Anion Conducting Multiblock Copolymers With Different Tethered Cations

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ABSTRACT: A multiblock copoly(arylene ether) polymer was used to quantitatively compare the ion conducting channels formed by three different, tethered cation head-groups. The synthesis allowed for the formation of an exact number of tethers on each repeat unit. Three head-groups, quaternary trimethylammonium (TMA), quinuclidium (ABCO), and tris(2,4,6-trimethoxyphenyl)-phosphonium (TTMPP) cation head-groups were compared in terms of size of the conducting channels, ionic conductivity of the mobile hydroxide ion, mechanical properties, quantity of productive and unproductive water, and chemical stability of the membrane in base. The interdomain spacing showed that multiblock copolymers with larger cations formed larger ion conductive channels in the membrane. Larger cations resulted lower ion exchange capacity (IEC) even though the polymer backbone and tether arrangements were identical. TMA was the most stable cation after exposure to 1 M NaOH at 60 °C for 20 days. ABCO had a lower number of bound water molecules and a 22% loss in ion conductivity after treatment in 1 M NaOH at 60 °C for 20 days due to the higher hydroxide ion concentration in the ion conductive blocks. Membranes with TMA head-groups also had the best mechanical properties. Two membrane preparation methods were compared. The presence of the cation head-groups assists in phase segregation.

INTRODUCTION Anion exchange membranes (AEMs) are used for separations and energy conversion devices including electrochemical cells, such as fuel cells, electrolyzers, flow batteries. Anion conductive polymers are used to compliment cation conductive polymer in dialysis or they can be used by themselves giving specific advantages. High ionic conductivity and chemical stability are universal goals which can be improved through phase segregation from a block copolymer structure. Block copolymers form efficient ion channels which confines the mobile hydroxide ion to ion conductive phase leading to better chemical stability, compared to random copolymers. Long alkyl side chains can improve the chemical stability of the tethered cation headgroup by facilitating ion channel formation. Benzyl trimethyl quaternary ammonium (BTMA) has been a common tethered cation in AEMs due to its convenient synthesis and lack of beta-hydrogens (i.e. hydrogens on the beta carbon). Beta-hydrogens are known to undergo Hoffman degradation. However, BTMA cations are susceptible to other degradation processes in alkaline conditions including direct nucleophilic substitution of hydroxide ions and elimination via ylide formation. Recent studies have shown that long, alkyl chain tethered trimethyl ammonium (TMA) have excellent stability in alkaline environments at elevated temperature. The long alkyl chain lowers the electron-withdrawing inductive effect and the resonance effect of the benzene ring when a benzyl attachment is used. The high electron density around the beta-hydrogens and the steric shielding in the β-positions lowers the risk of Hofmann elimination. In addition to trimethyl quaternary ammonium cations, other cation groups, such as quinuclidium, phosphonium, imidazolium, and guanidinium have also been reported to each have advantages. However, the test conditions and polymer structure in the different publications varies making it sometimes difficult to quantitatively compare the performance of the different head-groups.

The conductivity of quinuclidium (1-azaoniumbicyclo[2,2,2]octane), a quaternary ammonium cation formed by quaternization of a polycyclic amine 1-azabicyclo[2,2,2]octane (ABCO), has been studied. Quinuclidium has a larger van der Waals volume than the TMA head group, which may facilitate the formation of larger ion conductive channels to enhance ion mobility in the membrane. Arges et al. studied the alkaline stability of quinuclidium...
with a poly(2,6-dimethyl 1,4-phenyleneoxide) (PPO) backbone. Although no degradation of quinuclidium was found by 1D or 2D NMR, the decrease in ion exchange capacity (IEC) after exposure to alkaline solutions indicates cation degradation. It was postulated that quinuclidium degraded through direct nucleophilic substitution (SN1) of OH\(^{-}\) ions (debenzylation – cleavage of the cation site to form benzyl alcohol).

