinctly contrasts our degradation observations at 80 °C wherein the poly(styrene) derivative (**QA-PS**) was found to degrade less than its poly(phenylene oxide) analog (**QA-PPO**) (Figure 5-4b).

**Influence of N-Alkyl Interstitial Spacers and Dielectric Effects on Cation Degradation**

In both small molecules and polymers, substitution at the benzyl position was the major degradation route. Therefore the effect of interstitial n-alkyl spacers between the aryl ring and the trimethylammonium cation was investigated. This strategy has shown promise in the literature and confirmation of these previous membrane studies with an incisive small molecule measurement was sought.

Chempath, et al. showed that the background dielectric constant for the benzyl substitution of BTMA has a large effect on the reaction barrier. We observe this dielectric constant effect in our experiments by substituting the solvent form pure D$_2$O to a 3:1 CD$_3$OD:D$_2$O mixture. The varying rates of degradation in D$_2$O and CD$_3$OD:D$_2$O can be explained by an analysis of the respective dielectric constants of the solutions. The dielectric constant of the D$_2$O mixture with NaOD is ~72 at 25 °C and ~42 at 120 °C. The dielectric constant of the CD$_3$OD:D$_2$O mixture with NaOD is ~45 and 25 °C and ~20 at 120 °C. This type of solution study is reasonable considering the total dielectric constant of a hydrated polymer has been shown to be between 10–30 depending on the water content of the system.
In Figure 5, the alkaline degradation of ArPrTMA in pure D₂O and in 3:1 CD₃OD:D₂O mixture is shown. With the inclusion of a three carbon interstitial spacer, ArPrTMA, loses 11.6% of its TAA after 3 h in CD₃OD:D₂O to substitutional displacement (Sₓ₂Aliph) of the trimethylamine and dealkylation (Sₓ₂NMe). In D₂O, ArPrTMA degrades 3.3% after 3 h to substitutional displacement of the trimethylamine alone.

When both a three carbon interstitial spacer and terminal chain are added in the case of ArPrHxDMA, an additive effect on stability is observed as the TAA loss totals just 6.6% resulting from dealkylation alone. In D₂O solution with NaOD, the degradation of ArPrHxDMA is expectedly less yielding a combined 2.7% degradation to substitutional displacement and dealkylation.

The addition of an interstitial n-alkyl spacer clearly increased the stability of both the ArPrHxDMA and ArPrTMA compounds. The terminal n-alkyl pendant in ArPrHxDMA yielded marginal gains in stability compared to ArPrTMA. It appears that both interstitial
spacers and terminal pendant n-alkyl moieties increase the stability of TAA cations, but the interstitial spacer appears to have the greatest influence on eliminating the ubiquitous benzyl substitution observed in BTMA small molecules and polymers.

Additionally, it is worth noting that kinetic isotope studies on the elimination reaction (E2) of 2-phenylethyltrimethylammonium ions (i.e., a small molecule containing a two carbon interstitial spacer) lies so far on the side of the products, styrene and trimethylamine, that measuring the equilibrium constants at 40 °C in EtO\textsuperscript{-}/EtOH presented a challenge. The researchers reasoned the increased carbanion character of the trimethylammonium group favors facile sp\textsuperscript{3} to sp\textsuperscript{2} rehybridization in the transition state with negligible solvent effects. This propensity for degradation is not expected in structures containing \( \geq 3 \) carbon interstitial spacers.\textsuperscript{45}

Terminal n-alkyl pendants have been observed to induce phase separation in random copolymer AEMs. The origin of the increases of alkaline stability in these benzyldimethyl n-alkyl ammonium materials is from the steric shielding of the cation due to the phase separation of alkyl pendants. In the presented solution studies whereby the samples remain completely soluble, the benzyldimethyl n-alkyl ammonium cations are highly accessible by hydroxide and therefore degrade. The increased degradation of benzyldimethyl n-alkyl ammonium pendant cations compared to benzyl trimethyl ammonium cations is due to a lower local dielectric constant in the n-alkyl materials which increases the reactivity of the hydroxide and decreases molecular rotation of the cation which will increase benzyl attack.
Evidence for Contribution of 1,4-eliminations to Poly(styrene) Analogs

Prior work conducted on self-immolative systems that generate 1,4-quinodimethane analogs\textsuperscript{32} invoked a curiosity to the potential elimination of trimethylamine in an anion-induced 1,4-elimination on styrenic small molecule AEM analogs. Specifically, we chose to compare \textbf{pMeBTMA} that contains acidic \(\alpha\)-hydrogens against \textbf{ArBTMA}, a small molecule analog that lacks \(\alpha\)-hydrogens for 1,4-eliminations.

In Figure \textit{5-6}, the alkaline degradation of \textbf{pMeBTMA} and \textbf{ArBTMA} as 30 mM solutions in CD\textsubscript{3}OD–D\textsubscript{2}O (3:1), 1,4-dioxane (int. std.), and NaOD (20 equiv., 0.6 M) from 0–3 h shown in hourly intervals at 120 °C.

In Figure \textit{5-6}, the alkaline degradation of \textbf{ArBTMA} resulted in a TAA loss of 20.3% after 3 h compared to a significantly higher degradation rate for \textbf{pMeBTMA} of 38.6%. This result is intriguing considering the electron donating properties of a para-methyl group on an aromatic ring.\textsuperscript{46} Inductive donation should yield a benzyl carbon with a greater partial negative charge and therefore result in a reduction of electrophilicity. Considering that the byproducts of a 1,4-elimination under our conditions are equivalent to that of benzyl substitutions and the primary
increase in degradation of pMeBTMA is from benzyl substitution. The conclusion suggests that an anion-induced 1,4-elimination mechanism is activated at 120 °C. Studies conducted at 80 °C concluded that QA-PS is less susceptible to alkaline degradation compared to QA-PPO, but the opposite trend was observed for BTMA-PS and BTMA-PPO at 120 °C. This would indicate that the increase in thermal energy at 120 °C is sufficient to overcome the energy barrier necessary to activate the 1,4-elimination mechanism.

Conclusions

In summary, a high temperature ¹H NMR-based method to study AEM polymers and analogs under high temperature conditions was introduced that ensures their degradation for meaningful comparisons. The findings indicate that BTMA cations and benzylidimethylammonium analogs with n-alkyl terminal pendants are significantly more susceptible to degradation than trimethylammonium cations with an n-interstitial spacer. Further but minor enhancements in alkaline stability were observed when an n-alkyl interstitial and n-alkyl pendant functionalities were combined on a single cation. The study presented suggests that an AEM poly(phenylene oxide) is more resistant to alkaline degradation at 120 °C than an AEM poly(styrene) polymer; a reversal of stability observed at 80 °C in a previous study. A follow up studies with AEM poly(styrene) small molecules suggests that an anion-induced 1,4-elimination degradation mechanism is activated at 120 °C in when α-hydrogens are present on a styrenic AEM polymer.

This conclusion has potential consequences for BTMA containing poly(styrene)-based polymers in AEMFC high-temperature applications. Although more studies are needed to confirm the findings and given the added stability shown by the addition of the inclusion of n-alkyl interstitial spacers, it is suggested BTMA-poly(styrene) polymers are replaced with more robust
polymer backbones and chemistries are developed for synthesizing AEMs with n-interstitial spacers.

References:


Chapter 6

ATR-FTIR Determination of Alkaline Stability in Fluorinated Polymers

Introduction

Thus far, this dissertation has introduced a method to quantitatively determine the alkaline stability of dissolved AEM polymers using $^1$H NMR spectroscopy. While these determinations are useful and versatile, AEMs are utilized in the solid state within AEMFCs whereby effects apart from backbone and cation degradation may have an influence. In the membrane form, morphological phase separation can exclude interactions of the alkaline media with chemically labile functional groups. Unfortunately, techniques such as solid state NMR typically yield poor resolution for quantitative measurements and secondary property measurements, such as IEC or conductivity, yield little insight into chemical changes. Herein, an alternative spectroscopic and quantitative method for studying alkaline degradation in solid AEMs is presented using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) vibrational spectroscopy. ATR-FTIR sampling is sufficiently sensitive and quantitative (under certain conditions) to identify chemical changes within solid AEM samples while revealing gains in alkaline stability that results from polymer morphology. The samples investigated include the previously examined AEMs, QA-Radel and QA-PPO, along with a novel series of AEM samples designed by Miyatake$^{1-3}$ of the fluorinated multiblock AEM copolymers, QPE-3, QPAF-6, and QPE-9 (Figure 6-1) that exhibit phase-separated morphology based on hydrophilic—hydrophobic segmentation as shown in their TEM images in Figure 6-2.
Herein, the keynote IR vibrational assignments of QPE-3, QPAF-6, QPE-9, QA-Radel and QA-PPO are identified and quantitatively measured as a function of exposure to alkaline media.

Figure 6-1: Chemical structures of solid AEM polymers studied using ATR-FTIR.

Figure 6-2: TEM images of (a) QPAF-6 and (b) QPE-9 stained with tetrachloroplatinate ions.
Brief Contextual Review of ATR-FTIR Spectroscopy

ATR-FTIR spectroscopy is a widely used sampling technique for polymers\textsuperscript{4-7} allows for both qualitative and quantitative analysis. The primary benefit of ATR-FTIR sampling originates from the ability to use polymers sample without the need for dilution (e.g., with an IR transparent salt). This contrasts the limitations of transmission methods (e.g., FTIR, Raman) that constrain pristine polymer sample thicknesses to 5–20 µm for suitable detection.\textsuperscript{8}

Typically, in an absorption spectrum, peak intensity is proportional to absorption coefficients, light path lengths, and concentration using the Beer—Lambert relation. Once an absorption coefficient is extrapolated (using multipoint calibration curves), the concentration of a target peak (e.g., a quaternary ammonium vibration) can be obtained from the peak intensity alone \textit{given a fixed light path length}.\textsuperscript{6} In IR spectroscopy using transmission methods, the IR beam is projected through the sample and light path length is determined from the sample thickness and orientation with respect to the source. ATR-FTIR methods direct the IR beam into a crystal–sample interface to induce an evanescent wave that travels orthogonally into the sample. The energy of the evanescent wave is partially absorbed by the sample and the remaining reflected radiation is returned to the detector. The effective light path length using ATR-FTIR sampling can then be fixed (given several assumptions) as a product of the depth of penetration by the orthogonal IR beam and the crystal–sample contact area. The given assumptions include fixed: crystal and sample refractive indices, angle of incidence, and peak intensity of interest. These values are constant for a given instrument configuration and allows for the determination of sample concentration from peak intensity using the Beer—Lambert law.\textsuperscript{8}

Table 6-1: Notation for referencing vibration modes using a generic formula, $\chi_{XY(\sigma)}$.\textsuperscript{9}
To facilitate discussion, a short hand notation is used to reference specific vibrations modes of functional groups under the general formula, $\chi_{XY(z)}$, where $\chi$ indicates the vibration mode, $a$ describes the sub-mode and $XY(z)$ denotes the affected bond with the functional group in subscript (Table 6-1). Specific rotational and translational modes of vibration are illustrated in Table 6-2.

