

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Anion Exchange Membranes by Bromination of Benzylmethyl-containing Poly (fluorene ether sulfone)s

Cite this: DOI: 10.1039/x0xx00000x

Wenhai Mei,^a Changli Lü,^b Jingling Yan,^{*a} and Zhen Wang^{*a}

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Fluorene-containing anion exchange membranes were synthesized via the bromination reaction of poly(sulfone)s derived from between 9, 9-bis(3,5-dimethyl-4-hydroxyphenyl)fluorene (DMHPF), 4-fluorophenyl sulfone and 4, 4'-biphenol, quaternization reaction using trimethylamine, and ion exchange; then the properties of these AEMs were fully characterized, and the structure-property relationship regarding this series of AEMs was elucidated. Brominated poly (fluorene ether sulfone)s (BrPFES) were characterized using proton nuclear magnetic resonance (¹H NMR), and the bromination conversion, degree of functionalization (DF), and conversion of benzylmethyl groups were calculated. BrPFES was then quaternized by heterogeneous amination using trimethylamine, and then converted to quaternary ammonium bicarbonate by ion exchange. The properties of these AEMs were studied in terms of water uptakes, conductivities, swelling ratios, and mechanical properties. Compared to their homopolymer counterparts with similar ion exchange capacities (IEC), AEMs based on copolymers showed slightly lower conductivities but much lower water uptakes and swelling ratios, which can be explained by the fact that the continuation of hydrophilic domains in copolymers was interrupted by the incorporation of hydrophobic 4, 4'-biphenol segments.

1. Introduction

Fuel cells are considered as promising energy conversion devices for both stationary and mobile applications. Proton exchange membrane fuel cells (PEMFCs) have been the predominant fuel cell technologies in the last two decades due to their high power density, high energy efficiency, low operation temperature, and environmental friendliness.¹⁻³ However, PEMFCs are still suffering from several drawbacks such as the dependence of precious metal catalyst (e.g. platinum) and sluggish oxygen reduction kinetics, which prevents their widespread commercialization.

Recently, anion exchange membrane fuel cells (AEMFCs) have been receiving considerable attentions from both academic and industrial communities. AEMFC can offer potential advantages over PEMFC, including improved oxygen reduction kinetics, the applicability of non-precious metal catalyst (e.g. nickel and cobalt), and fuel flexibility.⁴⁻⁶ High performance anion exchange membranes (AEMs) are the key components in the development of AEMFCs. Since the commercially available sources of AEM materials are limited, many research efforts have been made to develop AEMs with high conductivity, good mechanical robustness, and long-term durability. A variety of quaternary ammonium-functionalized polymers have been investigated as AEM materials or the catalyst layer ionomers, including poly(styrene),^{7,8}

poly(sulfone),⁹⁻¹¹ poly(imide),^{12,13} poly(phenylene oxide),^{14,15} poly(norbornene),¹⁶ poly(phenylene).¹⁷ In most studies, halomethyl groups were introduced into the polymer backbone through either chloromethylation of aromatic rings or bromination of benzylmethyl groups, followed by the quaternization by a tertiary amine to form a pendent cation. Chloromethylation is a well-established, facile approach to creating anion exchange groups in the aromatic polymers. However, there are several undesired characteristics associated with chloromethylation, such as the involvement of excess highly toxic reagent, long reaction time, and low selectivity.¹⁸ Compared to chloromethylation, bromination of benzylmethyl-containing polymers showed faster reaction rates (several hours versus several days), high efficiency (up to 90% based on the conversion of bromine in NBS to bromine in bromomethyl group), and high selectivity which bromine and thus quaternary ammonium groups can be directed to specific locations. This process has been well demonstrated by Hickner, Hibbs, and other researchers.^{18, 19}