Phosphonium cations with a central phosphorus atom have been studied by Yan et al.\(^{16,17}\) A stabilized quaternary phosphonium cation, benzyl tri(2,4,6-trimethoxyphenyl)phosphonium, with nine methoxy groups was reported to provide electron donation and steric hindrance. High ionic conductivity, water uptake, alkaline stability, and mechanical properties and with an exact number and placement of head-groups was used to quantitatively compare the performance of the polymer. There may also be experimental uncertainty in the density or distribution of head-groups within some polymer backbones. In this study, a multiblock copoly(arylene ether) (mPEs) exhibiting excellent ion conducting channels (e.g. a random copolymer) because low conductivity may be due to inadequate phase segregation within the polymer. Thus, the direct comparison of stability, mechanical properties, and conductivity of different head-groups is complicated because of the number of uncontrolled variables between the previous studies. Comparison on a common polymer backbone is also complicated if the polymer forms inefficient ion conducting channels (e.g. a random copolymer) because low conductivity may be due to inadequate phase segregation within the polymer. There may also be experimental uncertainty in the density or distribution of head-groups within some polymer backbones. In this study, a multiblock copoly(arylene ether) (mPEs) exhibiting excellent ion channel formation properties and with an exact number and placement of head-groups was used to quantitatively compare the performance of three head-groups made from quaternary trimethyl ammonium (TMA), quinuclidium (ABCO), and tris(2,4,6-trimethoxyphenyl)phosphonium (TTMPP). The channel morphology, ionic conductivity, water uptake, alkaline stability, and mechanical and thermal properties of the AEM on the same block copolymer with the exact same number of each head-group was compared in order to understand the effects of head-group size and type on AEM properties. Two methods of membrane preparation were also compared. To our knowledge, this is the first study of the use of phosphonium cations with long, alkyl tethers in an AEM.

**EXPERIMENTAL**

**Materials**

\(\text{N,N'}\)-dimethylacetamide (DMAc) was obtained from Alfa Aesar and dried by vacuum distillation at 130 °C over \(\text{CaH}_2\). Decafluorobiphenyl (DFBP), 4,4\(^{'-}\)(hexafluoroisopropylidene) diphenol (HFBPA), 6-bromohexanoyl chloride, \(\text{AlCl}_3\), 1,2-dichloroethane, triethylsilane, and trifluoroacetic acid were obtained from Alfa Aesar. 4,4\(^{'-}\)(9-fluorenylidene)diphenol (BPFL) was obtained from TCI Co. Ltd. Potassium carbonate (\(\text{K}_2\text{CO}_3\)) and dichloromethane (DCM) were purchased from BDH chemicals. All chemicals were used as received unless otherwise noted.

**Synthesis of Hydrophobic and Hydrophilic Oligomers**

The synthetic procedure for the hydrophobic oligomer with three repeat units (\(x = 3\)) is as follows: DFBP (1.67 g, 5 mmol) and HFBPA (1.68 g, 5 mmol) were dissolved in 20 mL DMAc in a 100 mL three-neck round bottom flask with a condenser under \(\text{N}_2\) atmosphere at room temperature. \(\text{K}_2\text{CO}_3\) (1.66 g, 12 mmol) was added to the solution and then the mixture was heated to 80°C for 1 hr. DFBP (0.5 g) was added to the mixture and allowed to react at 40°C for 4 h to ensure that all the oligomers were hydroxyl-terminated. The viscous solution was poured into deionized water to precipitate the product. The white solid was isolated by filtration, washed three times with deionized water and dried overnight at 80 °C in a vacuum oven. Hydrophobic oligomers with a different number of repeat units were synthesized by controlling the reaction time.

Fluoro-terminated hydrophilic oligomer with five repeat units (\(y = 7\)) was synthesized via a similar procedure. BPFL (1.75 g, 5 mmol) and DFBP (1.67 g, 5 mmol) were dissolved in 20 mL DMAc under \(\text{N}_2\) atmosphere. \(\text{K}_2\text{CO}_3\) (1.66 g, 12 mmol) was added to the solution and the mixture was reacted at 80 °C for 2.5 h. BPFL (0.6 g) was added to the mixture and reacted at 40 °C for 4 h. After precipitation, filtration and drying, a white solid was yielded.

**Synthesis of Multiblock Copoly(Arylene Ether)s (mPEs)**

The hydrophobic oligomer (1.11 g, 0.5 mmol, \(x = 3\)) and hydrophilic oligomer (2.42 g, 0.5 mmol, \(y = 7\)) were dissolved in 20 mL DMAc at room temperature under \(\text{N}_2\) atmosphere. \(\text{K}_2\text{CO}_3\) (0.15 g, 1.1 mmol) was added to the solution and the mixture was reacted at 80 °C for 4 h. The viscous solution was poured into deionized water and white solid was precipitated out. The product was filtrated, washed with deionized water and dried overnight at 80 °C in a vacuum oven.

