The influence of an alkyl side chain attached to the nitrogen-centered cationic group on the properties and chemical stability of poly(phenylene oxide) based anion exchange membrane is the focus of this study. Two different cationic groups were investigated: one is the common benzyl trimethyl ammonium (BTMA) cationic group, and the other is benzyl dimethyldecyl ammonium with a C10 alkyl chain pendant to the cation-centered quaternary nitrogen. Swelling measurements were performed over a range of temperatures for both types of samples. Water uptake was found to be lower for the C10 (21 wt%) membrane than for the BTMA (53 wt%) membrane, due to the hydrophobicity of the long alkyl side chain and hydrophilic/hydrophobic phase separation. Degradation measurements under alkaline conditions indicated that the C10 membrane degraded more slowly than the BTMA sample at 60 °C. At 80 °C the C10 sample showed degradation likely due to the irreversible swelling and poor mechanical properties of the C10 membrane at high temperature due to the weakening of the poly(phenylene oxide) backbone interchain interactions by the C10 pendant group.

Another challenge regarding AEMs is their low ionic conductivity. High anion conductivity will improve the performance of AEMFCs mainly through lower ohmic losses. Clearly, one of the challenges in AEMFC technology is to develop new AEMs with high ionic conductivity due to high phase separation. Li, et al. has reported on a synthesis of multiple long alkyl side chains from C6 to C16 attached to PPO membrane. In this research, they showed that these types of membranes with these range of alkyl side chains showed reasonable stability up to 2000 h in 1 M NaOH at 80 °C. The C16 membranes having the longest chain showed lower water uptake, and higher hydroxide conductivity, compared to C6 membranes. However, C16 membrane was challenging in terms of forming robust film, probably due to poor compatibility between long alkyl side chain and stiff polymer backbone structure. Dang et al. reported the synthesis of QA groups attached to PPO either directly in benzylic positions, or via flexible pentyl and heptyl spacer units and in addition the configured with or without octyl extender chains pendant to the QA groups. They determined from analysis of small-angle X-ray scattering data that the flexible spacer units greatly facilitated efficient ionic phase separation, regardless of the presence of the extender chain. Despite a markedly lower water uptake, AEMs configured with additional extender chains still reached a high conductivity, 0.07 S cm−1 at 80 °C. They found that the addition of a spacer between the polymer backbone and QA group increased the thermal stability, while the addition of an extender seemed to decrease the thermal stability. This study reports on the difference in the characteristics of benzyl trimethylammonium (BTMA) and benzyl dimethyldecyl ammonium C10 pendant cationic groups attached to poly(phenylene oxide) backbone-based membranes. Poly(phenylene oxide) was chosen as the polymer backbone due to its good chemical and thermal stability in alkaline media, while the C10 alkyl chain pendant to the cationic group was selected to induce phase separation in the material. The long alkyl side chain and phase separation increases the stability and conductivity of the reported material.

Experimental

Synthesis.—Scheme 1 shows the chemical structure of a QA based AEMs, synthesized as described in previous reported methods. 

The worldwide demand for clean energy conversion technologies and renewable energy systems is growing apace. Research on fuel cell devices for a variety of applications has grown considerably in recent years, mostly due to fuel cells’ high thermodynamic energy efficiency (83–97%) and zero pollution. Among the various kinds of renewable energy conversion systems, fuel cells, or specifically polymer electrolyte fuel cells (PEFCs) incorporating proton or anion exchange membranes, have been developed for residential, portable, and transportation applications. Alkaline fuel cells using anion exchange membranes (AEM) have several potential advantages over proton exchange membrane fuel cells (PEMFC). The drawbacks of PEMFCs are mostly associated with the state-of-the-art Nafion membrane that operates under acidic conditions which require corrosion resistant catalysts and cell hardware. The basic environment of alkaline fuel cells offers important benefits, such as enhanced kinetics for oxygen reduction, reduced corrosion of the fuel cell components, and the use of low loadings of noble metal catalyst or the use of non-precious catalysts for hydrogen oxidation. The advantages of AEMFCs have proven to be alluring to the research community and there has been a push toward commercially viable devices. Currently, there are many obstacles to overcome in AEMFC technology, mainly regarding the chemical stability of the AEM backbone and the cationic groups under alkaline, thermal, and electrochemical conditions. The main degradation pathways for quaternary ammonium groups, (the most commonly used cationic groups in AEMs), under high pH conditions were found to be Hofmann elimination, nucleophilic substitution and ylide intermediate formation.