<table>
<thead>
<tr>
<th>Vibration mode</th>
<th>Sub-mode</th>
<th>$XY(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ – stretching</td>
<td>sym - symmetric</td>
<td></td>
</tr>
<tr>
<td></td>
<td>asym - asymmetric</td>
<td></td>
</tr>
<tr>
<td>$\delta$ – in-plane deformation</td>
<td>$\rho$ – rocking</td>
<td></td>
</tr>
<tr>
<td>$\gamma$ – out-of-plane deformation</td>
<td>$\tau$ – twisting or torsion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\omega$ – wagging</td>
<td></td>
</tr>
</tbody>
</table>

Chemical linkage for vibration mode. For example, $\nu_{\text{asym}} \text{C}_4\text{N}^+(QA)$.
Table 6-2: Model illustration of rotational and translational modes of vibration with directional motion indicated by arrows.\textsuperscript{10}

<table>
<thead>
<tr>
<th>Vibration Mode</th>
<th>Sub-mode</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>stretching ($u$)</td>
<td>symmetric stretching ($v_1$)</td>
<td><img src="image1" alt="Symmetric Stretching" /></td>
</tr>
<tr>
<td></td>
<td>bending ($v_2$)</td>
<td><img src="image2" alt="Bending" /></td>
</tr>
<tr>
<td></td>
<td>asymmetric stretching ($v_3$)</td>
<td><img src="image3" alt="Asymmetric Stretching" /></td>
</tr>
<tr>
<td>in-plane deformation ($\delta$)</td>
<td>rocking ($\rho$)</td>
<td><img src="image4" alt="Rocking" /></td>
</tr>
<tr>
<td>out-of-plane deformation ($\gamma$)</td>
<td>twisting ($\tau$)</td>
<td><img src="image5" alt="Twisting" /></td>
</tr>
<tr>
<td></td>
<td>wagging ($\omega$)</td>
<td><img src="image6" alt="Wagging" /></td>
</tr>
</tbody>
</table>
IR Assignments of Quaternary Ammoniums in AEMs

To date, only a single study has identified and reported a *comprehensive* analysis of IR spectral assignments for AEM polymers.\(^9\) The rarity of this analysis is in part due to the difficulty in assigning peaks given the obscuring overlap of vibrational frequencies arising from the polymer backbone and cation.

![Chemical structures of quaternary-ammonium functionalized AEM samples](Figure 6-3) Chemical structures of quaternary-ammonium functionalized AEM samples used for IR peak identification.\(^9\)

Mendoza\(^9\) reported the comprehensive vibrational assignments of pristine samples and the resulting changes from thermal, oxidative and electrochemical degradation of QA-SEBS, and QA-PS (Figure 6-3) using IR and Raman spectroscopy. With the use of small molecule analogs for these AEMs and literature assignments,\(^11-14\) Mendoza interpreted the IR spectra of QA-SEBS and QA-PS shown in Figure 6-4 with added annotations and specific peak assignments reproduced in Table 6-3.\(^9\)
Key vibrations to note in the Q-SEBS and Q-PS spectra that are relevant to the forthcoming samples examined, QA-PPO, QA-Radel, QPE-9, QPAF-6, and QPE-3 are those specific to the quaternary ammonium, $\nu_{asym}CN^{+}$, centered at 955, and aromatic stretching, $\nu_{CC(R,QA)}$ in the 1580–1615 cm$^{-1}$ region that serves as a persistent intrinsic internal standard (i.e., peak for normalization) for quantitative analysis. Other vibrations include deformation of the skeleton, $\delta$CNC, deformation of the entire cation, $\delta$C$_4$N$^{+}$, and vibrations of the methyl groups: $\gamma$CH$_3$, $\delta$CH$_3$, $\nu_{asym}$CH$_3$, $\nu_{sym}$CH$_3$. Reported characterization beyond these absorptions on AEMs

Figure 6-4: Annotated infrared spectra of Q-SEBS and Q-PS, comparing IR vibrational assignments. The notations used are $\nu$, stretching; $\delta$, in-plane deformation; $\gamma$, out-of-plane deformation; $\omega$, wagging; QA, quaternary ammonium; R, benzene or styrene; al, aliphatic. * Affected by (R) symmetry and substitution patterns. † The 1030–1250 cm$^{-1}$ region contains weak overlapping peaks. ‡ Conflicting literature assignments assign 1284 cm$^{-1}$ and 1580–1720 cm$^{-1}$ to HCO$_3$ counterion vibrations ($\nu_{asym}CO_2$) and indiscriminate $\omega$CH$_2$. 
are rare due to the obscurity by overlapping vibration modes originating from the polymer backbone.\(^9\)

**Table 6.3: IR absorption assignments of QA-PS and QA-SEBS.**\(^9\)

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))(^a)</th>
<th>Assignment(^b)</th>
<th>Description of Benzene Vibration</th>
<th>Functional Group(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1616</td>
<td>vCC</td>
<td>Ring stretching</td>
<td>Styrene-QA</td>
</tr>
<tr>
<td>1512</td>
<td>vCC + δCC</td>
<td>Ring stretching + deformation</td>
<td>Styrene-QA</td>
</tr>
<tr>
<td>1488</td>
<td>δCH(_3)</td>
<td></td>
<td>QA</td>
</tr>
<tr>
<td>1460</td>
<td>δCH(_2)</td>
<td></td>
<td>Aliphatic backbone</td>
</tr>
<tr>
<td>1384</td>
<td>δCH, γCH(_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1244</td>
<td>δCH</td>
<td>CH in-plane deformation</td>
<td>Styrene-QA</td>
</tr>
<tr>
<td>1222</td>
<td>δCH</td>
<td>CH in-plane deformation</td>
<td>Styrene-QA</td>
</tr>
<tr>
<td>1190</td>
<td>δCC</td>
<td>Ring deformation</td>
<td>Styrene</td>
</tr>
<tr>
<td>1070</td>
<td>δCC</td>
<td>Ring deformation</td>
<td>Styrene</td>
</tr>
<tr>
<td>1030</td>
<td>δCH</td>
<td>CH in-plane deformation</td>
<td>Styrene</td>
</tr>
<tr>
<td>1020</td>
<td>δCH(_3)</td>
<td></td>
<td>QA</td>
</tr>
<tr>
<td>992</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>976</td>
<td>ν(_{\text{asym}})C(_4)N(^+)</td>
<td></td>
<td>QA</td>
</tr>
<tr>
<td>955sh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>925</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>889</td>
<td>2 * δC(_4)N(^+)</td>
<td></td>
<td>QA</td>
</tr>
<tr>
<td>858</td>
<td>γCH</td>
<td>CH out-of-plane deformation</td>
<td>Styrene-QA</td>
</tr>
<tr>
<td>832</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>760</td>
<td>γCH</td>
<td>CH out-of-plane deformation</td>
<td>Styrene</td>
</tr>
<tr>
<td>720</td>
<td>δCH(_2)</td>
<td></td>
<td>Aliphatic-Styrene</td>
</tr>
<tr>
<td>701</td>
<td>δCC</td>
<td>Ring deformation</td>
<td>Styrene</td>
</tr>
</tbody>
</table>

\(^a\)sh – shoulder peak  
\(^b\)The symbols used are: \(v\), stretching; \(δ\), in-plane deformation; \(γ\), out-of-plane deformation.  
\(^c\)Mixed styrene functionality has distinct benzene vibrations: QA, quaternary ammonium; R, general benzene mode.
Application of Known Vibrational Frequencies to Studied Samples

The IR spectra of five pristine samples, QA-PPO, QA-Radel, QPE-9, QPAF-6 and QPE-3 were carefully examined for vibrational correlations to those reported by Mendoza in QA-SEBS and QA-PS and for structure-specific vibrations unique to each sample. The stacked and annotated spectra of these five pristine samples, obtained using ATR-FTIR methods, are shown in Figure 6-5.

Figure 6-5: Stacked annotated infrared spectra of QA-PPO, QA-Radel, QPE-9, QPAF-6, and QPE-3 showing regions of specific assignment common to all samples. The notations used are ν, stretching; δ, in-plane deformation; γ, out-of-plane deformation; ω, wagging; QA, quaternary ammonium; R, benzene or styrene; al, aliphatic. *Affected by (R) symmetry and substitution patterns. †The 1030–1250 cm⁻¹ region contains weak overlapping peaks. Dashed areas demarked with α, β, and γ; indicate regions of overlap with the sample-specific vibrational frequencies.
Comparative analysis to Mendoza’s work reveals similar vibrations for $v_{\text{asym}N^+}$ in the 905–990 cm$^{-1}$ region, overtones $2\delta C_4N^+(\text{QA})$ spanning 840–904 cm$^{-1}$, and $\delta CH_3(\text{QA})$ absorptions extending through the 998–1016 cm$^{-1}$ region. Ring stretching modes, $v_{CC}$, are present in the 1550–1625 cm$^{-1}$ region, suggesting a persistent vibration for normalization that can be used for quantitative analyses of remaining quaternary ammonium functionalities in alkaline degradation assays. Absent peaks, with the exception of the QA-PPO sample, are $\gamma CH_2(\text{al})$ and $\delta CH(\text{al})$ vibrations in the 1362–1392 cm$^{-1}$ region that are associated with the aliphatic backbones of QA-SEBS and QA-PS, but expressed in QA-PPO by the CH$_3$ functionality. Benzyl in-plane deformation, $\delta CH$, and out-of-plane wagging, $\omega CH_2$, are found as weak vibrations in the 1277–1342 cm$^{-1}$ region.

Aromatic (diaryl) ethers usually display a single strong asymmetric stretch, $v_{\text{asym}COC(R-O-R)}$, in the 1230–1310 cm$^{-1}$ region. This stretching, however, is strongly affected by the electronic effects of aryl substituents. Electron withdrawing substituents such as the fluorines (Ar–F) present in the structures of QPE-3, QPE-9 and the sulfone (Ar–SO$_2$–Ar) of QA-Radel—especially in the ortho and para positions—tend to increase the observed frequency resulting in an observed $v_{\text{asym}COC(R-O-R)}$ range of 1194–1272 cm$^{-1}$. The reverse trend is true for electron-donating groups, therefore QA-PPO with its 2,6-dimethyl substitutions would be expected to resonate at a reduced frequency; however, the structure of QA-PPO has unique properties that negate this trend. Compared to QPE-3, QPE-9, and QA-Radel, the C–O–C linkage has a lower rotational barrier, lower excluded volume and decreased van der Waals forces that combined, allow the C–O–C linkage to be highly flexible. In diaryl ethers, the conjugation of the benzene $\pi$ electrons with the lone pair of the oxygen depends on the angle of the C–O–C bond. The greatest conjugation occurs at 0° and the least at 90°. Given the greater segmental mobility of QA-PPO, both aryl rings can approach a greater conjugated state that results in a corresponding increase in the force constant of the C–O bond that results in an increase in the vibration
frequency to an observed ν\text{asym} COC(R-O-R) of 1182 cm\(^{-1}\).\(^{17}\) Unfortunately the aryl ether vibrations QA-PPO, QA-Radel, QPE-9 and QPE-3 overlap with δCH\(_{(R-QA)}\) and C–F domains and may not be reliable for any assessment of hydrolytic backbone degradation.

