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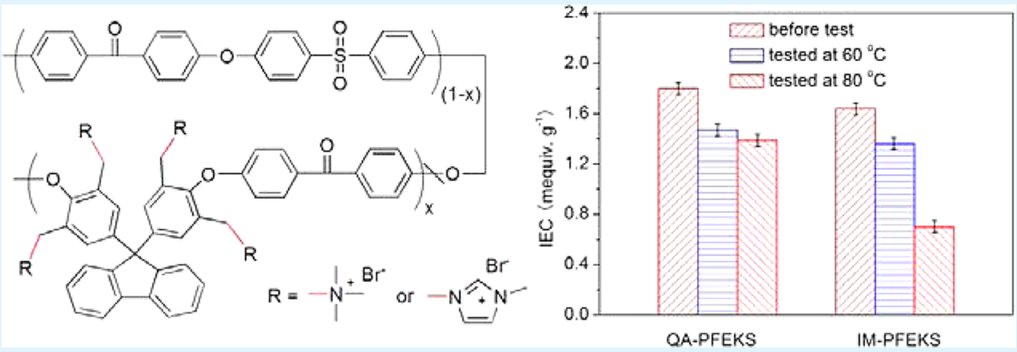
Degradation of Imidazolium- and Quaternary Ammonium-Functionalized Poly(fluorenyl ether ketone sulfone) Anion Exchange Membranes

Dongyang Chen and Michael A. Hickner*

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States



ABSTRACT: Imidazolium and quaternary ammonium-functionalized poly(fluorenyl ether ketone sulfone)s were synthesized successfully with the same degree of cationic functionalization and identical polymer backbones for a comparative study of anion exchange membranes (AEMs) for solid-state alkaline membrane fuel cells (AMFCs). Both anion exchange membranes were synthesized using a new methyl-containing monomer that avoided the use of toxic chloromethylation reagents. The polymer chemical structures were confirmed by ^{1}H NMR and FTIR. The derived AEMs were fully characterized by water uptake, anion conductivity, stability under aqueous basic conditions, and thermal stability. Interestingly, both the cationic groups and the polymer backbone were found to be degraded in 1 M NaOH solution at 60 °C over 48 h as measured by changes of ion exchange capacity and intrinsic viscosity. Imidazolium-functionalized poly(fluorenyl ether ketone sulfone)s had similar aqueous alkaline stability to quaternary ammonium-functionalized materials at 60 °C but much lower stability at 80 °C. This work demonstrates that quaternary ammonium and imidazolium cationic groups are not stable on poly(arylene ether sulfone) backbones under relatively mild conditions. Additionally, the poly(arylene ether sulfone) backbone, which is one of the most common polymers used in ion exchange membrane applications, is not stable in the types of molecular configurations analyzed.

KEYWORDS: *anion exchange membrane, polymer degradation, alkaline fuel cell, membrane stability, imidazolium, quaternary ammonium, poly(sulfone), poly(ketone)*

1. INTRODUCTION

Solid-state alkaline membrane fuel cells (AMFCs) hold promise as low cost, clean, and highly energy efficient power sources. New efforts have been devoted to foster AMFCs as alternatives to proton exchange membrane fuel cells (PEMFCs) as one route to fuel cell technology that is free from precious metal catalysts.[1−3] One of the challenging issues for the current development of AMFCs is to synthesize anion exchange membranes (AEMs) that feature the simultaneous requirements of high hydroxide anion conductivity, good mechanical integrity, and robust alkaline stability under electrochemical conditions. Many strategies in the design of high-performance proton exchange membranes find common ground in the preparation of AEMs, such as the use of hydrophilic−hydrophobic block structures to increase ion conductivity[4,5] and employment of cross-linking to mitigate the excess swelling of the membrane in water.[6,7] However, unless stability considerations are addressed, it is difficult to undertake development and optimization of new fuel cell devices.[8−10]

Different polymer backbone structures, namely aliphatic[6,11] versus aromatic,[4,12] and cation species including quaternary ammonium,[13] imidazolium,[14,15] phosphonium,[16] guanidinium,[17] sulfonium,[18] and pyridinium[19] have been explored as AEMs. These initial reports have given the field direction toward new materials targets, however, there are discrepancies across the field, especially concerning membrane stability. The stability of the quaternary ammonium group has been well-investigated experimentally and theoretically[20] and the benzyltrimethylammonium group has been commercialized in ion-exchange resin technology for its relatively high stability. It