**Synthesis of 1-Tether BrK6-mPEs**

Multiblock copolymer mPE-\(X_3\)\(Y_7\) (1.01 g) was dissolved in 20 mL DCM in a flask under nitrogen atmosphere. The flask was chilled in an ice bath. 6-bromohexanoyl chloride (0.6 mL, 4 mmol) and \(\text{AlCl}_3\) (0.54 g, 4 mmol) were added to the solution and warmed to room temperature. The mixture was reacted for 5 h at room temperature. The solution was poured into 200 mL deionized water and heated to 60 °C to evaporate the solvent. The product was dissolved in DCM and precipitated in deionized water three times to obtain a purified light yellow solid.

**Synthesis of 1-Tether BrK6-mPEs**

BrK6-mPE-\(X_3\)\(Y_7\) (1.17 g) was dissolved in 20 mL 1,2-dichloroethane in a three-neck round bottom flask with a condenser at room temperature under nitrogen. Trifluoroacetic acid (3.8 mL, 50 mmol) and triethylsilane (0.8 mL, 5 mmol) were added to the solution. The solution was heated to reflux for
24 h. After cooling to room temperature, it was poured into a NaOH solution (2 g NaOH, 200 mL deionized water). The mixture was heated to 80 °C to evaporate the solvent. The product was isolated by filtration. The product was dissolved in DCE and precipitated in deionized water three times producing a white solid product.

**Synthesis of 2-Tether BrKC6-mPES and BrC6-mPES**

2-tether BrKC6-mPES and BrC6-mPES were synthesized via Friedel-Crafts reaction and reduction reaction described in the previous steps.

**Membrane Casting Followed by Quaternization, and Ion Exchange of Quaternary Ammonium Head-Group**

BrC6-mPES (0.20 g) was dissolved in 5 mL 1,2-dichloroethane and the resulting solution was filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) membrane syringe filter into a 4-cm diameter aluminum dish. The solvent was evaporated in a tube furnace at 40 °C under nitrogen for 18 h. The free-standing membrane was about 40-μm thick. The membrane was quaternized by immersion in 45 wt% trimethylamine aqueous solution at room temperature for 48 h. After removal from the solution, the quaternized membrane with a bromide counter ion was washed with deionized water three times. The membrane was soaked in 1 M KOH solution under nitrogen for 24 h to exchange the bromide ions for hydroxide ions. After being washed with deionized water three times, the membrane was stored in deionized water.

**Quaternization Followed by Membrane Casting of Membranes with Trimethyl Quaternary Ammonium Head-Group**

0.5 g BrC6-mPES polymer was soaked in 45% trimethylamine aqueous solution at room temperature for 48 h. After being dried, the polymer was dissolved in 10 mL 1-methyl-2-pyrrolidone (NMP). The solvent was removed by pouring the mixture into a 4-cm diameter aluminum dish to dry in a tube furnace at 40 °C under nitrogen for 5 days to obtain the membrane.

**Quaternization Followed by Casting Membranes with Quaternary Quinuclidium Head-Groups**

0.5 g BrC6-mPES polymer was dissolved in 10 mL 1-methyl-2-pyrrolidone (NMP), followed by the addition of quinuclidine (1:1 molar ratio). The reaction mixture was stirred at 60 °C for 48 h in an N2 atmosphere. After reaction, the solvent was removed by pouring the mixture into a 4-cm diameter aluminum dish to dry in a tube furnace at 40 °C under nitrogen for 5 days.

**Quaternization Followed by Membrane Casting with Quaternary Phosphonium Head-Groups**

0.5 g BrC6-mPES polymer was dissolved in 10 mL 1-methyl-2-pyrrolidone (NMP), followed by the addition of tris(2,4,6-trimethoxyphenyl)phosphine (1:1 molar ratio). The mixture was reacted at 80 °C for 12 h under nitrogen. The mixture was then poured into a 4-cm diameter aluminum dish. The solvent was evaporated in a tube furnace at 40 °C under nitrogen for 5 days.

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**Characterization**

The chemical structure of the oligomers and polymers were analyzed by a variety of NMR techniques, including one-dimensional 1H NMR and 19F NMR using a Varian Mercury Vx 400 MHz spectrometer. Chloroform-d was used as the NMR solvent. Quantitative 19F NMR spectra were collected at 376.273 MHz with a 12.5 s relaxation delay.

The molecular weight of the polymers was determined by gel permeation chromatography (GPC) (Shimadzu) equipped with an LC-20 AD HPLC pump and a refractive index detector (RID-10 A, 120 V). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min at 35 °C. The molecular weight was measured against a polystyrene standard.