Peaks related to the QA-Radel-specific sulfur vibrations, ν\text{sym} SO\(_2\), ν\text{asym} CS, and ν\text{sym} CS, indicated by β, are expressed at 1150, 1106 and 1071 cm\(^{-1}\) and overlap with δCH\(_{(R-QA)}\), δCH\(_{(R)}\), and δCC\(_{(R)}\) regions.\(^9\) The fluorinated aromatic and aliphatic vibrations C–F vibrations of QPE-3, QPAF-6 and QPE-9 are found over a wide frequency range, 1000–1360 cm\(^{-1}\), overlapping with several other regions.\(^{17}\) Given the abundance of overlapping absorptions, the 1050–1360 cm\(^{-1}\) frequency range is not ideal for determining peak assignments or on a measurable basis for quantitative analysis in alkaline degradation assays.

Normalization

ATR-FTIR analyses enable the quantitative analysis of chemical changes in solid samples using constant instrument parameters at specific wavelengths. Characteristic peak intensities of an absorption spectrum are proportional to the peak absorption coefficient, light path length and concentration in a relationship analogous to the Beer—Lambert relation. Scaling differences from path length effects, scattering effects, and instrument sensitivities are corrected using multivariate analysis normalization. Multivariate analysis normalization entails the use of peak intensity ratios (normalized intensity) that is the peak intensity of the target peak divided by the peak intensity of a pseudo-constant reference peak component. Quantitative interpretations of chemical changes within the sample are then obtained with a calibration curve of peak intensity and known sample-specific concentrations.

Shown in Figure 6-6a is the νCC benzene stretching modes of QPE-3 membranes with IECs of 1.7 and 2.3 mmol/g, herein denoted in parenthesis (e.g., QPE-3 (1.7)), located at a peak
frequency of 1606 cm\(^{-1}\). This frequency is not expected to change under alkaline degradation conditions and serves as a pseudo-constant reference peak that is intensity normalized for quantitative scaling of the target peaks of interest. Figure 6-6b displays the intensity scaling result of the \(2\delta C_4N_{(QA)}\) peak at 883 cm\(^{-1}\) of QPE-3 (1.7) and (2.3) after normalization of the νCC frequency at 1606 cm\(^{-1}\). Also shown in the stacked overlay in Figure 6-6b is QPE-3\(_{CM}\) that is the non-quaternary ammonium functionalized QPE-3 backbone illustrating the specificity of the peak identity to the quaternary-ammonium functionality.

![Graph](image)

Figure 6-6: Superimposed infrared spectra of non-functionalized (NF) QPE-3 and functionalized QPE-3 with IECs (mmol/g) indicated in parenthesis of 1.7 mmol/g and 2.3 mmol/g. a) The νCC + δCC region displays a decrease in intensity for monosubstitution at 1606 cm\(^{-1}\) and increasing dissubstitution at 1650 cm\(^{-1}\) for increasing IEC. b) The \(2\delta C_4N_{(QA)}\) vibration at 884 cm\(^{-1}\) is absent in non-functionalized QPE-3 and increases progressively for higher IEC values.
Effect of IEC on Vibrational Spectra and Normalization for Quantitative Extraction

The degree of substitution by quaternary ammoniums on AEMs give rise to characteristic substitution peak vibrations indicative of the degree of substitution on the aromatic rings. The effect of this functionalization is shown in the spectral overlay of $\text{QPE-3}$ (1.7) and $\text{QPE-3}$ (2.3) in Figure 6-6a. The benzene $\nu_{CC} + \delta_{CC}$ peak of the fused aromatic fluorene substructure at 1606 cm$^{-1}$ decreases with increasing IEC that indicates a decrease in monosubstitution and an increase of dissubstituted $\nu_{CC} + \delta_{CC}$ modes at 1650 cm$^{-1}$. These peaks are general benzene vibrations and their combined peak intensities are well established as points of normalization$^9$ that are referred to as *substituent-insensitive standing waves*. Figure 6-6b shows the superimposed spectra of unfunctionalized $\text{QPE-3}$ backbone (QPE-3$_{CM}$), $\text{QPE-3}$ (1.7), and $\text{QPE-3}$ (2.3) in the $2^* \delta_{C_4N^+(QA)}$ vibration region. This overtone peak at 884 cm$^{-1}$ is sensitive to increased cation functionalization and shifts from an 879 cm$^{-1}$ maxima with increasing dissubstitution of the fluorene substructure. Accordingly, any changes to the quaternary ammonium functionality can be absolutely assessed on a multipoint calibration curve of the peak area for $2^* \delta_{C_4N^+(QA)}$ and known IEC values using the Beer—Lambert relation. The inlaid plot of normalized intensity and IEC in Figure 6-5b is one such example of a multipoint calibration curve for using FTIR-ATR methods to quantitatively determine the amount of functionalization given a quantitative assessment of IEC by other means, in this case, the IEC was determined by both Mohr titration and $^1\text{H NMR}$.
ATR-FTIR Determination of Alkaline Stability in Solid AEM Membranes

The alkaline degradation of four fluorinated AEM polymers exhibiting phase-separated morphology, QPE-3 (1.7), QPE-3 (2.3), QPE-6 (1.2) and QPE-9 (1.3), and two AEM polymers for comparison, QA-PPO (1.6) and QA-Radel (2.0) were examined for their relative stability in membrane form. Three alkaline degradation conditions were used that include membrane immersion in: (i) 0.6 M NaOH\((a)\) at 100 °C for 1, 3, and 6, (ii) 0.6 M NaOH\((a)\) at 120 °C for 6 hours, and (iii) 7.0 M KOH\((a)\) at 120 °C for 6 hours. The membranes used were cut to a specific weight that in all cases of 0.6 M NaOH solutions was equivalent to a 20-fold excess of NaOH to the quaternary ammonium and a greater than 200-fold excess for 7.0 M KOH to the quaternary ammonium. For each AEM sample, the stable νCC region was used as an internal standard for normalization and the peak areas for $2^\circ \delta C_4 N^+(QA)$ or $\nu_{asym} C_4 N^+$ vibrations were extracted to assess relative stabilities.

Alkaline Stability of QPE-3 determined by ATR-FTIR

QPE-3 (1.7), a polyphenylether copolymer containing alkyltrimethyl ammonium-functionalized fluorenes was exposed to: (i) 0.6 M NaOH\((a)\) at 100 °C for 1, 3, 6, and 12 hours, (ii) 0.6 M NaOH\((a)\) at 120 °C for 6 hours, and (iii) 7.0 M KOH\((a)\) at 120 °C for 6 hours.
After normalization of the $\nu_{CC}$ peak at 1606 cm$^{-1}$, the peak at 883 cm$^{-1}$ representative of the $2^\delta C_4N^+_{(QA)}$ overtone is observed to shift to 880 cm$^{-1}$ on exposure to all alkaline conditions as shown in Figures 6-7.

The stability of QPE-3 (1.7) when exposed to 100 °C in 0.6 M NaOH for 1, 3, and 6 hours is nominal with 98.5%, 96.0%, and 94.9% loss of the $2^\delta C_4N^+_{(QA)}$, respectively (Figure 6-8a). At an elevated temperature of 120 °C in 0.6 M NaOH the $2^\delta C_4N^+_{(QA)}$ overtone diminishes to 89.5% after 6 hours, and at the equivalent temperature in 7.0 M KOH, marginally more so at 86.7% after 6 hours (Figure 6-8b).

Figure 6-7: Stacked FTIR-ATR spectral overlays of QPE-3 (1.7) membrane samples in untreated form exhibiting the change in intensity for the $2^\delta C_4N^+_{(QA)}$ overtone when subjected to a) 100 °C in 0.6 M NaOH, and b) 120 °C in 0.6 M NaOH (i) and 120 °C in 7.0 M KOH (ii).
The rates of degradation were determined from the linear plot of the polymer concentration and time using a first-order approximation allowed by the excess of alkali in each case. The half-lives of the quaternary ammonium species as indicated by the $2\delta\text{C}_4\text{N}^+\text{(QA)}$ overtone at 883 cm$^{-1}$ after 6 hours was 103.2 hours for 0.6 M NaOH at 100 °C, 37.5 hours in 0.6 M NaOH at 120 °C, and 29.1 hours for 7.0 M KOH at 120 °C (Figure 6-8b).

A visual representation of each QPE-3 (1.7) polymer sample is shown in Figure 6-9 in untreated form and sample membranes expose to alkali conditions. The untreated dry membrane is flexible and translucent and only slightly discolors after 12 hours in 0.6 M NaOH at 100 °C.

![Figure 6-8](image1.png)  
**Figure 6-8:** The normalized rates of alkaline degradation of the $2\delta\text{C}_4\text{N}^+\text{(QA)}$ absorption peaks of QPE-3 (1.7) as measured by ATR-FTIR. a) Measurements of the relative degradation of QPE-3 (1.7) at various time intervals up to 6 h in the denoted alkaline conditions. b) Linear plots showing the rates of degradation of the remaining IEC (mmol/g) after 6 h for each alkaline condition indicated with the corresponding half-life ($t_{1/2}$).

![Figure 6-9](image2.png)  
**Figure 6-9:** Visual illustration QPE-3 (1.7) membrane samples in untreated form and after immersion in the indicated degradation conditions.
However, after only 6 hours in 0.6 M NaOH at 120 °C the QPE-3 (1.7) membrane sample is noticeably discolored and has reduced elasticity over the membrane subjected to 100 °C. When exposed to 7.0 M KOH at 120 °C for 6 hours, the membrane sample shows the greatest discoloration and reduction in membrane elasticity.

Figure 6-10: Stacked FTIR-ATR spectral overlays of QPE-3 (2.3) membrane samples in untreated form exhibiting the change in intensity for the 2$^\text{a}$$\delta$$\text{C}_4\text{N}^\text{+}(\text{QA})$ overtone when subjected to a) 100 °C in 0.6 M NaOH, and b) 120 °C in 0.6 M NaOH (i) and 120 °C in 7.0 M KOH (ii).

Examination of QPE-3 (2.3) displays the 2$^\text{a}$$\delta$$\text{C}_4\text{N}^\text{+}(\text{QA})$ overtone centered at 883 cm$^{-1}$, with a progressive shift toward 880 cm$^{-1}$ in 0.6 M NaOH at 100 °C and 779 cm$^{-1}$ in 0.6 M NaOH at 120 °C (Figure 6-10).
The stability of QPE-3 (2.3) when exposed to 0.6 M NaOH at 100 °C for 1, 3, and 6 hours is more pronounced than the less functionalized QPE-3 (1.7) variant with reductions of the $2^*\delta C_4N^{+}(QA)$ peak amounting to 89.1%, 81.4%, and 79.5%, respectively (Figure 6.1a). In 0.6 M NaOH solution at 120 °C after 6 hours a nominal difference in peak intensity is observed amounting to 77.0%. The modest change in stability between the different degrees of functionalization, although quantitatively different in terms of concentration, may result from changes in solubility near the surface of the polymer that disallows progressively increasing degradation.