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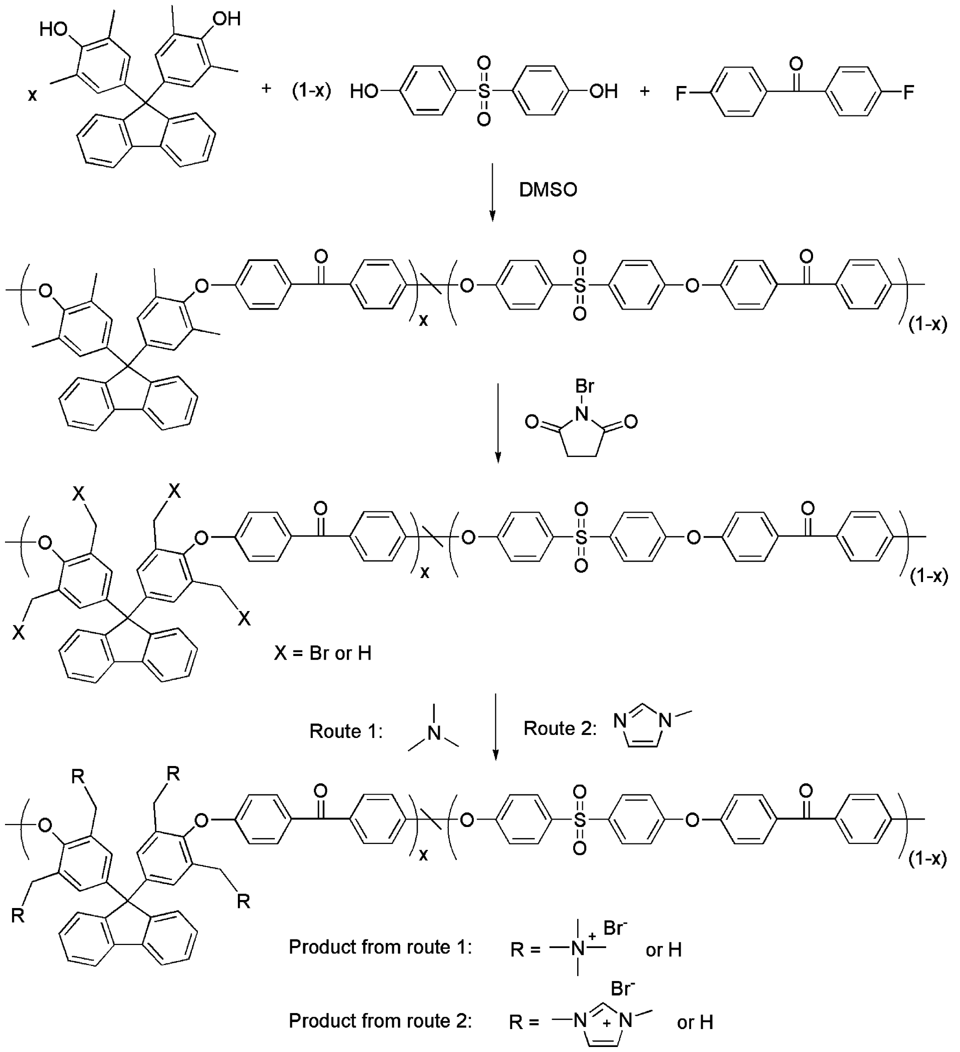
Scheme 1. Synthesis Route of Imidazolium and Quaternary Ammonium-Functionalized Poly(fluorenyl ether ketone sulfone)s



was reported that the imidazolium group has much better alkaline stability than the benzyltrimethylammonium group.[14,15] To develop high-performance AEMs for AEMFCs, herein, we reported the synthesis and comparison of imidazolium and benzyltrimethylammonium functionalized poly(fluorenyl ether ketone sulfone)s (Scheme 1) with an identical degree of functionalization and polymer backbone chemical structure. We feel this approach gives the best chance at developing detailed stability knowledge of the polymer backbone, linker group, and tethered cationic moiety for further development of highly stable AEMs.

The synthesis of AEMs generally involves halomethylation of a polymer and subsequent treatment with the desired cation precursor.[4,21] Direct addition of or in situ generated chloromethyl methyl ether is carcinogenic, but this reagent is highly reactive for chloromethylation of the aryl rings in a polymer, thus providing a facile route to the production of AEMs. Often, only one site on a backbone aromatic ring is functionalizable by direct chloromethylation before side reactions and cross-linking occur, which limits the ionic functionality of the polymer. N-bromosuccinimide (NBS), instead, is much safer to handle and can introduce benzyl bromide moieties at benzyl positions along the polymer backbone, giving an opportunity to synthesize multifunctionalized phenyl rings depending on the number of methyl groups. Therefore, NBS was chosen as halomethylation agent in this work and 9,9′-Bis(3,5-dimethyl-4-hydroxylphenyl)fluorene was synthesized to incorporate benzylic groups in the resulting polymer for halomethylation and also to endow good solubility to the polymer backbone because of this monomer's non-coplanar fluorene structure. Differences between quaternary ammonium-based and imidazolium-based AEMs derived from the brominated poly(arylene ether sulfone) backbone are reported for the critical AEM properties of water uptake, anion conductivity, and aqueous alkaline and thermal stability.