Proper molecular design of the backbone and tether can be used to enhance the alkaline stability of the cationic groups. Such strategies include attaching cationic groups in the benzyllic positions to avoid Hofmann elimination, adding electron-donating groups near the cationic group for stabilization, and attaching bulky shielding substituents near the cations to decrease the potential of hydroxide attack. Due to the Hofmann elimination mechanism, quaternary ammonium (QA) groups were usually attached in benzylic positions, however, Hibbs reported enhanced alkaline stability by inserting an alkyl or alkyl ether spacer chains, to separate the aromatic backbone and the QA groups.
Attenuated total reflection fourier transform infra-red (ATR-FTIR).—ATR-FTIR spectra of the membranes were obtained on a Nicolet iS5 spectrometer equipped with a DTGS detector. A reflection ATR accessory equipped with a diamond crystal at an incident angle of 45° was used. The membrane sample was pressed to the crystal by a clamp-kit to ensure reproducible contact between the sample and the ATR crystal. The spectrum was collected after 128 scans with a resolution of 4 cm⁻¹. This mode of FTIR was preferred for two main reasons; the simplicity of the measurement in this configuration and the assumption that the initial degradation process will occur predominantly on the surface of the membrane.

Water uptake.—Water uptake of HCO₃⁻ form membranes was defined as the weight ratio of the absorbed water to that of the dry membrane, as given by:

\[ W(\%) = \left( \frac{m_w - m_d}{m_d} \right) \times 100 \]

where, \( m_w \) and \( m_d \) are the mass of the membrane, prior to and subsequent to water absorption, respectively. The procedure of weighing wet membranes includes surface water elimination by a rapid surface drying with a Kimwipe followed by drying in a vacuum oven for 24 hours at a temperature of 60°C.

High resolution scanning electron microscopy (HRSEM).—High resolution scanning electron microscopy (HRSEM) analysis was carried out using a Zeiss Ultra-Plus FE-SEM. Samples of the membrane were cut into squares of approximately 5 mm × 5 mm and were fixed to an aluminum stub with a double-sided conductive tape. Subsequently, the samples were sputter coated with carbon to decrease charging of the sample. Cross-section was done by freeze fracturing consequently, the samples were sputter coated with carbon to decrease charging of the sample. The observation was conducted with an acceleration voltage of 3 kV.

Atomic force microscopy (AFM).—Atomic force microscopy (AFM) in tapping mode was performed with an Agilent Technologies 5100 SPM, using micro-fabricated cantilevers with a force constant of approximately 40 N m⁻¹.

Mechanical properties.—Tensile measurements were performed on samples equilibrated in liquid water and ambient air at room temperature. The wet membranes were cut into a dumbbell shape (12 mm × 3 mm in test area) and tensile measurements were performed on an Instron-5866 instrument at a crosshead speed of 5 mm/min at room temperature (25°C). The wet membrane samples were immersed in deionized water for 24 h before measurement.

Ionic conductivity.—The ionic conductivity (\( \sigma \)) of HCO₃⁻ forms of the membrane (size: 10 mm × 20 mm) was measured by two probe in-plane impedance spectroscopy using \( \sigma = \frac{d}{L_{\text{w}} W R} \) (d is the distance between reference electrodes, \( L_{\text{w}} \), and \( W \) is the thickness and width of the membrane, respectively). The membrane impedance was measured over the frequency range from 10 kHz to 10 mHz, with an AC amplitude of 10 mV and a 0 mV DC bias, using an PARSTAT 2273 (Princeton Applied Research). The resistance of the membranes was determined from the real part of the impedance at the minimum imaginary value. The measurements were conducted under fully hydrated conditions, with the sample membranes being immersed in water at elevated temperatures.

