Alkaline Stability of Poly(phenylene)-Based Anion Exchange Membranes With Various Cations

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ABSTRACT: Anion exchange membranes comprised of a poly(phenylene) backbone and one of five different cationic head-groups are prepared, briefly characterized, and tested for stability in 4 M KOH at 90 °C. The two membranes with resonance-stabilized cations (benzyl pentamethylguanidinium and benzyl N-methylimidazolium) show large (>25%) decreases in both conductivity and ion exchange capacity (IEC) after just one day of testing. The membrane with benzyl trimethylammonium cations shows a 33% loss of conductivity (14% decrease in IEC) after 14 days while the membrane with trimethylammonium cations attached by a hexamethylene spacer shows the least degradation: a 5% loss of conductivity over 14 days with no accompanying loss in IEC. A similar membrane which has a six-carbon spacer and a ketone adjacent to the phenyl ring shows much lower stability, suggesting that the ketone takes part in degradation reactions. © 2012 Wiley Periodicals, Inc.

KEYWORDS: alkaline fuel cell; anion exchange membrane; guanidinium; imidazolium; ionomers; membrane; sidechain; stability; stabilization

INTRODUCTION Recently, there has been increased interest in the development of anion exchange membrane fuel cells (AEMFCs). The fundamental difference between AEMFCs and the more widely studied proton exchange membrane fuel cells is that the former operate at high pH thus requiring the membrane to conduct hydroxide ions from the cathode to the anode. The key advantage of operating a fuel cell under alkaline conditions is the potential to forgo noble metal catalysts due to the low overpotentials associated with many electrochemical reactions at high pH.1 The improved electrokinetics also allow for the possible use of high energy density fuels such as ethanol which is also a renewable resource as it can be produced directly by fermentation of biomass. A major challenge in the development of AEMFCs is the need for an anion exchange membrane (AEM) that is chemically stable under the conditions within an AEMFC.2,3

AEMs are typically made with polymers that have pendant cationic groups. By far, the most commonly reported cationic group is the benzyl trimethylammonium (BTMA) cation. AEMs have been prepared with BTMA cations attached to polymer backbones such as poly(phenylene),4 poly(phenylene oxide),5 poly(phenylene oxide),6 poly(arylene ether sulfone),7–10 and poly(ether ether ketone)11 and BTMA-containing oligomers have been grafted onto backbones such as poly(tetrafluoroethylene-co-hexafluoropropylene).12

Many of these BTMA-containing membranes are reported to have good chemical stability. For example, the ion exchange capacity of a radiation-grafted perfluorinated AEM with BTMA cations was shown to decrease by less than 5% after a 233 h fuel cell test at 50 °C.13 Another study of the degradation mechanisms of tetra-alkylammonium compounds concluded that maintaining hydration around the cations is critical to stability and that, under the correct conditions, such cations possess reasonable stability at temperatures above 60 °C.14 Despite reports such as this, BTMA cations are generally considered to have insufficient stability for long-term use in AEMFCs. Thus the investigation of cationic groups with improved chemical stability is of paramount importance to the development of AEMFCs.

One relatively early study of cation stabilities found that quaternized 4,4'-diazobicyclo-[2.2.2]-octane cations had improved stability to alkaline conditions when compared to BTMA cations.15 Another approach to preparing more stable cations is to reduce susceptibility to nucleophilic attack by using resonance-stabilized cations such as guanidinium16,17 or imidazolium18,19 groups. Other reports have included the use of coordinated metal cations20 or phosphonium cations with bulky electron-donating substituents to both sterically protect the ion from nucleophilic attack and to lessen the charge density on the phosphorus atom.21 Additionally, it has been reported that attachment of quaternary ammonium groups to the polymer backbone via an alkylene spacer of >3 carbon atoms can lead to improved chemical stability.22 Attachment of imidazolium23...
and guanidinium\textsuperscript{24} groups with alkylene spacers have also been reported.

We have previously described the preparation of AEMs with BTMA cations on a poly(phenylene) backbone that is very stable under alkaline conditions and in AEMFC testing.\textsuperscript{25} This article will discuss the attachment and stability of benzylic resonance-stabilized cations on the poly(phenylene) backbone as well as ammonium cations attached by flexible spacers.