2. EXPERIMENTAL SECTION

2.1. Materials. 9,9′-bis(3,5-dimethyl-4-hydroyphenyl)fluorene (DMHPF) was synthesized according to a previously reported method.[22] All the reagents were purchased from common commercial suppliers. 4,4′-difluorobenzophenone was recrystallized from ethanol. All the other reagents were used without further purification.

2.2. Synthesis of Poly(fluorenyl ether ketone sulfone) (PFEKS). To a 100 mL three necked round-bottom flask equipped with a Dean–Stark trap, an argon inlet and outlet, a condenser, a magnetic stirrer was charged 2.0850 g of (15.0 mmol) K_2CO_3, 30 mL of DMSO, 15 mL of toluene, 1.6261 g (4.0 mmol) of DMHPE, 1.5016 g (6.0 mmol) of bis(4-hydroxylphenyl)sulfone, and 2.1820 g (10.0 mmol) of 4,4′-difluorobenzophenone. The reaction was first carried out at 145–150 °C for 3 h. The toluene was distilled from the reaction

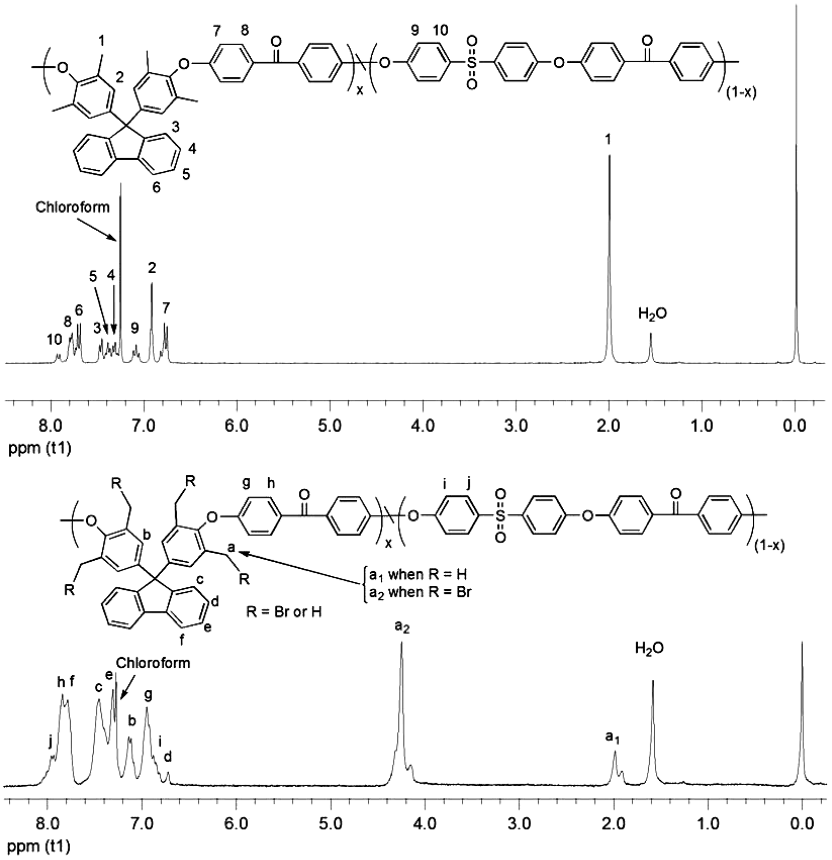


Figure 1. ^{1}H NMR spectra of PFEKS and Br-PFEKS (both in $CDCl_3$).

mixture to remove the product water and the temperature was raised to 170 °C and maintained for 15 h. The viscous mixture was poured into water to form the fibrous product PFEKS, which was collected by filtration. The measured intrinsic viscosity (IV) was 0.40 dL g^{-1}.

2.3. Bromination of PFEKS. The PFEKS was brominated using a radical-initiated route as reported in ref 13. To a 250 mL flask was added 5.0 g of PFEKS, 100 mL of dichloroethane, 2.7 g of N-bromosuccinimide (NBS) (15.0 mmol) and 0.2 g benzoyl peroxide (BPO) (0.8 mmol). The reaction was carried out at 85 °C for 5 h under the protection of Ar gas. Upon cooling to room temperature, the reaction mixture was poured into 500 mL of methanol. Fibrous product was formed and collected by filtration. The product was washed by 100 mL of acetone three times, dissolved in chloroform, precipitated in methanol, collected by filtration, and dried under vacuum at room temperature. The resulting IV of the product brominated polymer was 1.01 dL g^{-1}.