The incorporation of fluorenyl groups into ion conductive polymers offers many desired characteristics such as higher ion conductivity, and improved chemical, thermal and mechanical durability. Miyatake and coworkers reported on a series of fluorene-containing, sulfonated polyimides and poly (acrylene ether)s and evaluated their properties as PEM materials.²⁰ They also demonstrated that these polymers are durable for 5,000

hours under fuel cell operating conditions with a mediate power density. With respect to AEMs, fluorene-containing polymers also were also extensively investigated since 2010. Miyatake et al successfully synthesized fluorene-containing AEMs by the chloromethylation of multi-block fluorene-containing poly (acrylene ether)s using chloromethyl methyl ether, and then the quaternization of chloromethyl group with trimethylamine.²¹ The ionic conductivity was improved by phase separation caused by the multi-block architecture with highly hydrophilic segments. Furthermore, these membranes showed reasonable performance in a noble metal-free alkaline fuel cell fuelled by hydrazine.²² Other studies by Miyatake and Kim also reported fluorene-containing, ammonium-functionalized poly(ether sulfone)s, and confirmed that the introduction of fluorene groups is efficient to improve AEM properties.^{23,24} Meng and coworkers prepared fluorene-containing AEMs by the polymerization of tertiary amine-functionalized bisphenol and decafluorobiphenyl, followed by the quaternization by iodomethane.²⁵ Ion exchange capacity (IEC) can be controlled by adjusting the feeding ratio of amine-functionalized monomer and unfunctionalized monomer. Chen and Hickner synthesized fluorene-containing AEMs by bromination of benzylmethyl containing poly(ether ether ketone), and investigated the effect of different ammoniums on the stability of the resulting AEMs.²⁶ The results indicated that quaternary ammonium was more stable than imidazolium in NaOH solution at elevated temperatures. More recently, Liu and coworkers reported fluorene-containing AEMs by bromination of benzylmethyl-containing poly(sulfone)s, followed by quaternization using *N, N, N', N'*-tetramethyl-1, 6-diaminohexane.²⁷ In general, most of fluorene-containing AEMs were prepared via chloromethylation of aromatic polymers, which lacks precise control of IEC and distribution of ionic groups along the polymer chain.

Herein, we report the synthesis and characterization of AEMs by bromination of benzylmethyl-containing poly (fluorenyl ether sulfone)s. Poly(sulfone)s with a variety of benzylmethyl content was synthesized by polycondensation of 4-fluorophenyl sulfone, 4, 4'-biphenol, and 9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene (DMHPF). Benzyltrimethyl ammonium functionality was then introduced by bromination of benzylmethyl group, followed by amination using trimethylamine. The properties of fluorene-containing AEMs were varied by adjusting the ratio of 4, 4'-biphenol and DMHPF, as well as the amount of brominating reagent. The properties of these AEMs were fully characterized, and the structure-property relationship for this series of AEMs was elucidated.

2. Experimental

2.1 Materials

9-Fluorenone, 2, 6-dimethylphenol, mercaptopropionic acid, 4-fluorophenyl sulfone, 4, 4'-biphenol, *N*-bromosuccinimide (NBS) and benzoyl peroxide (BPO) were purchased from J&K Chemical. All other chemicals were purchased from Sigma-

Aldrich Corporation. 4-Fluorophenyl sulfone and 4, 4'-biphenol were purified by recrystallization from ethanol. All other chemicals were of analytical grade, and used as received unless specified.

2.2 Synthesis of 9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene (DMHPF)

9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene (DMHPF) was prepared according to a procedure in the literature,²⁶ yield: 56%. ¹H NMR (400 MHz, DMSO-*d*₆) δ(ppm): 8.08 (s, 2H), 7.86-7.84 (d, 2H), 7.37-7.25 (m, 6H), 6.92 (s, 4H), 2.01 (s, 12H).