Ion exchange capacity (IEC).—Ion exchange capacity was measured using potentiometric method. Using silver electrode, and measuring the potential versus calomel electrode. This method enhances the accuracy of the titration method for IEC determination, especially when small quantities are measured.

A membrane sample (in Cl⁻ form) of 30 × 30 mm², with thickness of 0.070–0.10 mm was immersed in 50 mL 0.2 M KNO₃ solution for 24 h (the solution was changed 3 times) and titrated with 0.02–0.1 M AgNO₃. The IEC was calculated via:

\[ \text{IEC} = \frac{\Delta V_{\text{AgNO3}} C_{\text{AgNO3}}}{m_d} \]

where, \( m_d \) is the mass of the dry membrane (in the Cl⁻ form) dried at 60°C in a vacuum oven for 24h, \( \Delta V_{\text{AgNO3}} \) is the consumed volume of AgNO₃ solution and \( C_{\text{AgNO3}} \) is the concentration of AgNO₃ solution.

Results and Discussion

Surface and cross-sectional images of the membranes.—The surface and cross-sectional images of the membranes are presented in Figure 1. The surfaces were found to be smooth and uniform, while showing only minor surface defects. Some small pits were observed in both of the samples, probably due to the solvent casting procedures during membrane formation. Significant differences were detected in the cross-sectional images of the membranes: the C10 membrane displayed some microstructure upon fracture, while BTMA did not display any defined structure.

This data may indicate that the tether and the cationic group type has an influence on the inner structure of the membrane, or at least on the mechanical properties of the sample during fracture. This type of cation seems to promote some structure in the material, which may influence the mechanical properties and transport characteristics.

ATR-FTIR spectroscopic analysis.—The chemical structure of the polymers was investigated by FTIR and the absorption spectra of the membranes are shown in Figure 2. Both membranes have similar FTIR spectra, and only a few minor changes regarding the difference
in the cationic groups could be measured. The C10 membrane has peaks in the 2955–2858 cm$^{-1}$ region, dominated by -CH$_2$- symmetric and asymmetric stretches. The peak at 1305 cm$^{-1}$ is assigned to the asymmetric vibrational mode of the ether linkage, while the C$_4$N$^+$ vibrations originating from the quaternary ammonium moieties are located at 918–982 cm$^{-1}$. The absorption spectrum of BTMA has IR bands in the 1420 cm$^{-1}$ and 1600 cm$^{-1}$ regions, dominated by C-C aromatic stretching.

Water uptake.—The water uptake and conductivity of the membrane are interconnected and have a major effect on the performance and stability of the fuel cell. Understanding and controlling the complexity associated with water management is a great challenge in developing an efficient alkaline fuel cell systems. Thus, in order to improve both conductivity and chemical stability of the polymer, the water-related properties of the membranes should be considered.

It is well-known that AEMs in the hydroxide form quickly convert to the less-conductive CO$_3^{2-}$ and HCO$_3^-$ forms when exposed to CO$_2$. Thus, in order to avoid confusion in the interpretation of the results to due mixed counterion forms, water uptake was conducted in the HCO$_3^-$ form of the samples. Figure 3 shows that water uptake of both membranes increases with temperature. The water uptake of the C10 membrane is lower than that of the BTMA membrane almost through the entire range of temperatures, likely due to the hydrophobicity of the C10 side chain and microphase separated structure of the C10 membrane. However, when the C10 membrane reached 80°C, a drastic increase in water uptake occurred. This behavior is in contrast to the water uptake of the BTMA membrane that gradually increased across the temperature range of 25–80°C, without any detectable sudden increase as was recorded with the C10 membrane.