**EXPERIMENTAL**

**Materials**

All reagents were purchased from commercial vendors and used without further purification unless specified. 1,1,2,3,3-Pentamethylguanidine (PMG) was prepared according to the procedure of Wang et al.\textsuperscript{16} Tetramethylpoly(phenylene) (TMPP), brominated tetramethylpoly(phenylene) (BTMPP), and aminated tetramethylpoly(phenylene) (ATMPP) were prepared as described previously\textsuperscript{4} and their structures are shown in Figure 1. The unfunctionalized Diels–Alder poly (phenylene) (DAPP) was prepared according to the procedure of Fujimoto et al.,\textsuperscript{26} and its structure is shown in Figure 2.

**Synthesis and Casting of ImTMPP**

BTMPP (1.25 g, 2.51 \(\text{CH}_2\text{Br/repeat unit}\)) was dissolved in \(N, N\)-dimethylacetamide (DMAc) (38 mL) in a flask under argon. N-Methylimidazole (0.75 mL, 9.4 mmol, 3 equivalents per \(\text{CH}_2\text{Br}\)) was added and the solution was heated to 80 \(^\circ\text{C}\) for 30 min. After cooling to room temperature, the solution was filtered and poured onto a glass casting dish (5 \(\times\) 5 inch). The dish was held in a vacuum oven at room temperature for 4 h and then at 50 \(^\circ\text{C}\) for 18 h. The resulting membrane was then immersed in 0.5 M HBr for 2 h and then in deionized water for at least 24 h to yield the ImTMPP membrane in its bromide counter-ion form.

**Synthesis and Casting of PMGTMPP**

BTMPP (1.25 g, 2.26 \(\text{CH}_2\text{Br/repeat unit}\)) was dissolved in DMAc (52 mL) in a flask under argon. PMG (3.3 g, 25 mmol, 9 equivalents per \(\text{CH}_2\text{Br}\)) was added and the solution was heated to 80 \(^\circ\text{C}\) for 30 min. After cooling to room temperature, the solution was filtered and poured onto a glass casting dish (5 \(\times\) 5 inch). The dish was held in a vacuum oven at room temperature for 4 h and then at 50 \(^\circ\text{C}\) for 18 h. The resulting membrane was then immersed in 0.5 M HBr for 2 h and then in deionized water for at least 24 h to yield the PMGTMPP membrane in its bromide counter-ion form.

**Synthesis of BrKC6PP**

The degree of functionalization (DF) could be controlled by varying the amount of acylation reagent. Details for the reaction resulting in BrKC6PP with DF = 2.48 are given here. DAPP (2.04 g, 2.68 mmol) was dissolved in dichloromethane (125 mL) in a flask under argon. The flask was chilled in an ice/water bath and 6-bromohexanoyl chloride (1.1 mL, 7.4 mmol) was added. Aluminum chloride (981 mg, 7.4 mmol) was added to the flask, the bath was removed, and the reaction was allowed to warm to room temperature over 5 h.
while stirring. The solution was poured into a beaker containing 200 mL deionized water and the beaker was heated to 60 °C to evaporate the organic solvent. After cooling to room temperature the mixture was filtered and the solid was blended with acetone in a Waring blender. The mixture was filtered and the solid was dried at room temperature under vacuum to yield BrKC6PP as an off-white solid (3.00 g, 90%).

**Synthesis of TMAKC6PP**
A solution of BrKC6PP (440 mg, DF = 2.48) in chloroform (10 mL) was filtered through a syringe filter into a circular glass dish with a 3.75 inch diameter. An inverted beaker was placed over the dish and the solvent was allowed to evaporate for 18 h. The resulting film was removed from the dish and immersed in a trimethylamine solution (50 wt % in water) for 48 h. The resulting membrane was then immersed in 0.5 M HBr for 2 h and then in deionized water for at least 24 h to yield the TMAKC6PP membrane in its bromide counter-ion form.

**Synthesis of BrC6PP**
To a solution of BrKC6PP (4.37 g, 3.5 mmol, DF = 2.70) in 1,2-dichloroethane (220 mL) was added trifluoroacetic acid (55 mL) and triethylsilane (7.0 mL, 43.8 mmol). The solution
was heated to reflux for 24 h, then cooled to room temperature and poured into a beaker containing NaOH (27 g) dissolved in water (300 mL). The beaker was heated to 80 °C to evaporate the organic solvent. After cooling to room temperature the mixture was filtered and the solid was blended with acetone in a Waring blender. The solid was then dissolved in dichloromethane and precipitated into acetone. The mixture was filtered and the solid was dried at room temperature under vacuum to yield BrC6PP as a white solid (3.86 g, 89%).