2.3 Synthesis of 9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene-based poly(sulfone)s

As depicted in Scheme 1, DMHPF-based poly(sulfone)s were prepared according to a literature procedure based on a weak base route.²⁸ The molar percentages of DMHPF in the total of bisphenols were 100%, 80%, and 60%. Thus, the benzylmethyl-bearing poly(sulfone)s were named by these ratios, e.g. PFES-80 was made from a mixture of DMHPF (80%) and 4, 4'-biphenol (20%). A typical procedure for poly(sulfone) synthesis follows. 9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene (1.626 g, 0.004 mol), 4-fluorophenyl sulfone (1.671 g, 0.005 mol), 4, 4'-biphenol (0.186 g, 0.001 mol), anhydrous potassium carbonate (0.800 g, 0.006 mol), 1-methyl-2-pyrrolidinone (15 mL), and toluene (25 mL) were placed into a 100 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a Dean-Stark trap, and gas inlet and outlet. The mixture was heated to 140 °C under an argon atmosphere. The water was azeotropically depleted from the solution. After 6 hours, toluene was removed from the system when the temperature was raised to 180 °C. Then the reaction mixture was held at 180 °C until the viscosity of the solution did not increase further. After cooled to room temperature, the mixture was poured into 200 mL deionized water. The resulting fibrous polymer was Soxhlet extracted with water for 24 hours and dried at 100 °C in vacuum for 24 hours to afford an off-white solid (3.119 g, 95%).

2.4 Bromination of 9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene-based poly(sulfone)s

The bromination of DMHPF-based poly(sulfone)s was performed in 1, 1, 2, 2-tetrachloroethane using *N*-bromosuccinimide (NBS) as the bromine source and benzoyl peroxide (BPO) as the initiator. A typical process follows. 1.0 g of polymer and 20 mL of 1, 1, 2, 2-tetrachloroethane were introduced into a 100 mL, three-necked, round-bottomed flask equipped with a condenser, a magnetic stirrer, and gas inlet and outlet. The mixture was heated to 85 °C in an argon atmosphere. Once the polymer completely dissolved, NBS (0.356 g, 0.002 mol) and BPO (0.0242 g, 0.0001mol) were added. The reaction was held at 85 °C for 5 hours. After cooled to room temperature, the mixture was poured into 100 mL of methanol. Then the crude product was collected by filtration, Soxhlet extracted with ethanol for 24 hours, and dried in vacuum at 80 °C to afford a yellow solid (1.09 g, 94%). The brominated polymers

were named after the composition of their poly(sulfone) precursor and the millimoles of NBS per 1 gram of poly(sulfone), e.g. BrPFES-80-3 were the product of brominating PFES-80 with 3 millimole of NBS per 1 gram of poly(sulfone).

2.5 Membrane preparation

Anion exchange membranes were prepared by the heterogeneous amination of brominated poly(sulfone)s using trimethylamine aqueous solution. A solution of brominated polymer in chloroform (10 wt%) was filtrated to remove insoluble impurities, and cast onto a flat glass plate. After the solvent was removed by evaporation at room temperature for 12 hours, the membrane was then dried at 60 °C for 6 hours to deplete chloroform. The dry membranes were then immersed into a 33% trimethylamine aqueous solution for 48 hours at room temperature. The aminated membranes were soaked in 1 M KOH for 48 hours, and washed completely with deionized water until the pH value of the water remained about 6-7. Hydroxide is very sensitive to CO₂ due to the rapid conversion from hydroxide to CO₃²⁻/HCO₃⁻, which makes the measurement of water uptake and conductivity in hydroxide form very difficult and less reliable.^{18, 29-30} Thus, all the membranes were converted to bicarbonate form by exposure to CO₂ in air for 50 hours.¹⁸ The quaternized polymers were named by their brominated precursors, e.g. QPFES-80-3 was the quaternized product of BrPFES-80-3. All the membranes were stored in DI water before characterizations.

2.6 Characterizations

¹H NMR spectra were obtained on a Bruker-400 spectrometer. The solvent for monomer and neutral polymers was CDCl₃-d₁, and DMSO-d₆ was used for quaternary ammonium-bearing polymers. Tetramethylsilane (TMS) was used as an internal standard. The degree of functionalization of brominated poly(sulfone)s was determined from the integral ratio of the brominated benzyl peaks (Peak 9' in Figure 1) to unbrominated benzyl peaks (Peak 8' in Figure 1). Ion exchange capacities (IEC) were calculated from the ratio of the ¹H NMR peaks from the methyl protons in the quaternary ammonium moiety (Peak 2 in Figure 2) and the sum of signals from aromatic protons. Thermal stability was evaluated using a Perkin-Elmer TGA 2 analysis system with a heating rate of 10 °C/min from room temperature to 700 °C under a continuous nitrogen flow. Molecular weights of poly(sulfone)s were measured using a PL-GPC 120 gel permeation chromatography. THF was used as the eluent, and molecular weights were determined by calibration with poly(styrene) standard.