Atomic force microscopy (AFM) imaging.—Tapping mode phase images of the membrane surfaces were recorded at 25°C over a 250 nm × 250 nm surface area. The dark regions shown in Figure 4 correspond to the soft hydrophilic ionic groups and the bright domains correspond to the rigid structures of the aromatic backbones. The hydrophilic/hydrophobic structure is related to the different side chains of the membranes. Compared to other anion exchange membranes, these membranes demonstrated a moderate degree of phase separation with small isolated hydrophilic domains.

Figure 4 demonstrates two different types of surface structures: BMTA has a short and shapeless hydrophilic structure, while C10 membrane is characterized by more defined, long and thin (5–12 nm width) hydrophilic channels. There is a slight visible difference in the hydrophilic/hydrophobic regions between the membranes and the C10 membrane seems to have more defined, organized and systematic structure.

Alkaline stability.—The membranes were immersed in an aqueous KOH (1 and 10 M) solutions at 60°C and 80°C for up to 1,000 hours. The solution of 1 M KOH was chosen in order to mimic the fuel cell conditions, while the high alkalinity of 10 M KOH was chosen for accelerated degradation conditions. Prior to each measurement, the membrane samples were removed from the solution and washed.
thoroughly by DI water until all KOH residues were removed. After rinsing, the alkaline stabilities of the AEMs were evaluated with HRSEM and FTIR.

**FTIR spectroscopy studies.**—Chemical changes in the structure of the membranes during alkaline stability studies were studied by FTIR (spectra are shown in Figure 5). In order to track changes in the quaternary ammonium group, two main peaks were selected: the QA group at 920 cm\(^{-1}\) as the functional group of interest, and the C-C aromatic group positioned at 1600 cm\(^{-1}\), representing a stable and durable chemical group, that will function here as a reference peak. The relative abundance of chemical groups can be quantified from the intensity of the FTIR absorption peaks. The ratio between these intensities reflects changes in the chemical structure of the membranes. As specified earlier, the alkaline stability of these AEMs was investigated under harsh pH conditions at 60°C in order to facilitate the degradation process. It can be observed in Figure 5 that the intensity of the QA band, corresponding to the C\(_4\)N\(^+\) stretch, decreases over time in the 10 M solution. It is evident that the decrease of QA in BTMA membrane is faster than that of the C10 membrane. This data was explained by Sn2 nucleophilic substitution at the benzyl position or an abstraction of the methyl groups from the quaternary ammonium center.\(^7\)\(^,\)\(^23\)

In addition, two new peaks were observed (Figure 6) in both of the degraded membranes in the 10 M KOH solution at 60°C 1000h. These two peaks are located at 2815 cm\(^{-1}\) and 2770 cm\(^{-1}\) and are assigned respectively to asymmetric and symmetric stretching of (C-H) in the –N(CH\(_3\))\(_2\) group. The presence of this amine is likely due to methyl abstraction from the quaternary ammonium center.

**Ion exchange capacity (IEC) and conductivity properties.**—In addition to FTIR studies, IEC and conductivity (Figures 7 and 8 respectively) were measured during the alkaline stability tests. Both of the membranes showed a fast initial drop of IEC and conductivity over the first 150 h, then the decrease became much more moderate. The conductivities of C10 membranes preserved \(~\sim\)80% of their initial values and \(~\sim\)84% of the IEC after 450h, while the conductivity of the BTMA membrane decreased to \(~\sim\)63% and the IEC to \(~\sim\)70% of the initial value after 60 h. Unfortunately, after 60h in an alkaline environment, it was impossible to measure the conductivity of BTMA due to cracks and the sample’s unstable mechanical properties. These results are compatible with the FTIR results that showed higher alkaline stability for the C10 type membrane versus the BTMA version. Although there are two \(\beta\)-hydrogen atoms around the quaternary ammonium groups in C10 membranes in which the Hofmann elimination could be the preferred decomposition pathway, the steric hindrance of the alkyl chains may hinder Hofmann elimination and protect the ammonium cations from being attacked by hydroxide ions.