2.4. Synthesis of QA-PFEKS and IM-PFEKS. Two and a half grams of brominated PFEKS was dissolved in 25 mL of N, N′-dimethylacetamide (DMAc) in a glass vial. Next, 5.3 g of trimethylamine solution (45 wt % in water) was added and the container was sealed. The mixture was magnetically stirred at room temperature for 24 h, and then poured into a Petri dish and dried at 70 °C under ambient pressure. A membrane was formed and peeled from the substrate in water, and then immersed in deionized water for 24 h with changing the water three times. The membrane was dried at room temperature under vacuum for 24 h, dissolved in DMAc as an 8 wt % solution, cast onto a glass plate, and dried at 70 °C for 24 h. The membrane (QA-PFEKS) was removed from the glass plate and stored in deionized water prior to use. For IM-PFEKS, 1-methylimidazole (3.3 g) was added instead of trimethylamine in the above procedure.

2.5. Membrane Preparation and Anion Exchange. The QA-PFEKS and IM-PFEKS were dissolved in N, N′-dimethylacetamide (DMAc) at approximately 8 wt /vol % and then cast on glass plates, dried at 80 °C under atmosphere pressure for 24 h. The QA-PFEKS and IM-PFEKS membranes were peeled off from the glass plates and immersed in 1 M $KHCO_3$ or KOH solution for 24 h, followed by immersion in deionized water for 24 h with changing the water three times. HCO_3^- or OH^- counterion form polymers were obtained. Due to equilibration of the OH^- form membrane with ambient CO_2 in water or air, the OH^- form polymers were characterized immediately.

2.6. Characterization. The intrinsic viscosities of the samples were measured in 1-methyl-2-pyrrolidinone (NMP) containing 0.05 M LiBr at room temperature using a Ubbelohde viscometer. The thermal stability of the Br^- form and HCO_3^- form membranes was analyzed using a Q50 TGA (TA Instruments Corp., USA). The temperature was increased from room temperature to 80 °C and held for 30 min to remove most of the residual water from the sample, and then increased to 800 °C at a heating rate of 10 °C min^{-1} under a N_2 atmosphere. FTIR spectra were recorded on a Bruker Vertex FTIR spectrometer. ^{1}H NMR was recorded on a Bruker AV-300 NMR instrument and the chemical shifts were listed in parts per million (ppm) downfield from tetramethylsilane (TMS).

For ion exchange capacity (IEC) titration, 0.2 g membrane (Br-form) was immersed in 50 mL 0.2 M $NaNO_3$ solution for 24 h and titrated with 0.1 M AgNO3 using K_2CrO_4 as colorimetric indicator. The IEC was calculated via

$$\text{IEC} = \frac{\Delta V_{\text{AgNO3}} C_{\text{AgNO3}}}{m_{\text{d}}}$$

where m_{d} is the mass of the dry membrane, ΔV_{AgNO3} is the consumed volume of $AgNO_3$ solution, and C_{AgNO3} is the concentration of $AgNO_3$ solution.

The water uptake of the membranes was defined as weight ratio of the absorbed water to that of the dry membrane as given by

$$W(\%) = \left(\frac{m_{\text{w}} - m_{\text{d}}}{m_{\text{d}}}\right) \times 100\%$$