The water uptakes of AEMs were obtained according to literature methods.¹⁸ AEMs were equilibrated in DI water at different temperatures for 24 hours before subjected to the measurements. The fully hydrated anion exchange membranes were taken out of water, blotted quickly to remove surface water, and weighed immediately. The membranes were then dried at 50 °C in vacuum for 24 hours and weighed again. The water uptakes were calculated by the following equation:

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

Where W_{wet} and W_{dry} were the hydrated mass and dry mass of the membranes, respectively.

Swelling ratios of AEMs were evaluated by measuring the dimensional difference in in-plane direction between the dry membranes and fully hydrated membranes. The swelling ratio was calculated by the following equation:

$$SW(\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\%$$

where L_{wet} , L_{dry} , are the lengths of the wet and dry membranes, respectively.

The membrane resistances were measured by four-probe electrochemical impedance spectroscopy (EIS) in DI water at 23, 40, 60, 80 °C using a CHI660D electrochemical workstation. EIS were performed by applying an alternating voltage of 10 mV in a frequency range of 0.1-1×10⁵ Hz. The bicarbonate conductivities were calculated by using the following equation:

$$\sigma = \frac{L}{R \times S}$$

where L is the distance between the two electrodes, R is the resistance of the membrane, and S is the conducting area. The activation energies for bicarbonate conduction using an Arrhenius relationship were determined according to a method in the literature.¹⁸

Tensile measurements were performed on an Instron 5982 system at room temperature with a stretching speed of 20 mm min⁻¹. Membrane samples were cut into rectangular shape with a test area of 20 × 5 mm. For the measurements in wet state, the fully hydrated samples were taken out from DI water, swept with tissues to remove the surface water, and immediately subjected to the tests. For measurements in dry state, the samples were dried at 80 °C for 12 hours in vacuum before tests. Five samples were measured for each membrane, and the averages were reported.

3. Results and discussion

3.1 Synthesis of polymers

The benzylmethyl-containing bisphenol, 9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene (DMHPF), was prepared according to a reported procedure,²⁶ using 9-fluorenone and 2,6-dimethylphenol as starting materials, and mercaptopropionic acid and concentrated sulfuric acid as the catalysts. As depicted in Scheme 1, benzylmethyl-containing poly (fluorenyl ether sulfone)s (PFES) were synthesized by polycondensing 4-fluorophenyl sulfone with varied molar ratios (1:0, 0.8:0.2, and 0.6:0.4) of DMHPF and 4, 4'-biphenol. The molecular weights of PFES were measured by gel permeation chromatography (GPC), and the results are listed in Table 1. PFES showed high molecular weight (Mw>143 kg/mol) and reasonable

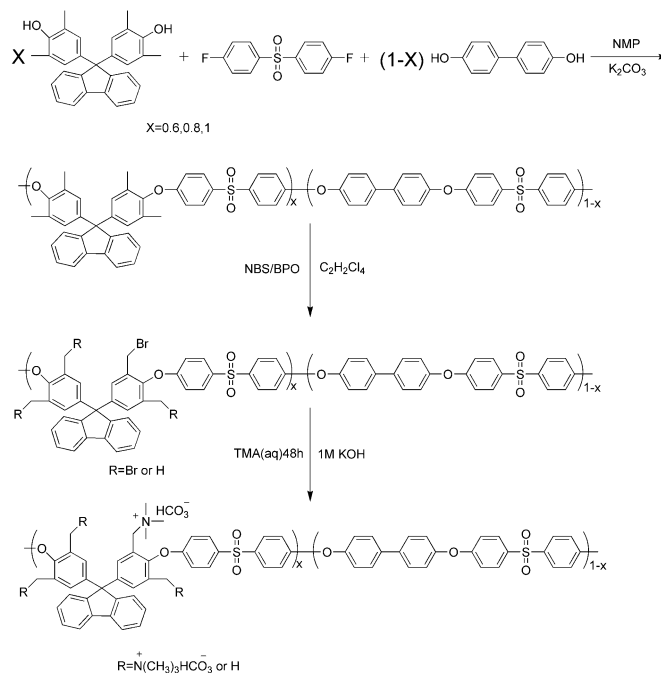
polydispersity index, which confirmed the successful synthesis of PFES.