![Figure 5](image5.png)  
Figure 5. Relative intensity of QA group vibration vs. aromatic C-C bond.

![Figure 6](image6.png)  
Figure 6. FTIR absorption spectra of BTMA (left) and C10 (right).

![Figure 7](image7.png)  
Figure 7. Ion exchange capacity (IEC) of the membranes after the membrane was held at 1M KOH, 60°C, for 600h.
Hydrolytic stability.—One of the alkaline fuel cell community’s aims is to increase the operation temperature of the fuel cell, not only to enhance the kinetic processes within the device, but also to avoid liquid water condensation in the system. Operating the cell at 95 °C would avoid most of the liquid water condensation in the gas diffusion layers and flow channels. Therefore, targeting higher temperatures and characterizing membranes near 100 °C is required to push alkaline fuel cell technology forward.

The hydrothermal stability of the membranes was examined by immersing the membranes in water held at 80 °C. We evaluated the hydrolytic stability at this temperature since this is the current target operative temperature of alkaline fuel cells. Figure 9 displays HRSEM images of the membranes after being held at 80 °C in liquid water for 1000 h. As can be seen from the images, the C10 membrane undergoes major degradation processes, being reflected in the formation of 5–15 μm holes in high density, through the entire membrane surface. On the other hand, in the BTMA membrane small cracks and 0.5–1.0 μm holes were formed in a much lower density.

The FTIR showed a decrease in the intensity of most of the peaks associated with the C-C aromatic group. As can be seen in Figure 10, the C10 membrane showed a significant decrease in all of the IR peaks, including QA and ether groups, while the most significant decrease was observed in the C-H group. On the other hand, the decrease in the IR peak intensity of BTMA membrane were less drastic, and the most significant decrease was found in the C-H group peak.

Mechanical properties.—Stress-strain measurements showed that the long alkyl side chain has an influence on the mechanical properties of the membrane. It was found that the elongation at break of BMTA was 6.9% (dry) and 10.2% (wet) and the elongation at break of the C10 membranes was 4.7% (dry) and 5.5% (wet). The stress at break of the BTMA sample decreased from 47.7 MPa when dry to 28.5 MPa when wet, indicating some plasticization of this sample with water. On the other hand, the C10 membrane showed a tensile stress at break of 37.2 MPa when dry and 34.9 MPa when wet. The C10 membrane appeared not to plasticize in the wet state which could result in a non-elastic swelling response as shown in the water uptake measurements. The long C10 side chains could weaken the interchain interactions in the material inducing irreversible swelling at high temperatures. This type of mechanical response during swelling must be considered in future membrane designs.

Conclusions

The effect of long alkyl side chain groups on the properties of poly(phenylene oxide)-based AEMs and their stability in alkaline and hydrothermal conditions was investigated and compared to analogous AEMs with the typical BTMA cationic group. Water uptake measurements showed that the C10 membrane has lower values of water uptake than BTMA membranes in the 25–70 °C temperature range, probably due to the long hydrophobic alkyl side chain which sterically protects the cationic group and decreases its hydrophilicity. AFM data showed the presence of phase separation in the C10 membrane. Chemical stability results indicated that in high pH environment, the C10 membrane shows slow degradation of the cationic groups as measured by a decrease in the relative intensity in the ATR-FTIR analysis and IEC and conductivity results. Hydrolytic stability at 80 °C was investigated and it was found that the C10 membrane is not stable in liquid water at this temperature – likely due to irreversible swelling and mechanical degradation of the membrane precipitated by increased solution uptake. HRSEM measurements showed large holes on the surface of the membrane and ATR-FTIR analysis revealed a decrease in most of the relative intensities of the backbone and the functional group peaks, compared to the PPO-BTMA control.

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