The ionic conductivity of the membranes was measured with an in-plane, four-point probe and electrochemical impedance spectrometer (PAR 2273 potentiostat) at frequencies from 1 Hz to 1 MHz. All samples were tested in HPLC-grade water with continuous nitrogen gas bubbling to minimize the exposure to CO2. The samples were equilibrated for 30 min prior to measurement. The in-plane ionic conductivity was calculated using eq. 1.

\[ \sigma = \frac{L}{WTR} \quad (1) \]

In eq. 1, \( \sigma \) is the ionic conductivity in S/cm, \( L \) is the length between sensing electrodes in cm, \( W \) and \( T \) are the width and thickness of the membrane in cm, respectively, and \( R \) is the resistance measured in ohms.

The ion exchange capacity (IEC) of the membranes was measured by titration. The membranes in Cl- form were dried (vacuum oven, 50 °C, 24 h), weighed, and then immersed in 0.5 M aq. NaNO3 (20 mL) for 48 h. The resulting solution was titrated with 0.02 M aq. AgNO3 to determine the Cl- ion concentration, using K2CrO4 as colorimetric indicator.

The IEC values were calculated from the amount of AgNO3 consumed (\( V_{\text{AgNO}} \)3) and the weight of the dry membrane sample (\( M_{\text{dry}} \)) using eq. 2.

\[ \text{IEC} = \frac{V_{\text{AgNO}}3 \times C_{\text{AgNO}}3}{M_{\text{dry}}} \quad (2) \]

The water uptake of the membranes was calculated from eq. 3.

\[ \text{WU}(\%) = \frac{M_w - M_d}{M_d} \times 100 \quad (3) \]

In eq. 3, \( M_d \) is the dry mass of the membranes measured after being dried in vacuum for 24 h and \( M_w \) is the wet mass of the membranes without surface water. Both dry and wet membranes were in the OH- form and the measurements were performed at room temperature. The number of water molecules per ionic group, hydration number \( \lambda \), was calculated using eq. 4.

\[ \lambda = \frac{1000 \times \text{WU} \%}{\text{IEC} \times 18} \quad (4) \]

The number of freezable water (\( N_{\text{freez}} \)) and bound water (or non-freezable water) (\( N_{\text{bound}} \)) were determined by differential...
scanning calorimetry (DSC). DSC measurements were carried out on a DSC Q200 (TA Instruments). The membrane samples were fully-hydrated by soaking in deionized water for at least one week. A 3 to 5 mg sample was quickly sealed in an aluminum pan after the excess water was wiped away. The sample was cooled to −50 °C and heated to room temperature at a rate of 5 °C/min under N2 (20 mL/min). The quantity of freezable and non-freezable water was determined by eqs. 5–7.21–23

\[ N_{\text{free}} = \frac{M_{\text{free}}}{M_{\text{tot}}} \times \lambda \]  

(5)

In eq. 5, \( N_{\text{free}} \) is the mass of freezable water and \( M_{\text{tot}} \) is the total mass of water in the membrane. The weight fraction of freezable water was calculated by eq. 6.

\[ \frac{M_{\text{free}}}{M_{\text{tot}}} = \frac{H_{f}}{H_{\text{ice}}} \left( \frac{M_{W}-M_{a}}{M_{W}} \right) \]  

(6)

\( H_{f} \) is the enthalpy of fusion corrected for the subzero freezing point according to eq. 7.

\[ H_{\text{ice}} = H_{\text{ice}}^{o} - \Delta C_{p} \Delta T_{f} \]  

(7)

\( \Delta C_{p} \) is the difference between the specific heat capacity of liquid water and ice, and \( \Delta T_{f} \) is the freezing point depression.

Small angle X-ray scattering (SAXS) was used to analyze the morphology of the AEMs. Dry membranes in Br− form were tested in a Malvern Panalytical Empyrean XRD (Netherlands) with a Pixel 3D detector. The scattering experiments were performed using Cu Kα radiation with a wavelength (\( \lambda \)) of 1.542 Å generated within a high brilliance micro focus sealed tube with shaped multilayer optics operating at 45 kV and 40 mA. The wave vector (\( q \)) was calculated from eq. 8.

\[ q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \]  

(8)

In eq. 8, \( 2\theta \) is the scattering angle. The characteristic separation length, or interdomain spacing (\( d \)) (i.e., the Bragg spacing) was calculated from eq. 9.

\[ d = \frac{2\pi}{q} \]  

(9)

Transmission electron microscopy (TEM) was also used to analyze the morphology of the membranes. TEM was performed on a JEOL JEM-1400 transmission electron microscope. The membranes in bromide ion form were stained with osmium tetroxide at room temperature prior to examination. The stained membranes were embedded within an epoxy resin, sectioned into approximately 50 nm thick samples with a Leica UC6t Ultramicrotome, and placed on a copper grid for observation.