Bromination of the benzylmethyl groups in PFES was then performed in 1, 1, 2, 2-tetrachloroethane at 85 °C. The reaction proceeded via a free radical mechanism with NBS as the bromine source and BPO as the initiator. The representative ¹H NMR spectra of plain PFES and brominated FPES (BrPFES) were compared in Figure 1. Bromination resulted in the decrease of benzylmethyl proton signals at around 2.0 ppm (Peak 8' in Figure 1), and instead new proton signals (peak 9' in Figure 1) for bromomethyl groups appeared in around 4.4 ppm. Due to the steric hindrance caused by fluorenyl segments, the two bromomethyl groups are configurationally different from each other. Therefore, two peaks appeared around 4.4 ppm, which was also observed by Hickner *et al.*²⁶ Meanwhile, the signals for aromatic proton adjacent to bromomethyl group shifted from about 6.8 ppm in plain PFES to around 7.2 ppm for BrPFES. Furthermore, the relative intensities for bromomethyl proton signals increased with the increasing amount of NBS. Degree of functionalization (DF) was calculated from the integral ratios between unreacted benzylmethyl groups and bromomethyl groups. DF of BrPFES spanned a range of 0.91-2.24. DF for BrPFES polymers could be controlled by the feeding amount of NBS. Furthermore, the distribution of bromomethyl groups could be tuned by varying the ratios of 4, 4'-biphenol. The brominated polymers with high 4, 4'-biphenol content had more clustered bromomethyl groups for a given DF. As summarized in Table 2, bromination conversion, determined from the feeding bromine in NBS and the resulting bromine in BrPFES, was higher than 90% when the benzylmethyl conversion was low. Generally, the bromination conversion decreased with the increase of NBS amount, which can be attributed to the decreasing benzylmethyl contents. However, the bromination conversion was higher than 70% even if high feeding ratio of NBS was applied. Benzylmethyl conversion was lower for BrPFES-100 polymers due to their high benzylmethyl contents, while the conversion for BrPFES-60 was much higher since much less benzylmethyl groups were available for bromination. Since 4, 4'-biphenol residue can't be brominated by NBS, the bromomethyl and quaternary ammonium groups can be selectively directed to DMHPF residue. In contrast, only randomly functionalized

Table 1. The molecular weights of plain poly (fluorenyl ether sulfone)s*

Polymer	Mn (kg/mol)	Mw (kg/mol)	PDI
PFES-100	80	152	1.85
PFES-80	79	143	1.81
PFES-60	117	212	1.81

*Measured by gel permeation chromatography (GPC) using polystyrene as a standard.



Scheme 1. Synthetic routes to PFES-based anion exchange membranes.

polymers can be produced via chloromethylation unless a major structural modification was applied to the polymer backbones.^{18, 31} These results demonstrated the high efficiency and selectivity of bromination of benzylmethyl groups over the chloromethylation of aromatic rings in the introduction of halomethyl groups into aromatic polymers for anion exchange membranes.

BrPFES was then quaternized by soaking the membranes in trimethylamine aqueous solution for 48 hours. Due to the limited solubility in polar aprotic solvents (such as NMP), the homogeneous amination of BrPFES was unsuccessful. As shown in Figure 2, the peak near 3.1 ppm in the ¹H NMR spectrum of quaternized polymers (peak 2 in Figure 2) were assigned to the methyl protons of in the quaternary ammonium groups. IEC was calculated from the integral of this peak to the sum of the aromatic peaks.