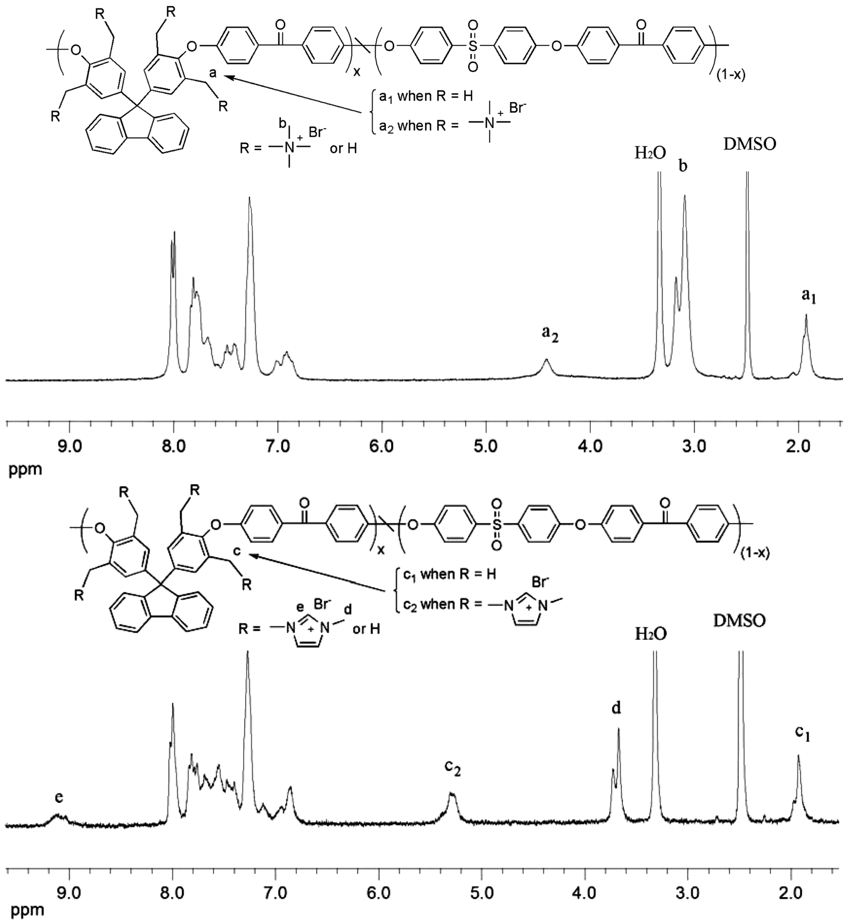


Figure 2. ^{1}H NMR spectra of QA-PFEKS and IM-PFEKS in DMSO-d$_6$. The representative peaks of quaternary ammonium cation and imidazolium cation are indicated in the spectra.

where m_d and m_w are the weight of membranes before and after water absorption, respectively. The hydration numbers (λ) were calculated from

$$\lambda = \left(\frac{m_w - m_d}{M_{H2O}}\right)\left(\frac{1000}{m_d \mathrm{IEC}}\right)$$

where M_{H2O} is the molecular weight of water.

The ion conductivities of membranes were measured by two-probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260A frequency response analyzer as previously reported.[23] The measurements were conducted with the sample submerged in deionized water at room temperature. The conductivity (σ) was calculated from the impedance plot according to the cross-sectional area available for ion transport (A) and the distance between electrodes (d), $\sigma = d/RA$, where the resistance R was derived from the intercept of the low-frequency complex impedance with the Re (Z') axis. For OH^- conductivity measurement, the samples were immersed in deionized water, which was degassed and blanketed with flowing Ar gas to exclude as much CO_2 as possible.

3. RESULTS AND DISCUSSION

3.1. Polymer Synthesis. The polymerization of benzyl group-containing poly(fluorenyl ether ketone sulfone) (PFEKS) and its postfunctionalization reactions are depicted in Scheme 1. ^{1}H NMR was used to confirm the chemical structures of the products and to determine the degree of functionalization (DF) of the backbones. The benzyl group on PFEKS had a singlet peak at 2.0 ppm, Figure 1. After selective bromination at the benzyl positions, the peak split into a doublet and shifted to 4.1−4.4 ppm. The remaining unreacted benzyl group also became a doublet while remaining at 1.9−2.1 ppm. From the integral area ratio of the brominated benzyl peaks to (brominated benzyl peaks + unreacted benzyl peaks), a 67% DF was calculated, similar to our previous report.[13] Treating this brominated polymer with trimethylamine or 1-methylimidazole in N,N′-dimethylacetamide solution at room temperature gave QA-PFEKS or IM-PFEKS, respectively. Complete conversion of the brominated benzyl groups to the corresponding cationic moiety was observed in ^{1}H NMR spectra of QA-PFEKS and IM-PFEKS, Figure 2, where the peaks of brominated benzyl group were totally replaced by the peaks of quaternary ammonium- or imidazolium-functionalized benzyl groups.

The FTIR spectra of QA-PFEKS and IM-PFEKS are shown in Figure 3. The peak at 3062 cm^{-1} was ascribed to the vibration of aromatic C−H bond. The peaks at 2955 and 2926 cm^{-1} were assigned to the vibration of the aliphatic C−H bond on the methyl or methylene groups. The peak at 1646 cm^{-1} was assigned to the vibration of C=C bond on the fluorenyl group and C−N bond on quaternary ammonium group or imidazolium group. The peaks at 1600 and 1488 cm^{-1} were attributed to the asymmetric and symmetric vibrations of C=C bond on phenyl rings, respectively. The peak at 1448 cm^{-1} was ascribed to the vibration of C−N bond on the quaternary ammonium group or imidazolium group. Both the ^{1}H NMR and FTIR results validated the successful synthesis of QA-PFEKS and IM-PFEKS.