A plot for the rate of degradation of QPE-3 (2.3) yields reduced half-lives of 23.2 hours for 0.6 M NaOH solution at 100 °C and 16.7 hours for 0.6 M NaOH at 120 °C (Figure 6-11b). Although 7.0 M KOH at 120 °C was not used for QPE-3 (2.3), the half lives were significantly less than QPE-3 (1.7) samples exposed to the harsher conditions of 7.0 M KOH at 120 °C.
Membrane samples of QPE-3 (2.3) were translucent and flexible in untreated form and slightly yellowed and were stiffer upon bending in 0.6 M NaOH at 100 °C for 12 hours, compared to its QPE-3 (1.7) analog (Figure 6-12). QPE-3 (2.3) exposed to 0.6 M NaOH at 120 °C for 6 hours was characteristically more discolored than the aforementioned sample and noticeably stiffer after exposure to 0.6 M NaOH at 120 °C for 6 hours than its QPE-3 (1.7) counterpart.

**Alkaline Stability of QPE-9 determined by ATR-FTIR**

QPE-9 (1.6), a polyphenyl ether copolymer similar to QPE-3, but containing alkyltrimethylammonium-functionalized poly(styrene) instead of fluorene moieties. After normalization of the νCC peak at 1607 cm⁻¹, the δCH₃(QA) absorption centered at 1071 cm⁻¹ was observed to remain constant under all alkaline degradation conditions as shown in Figures 6-13a and 6-13b.

The stability of QPE-9 when exposed to 100 °C in 0.6 M NaOH for 1, 3, and 6 hours is nominal with 98.5%, 96.0%, and 94.9% loss of the δCH₃(QA), respectively (Figure 6-14a). At an elevated temperature of 120 °C in 0.6 M NaOH the δCH₃(QA) overtone diminishes to 89.5% after...
6 hours, and at the equivalent temperature in 7.0 M KOH, marginally more so at 86.7% after 6 hours.

![Figure 6-13](image)

**Figure 6-13:** Stacked FTIR-ATR spectral overlays of QPE-9 (1.6) membrane samples in untreated form exhibiting the change in intensity for the δCH$_{3(QA)}$ overtone when subjected to a) 100 °C in 0.6 M NaOH, and b) 120 °C in 0.6 M NaOH (i) and 120 °C in 7.0 M KOH (ii). Replace this with figure caption below the figure.

The rate of degradation of QPE-9 (1.6) yields kinetics comparable to QPE-3 (1.7) with half-lives of 35.0 hours for conditions of 100 °C in 0.6 M NaOH, 27.4 hours for 120 °C in 0.6 M NaOH and 17.7 hours for 120 °C in 7.0 M KOH (Figure 6-14b). Given that QPE-3 (1.7) and QPE-9 (1.6) have similar IECs, benzyltrimethylammonium linkages, and co-polymer backbones, this result seems to indicate that the relative stabilities of the individual tethering units, unfused trisubstituted benzene and the fused structure of fluorine, have little effect on the overall stability of the AEM samples.
Membrane samples of QPE-9 (1.6) discolored to a greater degree than samples of QPE-3 (1.7) with significant discoloration and stiffening from the untreated form upon exposure to 100 °C in 0.6 M NaOH for 12 hours (Figure 6-15). QPE-9 (1.6) samples exposed to 120 °C in 0.6 M NaOH for only 6 hours displayed qualitative properties similar to the aforementioned sample and membranes samples exposed to 120 °C in 7.0 M KOH for 6 hours displayed considerable discoloration and when manipulated they exhibited brittleness.

Figure 6-15: Visual illustration QPE-9 (1.6) membrane samples in untreated form and after immersion in the indicated degradation conditions.
Alkaline Stability of QPE-6 Determined by ATR-FTIR

QPE-6 (1.2), consisting of an aliphatic fluorocarbon chain that is copolymerized with alkyltrimethylammonium-functionalized poly(styrene) similar to QPE-9. Normalization of the νCC peak intensity at 1608 cm\(^{-1}\) allowed for the quantitative assessment of the δCH\(_3\)(QA) centered at 890 cm\(^{-1}\) (Figure 6-16a). A minor shift of the δCH\(_3\)(QA) to 892 cm\(^{-1}\) was observed for samples subjected to 100 °C in 0.6 M NaOH and 894 cm\(^{-1}\) for samples exposed to 120 °C in 7.0 M KOH (Figure 6-16b).

![Figure 6-16](image)

Figure 6-16: Stacked FTIR-ATR spectral overlays of QPE-6 (1.2) membrane samples in untreated form exhibiting the change in intensity for the 2\(\delta\)C\(_4\)N\(^+\)(QA) overtone when subjected to a) 100 °C in 0.6 M NaOH, and b) 120 °C in 0.6 M NaOH (i) and 120 °C in 7.0 M KOH (ii).

The stability of QPE-6 (1.2) after exposure to 100 °C in 0.6 M NaOH for 1, 3, and 6 hours was 87.9%, 84.4%, and 80.9% as observed in the decrease of the δCH\(_3\)(QA) absorbance (Figure 6-17a). At 120 °C in 0.6 M NaOH after 6 hours, the δCH\(_3\)(QA) peak is reduced to 74.0%
(Figure 6-17b), and finally, when subjected to 120 °C in 7.0 M KOH, QPE-6 (1.2) is reduced to 57% after 6 hours.

Figure 6-17: The normalized rates of alkaline degradation of the $2\delta C_4N^{+\text{QA}}$ absorption peaks of QPE-6 (1.2) as measured by ATR-FTIR. a) Measurements of the relative degradation of QPE-6 (1.2) at various time intervals up to 6 h in the denoted alkaline conditions. b) Linear plots showing the rates of degradation of the remaining IEC (mmol/g) after 6 h for each alkaline condition indicated with the corresponding half-life ($t_{1/2}$).

QPE-6 (1.2) yields significantly reduced rates of degradation when compared to any of the aforementioned polymers with half-lives of 22.8 hours upon exposure to 100 °C in 0.6 M NaOH, 14.0 hours for 120 °C in 0.6 M NaOH and a meager 7.4 hours for 120 °C in 7.0 M KOH. Given the low IEC of 1.2 mmol/g, QPE-6 and degradation data on the similar structure of QPE-9, the significant difference in stabilities suggests that the aromatic block in QPE-9 decreases its lability, while the aliphatic fluorocarbon chain increases lability. However, the QPE-6 (1.2) membrane sample tested was of a lower Mw of 35,000 compared to an Mw of >100,000 for all other membrane samples tested. Additional studies using QPE-6 samples of larger Mw are needed to draw any decisive conclusions regarding the reduced alkaline stability of QPE-6.

The increased susceptibility of QPE-6 (1.2) to alkaline degradation was also manifested upon visual examination of the samples (Figure 6-18). In untreated form, QPE-6 (1.2) was
qualitatively quite flexible and showed significant browning and a reduction in flexibility upon exposure to 100 °C in 0.6 M NaOH for 12 hours. Surprisingly, treatment of a membrane sample at 120 °C in 0.6 M NaOH solution for 6 hours displayed less discoloration and increased flexibility over the previously mentioned sample. Finally, the \textbf{QPE-6} (1.2) sample treated exposed to 100 °C in 0.6 M NaOH for 6 hours showed the greatest discoloration and stiffness.

![Membrane Samples](image)

Figure 6-18: Visual illustration \textbf{QPE-6} (1.2) membrane samples in untreated form and after immersion in the indicated degradation conditions.

\textbf{Alkaline Stability of QA-Radel Determined by ATR-FTIR}

\textbf{QA-Radel} (2.0), a well-studied poly(aromatic sulfone) ether containing benzyltrimethylammonium ion groups was included in this study along with \textbf{QA-PPO} as reference standards for ATR-FTIR degradation. Normalization of the νCC peak occurs at 1582 cm\(^{-1}\), and the \(2\delta\text{C}_4\text{N}^+\text{QA}\) is observed with nominal shifting from 919 cm\(^{-1}\) to 918 cm\(^{-1}\) under all conditions studied (Figure 6-19).
The stability of QA-Radel (2.0) exposed to 100 °C in 0.6 M NaOH for 1, 3, and 6 hours is 89%, 70%, and 67%, respectively (Figure 6-20a). At 120 °C in 0.6 M NaOH at 6 hours, the QA-Radel (2.0) membrane sample exhibits only 55.0% of the $2\delta C_4N^+_{(QA)}$ intensity remaining. QA-Radel (2.0) samples exposed to 120 °C in 7.0 M were dissolved by the strong alkaline conditions and not included.

The rates of degradation of QA-Radel (2.0) indicated the lowest alkaline stability of membrane samples studied with half-lives of 8.5 hours and 7.0 hours for 100 °C and 120 °C in 0.6 M NaOH, respectively (Figure 6-20b). This reduced susceptibility to alkaline media is also reported for dissolved samples in $^1$H NMR studies discussed in prior chapters. Although the commercial Radel® poly(sulfone) backbone very resilient to alkaline media, when functionalized

![Figure 6-19: Stacked FTIR-ATR spectral overlays of QA-Radel (2.0) membrane samples in untreated form exhibiting the change in intensity for the $2\delta C_4N^+_{(QA)}$ overtone when subjected to a) 100 °C in 0.6 M NaOH, and b) 120 °C in 0.6 M NaOH (i) and 120 °C in 7.0 M KOH (ii).]
with benzytrimethylammonium groups, the sulfone moiety is believed to inductively withdraw electron density from the benzy methylene to allow greater susceptibility to nucleophilic attack.

A qualitative assessment of the QA-Radel (2.0) samples resulted in significant discoloration and prominent stiffening of the membrane after exposure to 100 °C in 0.6 M NaOH. Exposure to 120 °C in 0.6 M NaOH yielded a yellowed membrane sample of sufficient brittleness to lose its structural integrity (Figure 6-21).

Figure 6-20: The normalized rates of alkaline degradation of the $2\delta C_4 N_{(QA)}^+$ absorption peaks of QA-Radel (2.0) as measured by ATR-FTIR. a) Measurements of the relative degradation of QA-Radel (2.0) at various time intervals up to 6 h in the denoted alkaline conditions. b) Linear plots showing the rates of degradation of the remaining IEC (mmol/g) after 6 h for each alkaline condition indicated with the corresponding half-life ($t_{1/2}$).

Figure 6-21: Visual illustration QA-Radel (2.0) membrane samples in untreated form and after immersion in the indicated degradation conditions.
Alkaline Stability of QA-PPO Determined by ATR-FTIR

QA-PPO (2.4) is a poly(aromatic) ether akin to QA-Radel, but instead consists of single-ring substituted aromatic ethers. The νCC peak is found at 1601 cm\(^{-1}\) for normalization and the \(2\delta\tilde{C}_4\tilde{N}^{+(QA)}\) absorbances appear bimodal with centers at 962 cm\(^{-1}\) and 970 cm\(^{-1}\) (Figure 6-22).