The thermal stability of the hydroxide form of the membranes was analyzed by thermogravimetric analysis (TGA) on a TA Instruments Q50 analyzer. The thermal degradation was evaluated at a heating rate of 5 °C/min up to 800 °C in nitrogen.

The stress-strain relationship of the membranes was investigated by dynamic mechanical analysis (DMA) using TA Instruments Q800 with controlled force mode. Rectangular membrane samples were fully hydrated and tested using tension clamps after removing surface water at 100% relative humidity. The experimental parameters were set as follows: preload force 0.05 N, isothermal conditions at 30 °C, soak time 1 min, force ramp rate 0.5 N/min and upper force limit up to 18 N.

The alkaline stability of the membranes was evaluated by soaking the membranes (in hydroxide form) in 1 M NaOH in a teflon-lined Parr reactor at 60 °C for up to 1000 h to measure the change in ionic conductivity. Before measurement, each membrane was thoroughly washed with deionized water. The ionic conductivity was determined in HPLC-grade water at room temperature under constant nitrogen gas purging.

**RESULTS AND DISCUSSION**

**Synthesis of Anion Conductive Multiblock Copolymer with Long, Alkyl Tethered TMA, ABCO, and TTMP**

The multiblock copolymer with long, alkyl side chains terminated with a cation head-group was synthesized via polycationization reaction and Friedel-Crafts acylation followed by reduction of the ketone, as described previously. In this study, a multiblock copolymer, \( X_{3}Y_{7-2} \), with a hydrophobic block (\( X \)) composed of 3 repeat units in each block, a hydrophilic block (\( Y \)) with 7 repeat units in each hydrophobic block, and 2 alkyl head-group tethers per hydrophilic repeat unit was used to study the effects of head-group type on membrane properties. The block copolymer was quaternized with trimethylamine, quinuclidine, and tris(2,4,6-trimethoxyphenyl)phosphine to form three different head-groups. The resulting cations were: alkyl tethered TMA, ABCO, and TTMP, respectively. Each had a bromide counter ion. The membranes were solvent cast after the quaternization reaction. Another membrane with alkyl TMA was quaternized after the membrane was cast. This was used as a comparison with the membranes quaternized before casting. The membranes were converted into the hydroxide ion form by soaking them in a NaOH solution. The structure of the multiblock copolymer with these three cations head-groups is shown in Figure 1.

**Morphology**

The morphology of the dry membranes with the three different cation head-groups in bromide form were characterized via small angle X-ray scattering (SAXS), as shown in Figure 2. The size of the ion conductive channels, which is the size of the continuous hydrophilic ion domains formed by phase segregation of the block copolymer, was evaluated by calculating the average separation length, or interdomain spacing, \( d \), between inhomogeneities in the membrane. The interdomain spacing was calculated from the position of the scattering maximum (\( q_{\text{max}} \)) via Bragg’s law. The multiblock copolymer AEMs with alkyl trimethylammonium \( X_{3}Y_{7-7} \), \( X_{3}Y_{7-8} \), quinuclidium \( X_{3}Y_{7-8} \), and phosphonium \( X_{3}Y_{7-P} \) showed scattering peaks.
with $q_{\text{max}}$ values of 0.124, 0.167, 0.153 and 0.132 nm$^{-1}$, respectively. This corresponds to inter-domain spacing ($d$) of 50.6, 37.6, 41.0 and 47.6 nm, respectively, as shown in Table 1. The $d$ values obtained from the SAXS data confirms phase segregation from the multiblock copolymers, rather than just small ion clusters in the membranes which would show a smaller value of $d$.