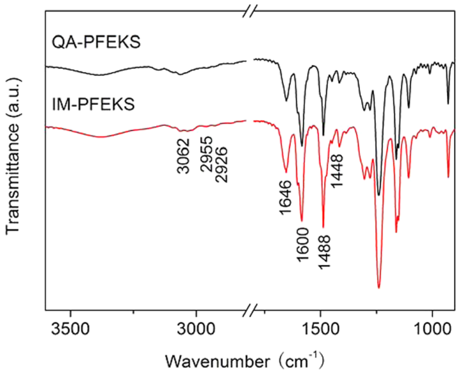


Figure 3. FTIR spectra of QA-PFEKS and IM-PFEKS.

The intrinsic viscosities (IVs) of QA-PFEKS and IM-PFEKS were measured using a procedure to minimize the polyelectrolyte effect.[24] Interestingly, the IV of IM-PFEKS was much lower than that of QA-PFEKS even though they have the same main chain structure, Table 1. We surmise that the lower IVs in the imidazolium-based polymers were due to lower Coulombic interaction between the delocalized imidazolium cations compared to the stronger forces experienced in quaternary ammonium-based materials. The ion exchange capacities (IECs) derived from the DF of brominated PFEKS for QA-PFEKS and IM-PFEKS were 1.89 and 1.82 mequiv. g^{-1}, respectively. This difference in IEC was due to the different masses of quaternary ammonium cation and imidazolium. The titrated IECs are shown in Table 1, which were slightly lower than the values calculated from ^{1}H NMR.

3.2. Anion Conductivity. It has been reported[13,25] that OH$^-$ form membranes absorb CO$_2$ from the atmosphere easily to yield HCO$_3^-$ form membranes. The dilute solution mobility of HCO$_3^-$ is much lower than the mobility of OH$^-$, hence the observed decrease in the ion conductivity versus time upon exposure of OH$^-$ form membranes to CO$_2$. The water uptake and ion conductivity of the membranes in OH$^-$ and HCO$_3^-$ forms were investigated and listed in Table 1. It can be found that the OH$^-$ form membranes had much higher water uptake than HCO$_3^-$ form membranes for both QA-PFEKS and IM-PFEKS. The water uptakes of QA-PFEKS were slightly higher than that of IM-PFEKS, probably because of the smaller size of quaternary ammonium cation compared to imidazolium cation as well as the slightly higher IEC of QA-PFEKS. The anion conductivities of QA-PFEKS were much higher than those of IM-PFEKS, which can be correlated to the different water uptake between these two materials, similar to the case of proton exchange membranes in which higher water uptake facilitates ion transport.[26,27] The HCO$_3^-$ conductivities were much lower than the OH$^-$ conductivities, and the ratio of OH$^-$ conductivity to HCO$_3^-$ conductivity is approximately 4.4 as predicted from the dilute solution mobility ratio of the anions. The OH$^-$ conductivity of QA-PFEKS in this work were comparable to the reported quaternary ammonium functionalized poly(fluorenyl ether)s with similar IEC.[13] Although the OH$^-$ conductivity can be optimized by many strategies, we are more interested in the alkaline stability of these membranes before further enhancements in conductivity are addressed.

3.3. Alkaline Stability. The alkaline stability of QA-PFEKS and IM-PFEKS was studied by immersing the membranes in 1 M NaOH solution at 60 or 80 °C for 48 h. Under both conditions, the QA-PFEKS samples broke into small pieces, which is an indication of a decrease in mechanical properties and polymer molecular weight, while IM-PFEKS samples remained intact as shown in Figure 4. After examination of the degradation fragments, we found many scale-like features on the surface of IM-PFEKS as an indication of degradation. This phenomenon was also observed when evaluating the stability of sulfonated poly(sulfone)[28] under the same alkaline conditions, which calls into question the alkaline stability of poly(arylene ether sulfone) or poly(arylene ether ketone) backbones after hydrophilic functionalization with ions that allows for intimate contact between the polymer backbone and nucleophiles in solution.

The IEC of all samples decreased during treatment of the samples at 60 or 80 °C, Figure 5a. The IEC of QA-PFEKS was reduced to 82% of its original IEC at 60 °C and 78% of the IEC remained at 80 °C; the IEC of IM-PFEKS was reduced to 83% of its original IEC at 60 °C and only 43% of the original IEC was maintained after treatment at 80 °C. Therefore, the degradation of the imidazolium cation was much more pronounced at 80 °C as compared to the benzyltrimethylammonium cation. Previous reports[14,15] have suggested high alkaline stability of imidazolium cations, but recent work[29,30] has revealed that imidazolium cations are even less stable than quaternary ammonium cations which is in good agreement with our observations. The intrinsic viscosities of the QA-PFEKS sample decreased significantly, Figure 5b, suggesting severe polymer backbone degradation occurred during treatment with aqueous base. Although the alkaline stability of poly(arylene ether sulfone) or poly(arylene ether ketone) backbones was not considered by recent publications[2,16,17] where anion exchange membranes were developed from these backbones, early work by Sata et al.[31] in 1996 reported the low stability of the poly(arylene ether sulfone) backbone compared to polystyrene backbone for AEMs presumably because of the hydrolysis of aromatic ether bond under alkaline conditions. Zhang et al.[32] also found decreases in viscosities of their AEMs after alkaline stability tests; however, they did not minimize the polyelectrolyte effect by adding salt to the IV solution to rule out the influence of IEC changes on IV.