![Stacked FTIR-ATR spectral overlays of QA-PPO (2.4) membrane samples in untreated form exhibiting the change in intensity for the \(2\delta\tilde{C}_4\tilde{N}^{+(QA)}\) overtone when subjected to a) 100 °C in 0.6 M NaOH, and b) 120 °C in 0.6 M NaOH (i) and 120 °C in 7.0 M KOH (ii).](image)

Figure 6-22: Stacked FTIR-ATR spectral overlays of QA-PPO (2.4) membrane samples in untreated form exhibiting the change in intensity for the \(2\delta\tilde{C}_4\tilde{N}^{+(QA)}\) overtone when subjected to a) 100 °C in 0.6 M NaOH, and b) 120 °C in 0.6 M NaOH (i) and 120 °C in 7.0 M KOH (ii).

The alkaline stability of QA-PPO (2.4) as measured by the \(2\delta\tilde{C}_4\tilde{N}^{+(QA)}\), upon exposure to 100 °C in 0.6 M NaOH for 1, 3, and 6 hours yields remaining absorbances at 960 cm\(^{-1}\) of 87%, 84%, and 83%, respectively. Six hour immersion times at 120 °C in 0.6 M NaOH yields a reduction to 84.0%, and at 120 °C in 7.0 M KOH, slightly more so to 76% (Figure 6-23a).
The rate of degradation of QA-PPO (1.6) results in half-lives of 28.3 hours at 100 °C in 0.6 M NaOH, 23.8 hours at 120 °C in 0.6 M NaOH and 15.4 hours at 120 °C in 7.0 M KOH (Figure 6-23a). The rates closely resemble those of QPE-9 (1.7) and exceed those of QA-Radel as shown in prior $^1$H NMR alkaline degradation studies.

Membrane samples of QA-PPO (1.6) darkened slightly upon exposure to 100 °C in 0.6 M NaOH for 12 hours, with similar results for samples immersed in 0.6 M NaOH at 120 °C for 6
hours (Figure 6-24). Degrading the QA-PPO sample in 7 M KOH at 120 °C for 6 hours yielded the greatest discoloration and stiffening of the membrane.

Summary and Conclusions

A comprehensive evaluation of all of the membrane samples exposed to 100 °C in 0.6 M NaOH and 120 °C in 0.6 M NaOH for 6 h as shown in Table 6-4, suggests that QPE-3 (1.7) and QPE-9 (1.6) have the greatest alkaline stability. However, with the exceptions of QPE-6 (1.2) (due to low M_w) and QA-Radel (due to several additional degradation pathways), QPE-3 (2.3) and QA-PPO (1.6) cannot be discounted as AEMs with alkaline resistance given that greater IECs are correlated with greater degrees of alkaline degradation. The suggestion is that QA-PPO in an IEC of ~1.6–1.7 mmol/g would have a proportional degree of degradation to QPE-3 (1.7) under the same conditions. It is worth restating that QPE-6 (1.2) should not be discounted as AEM candidate with high alkaline resistance until future studies using membrane samples of higher M_w comparable to the other samples studied can be evaluated using identical FTIR-ATR methods.

An examination of the AEM samples exposed to 120 °C in 7.0 M KOH reveals a similar trend to the milder alkaline conditions with impressive results given the higher temperature and >200-fold excess of alkali to ionic group used. Although a comparison of the effects of different alkali media were not examined, QPE-3 (1.7) and QPE-9 (1.6) showed the greatest sensitivity to increases in temperature, while QA-PPO (1.6) was more responsive to the change in alkali with respect to overall alkaline degradation.
This investigation provided greater insight into a quantitative method of studying AEM performance in alkaline media using ATR-FTIR spectroscopy. A distinct advantage of ATR-FTIR spectroscopy for studying AEMs is the ability to study samples in their solid state, as they would be utilized in an AEMFC. As such, this simple method allows for the examination of any differences to the alkaline stability of AEMs that arise from phase separation and internal dielectric constants.
References


ADVANCED SYNTHETIC DESIGN FOR AEM POLYMER BACKBONES

Introduction

In prior Chapters, compelling evidence was presented to suggest that alkaline stability increases when ammonium cations are shielded with n-alkyl interstitial linkages and/or n-alkyl aliphatic pendants. Similarly, we presented evidence suggesting that poly(phenylene oxide) (PPO) offers a significant advantage over alternative polymer backbones at 120 °C. There are very few examples of n-alkyl interstitial spacer functionalized AEM polymers in the literature primarily due to the crosslinking tendencies of synthetic halogenated polymer intermediates by metal–halogen exchange reactions as shown with the example of a brominated PPO (ArBr-PPO) in Figure 7-1.

Figure 7-1: Crosslinked products of subjecting ArBr-PPO to an alkyl lithium or Grignard
The single existing precedent from Jannash\textsuperscript{1} overcame crosslinking issues with the use of very dilute polymer solutions at -78 °C (presumably due to limited solubility) and large excesses of alkyl lithium reagents to substitute a benzyl-brominated PPO variant. These limitations combined with the lack of progress in the field of n-alkyl functionalization of AEMs since Tomoi’s 2001 article\textsuperscript{2} outlined a need for new polymer chemistry solutions. Specifically, chemistries that could use either existing commercial backbones such as PPO, or the easily-brominated variant, $\text{ArBrPPO}$, to facilitate a metal–halogen exchange and the nucleophilic addition of an n-alkyl interstitial spacer electrophile. Thus a reagent approximating the reactivity of a Grignard reagent with the ability to exchange with electron-rich aryl halides and the steric bulk to avoid typical crosslinking results was needed.

**Oshima Magnesate–Halogen Exchange Reactions**

Koichiro Oshima developed one such solution\textsuperscript{3} on small molecules by expanding earlier work performed by Wittig\textsuperscript{4} on halogen–magnesium exchange reactions with magnesium ‘ate’ complexes of the formula, $\text{R}_3\text{MgLi}$. These lithium trialkyl magnesates are prepared \textit{in situ} by the addition of an alkyl lithium (2 equivalents) to an alkyl magnesium halide (1 equivalent) and generally exhibits fast lithium–halogen exchange with less sensitivity to electronic effects.\textsuperscript{5}
Figure 7-2: Metal–halogen exchange reactions of lithium trialkyl magnesium ate complexes (Oshima magnesate) with various small molecules with differing electronic effects. © American Chemical Society, 2001.²

Figure 7-2 shows several such examples of Oshima’s magnesate–halogen exchange with small molecule halides of varying electronic effects electronic effects. Additionally, Struk developed a practical protocol for preparing magnesate reagents of varying reactivity by substituting the alkyl group of the Grignard reactant for functionalization of 2-methylpyridines.⁶

Figure 7-3: Methodologies developed by Struk for the formation of Oshima magnesates of various reactivities. © Georg Thieme Verlag Stuttgart, 2012.⁶
Successful applications of n-alkyl polymer functionalizations using Oshima magnesates has been demonstrated on crosslinked polymer resins (Figure 7-4a) with a variety of electrophiles (Figure 7-4b) with excellent conversion (Figure 7-4c).\(^6\)

\[\text{c)\ ]

<table>
<thead>
<tr>
<th>Bead size</th>
<th>Reagent</th>
<th>Time</th>
<th>% Br$^+$</th>
<th>% P$^+$</th>
<th>equiv g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-300 µm</td>
<td>i-PrMgCl</td>
<td>5 h</td>
<td>10.6</td>
<td>0.45</td>
<td>0.15</td>
</tr>
<tr>
<td>150-300 µm</td>
<td>α-BuLi</td>
<td>5 h</td>
<td>6.7</td>
<td>2.80</td>
<td>0.90</td>
</tr>
<tr>
<td>150-300 µm</td>
<td>i-Pr(α-Bu)₂MgLi</td>
<td>5 h</td>
<td>0.0</td>
<td>4.20</td>
<td>1.36</td>
</tr>
<tr>
<td>400-500 µm</td>
<td>i-Pr(α-Bu)₂MgLi</td>
<td>12 h</td>
<td>0.0</td>
<td>4.60</td>
<td>1.49</td>
</tr>
<tr>
<td>500-600 µm</td>
<td>i-Pr(α-Bu)₂MgLi</td>
<td>12 h</td>
<td>0.0</td>
<td>4.15</td>
<td>1.34</td>
</tr>
</tbody>
</table>

*Starting bromopolystyrene = 16.0% Br; 0% P. The theoretical maximum phosphorous content in product polymer = 5.1%.*

Figure 7-4: Functionalization of brominated polystyrene crosslinked resins: a) general scheme, b) demonstrated electrophiles that resulted in the desired product, and c) conversion rates for resin beads of various size, under different metal–halogen exchange conditions and duration. © The Royal Society of Chemistry, 2004.\(^7\)
In an attempt to employ the use of Oshima magnesate strategy (Figure 7-5) on a non-resinous polymer, commercial PPO was chosen as a starting point for its proven backbone stability. Next, an aryl bromide intermediate, **ArBr-PPO**, was selected as an intermediate for the reliable conversion rates and selectivity offered over bromination at the benzyl position with NBS and AIBN that often yields inconsistent degrees of functionalization (Df) and a mixture of benzyl- and aryl-brominated products. Treatment of PPO in chloroform (CHCl₃) with a stoichiometric quantity of Br₂ (with respect to the targeted Df) under ambient atmospheric conditions yielded **ArBr-PPO** (¹H NMR shown in Figure 7-6) in the desired Df as described by the literature⁸,⁹ and shown in Figure 7-7.
Figure 7-6: $^1$H NMR (300 MHz, CDCl$_3$) of ArBr-PPO showing unfunctionalized PPO aryl hydrogens and benzyl groups at 6.47 and 2.33 ppm, respectively. Bromine-functionalized aryl hydrogens and benzyl groups appear at 6.11 and 2.10 ppm, respectively.

Figure 7-7: Degree of functionalization observed with respect to Br$_2$ stoichiometry for aryl bromation of PPO to ArBr-PPO.
Next, the Oshima magnesate was prepared with the slow addition of \( n \)-butyl lithium (2 equiv.) to isopropylmagnesium chloride (1 equiv.) at -10 °C in anhydrous THF. The resulting \( i\)-Pr\((n\text{-Bu})_2\text{Mg}^\bullet(\text{LiCl})_2 \) solution was cooled to -78 °C (although -20 °C is sufficient) and to it was slowly added a solution of ArBr-PPO in anhydrous THF. The reaction mixture is then typically warmed to room temperature to presumably result in a magnesate–polymer intermediate complex. However, cooling of the intermediate mixture to -20 °C and subsequently adding the electrophile, 1-bromo-4-chlorobutane, produced little conversion to the desired product, \( \text{Alk}_4\text{Cl-PPO} \).