Since the membranes had the same backbone structure (i.e. same length of hydrophobic and hydrophilic blocks) and the same number of head-group tethers on each hydrophilic repeat unit, the difference in the interdomain spacing $d$ was primarily due to the different cation head-groups. The IEC of each membrane was evaluated by titration and is reported in Table 1. The data shows that essentially full conversion of the tethers to the cation head-group was achieved, as discussed in the next paragraph. By comparing $X_3Y_7$-$A_2$, $X_3Y_7$-$Q$, and $X_3Y_7$-$P$, it was found that the interdomain spacing increased with the size of the cation head-group. In addition, the preparation method of the membrane also affected the phase segregation and the size of the ion conductive domains. The membrane quaternized after casting, $X_3Y_7$-$A_1$, showed much larger interdomain spacing $d$ than that of the membrane quaternized before casting, $X_3Y_7$-$A_2$. Quaternization before casting allowed better phase segregation of the block copolymers because the block copolymer with the ionic groups attached has a higher $\chi$, the Flory Huggins interaction parameter characterizing the effective interaction of monomers in the hydrophilic and hydrophobic blocks. In addition, casting the membrane before quaternization may not provide the needed volume expansion for formation of the cation head-group.

The IEC of the membranes with different cation head-groups is summarized in Table 1. Since all the membranes had the same structure, other than the cation head-group, the difference in the IEC values is the direct result of the molecular weight of the cation head-groups. TMA has an intrinsic advantage because of its low mass, Figure 1. As the size and mass of cation group increased, the IEC decreased. For example, the membrane with alkyl TMA, $X_3Y_7$-$A_1$ and $X_3Y_7$-$A_2$ had an IEC of 1.49 meq/g, while the membrane with alkyl TTMPP, $X_3Y_7$-$P$, had an IEC of 0.87 meq/g, 42% less than the TMA-containing AEM.

The hydroxide conductivity of the membranes at 20, 40, 60 and 80 °C is shown in Figure 3. The ionic conductivity increased with temperature and followed an Arrhenius relationship.
The slope of the Arrhenius plot corresponds to the activation energy for ionic conductivity. The energy of activation was found to be 19.6, 20.6, 18.8, and 18.9 kJ/mol for X3Y7-A1, X3Y7-A2, X3Y7-Q, and X3Y7-P, respectively.

By comparing the ionic conductivity of the membranes with different cation head-groups, it can be seen that the ionic conductivity increased with IEC even though the materials had the same backbone, tether length, and the same number of ionic head-groups attached to each repeat unit in the hydrophilic block of the polymer. The membrane conductivity closely follows the IEC, however, there also appears to be a difference in hydroxide mobility. This can be seen by comparing the conductivity per IEC for the four membranes shown in Table 1. The conductivity per IEC from Table 1 are as follows: 61.8, 67.9, 49.4 and 52.9. This shows that the hydroxide ions with the TMA head-group had the highest mobility. Thus, quaternary TMA is a more efficient and compact head-group (i.e. smaller van der Waals volume) and formed the smallest channels.

In addition, the preparation method of the membranes also affects the ionic conductivity. The membrane quaternized after casting, X3Y7-A1, exhibited lower ionic conductivity than the membrane quaternized before casting, X3Y7-A2. This difference in conductivity and conductivity per IEC is due to hydroxide mobility because the membranes were otherwise identical. The casting before quaternization, X3Y7-A1, resulted in larger ion conductive channels. It is noted that this larger channel size did not result in higher conductivity. X3Y7-A2 had the highest conductivity (i.e. higher mobility than X3Y7-A1) which can be attributed to a more efficient ion channel pathway.

**Table 1** Properties of the AEMs with alkyl trimethylammonium (TMA), quinuclidium (ABCO), and trim(2,4,6-trimethoxyphenyl)-phosphonium (TTMPP) cations

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Interdomain spacing d (nm)</th>
<th>Theoretical IEC (meq/g)</th>
<th>Titration IEC (meq/g)</th>
<th>Ionic conductivity (mS/cm)</th>
<th>r/IEC</th>
<th>Water uptake (%)</th>
<th>Hydration number, λ</th>
<th>Nfree</th>
<th>Nbound</th>
</tr>
</thead>
<tbody>
<tr>
<td>X3Y7-A1</td>
<td>40</td>
<td>1.49</td>
<td>1.39</td>
<td>26.7</td>
<td>92.2</td>
<td>61.8</td>
<td>26.0</td>
<td>9.7</td>
<td>0.6</td>
</tr>
<tr>
<td>X3Y7-A2</td>
<td>36</td>
<td>1.49</td>
<td>1.42</td>
<td>27.8</td>
<td>101.2</td>
<td>67.9</td>
<td>24.4</td>
<td>9.1</td>
<td>0.4</td>
</tr>
<tr>
<td>X3Y7-Q</td>
<td>35</td>
<td>1.38</td>
<td>1.27</td>
<td>21.1</td>
<td>68.2</td>
<td>49.4</td>
<td>11.1</td>
<td>4.5</td>
<td>0.2</td>
</tr>
<tr>
<td>X3Y7-P</td>
<td>45</td>
<td>0.87</td>
<td>0.87</td>
<td>14.2</td>
<td>46.1</td>
<td>22.4</td>
<td>14.3</td>
<td>1.7</td>
<td>12.6</td>
</tr>
</tbody>
</table>