The ^{1}H NMR of degraded QA-PFEKS is shown in Figure 6, where few changes at the aromatic proton area were observed as compared to ^{1}H NMR of pristine QA-PFEKS. However, the exact reactions that occurred during degradation were too complex to be clarified by ^{1}H NMR. Since these polymers do not contain β-hydrogens to the quaternary ammonium group, we surmise that degradation of the QA-PFEKS proceeds by dealkylation of the pendant methyl groups and/or substitution at the benzyl position. IM-PFEKS samples were insoluble in all

Table 1. Intrinsic Viscosity, Water Uptake, and OH$^-$ Conductivity of QA-PFEKS and IM-PFEKS

			water uptake (%)		λ		conductivity (mS cm^{-1})	
sample	intrinsic viscosity (dL g^{-1})	IEC (mequiv g^{-1})	OH$^-$	HCO$_3^-$	OH$^-$	HCO$_3^-$	OH$^-$	HCO$_3^-$
QA-FEKS	0.54	1.80	59	36	18.2	11.1	22.3	5.1
IM-PFEKS	0.34	1.64	48	32	14.8	9.9	17.1	3.9

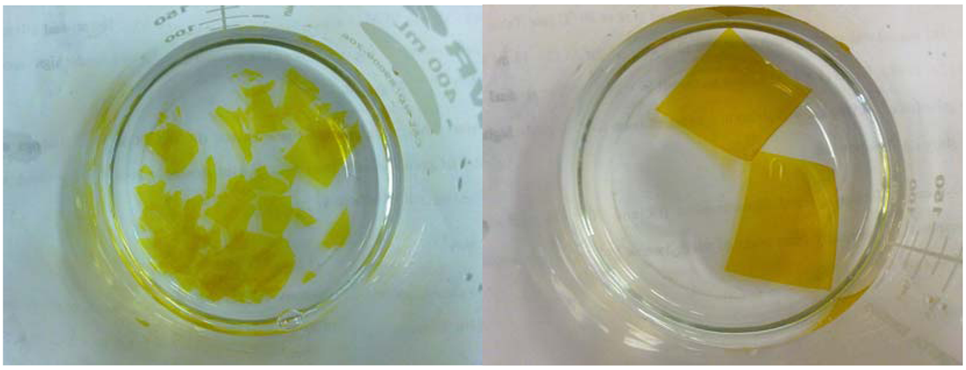


Figure 4. Optical images of QA-PFEKS (left) and IM-PFEKS (right) after degradation test.

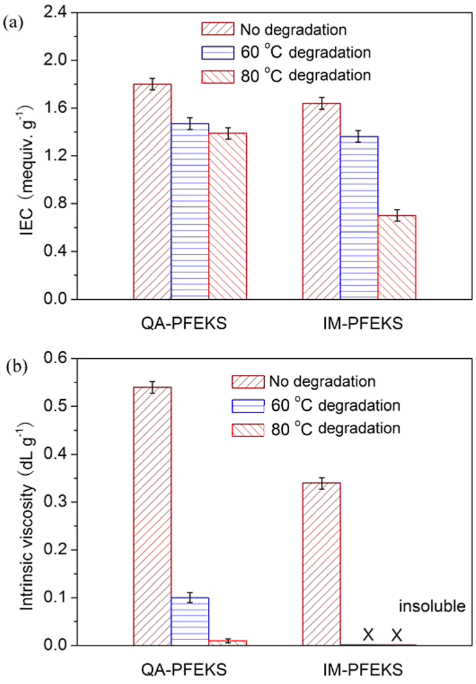


Figure 5. Stability of QA-PFEKS and IM-PFEKS in 1 M NaOH at 60 and 80 °C. (a) IEC; (b) intrinsic viscosity.

solvents after stability tests indicating cross-linking, therefore, no IV could be obtained for these samples. Despite its distributed charge density, the planar structure of imidazolium has little steric hindrance for attack by OH^-, which may negatively influence its alkaline stability. Ye et al.[33] reported the degradation mechanism of the imidazolium cation where an aldehyde group was observed in their ^1H NMR results. Although the mechanism of cross-linking of IM-PFEKS is difficult to elucidate, the highly reactive aldehyde group may be one of the sources of cross-links in the degraded polymer.