Further investigation into promoting alkylative substitution by the polymer–magnesate complex revealed that in instances of highly substituted and electron-rich systems (as in the case with our intermediate), the addition of sub-stoichiometric amounts of \( \text{CuCN\bullet2LiCl} \) (0.3 equiv.) improved the efficiency of the trapping reaction with the electrophile (Figure 7-8). The subsequent addition of \( \text{CuCN–2LiCl} \) (0.3 equivalents) effectively promoted the reactivity of the

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Figure 7-8: Bromine–magnesium exchange of highly substituted electron-rich aryl bromides requires the addition of \( \text{CuCN\bullet2LiCl} \) for high conversion yields. © American Chemical Society, 2001.
magnesate–polymer complex toward the selective alkylation of 1-bromo-4-chlorobutane to result in $\text{Alk}_4\text{Cl-PPO}$. Addition of the polymer-magnesate to an electrophile is not limited to the substitution of $n$-halogenated alkanes. In fact, the magnesate–polymer–catalyst complex was treated with allyl bromide to yield an allyl functionalized poly(phenylene oxide) (not shown) but terminal bromination of the alkene proved unsuccessful using BH$_3$–THF/HBr or O$_2$/HBr. Other variants may include those performed on Struk’s resins$^6$ shown in Figure 7-4b.

Figure 7-9 exhibits the $^1$H NMR of $\text{Alk}_4\text{Cl-PPO}$ that is sufficiently soluble in deuterated chloroform for characterization. Aromatic hydrogens corresponding to unsubstituted monomer units appear at 6.46 ppm and those corresponding to substituted hydrogens as a broad singlet at 5.98 ppm. The protium on the $\alpha$-carbon of the alkyl chloride appears at 3.61 ppm and the benzyl protium of the interstitial spacer as a broad peak at 2.85 ppm. Hydrogens corresponding to the remaining benzyl groups (6 H) and the $\beta/\gamma$-hydrogens of the interstitial spacer appear as a multiplet at 1.79–2.17 ppm.

Figure 7-9: $^1$H NMR (360 MHz, CDCl$_3$) spectrum of $\text{Alk}_4\text{Cl-PPO}$ intermediate.
Alkyl chlorides are notoriously difficult to react in substitution reactions in high yields. The difficulty manifested itself in dozens of failed reactions that included tandem Finkelstein reactions, the use of various Cu catalysts, and an assortment of solvents systems and temperatures. After this extensive synthetic optimization period, optimal yields (> 90%) were afforded by the addition of aqueous TMA (45 wt%, 10 equivalents) in N-methyl-2-pyrrolidone (NMP) for 16 h at 70 °C in a pressure vessel (thereby avoiding evaporation of the gaseous trimethylamine) to yield Alk₄TMA-PPO. Interestingly, marginally higher temperatures of 75 °C under these conditions led to undesired Hofmann elimination byproduct of the alkyl chloride starting material.

Figure 7-10: Annotated ¹H NMR (300 MHz, 10% D₂O in DMSO–d₆) spectrum of Alk₄TMA-PPO intermediate.

The Alk₄TMA-PPO product appears as a light yellow hygroscopic polymer with very limited solubility in most commercial deuterated solvents, including the 10% D₂O in DMSO–d₆ mixture for the spectrum shown in Figure 7-10. Due to this limited solubility, successive studies
involving membrane casting, material properties and an alkaline degradation analysis are underway.

Given the early successes of the Oshima magnesate-mediated n-alkyl interstitial functionalization of PPO, applicability of the chemistry to other polymer backbones was examined. SEBS, a synthetic rubber, is the principle polymer backbone of several commercial AEMs and has proven alkaline stability, but its known post-polymer modification chemistry is limited. Specifically, radical-mediated reactions are particularly troublesome due to multiple reaction sites at the benzyl position and aliphatic backbone. Provided that the bromination of SEBS was possible, the halogen-magnesium exchange and subsequent alkylation was expected to be successful (Figure 7-11).

![Figure 7-11: Synthetic strategy for the n-alkyl interstitial spacer functionalization of SEBS.](image)

Precedent for the aryl bromination of SEBS is limited without also brominating at the α-hydrogen of the styrene ring. This undesired secondary bromination is often “solved” in the literature by a successive reduction reaction with LiAlH4 to restore the α-hydrogen and avoid crosslinking in latter metalation reactions. However, a catalytic amount of FeCl3 and Br2 in chloroform under strict anhydrous and light-free conditions was found to result in Br-SEBS as shown in the comparison with SEBS in Figure 7-12.
The procedures for Oshima-Magnesate mediated alkyl functionalization of Br-SEBS and Br-PPO are similar with two differences: (i) the synthesis of Alk₄Cl-SEBS does not require the addition of CuCN–2LiCl as a catalyst for reaction with 1-chloro-4-bromobutane, and (ii) in the absence of using CuCN–2LiCl as a catalyst, reaction temperatures of -20 °C are suitable for both the addition of i-Pr(n-Bu)₂MgLi to Br-SEBS and for the addition 1-chloro-4-bromobutane to the resulting polymer–magnesate complex that results with the substituted product, Alk₄Cl-SEBS (Figure 7-13). Although not attempted, the synthesis of Alk₄TMA-SEBS is expected to be successful under the identical conditions to those described for trimethylamine quaternization of Alk₄TMA-PPO.

Figure 7-12: Annotated ¹H NMR (360 MHz, 10% D₂O in DMSO–d₆) spectrum SEBS and Br-SEBS.
Conclusions

Although further studies are required to evaluate the material and AEM properties of Alk₄TMA-PPO, the results presented show an effective synthetic methodology to impart n-alkyl interstitial spacers on two robust polymer backbone, PPO and SEBS. This accessible modification introduces the potential for added alkaline stability on the polymer backbones (and possibly others) as suggested by small molecule studies in prior chapters.

Figure 7-13: Annotated ¹H NMR (300 MHz, CDCl₃) spectrum of Alk₄TMA-PPO intermediate.
References


AEMFCs for applications in stationary, mobile and aerospace applications continue to provide a viable solution for meeting the growing worldwide energy needs (1.8% YOY) from renewable resources. Research and development in the area of AEMFCs has focused on increasing AEM polymer performance by addressing the underlying causes of alkaline instability. In that quest, measurements of alkaline stability have primarily consisted of secondary measurements of alkaline stability, that is, measurements of mostly ion-exchange capacities and ionic conductivities. Fewer efforts of primary measurements to quantify alkaline stability such as $^1$H NMR, 2D NMR, and FT-IR/Raman spectroscopy have been demonstrated and regularly reproduced. Even more rare have been standardized methods to quantify and compare various iterations of AEM designs to one another. This lack of understanding has led to conflicting reports of stability and a lack of consensus on the comparative alkaline stability of various cation and polymer backbone combinations.
The works presented within this dissertation were an examination and study of the various interrelationships that constitute AEM alkaline degradation (Figure 8-1) with the use of standardized methods, and quantitative spectroscopic techniques. The objectives of the presented studies were to isolate and examine each of the proposed factors contributing to the alkaline degradation of AEMs and to gain insight and develop into new synthetic designs (and chemistries) based on the results.

Figure 8-1: Interrelationship of factors contributing to alkaline degradation in AEMs as summarized by the results presented.
$^1$H NMR Studies of Dissolved AEM Polymers at 80 °C

*In-situ* $^1$H NMR studies of dissolved benzyltrimethylammonium-functionalized AEMs and the small molecule analog, pMeBTMA, at 80 °C was intended to systematically investigate the relative stability of polymer backbones under controlled and reproducible test conditions. Using a mixed solvent system of CD$_3$OD/D$_2$O (3:1), an AEM polymer concentration of 30 mM, and the addition of 20 equivalents (0.6 M overall) of NaOD, allowed a variety of the polymer samples examined to remain dissolved throughout the course of the experiment. Additionally, the inclusion of a non-reactive internal standard for normalization (1,4-dioxane) allowed for the quantitative extraction of degradation kinetics (using pseudo-first order approximations) and the speciation of the degradation byproducts.

Results from *in-situ* $^1$H NMR studies conducted at 80 °C, wherein 20 equivalents of NaOD were used with respect to the AEM concentration, showed the greatest stability arose from the para-substituted styrenic samples, pMeBTMA and QA-Styrene with half lives of 2887 and 231 hours, respectively. QA-PPO displayed modest alkaline hydrolyses with 84.2% of the benzyltrimethylammonium cation remaining after 779 minutes and a half-life of 57.8 hours. QA-PAES, an AEM with relatively desirable membrane properties, showed surprisingly low stability with bimodal degradation kinetics and a primary half-life of 2.7 hours and 9.9% of the benzyltrimethylammonium remaining after 779 minutes. The results clearly gives credence to the contribution of the polymer backbone on alkaline stability of benzyltrimethylammonium functionalities that could be extended to the study of other cations (e.g., imidazoliums, sulfoniums, phosphazeniums, etc.).

The key result for this study, however, was the development of the spectroscopic method to measure AEM degradation under controlled and reproducible test conditions, thereby consistently affording knowledge of benzyltrimethylammonium stability. The approach presented...
empowers the AEMFC research community with a systematic investigation to compare AEM stabilities, identify the products of degradation, while also providing evidence of the underlying cause of degradation.

**1H NMR Studies of Dissolved AEM Polymer at 120 °C**

The in-situ 1H NMR studies conducted at 80°C highlight the utility of small molecule analogs to approximate AEM polymer degradation, and substantiate the contribution of polymer backbones on alkaline stability. An additional emphasis was given to ranking alkaline stability under conditions that would induce such degradation. However, in the case of the pMeBTMA and QA-Styrene samples examined at 80 °C, the overall quantity of alkaline degradation was only nominally significant. Given that comparative degradation rates cannot be readily assessed unless the conditions exist to induce significant degradation, follow-up studies focused on using a similar method at an elevated temperature of 120 °C; designed to induce degradation of both the polymer and tetraalkylammonium cation architecture. Furthermore, polymeric AEMs and small molecule analogs containing combinations of n-alkyl interstitial, and n-alkyl terminal pendant cation spacers were introduced to assess reports that these functionalities increase alkaline stability.

The objectives were focused on identifying specific degradation mechanisms occurring for each sample. Preliminary degradation results showed that n-hexyl terminal pendant spacers decrease the alkaline stability of small molecule AEM analogs, PS, and PPO in the absence of an n-alkyl interstitial spacer. The prevalence of the S_N2_Bn mechanism was greater in PS samples, while PPO samples were more susceptible to the S_N2_NMe mechanism. Hofmann elimination (E2) was predominantly observed in the polymer samples QA6-PS and QA6-PPO, and in no case
existed in greater quantities than either Sn2Bn or Sn2Bn. Small molecule analogs containing a 3-carbon n-alkyl interstitial spacer (ArPrTMA) and one containing both a 3-carbon n-alkyl interstitial spacer and an 6 carbon n-alkyl terminal spacer (ArPrHxDMA) exhibited the greatest stability of all samples examined. Specifically, ArPrTMA yielded an overall degradation of only 12% after 3 hours of alkaline exposure at 120 °C, and only a marginal decrease in degradation with the presence of both spacers (ArPrHxDMA) with 7% overall degradation. Interestingly, a parallel examination of these two small molecules in the absence of CD3OD (only D2O and KOD) revealed that the reduced dielectric constant of the mixed solvent system leads to a three-fold greater rate of degradation over purely aqueous systems. It appears that both interstitial spacers and terminal pendant n-alkyl moieties increase the stability of tetraalkylammonium cations, but the interstitial spacer has the greatest influence on eliminating the ubiquitous benzyl substitution observed in BTMA small molecules and polymers.