* X: hydrophobic block (3 repeat units); Y: hydrophilic block (7 repeat units).
  * Interdomain spacing: average separation length between inhomogeneities (d) measured from SAXS.
  * Theoretical IEC: calculated assuming 100% quaternization.
  * Ionic conductivity: tested in hydroxide ion form.
  * r/IEC: ratio of ionic conductivity at 80 °C to IEC.
  * Water uptake: measured at room temperature in hydroxide ion form.

Hydration number (λ) is the number of water molecules per cation/anion pair. Hydration number includes all the water molecules in the membrane: freezable water molecules which are only slightly associated with the ions, and non-freezable water (i.e., bound water) which serve as the ion hydration shell. The number of freezable (Nfree) and non-freezable (Nbound) water molecules was investigated by DSC and are summarized in Table 1 and Figure 4. In the DSC thermograms, the freezable water showed a characteristic

**Figure 3** Arrhenius plot of ionic conductivity vs. inverse temperature. [Color figure can be viewed at wileyonlinelibrary.com]
freezing peak at subzero temperature while non-freezable water did not.

The membranes with alkyl trimethylammonium head-groups, X₃Y₇-A₁ and X₃Y₇-A₂, had a hydration number of about 9 bound water molecules per ionic pair and very little free-water. This is consistent with the previous results where two-tether, multiblock copolymer membranes with alkyl tethered quaternary ammonium groups. However, in the case of alkyl quinuclidium, X₃Y₇-Q, the hydration number was low, 4.5, with very little freezable water. The membrane with alkyl phosphonium, X₃Y₇-P, had a high hydration number, up to 14.3 with a bound water value of 12.6. The lower IEC for the TTMPP head-group contributed to the lower conductivity and water uptake. One can consider adding additional tethers to each hydrophilic head-group in the polymer backbone to increase the IEC for the TTMPP head-group AEMs. However, if the number of tethers was increased for TTMPP to increase its IEC and conductivity, the number of tethers for the TMA and ABCO containing polymers should also be performed, if a fair-basis for comparison were used. This would clearly lead to even higher conductivities for ABCO and TMA head-group polymers. This clearly shows that there is an IEC and conductivity penalty for large, bulky head-groups in comparison to small ones.

**Relationship of Morphology, IEC, Ionic Conductivity, and Water Uptake**

The size of cation head-groups affects the morphology and properties of the AEMs. Alkyl trimethylammonium (TMA) has the smallest size and forms the smallest ion conducting channels, as determined by SAXS measurements. It has the highest ionic conductivity, up to 101.2 mS/cm at 80 °C and highest water uptake, 24.4% due to its high IEC (1.49 meq/g). Alkyl ABCO also has low water uptake, only 11.1%. This corresponds to four bound waters per cation/anion pair. Alkyl TTMPP has the largest size and forms the largest ion conductive channels. It has relatively low ionic conductivity, and higher water uptake than ABCO. Thus, alkyl TMA is the preferred head group for this backbone in terms of IEC, ionic conductivity and water uptake.

**Chemical Stability**

The alkaline stability of the membranes with the three cations were evaluated by measuring the change of ionic conductivity with exposure time in 1 M NaOH at 60 °C. As shown in Figure 5, the X₃Y₇-A2 membrane with alkyl trimethylammonium showed the best alkaline stability, with only 1% ionic loss over 480 h. This was consistent with the result...
of the alkyl trimethylammonium group stability reported previously. Several other studies also confirmed that alkyl trimethylammonium has little or no degradation at 60 °C after 30 days.\textsuperscript{3,12}

X_3Y_7-P with alkyl TTMPP showed 4.8% ionic conductivity loss in 480 h. Yan et al.\textsuperscript{16} reported no ionic conductivity loss for benzyl TTMPP after exposure to 1 M KOH at 60 °C for 30 days. However, Arges et al.\textsuperscript{24} reported (using NMR analysis) that only about 90% of the cations remained after the same exposure. In addition, they proposed that the degradation pathway is by direct nucleophilic SN2 substitution of the OH– ion creating a tertiary phosphate followed by oxidation to phosphorus oxide. It is believed that the same degradation mechanism also occurred in this case, but the long alkyl side chain mitigates the degradation. Yan et al.\textsuperscript{25} suggested an alternate structure of alkyl tris(2,4,6-trimethylphenyl)phosphonium without the methoxy groups for better alkaline stability.