3.4. Thermal Stability. The thermal stability of HCO_3^- form and Br^- form QA-PFEKS and IM-PFEKS were investigated by thermogravimetric analysis (TGA) as shown in Figure 7. Two-step decomposition was observed for Br^- form samples, which was ascribed to the decomposition of cationic groups in the first step and the decomposition of polymer backbone in the second step.[12,34] The 5% weight loss temperatures were 261 and 293 °C for Br^- form QA-PFEKS and IM-PFEKS, respectively. The HCO_3^- form samples exhibited an additional decomposition event at between 100 to 240 °C, which was attributed to the decomposition of HCO_3^- ion. Although there are TGA curves of OH^- form AEMs in the literature[35] where the thermal stabilities were concluded as high as more than 200 °C, we do not believe it is appropriate to use TGA to investigate the thermal stability of OH^- form AEMs because the real thermal stability of OH^-

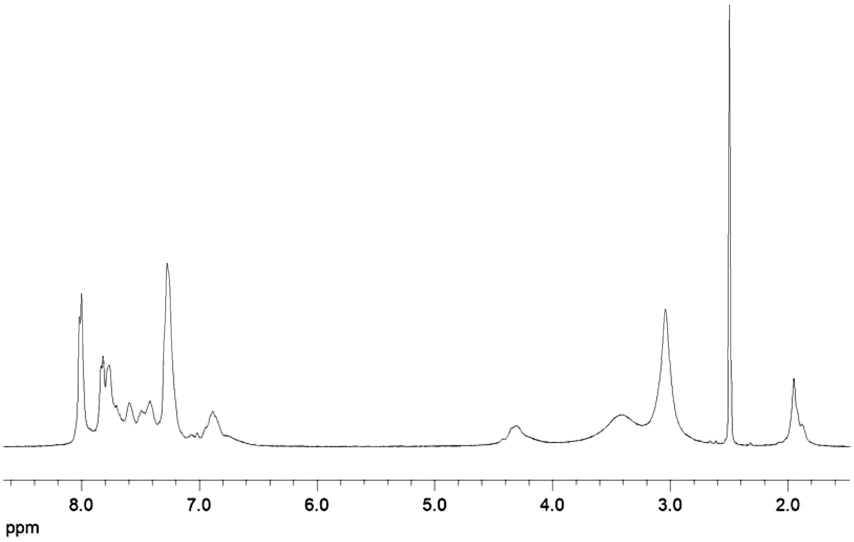


Figure 6. ^1H NMR of degraded QA-PFEKS in DMSO-d6. Degradation conditions: 1 M NaOH, 80 °C, 48 h.

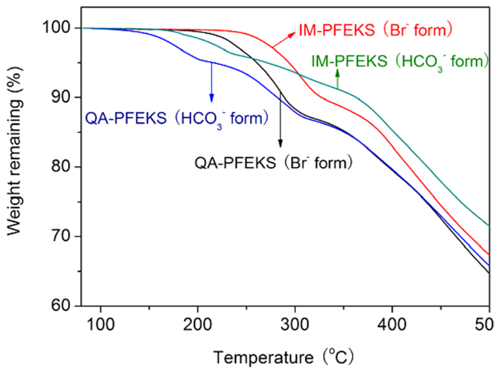


Figure 7. TGA curves of HCO$_3^-$ and Br$^-$ forms QA-PFEKS and IM-PFEKS.

form AEMs was known to be much less than what is indicated in TGA measurements.[4,36]

4. CONCLUSIONS

Imidazolium- and quaternary ammonium-functionalized poly(fluorenyl ether ketone sulfone)s with the same degree of functionalization and identical polymer backbone structure were synthesized successfully as anion exchange membranes for AMFC applications. The water uptake and ion conductivity of QA-PFEKS were higher than those of IM-PFEKS. Both QA-PFEKS and IM-PFEKS were found to be unstable in 1 M NaOH solution at 60 or 80 °C. Reduced IEC and lower intrinsic viscosity for QA-PFEKS were found after stability tests, suggesting degradation of both the cationic group and polymer backbone upon exposure to aqueous base. The IM-PFEKS experienced a similar decrease in IEC at 60 °C and a much larger decrease in IEC at 80 °C as compared to QA-PFEKS. The tested IM-PFEKS samples were found to be insoluble in any solvents after degradation. These results outline the challenges of alkaline stability of both cationic groups and polymer backbones for AMFC applications.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hickner@matse.psu.edu. Tel.: 814-933-2204. Fax: 814-865-2917.

Notes

The authors declare no competing financial interest.

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