One particularly interesting observation was the inverse relationship between the overall degradation rates of PS and PPO at 80 °C and 120 °C. At 80 °C, QA-PPO degrades more rapidly than QA-PS, while the inverse is true at 120 °C. This curious result propelled the examination of a new possible mechanism, a 1,4-emilination that may be activated at higher temperatures. Examination of pMeBTMA and a simple small molecule analog lacking acidic α hydrogens (ArBTMA), indeed showed faster alkaline degradation of pMeBTMA that is suggestive of the activation of additional mechanism of degradation.

This conclusion has potential consequences for BTMA poly(styrene)-based polymers in AEMFC high-temperature applications. Although more studies are needed to confirm the findings and given the added stability shown by the inclusion of n-alkyl interstitial spacers, it was suggested BTMA-poly(styrene) polymers are replaced with more robust polymer backbones and new chemistries were developed for synthesizing AEMs with n-interstitial spacers.
ATR-FTIR Studies of AEM Samples

While quantitative methods to determine the alkaline stability of dissolved AEMs are useful and versatile, AEMs are utilized in the solid state within AEMFCs where morphological effects (e.g., phase separation) may have some influence. Therefore, developing a method of study for the quantitative assessment of alkaline stability in solid membrane samples was key to gain an understanding of any contributions gained by morphological effects and solvation. ATR-FTIR spectroscopy enabled the study of solid fluorinated and non-fluorinate AEM samples using a simple method in purely aqueous media. Incorporating meticulous works performed by Mendoza on AEM degradation using FTIR and Raman spectroscopy, the samples of interest were appropriately characterized for pseudo-constant normalization absorbances and peaks pertaining to tetraalkylammonium vibrations in order to quantify degradation of the cation.

Analysis of the membrane samples exposed to 100 °C in 0.6 M NaOH, and those exposed to 120 °C in 0.6 M NaOH for 6 h suggested that benzyltrimethylammonium-functionalized QPE-3 (1.7) and QPE-9 (1.6) exhibit greater stability than QA-PPO (1.6)—a result that may be the result of phase separation. AEM samples of higher IECs, as in the case of QPE-3 (1.7) and QPE-3 (2.3), were observed to have a higher degree of alkaline degradation. Finally, QA-PPO (1.6) exhibited an order of magnitude greater alkaline stability in membrane form over those dissolved and analyzed by $^1$H NMR at 120 °C.

The use of ATR-FTIR spectroscopy to study solid membranes affords AEMFC researchers yet another simple spectroscopic technique and method to quantitatively assess alkaline stability.
**Oshima Magnesate Mediated N-alkyl functionalization of PPO and SEBS**

Prior results yielded compelling evidence that alkaline stability increases when ammonium cations are shielded with n-alkyl interstitial linkages and/or n-alkyl aliphatic pendants. Likewise, the data indicates that PPO provides the greatest stability at 120 °C of the polymers that have potential for post-polymer synthetic modifications in addition to desirable membrane properties. Given the failures of functionalizing brominated PPO backbones (ArBrPPO) with either Grignard or organolithium reagents (due to crosslinking), alternative synthetic approaches were sought. Oshima magnesate chemistry afforded the ability to perform halogen–magnesium exchanges on ArBrPPO intermediates for selective alkylation with 1-bromo-4-chlorobutane to install an n-alkyl interstitial spacer. The resulting precursor was aminated with aqueous TMA in NMP at 70 °C to afford the novel Alk₄TMA-PPO polymer containing an n-alkyl interstitial spacer. Given this success, the methodology was applied to SEBS by first, selectively brominating the polymer with Br₂ and FeCl₃ and following with a sequential treatment using the same Oshima magenesate methodology applied to ArBrPPO to afford Alk₄Cl-SEBS as a precursor for future studies.

While the Oshima magnesate methodology proved successful for the installation of an n-alkyl interstitial spacer on AEM polymer backbones, successive experiments are required to examine the membrane properties and alkaline degradation performance of these new synthetic targets.
Appendix A

\(^1\)H NMR DETERMINATION OF ALKALINE STABILITY OF AEMS FUNCTIONALIZED WITH BTMA CATIONS AT 80 °C

Figures and Tables of Data for Kinetic NMR Experiments

Table A-1: Percent quaternary-ammonium functionalities remaining of QA-PAES in CD\(_3\)OD–D\(_2\)O (3:1), 1,4-dioxane (internal standard), KOD (20 equiv.), from 7–779 min in ~64 min intervals at 80 °C.

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Figure A-1: Stacked overlay of $^1$H NMR spectra of QA-PAES in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), without KOD, from 7–779 min in ~64 min intervals at 80 °C.

Table A-2: Percent quaternary-ammonium functionalities remaining of QA-PAES in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), without KOD from 7–779 min in ~64 min intervals at 80 °C.

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Figure A-2: Stacked overlay of $^1$H NMR spectra of QA-Styrene in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), KOD (20 equiv.), from 7–779 min in ~64 min intervals at 80 °C.

Table A-3: Percent quaternary-ammonium functionalities remaining of QA-Styrene in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), KOD (20 equiv.), from 7–779 min in ~64 min intervals at 80 °C.

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Figure A-3: Stacked overlay of $^1$H NMR spectra of QA-Styrene in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), without KOD from 7–779 min in ~64 min intervals at 80 °C.

Table A-4: Percent quaternary-ammonium functionalities remaining of QA-PPO in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), KOD (20 equiv.), from 7–779 min in ~64 min intervals at 80 °C.

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Figure A-4: Stacked overlay of $^1$H NMR spectra of QA-PPO in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), without KOD from 7–779 min in ~64 min intervals at 80 °C

Table A-5: Percent quaternary-ammonium functionalities remaining of QA-PPO in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), without KOD from 7–779 min in ~64 min intervals at 80 °C.

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Figure A-5: Stacked overlay of $^1$H NMR spectra of pMeBTMA in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), KOD (20 equiv.), from 7–779 min in ~64 min intervals at 80 °C.

Table A-6: Percent quaternary-ammonium functionalities remaining of pMeBTMA in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), KOD (20 equiv.), from 7–779 min in ~64 min intervals at 80 °C.

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<td>99.52%</td>
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<td>1.3%</td>
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<td>99.34%</td>
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<td>98.9%</td>
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<tr>
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<tr>
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</tr>
<tr>
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<td>99.50%</td>
<td>100.4%</td>
<td>99.5%</td>
<td>0.9%</td>
</tr>
</tbody>
</table>
Figure A-6: Stacked overlay of $^1$H NMR spectra of pMeBTMA in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), without KOD from 7–779 min in ~64 min intervals at 80 °C.

Table A-7: Percent quaternary-ammonium functionalities remaining of pMeBTMA in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), without KOD from 7–779 min in ~64 min intervals at 80 °C.

<table>
<thead>
<tr>
<th>time (m)</th>
<th>trial 1</th>
<th>trial 2</th>
<th>trial 3</th>
<th>avg. (three trials)</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
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<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>71.5</td>
<td>99.4%</td>
<td>99.1%</td>
<td>99.9%</td>
<td>99.5%</td>
<td>0.4%</td>
</tr>
<tr>
<td>135.8</td>
<td>98.5%</td>
<td>99.8%</td>
<td>98.7%</td>
<td>99.0%</td>
<td>0.7%</td>
</tr>
<tr>
<td>200.2</td>
<td>99.9%</td>
<td>99.2%</td>
<td>100.1%</td>
<td>99.7%</td>
<td>0.5%</td>
</tr>
<tr>
<td>264.5</td>
<td>100.5%</td>
<td>98.2%</td>
<td>99.7%</td>
<td>99.4%</td>
<td>1.2%</td>
</tr>
<tr>
<td>328.8</td>
<td>101.3%</td>
<td>100.1%</td>
<td>99.1%</td>
<td>100.2%</td>
<td>1.1%</td>
</tr>
<tr>
<td>393.2</td>
<td>101.4%</td>
<td>99.1%</td>
<td>98.9%</td>
<td>99.8%</td>
<td>1.4%</td>
</tr>
<tr>
<td>457.5</td>
<td>100.7%</td>
<td>99.0%</td>
<td>99.8%</td>
<td>99.8%</td>
<td>0.9%</td>
</tr>
<tr>
<td>521.8</td>
<td>101.0%</td>
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<td>99.1%</td>
<td>99.8%</td>
<td>1.0%</td>
</tr>
<tr>
<td>586.0</td>
<td>99.4%</td>
<td>99.4%</td>
<td>100.2%</td>
<td>99.7%</td>
<td>0.5%</td>
</tr>
<tr>
<td>650.5</td>
<td>100.2%</td>
<td>99.9%</td>
<td>101.0%</td>
<td>100.3%</td>
<td>0.5%</td>
</tr>
<tr>
<td>714.8</td>
<td>102.9%</td>
<td>99.1%</td>
<td>100.2%</td>
<td>100.7%</td>
<td>2.0%</td>
</tr>
<tr>
<td>779.2</td>
<td>100.5%</td>
<td>99.2%</td>
<td>99.8%</td>
<td>99.8%</td>
<td>0.6%</td>
</tr>
</tbody>
</table>
Figure A-7: $^1$H NMR Spectrum of chloromethylated Radel.
Figure A-8: $^{13}$C spectrum of chloromethylated Radel.
Figure A-9: $^1$H NMR spectrum of QA-PAES.
$^{13}$C NMR (CH$_3$)$_2$SO, 300 MHz

Figure A-10: $^{13}$C NMR Spectrum of QA-PAES.
Figure A-11: $^1$H NMR spectrum of QA-PPO.
$^{13}$C NMR (CH$_3$)$_2$SO, 300 MHz

Figure A-12: $^{13}$C NMR spectrum of QA-PPO.
$^{1}H$ NMR (CD$_3$OD), 300 MHz)

Figure A-13: $^{1}H$ NMR spectrum of QA-Styrene.
Figure A-14: $^{13}$C NMR spectrum of QA-Styrene.
Figure A-15: $^1$H NMR spectrum of pMeBTMA.
$^{13}$C NMR (CD$_3$OD), 300 MHz

Figure A-16: $^{13}$C NMR spectrum of pMeBTMA.
Appendix B

$^1$H NMR DETERMINATION OF ALKALINE STABILITY OF TETRAALKYLAMMONIUM CATIONS AT 120 °C

Figure B-1: Stacked overlay of $^1$H NMR spectra of pMeBTMA in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), with NaOD (20 equiv.), from 0–3 h at 120 °C.
Figure B-2: Stacked overlay of $^1$H NMR spectra of QA-PPO in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), NaOD (20 equiv.) from 0–3 h at 120 °C.

Figure B-3: Stacked overlay of $^1$H NMR spectra of QA6-PS in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), NaOD (20 equiv.) from 0–3 h at 120 °C.
Figure B-4: Stacked overlay of $^1$H NMR spectra of pMeBQA6 in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), NaOD (20 equiv.) from 0–3 h at 120 °C.

Figure B-5: Stacked overlay of $^1$H NMR spectra of QA-PS in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), NaOD (20 equiv.) from 0–3 h at 120 °C.
Figure B-6: Stacked overlay of $^1$H NMR spectra of **ArPrTMA** in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), NaOD (20 equiv.) from 0–3 h at 120 °C.