X_3Y_7-Q with alkyl quinuclidium showed 22% ionic conductivity loss after 480 h at 60 °C. Degradation was also observed in other studies by Arges et al.\textsuperscript{20} on benzyl quinuclidinium where the IEC dropped from 1.8 to 0.5 meq/g in 1 M NaOH at 60 °C after 30 days. This was due to direct nucleophilic SN1 substitution at the benzylic methyl (debenzylation). Mohanty et al.\textsuperscript{3} reported no degradation for a series small molecules based long alkyl tether quaternary ammonium groups in 1 M NaOH at 60 °C. The degradation in ionic conductivity for the alkyl quinuclidinium head-group in this study may be the result of the small hydration number (i.e. bound water molecules for each cation/anion pair). Thus, the local hydroxide concentration in the ion conductive channels appears to be twice as high as the TMA head-groups.

Figure 6 shows the thermal degradation behavior of the membranes with the three head-groups in the hydroxide ion form as measured by TGA. All four samples showed a three-stage degradation upon heating in nitrogen. The initial weight loss below 100 °C is attributed to the evaporation of bound water in the membrane and not membrane degradation. The first degradation stage was the thermal degradation of ion exchange groups which occurred at slightly different temperatures for the three cations. The starting temperature for the degradation was 180 °C, 200 °C, and 190 °C for TMA, ABCO, and TTMPP cations, respectively. The second degradation stage was due to the long alkyl side chains in the temperature range of 250 °C to 400 °C. Above 400 °C, the degradation of polymer backbone occurred. The thermal degradation was not affected by the film casting method, as the chemical structure of the X_3Y_7-A1 and X_3Y_7-A2 were the same. It is noted that all of the membranes were thermally stable at the usual fuel cell and electrolyzer operating temperatures, below 100 °C.

The mechanical properties of the membranes with the three cation head-groups in hydroxide ion form were obtained from the stress-strain curve, as summarized in Table 2. The membranes were soaked in deionized water before testing and excess water was wiped off the surface before the test. The values for tensile strength, Young's modulus, and elongation at break show that these membranes had adequate mechanical strength and flexibility. The membrane with quinuclidinium head-groups showed the highest mechanical strength as measured by elongation-to-break, while the membrane with TTMPP showed the lowest. It was also observed that the solvent casting method affected the mechanical properties of the membrane. X_3Y_7-A2, quaternized before solvent casting, showed better mechanical properties than X_3Y_7-A1, quaternized after membrane casting. This is due to tighter entanglement and better rearrangement of polymer chains in the membrane if it was cast after quaternization.

### CONCLUSIONS

Multiblock copoly(arylene ether) based anion exchange membranes with alkyl tethered TMA, ABCO, and TTMPP cations were synthesized and quantitatively compared. The relationship between the size and structure of the cations with the morphology and properties of the AEMs was investigated. A larger cation head-group led to larger ion channels. However, the larger head-group also caused lower IEC and consequently lower ionic conductivity regardless of the cation channel size. Quinuclidinium showed lower water uptake with fewer bound water molecules for each ion pair. TMA is the most stable cation head-group during exposure to 1 M NaOH solution at 60 °C (20-day exposure), while the quinuclidinium head-group showed a 22% drop in ion conductivity, which was most likely due to the high local hydroxide concentration because it has less water uptake per hydroxide ion. The TMA head-group also had the best mechanical properties. Thus, the TMA head-group appears to be the best and most efficient cation head-group among those studied here for this backbone. Finally, the membrane preparation method affects the morphology and properties of the AEMs. Quaternization before membrane casting resulted in better properties than quaternization after membrane casting due to a better arrangement of the ion conducting channels.

In summary, quaternary ammonium head-groups tethered to a polymer backbone via long alkyl chains showed superior properties, including stability and ionic conductivity. TMA forms efficient ion conducting channels and has a low mass giving it a natural IEC advantage. While the operating temperature,
stability and conductivity targets for the different electrochemical devices varies (e.g. electrolyzers are higher current but modest operating temperature, fuel cells are higher temperature but lower current, and flow batteries are lower temperature but very sensitive to ionic resistive losses), each device benefits from higher stability and ionic conductivity. Long-tethered TMA on a block copolymer is the preferred ion head-group for each of these applications based on the structures and tests performed in this study.

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REFERENCES