**Synthesis of TMAC6PP**
A solution of BrC6PP (1.20 g, DF = 2.70) in chloroform (30 mL) was filtered through a syringe filter into a glass casting dish (5 × 5 inch). An inverted beaker was placed over the dish and the solvent was allowed to evaporate for 18 h. The resulting film was removed from the dish and immersed in a trimethylamine solution (50 wt % in water) for 48 h. The resulting membrane was then immersed in 0.5 M HBr for 2 h and then in deionized water for at least 24 h to yield the TMAC6PP membrane in its bromide counter-ion form.

**Conversion of Membranes to Chloride or Hydroxide Form**
Membranes with bromide counter-ions were soaked in either 1 M NaCl or 1 M KOH aqueous solutions at room temperature for 48 h to exchange the bromide ions for chloride or hydroxide ions. Afterward the membranes were immersed in deionized water for at least 24 h prior to analysis. When handling membranes in their hydroxide form, no effort was made to exclude carbon dioxide from the water in the storage containers. The hydroxide form membranes were only used for the ion exchange capacity (IEC) measurements and in that case, the conversion of hydroxide ions to bicarbonate or carbonate ions was inconsequential since any of those anions would react with HCl.

**Hydroxide Stability Testing**
Membranes in bromide form were immersed in a 4 M KOH aqueous solution in a stirred reactor under argon for 14 days at 90 °C. At designated intervals, samples were removed from the reactor and were checked for IEC and Cl⁻ conductivity. Used samples were not returned to the reactor. Samples for IEC measurements were immersed in deionized water for at least 48 h with the water frequently replaced prior to analysis. Samples for chloride ion conductivity measurements were immersed in 1 M HCl for 48 h and then in deionized water for at least 24 h prior to analysis.

**Characterization and Measurements**
Gel permeation chromatography (GPC) was performed with a liquid chromatograph equipped with a Viscotek VE2001 isocratic pump and autosampler and a Viscotek VE3580 refractive index detector. The mobile phase was tetrahydrofuran and the system was operated at 25°C with a flow rate of 1.0 mL min⁻¹. The weight-average molecular weights were measured by calibration with polystyrene standards.

³H NMR spectra of the polymers were obtained on a Bruker 500 MHz spectrometer using 5 mm o.d. tubes. Sample concentrations were about 5% (wt/vol) in CDCl₃ or CD₂Cl₂ for non-ionic samples. DMSO-d₆ was used for polymers with attached cations and the spectra were obtained at 90 °C.

IECs were determined by a back titration procedure described previously.²² All measurements were performed in deionized water at room temperature with the membranes in chloride form.

**RESULTS AND DISCUSSION**
The preparation of poly(phenylene)s with three different benzyl cations is shown in Figure 1. All three are prepared by the nucleophilic substitution of a benzyl bromine atom by a nitrogen-containing base. The preparation of the polymer with BTMA cations (ATMPPP) differs from the other two because the BTMA cations are formed with the polymer in the solid state.⁴ Attempts to make AEMs by immersing films of BTMPPP in aqueous solutions of either N-methylimidazole or PMG failed, yielding only polymers with few, if any, attached cationic groups. N-Methylimidazole and PMG are each much larger molecules than trimethylamine and the lack of substitution products in these cases is probably due to their inability to penetrate the solid polymer matrix to react with the bromomethyl groups. Instead, ImTMPP and TMGTMPP were prepared by addition of the appropriate base to a solution of BTMPPP in DMAC. Membranes could be cast directly from the reaction solution and excess base was removed by soaking the membranes in aqueous acid. Conversion of the bromomethyl groups to resonance-stabilized cations was nearly quantitative, as indicated by the close agreement between the theoretical and NMR-measured IEC values in Table 1. The structures of the imidazolium- and guanidine-containing polymers were confirmed by ³¹H NMR spectroscopy and the peak assignments were in good agreement with the previously reported results for polymers with the same pendant ionic groups.¹⁶,²⁷ For simplification, the ionomer structures in Figure 1 each show exactly two cations per repeat unit. In reality, the number of cationic groups is controlled by the number of bromomethyl groups formed in the first reaction step and the average number of cations per repeat unit can range from zero to four. The exact number of bromomethyl groups per repeat unit (DF) for each polymer discussed here was determined by NMR and the results are given in Table 1.