Figure B-7: Stacked overlay of $^1$H NMR spectra of **ArPrHxDMA** in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), NaOD (20 equiv.) from 0–3 h at 120 °C.
Figure B-8: Stacked overlay of $^1$H NMR spectra of QA6-PPO in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), NaOD (20 equiv.) from 0–2 h at 120 °C.

Figure B-9: Stacked overlay of $^1$H NMR spectra of ArPrTMA in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), NaOD (20 equiv.) from 0–3 h at 120 °C.
Figure B-10: Stacked overlay of $^1$H NMR spectra of ArBTMA in CD$_3$OD–D$_2$O (3:1), 1,4-dioxane (internal standard), NaOD (20 equiv.) from 0–3 h at 120 °C.

Figure B-11: $^1$H NMR spectrum of pMeBQA6.
Figure B-12: $^1$H NMR spectrum of pMeBTMA.
Figure B-13: $^1$H NMR spectrum of ArPrHxDMA.
Figure B-14: $^1$H NMR spectrum of BTMA-PS.
Figure B-15: $^1$H NMR spectrum of QA6-PS.
Figure B-16: $^1$H NMR spectrum of ArPrTMA.
Figure B-17: $^1$H NMR spectrum of ArBTMA.
Figure B-18: $^1$H NMR spectrum of BTMA-PPO.
Figure B-19: $^1$H NMR spectrum of QA6-PPO.
Figure B-20: Left: CAD dimensions of custom milled aluminum block for heating pressure NMR tubes. Right: Schematic of custom heating block for pressure NMR tubes.
Figure B-21: Representative samples in pressure vessels for $^1$H NMR analysis at 120 °C.
Appendix C

$^1$H NMR and ATR-FTIR Determination of Alkaline Stability in Fluorinated Polymers

$^1$H NMR Degradation Study of Dissolved QPE3-2.3 in Alkaline Solution at 100 °C

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>δ (ppm)</th>
<th>t = 0 min 25 °C</th>
<th>t = 30 min 100 °C</th>
<th>Relative Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA</td>
<td>N(CH$_3$)$_3$</td>
<td>2.16-2.23</td>
<td>2.4%</td>
<td>4.9%</td>
</tr>
<tr>
<td>QA</td>
<td>CH$_2$N(CH$_3$)$_3$</td>
<td>2.94-3.18</td>
<td>100%</td>
<td>89.8%</td>
</tr>
<tr>
<td>Fluorene Ether $H_1$</td>
<td>6.38-6.55$^1$</td>
<td>1.1%</td>
<td>6.0%</td>
<td></td>
</tr>
</tbody>
</table>

- TMA is present upon addition of NaOD at 25 °C
- Benzy1 substitution is the only observed mechanism

$t_{50^0C} = 193$ min

Figure C-1: $^1$H NMR alkaline degradation examination and analysis of QPE-3 (2.3) at 100 °C for 30 min.
Figure C-2: $^1$H NMR alkaline degradation examination and analysis of QPE-6 (1.2) at 100 °C for 30 min.
Figure C-3: $^1$H NMR alkaline degradation examination and analysis of QA-PPO (1.6) at 100 °C for 30 min.
Figure C-4: $^1$H NMR alkaline degradation comparison of half-lives determined at 120 °C and 100 °C for selected Miyatake polymers.
To develop the quantitative analysis method, a number of standard polymers of varying IEC can be prepared and spectra collected from the solid membrane. Specified absorption bands are identified and the peak heights or areas calculated for the various standards. The resulting quantitative data is examined by least squares analysis based on Beer's Law.

\[ A = \text{abs.} \]

- \( A \) = absorbance;
- \( a \) = molar absorptivity of the analyte (a constant)
- \( b \) = pathlength
- \( c \) = analyte concentration.

- Refractive indices of the ATR crystal and the sample
- Angle of incidence of the IR beam
- Critical angle
- Depth of penetration
- Wavelength of the IR beam
- Effective path length—calculated (~500 nm)
- Number of reflections
- Quality of the sample contact with ATR crystal

Figure C-5: Principles of ATR-FTIR spectroscopy.
Figure C-6: Stacked ATR-FTIR full spectra of QPE-3 (1.7) under the alkaline degradation conditions indicated.
Figure C-7: Stacked ATR-FTIR full spectra of QPE-3 (2.3) under the alkaline degradation conditions indicated.
Figure C-8: Stacked ATR-FTIR full spectra of QPE-9 (1.3) under the alkaline degradation conditions indicated.
Figure C-9: Stacked ATR-FTIR full spectra of QPE-6 (1.2) under the alkaline degradation conditions indicated.
Figure C-10: Stacked ATR-FTIR full spectra of QA-Radel under the alkaline degradation conditions indicated.
Figure C-11: Stacked ATR-FTIR full spectra of QA-PPO under the alkaline degradation conditions indicated.
### FTIR Frequencies of Common Tetraalkylammonium Ions

**Table 1. Frequencies and Assignments of Substituted Tetramethyl-Ammonium Ions**

<table>
<thead>
<tr>
<th>R-</th>
<th>N+(CH₃)₄</th>
<th>δ(CN⁺)</th>
<th>(\nu) (cm⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>O</td>
<td>921 s</td>
<td>461 w</td>
<td></td>
</tr>
<tr>
<td>CH₃-(CH₃)₂-CO-CH₃-CH₃-</td>
<td>915 s</td>
<td>945 s</td>
<td>961 vs</td>
</tr>
<tr>
<td>CH₃-C-CH₃-O-CH₃-CH₃-</td>
<td>915 s</td>
<td>945 s</td>
<td>961 vs</td>
</tr>
<tr>
<td>S</td>
<td>912 m</td>
<td>455 m</td>
<td></td>
</tr>
<tr>
<td>O-CH₃-CH₃-</td>
<td>912 m</td>
<td>945 s</td>
<td>961 vs</td>
</tr>
<tr>
<td>CH₃-CH₃-</td>
<td>912 m</td>
<td>945 s</td>
<td>961 vs</td>
</tr>
<tr>
<td>CH₃-(CH₃)₂-CO-CH₃-CH₃-</td>
<td>915 s</td>
<td>945 s</td>
<td>961 vs</td>
</tr>
<tr>
<td>CH₃-</td>
<td>915 m</td>
<td>927*</td>
<td>945 s</td>
</tr>
</tbody>
</table>

\(\nu = \text{stretching; } \delta = \text{bending; } s = \text{strong; } \text{vs} = \text{very strong; } m = \text{medium; } w = \text{weak.}

* Frequency assigned in this region by Lorenzelli and Müeller [2].

Three peaks result for each substitution due to degenerate \(\nu_{\text{asym}}\text{CN}^+\) asymmetric stretching.

* * *

**Spectrochimica Acta Part A** 1968, 24(6), 786–788

Figure C-12: FTIR frequencies of common tetraalkylammonium ions.
Infrared Spectroscopy for Polymer Applications – Degradation of Perfluorinated PEMs in Fenton’s Reagent

Highlighted carbon-fluorine band (C–F) in the IR spectra over time showing (a) at 0 V and (b) -0.9 V. E. vs. RHE. (c) The rate of (C–F) degradation (resulting from changes to 1150 cm\(^{-1}\) absorption band) increases as higher potential is applied.

PEMs degrade faster with applied potentials and electrochemical degradation rate increased when higher potentials were applied.

*Polymer Degradation and Stability* 2009, 94(10), 1707–1713

Figure C-13: FTIR frequencies of fluorinated aliphatic chains.
# Infrared Spectroscopy for Polymer Applications – Vibrational Assignments for Q-PVBC and Q-SEBS

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>Description of Benzene Vibration</th>
<th>Functional Group</th>
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<tr>
<td>1580-1720</td>
<td>ν_{c=O}CO₂</td>
<td></td>
<td>Bicarbonate anion</td>
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<tr>
<td>1616</td>
<td>νCC</td>
<td>Ring stretching (8a)</td>
<td>Styrene-QA</td>
</tr>
<tr>
<td>1512</td>
<td>(νCC + δCC)</td>
<td>Ring stretching + deformation (19a)</td>
<td>Styrene - R</td>
</tr>
<tr>
<td>1488</td>
<td>δCH₂</td>
<td></td>
<td>QA</td>
</tr>
<tr>
<td>1460</td>
<td>δCH₂</td>
<td></td>
<td>Aliphatic backbone</td>
</tr>
<tr>
<td>1384</td>
<td>δCH₂, γCH₂</td>
<td></td>
<td>Bicarbonate anion</td>
</tr>
<tr>
<td>1284</td>
<td>1HCO₂⁻**</td>
<td></td>
<td></td>
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<tr>
<td>1244</td>
<td>δCH</td>
<td>CH in-plane deformation (*)</td>
<td>Styrene-QA</td>
</tr>
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<td></td>
</tr>
<tr>
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<tr>
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<td>δCH</td>
<td>CH in-plane deformation</td>
<td>QA</td>
</tr>
<tr>
<td>1020</td>
<td>δCH₂</td>
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<td>QA</td>
</tr>
<tr>
<td>976</td>
<td>ν_{c=O}C=N</td>
<td></td>
<td>QA</td>
</tr>
<tr>
<td>925</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>889</td>
<td>2 * δC,N</td>
<td></td>
<td>QA</td>
</tr>
<tr>
<td>858</td>
<td>γCH</td>
<td>CH out-of-plane deformation (10b)</td>
<td>Styrene-QA</td>
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<tr>
<td>832</td>
<td>γCH</td>
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<td>Styrene</td>
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<tr>
<td>760</td>
<td>γCH</td>
<td>CH out-of-plane deformation (11)</td>
<td>Styrene</td>
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<td>720</td>
<td>δCH₂</td>
<td>Aliphatic-Styrene</td>
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</tr>
<tr>
<td>701</td>
<td>δCC</td>
<td>Ring deformation (4)</td>
<td>Styrene</td>
</tr>
</tbody>
</table>

* ν – normal mode
* δ – bending mode
* The symbols used are: ν, stretching; δ, in-plane deformation; γ, out-of-plane deformation.
* Wilson number indicated for reference purposes.
* Mixed styrene functionality has distinct benzene vibrations: QA, quaternary ammonium; R, general benzene mode.

Figure C-14: Complete FTIR frequency assignments for QA-PVBC and QA-Radel.
VITA

Sean A. Nuñez, Ph.D.

Sean Andrew Nuñez was born in Manhattan, New York. After completing his work at Arlington High School, Lagrangeville, New York, in 2002, he entered Dutchess Community College (S.U.N.Y.) where he earned a degree in Liberal Arts Science (A.S.). He was accepted at the State University at Buffalo (S.U.N.Y.) in 2005 where he earned a double degree in Chemistry (B.A.) and Medicinal Chemistry (B.S.). In 2008, he was accepted into the Chemistry Department at The Pennsylvania State University where he earned a degree in Organic Chemistry (M.S.). Sean then was accepted to the Materials Science and Engineering Department where he proceeded to procure a Ph.D. in 2015.