The attachment of sidechains to the poly(phenylene) backbone was accomplished by a Friedel-Crafts acylation of 6-bromo-1-hexanoyl chloride on the parent polymer, DAPP. In Figure 2, the acylated polymer, BrKC6PP, is depicted as having one sidechain per repeat unit for simplicity, although samples with up to 2.7 sidechains per repeat unit were
prepared. The acylation could take place at any available position on any of the aryl rings in DAPP, however because of their steric bulk, the six pendant rings probably prevent the backbone rings from taking part in the reaction. The distribution of aryl substitution patterns could not be determined due to the overlapping peaks in the aryl region of the \(^1\)H NMR spectrum of BrKC6PP (Fig. 3). The average number of sidechains attached to each repeat unit (DF) for BrKC6PP was determined from the \(^1\)H NMR spectrum by comparing the total aromatic peak area to the combined areas of the peaks assigned to the methylene units in the sidechains and these values are listed in Table 1.

Protons in the \(\alpha\)-position of ketones are known to be somewhat acidic due to the formation of enolate ions. Since this study is concerned with chemical stability under strongly alkaline conditions, it was foreseen that the \(\alpha\)-protons on the sidechains in BrKC6PP might be a weak point that could lead to unwanted degradation reactions. To test this possibility and to potentially avoid it, BrKC6PP was treated with triethylsilane to reduce the ketone to a methylene group. In Figure 3, the disappearance of the peak assigned to the \(\alpha\)-protons (e) and the appearance of the peak assigned to the protons adjacent to phenyl ring (f) are clear evidence for the reduction. The resulting polymer, BrC6PP, has purely alkyl sidechains which cannot form enolate ions. Formation of hexane-1-one-6-trimethylammonium ions on BrKC6PP and hexane-6-trimethylammonium (HTMA) ions on BrC6PP was accomplished by casting films of the parent polymers and then soaking them in aqueous trimethylamine.

The data in Table 1 show that the measured IEC values for all of the polymers were lower than the theoretical values (70–80% of theoretical) and this is consistent with reported results for several other AEMs.\(^{7,12,28}\) All of the ionomers in Table 1 except for TMAKC6PP were soluble in either DMF or DMSO, so their IECs could also be checked by \(^1\)H NMR spectroscopy. In all four cases, the NMR-measured IEC values were in close agreement with the theoretical values, indicating that the bromomethyl and bromoalkyl groups in the parent polymers were essentially all converted to ammonium groups. Thus the titration-measured IECs must be low because of a systemic error during the titration itself; possibly incomplete ion exchange, incomplete drying, or removal of water-soluble oligomers with high IEC values. The titration-measured IECs are self-consistent, however, since titrations of replicate samples gave results within ±5% of each other.

Ionic conductivities were measured with the membranes in chloride form in order to avoid issues with the formation of carbonate ions in hydroxide form membranes when exposed to atmospheric CO\(_2\). Based on the dilute-solution mobilities of hydroxide and chloride anions, the conductivity for AEMs in OH\(^-\)/CO\(_2\) form can be predicted to be about 2.6 times greater than the chloride form conductivity.\(^{29,30}\) This has been demonstrated for a different class of AEMs and it can reasonably be assumed that a similar relationship holds for the conductivities listed in Tables 1 and 2.\(^{20}\) The chloride conductivities in Table 1 trend very well with the water uptakes,

### TABLE 1 Anion Exchange Membrane Properties

<table>
<thead>
<tr>
<th></th>
<th>DF</th>
<th>Theoretical IEC (meq/g)</th>
<th>Measured IEC (meq/g)</th>
<th>Water Uptake(^a) (wt %)</th>
<th>Cl(^-) Conductivity (mS cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATMPP</td>
<td>2.38</td>
<td>2.39</td>
<td>1.90</td>
<td>2.35</td>
<td>159</td>
</tr>
<tr>
<td>PMGTMP</td>
<td>2.26</td>
<td>1.98</td>
<td>1.51</td>
<td>1.87</td>
<td>66</td>
</tr>
<tr>
<td>ImTPM</td>
<td>2.51</td>
<td>2.40</td>
<td>1.79</td>
<td>2.40</td>
<td>59</td>
</tr>
<tr>
<td>TMAKC6PP</td>
<td>2.48</td>
<td>2.08</td>
<td>1.46</td>
<td>N/A(^b)</td>
<td>91</td>
</tr>
<tr>
<td>TMAC6PP</td>
<td>2.70</td>
<td>2.27</td>
<td>1.74</td>
<td>2.20</td>
<td>126</td>
</tr>
</tbody>
</table>

\(^a\) Hydroxide form.

\(^b\) Membrane was not soluble in any solvent tested.

![FIGURE 3 \(^1\)H NMR spectra of BrKC6PP (top) and BrC6PP (bottom).](image)

### TABLE 2 Stability of Anion Exchange Membranes in 4 M KOH at 90 °C (Cl\(^-\) Conductivity/IECa) using the same units as Table 1

<table>
<thead>
<tr>
<th></th>
<th>0 Days</th>
<th>1 Day</th>
<th>2 Days</th>
<th>7 Days</th>
<th>14 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATMPP</td>
<td>18.0/1.9</td>
<td>16.5/1.8</td>
<td>15.5/1.8</td>
<td>13.9/1.7</td>
<td>12.0/1.5</td>
</tr>
<tr>
<td>PMGTMP</td>
<td>10.0/0.70</td>
<td>0.60/0.06</td>
<td>0.60/0.01</td>
<td>0.40/0.004</td>
<td>0.40/0.001</td>
</tr>
<tr>
<td>ImTPM</td>
<td>9.7/1.5</td>
<td>4.0/1.1</td>
<td>4.0/1.1</td>
<td>3.8/1.1</td>
<td>2.3/1.0</td>
</tr>
<tr>
<td>TMAKC6PP</td>
<td>13.0/1.4</td>
<td>6.0/1.0</td>
<td>5.4/0.92</td>
<td>1.1/0.70</td>
<td>0.80/0.65</td>
</tr>
<tr>
<td>TMAC6PP</td>
<td>17.4/1.8</td>
<td>17.5/1.8</td>
<td>17.1/1.8</td>
<td>16.6/1.8</td>
<td>16.6/1.8</td>
</tr>
</tbody>
</table>

\(^a\) Measured by titration because all samples were insoluble after testing.

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of the membranes remained tough and flexible throughout.

conductivity losses are due to cation degradation and not cations (which lack and hydrophobic domains since the IEC of TMAC6PP over the second week. This leveling-out behavior was unexpected and might be due to a reorganization of hydrophilic and hydrophobic domains since the IEC of TMAC6PP remained constant throughout the test. It is interesting to note that TMAC6PP retains a greater portion of its conductivity than ATMPP despite the fact that HTMA cations are susceptible to Hofmann elimination reactions while BTMA cations (which lack β-hydrogens) are not. This finding is supported by a recent computational study which predicts that n-alkyltrimethylammonium groups are more stable than BTMA when n > 3.31 This stability is the result of both steric shielding of the β-hydrogens when n > 3 and an increased susceptibility to SN2 attack at the nonmethyl substituent on the nitrogen atom in BTMA. Thus the stability advantage that HMTA cations gain by not having the methylene which is both benzylic and adjacent to a positive charge in BTMA cations is greater than the disadvantage imposed by the presence of two β-hydrogen atoms.

TMAC6PP showed poor stability (90% conductivity loss over 7 days) and this must be due to the ketone functional group, given the good stability of TMAC6PP. The exact role of the ketone in the degradation reactions is unclear but a likely explanation is the formation of an enolate anion which can than act as a nucleophile in an intramolecular reaction with the cation at the end of the chain.

Both ImTMPP and PMGTMPP showed very large decreases in conductivity after only one day of testing (59 and 94%, respectively). This was unexpected given previous reports of the alkaline stabilities of AEMs with benzyl guanidinium and imidazolium groups.16,18 The KOH concentration and the temperature of the test in this study were both higher than in the previous studies and this might account for the apparent differences in stability; however a recent and very thorough study by Deavin et al. has reported that imidazolium cations as both small molecules and as tethered cationic head-groups are susceptible to significant degradation under relatively mild conditions (1 M KOH, 60 °C).32 Both BTMA and HTMA cations showed much greater stability than the resonance-stabilized cations when attached to the poly(phenylene) backbone and the TMAC6PP AEM appears to be a very promising candidate for use in AEMFCs.

CONCLUSIONS

A series of AEMs based on a DAPP backbone and having a variety of different attached cations have been synthesized. All five membranes were tough and flexible before and after exposure to KOH solution at elevated temperature. All five membranes had water uptake and ionic conductivity values that are considered reasonable for use in AEMFCs. The membranes with resonance-stabilized cations (benzylic guanidinium and imidazolium groups) and the membrane with hexane-1-one-6-trimethylammonium sidechains showed poor stability under alkaline conditions (>50% loss of conductivity after 1 day). The membrane with hexane-6-trimethylammonium sidechains was the only one that showed greater stability than the previously-reported AEM with BTMA cations (5% vs. 33% conductivity loss after 14 days). Thus the replacement of a benzylic methylene spacer with a hexamethylene spacer results in greater stability despite the possibility of Hofmann elimination reactions which are not possible in the former case. For future reports, we intend to study the degradation mechanisms of these cations in order to further develop stable AEMs for AEMFCs.

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REFERENCES AND NOTES