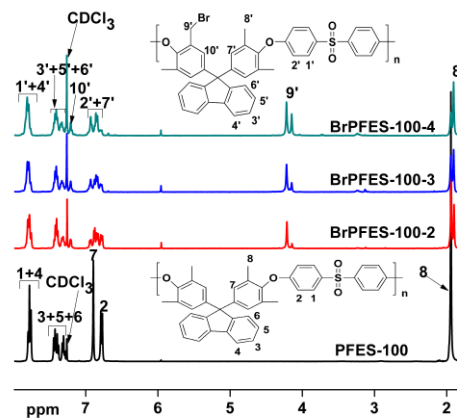


Figure 1. The ¹H NMR spectra of PFES-100 and BrPFES-100.

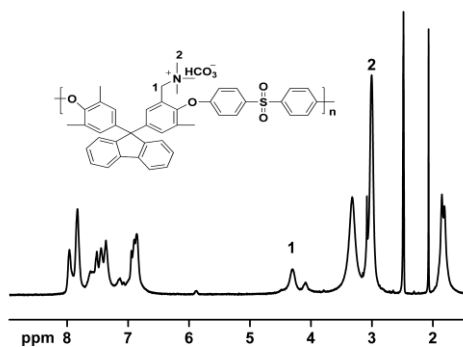


Figure 2. The ^1H NMR spectrum of QPFES-100-3.

Table 2. The bromination conversion, degree of functionalization and benzylmethyl conversion of brominated PFES

Polymer ^a	Bromination conversion (%) ^b	Degree of functionalization ^c	Benzylmethyl conversion (%) ^d
BrPFES-100-2	94	1.17	29
BrPFES-100-3	99	1.86	46
BrPFES-100-4	85	2.10	52
BrPFES-80-2	97	1.12	35
BrPFES-80-3	92	1.59	50
BrPFES-80-4	76	1.73	54
BrPFES-80-5	78	2.24	70
BrPFES-60-2	86	0.91	38
BrPFES-60-3	95	1.50	62
BrPFES-60-4	82	1.72	72
BrPFES-60-5	70	1.82	76

^a The first and second numbers stand for the molar percentage of DMHPF in the total of bisphenols, and the millimolar equivalents of NBS used per gram PFES, respectively.

^b Calculated from the bromine in the feeding NBS and the resulting BrPFES determined by ^1H NMR.

^c Number of bromomethyl groups per repeat unit by ^1H NMR.

^d Calculated by ^1H NMR.

3.2 Thermal stability

The thermal stability of quaternized PFES (QPFES) and their precursors, PFES and BrPFES were assessed by thermogravimetric analysis (TGA) in nitrogen atmosphere. As shown in Figure 3, there was no detectable weight loss below 380 °C for PFES. BrPFES showed two-stage weight loss profile in TGA curve. The weight loss between 120 and 350 °C were assigned to the decomposition of bromomethyl groups. Then the degradation of polymer backbone happened when the

temperature was higher than 400 °C. As for QPFES, the initial weight loss between room temperature and 270 °C was attributed to the evaporation of absorbed water in ionic polymers. The rapid weight loss at around 270 °C was due to the elimination of the quaternary ammonium groups. The third step of weight loss was above 380 °C and assignable to the decomposition of poly(sulfone) backbone.

3.3 IEC, water uptake and swelling ratio

As suggested by previous reports,^{18, 29-30} OH^- can be rapidly converted to $\text{CO}_3^{2-}/\text{HCO}_3^-$ due to the absorption of CO_2 in water and air. Consequently, the measurements of water uptake and conductivity in OH^- form are difficult and less reliable. Therefore, all the membranes were converted to bicarbonate form by exposure to CO_2 since quaternary ammonium bicarbonate is not sensitive to CO_2 in water or air. The bulk water uptake as a function of IEC is plotted in Figure 4. As expected, the water uptakes of PFES-based AEMs increased with the increase of IEC in a non-monotonic style. For AEMs based QPFES-100 and Q-FPES-80, water uptake increased rapidly when IEC was higher than 2.2 meq/g, which can be regarded as a critical ion content to achieve good connectivity between hydrophilic domains. There was no clear critical IEC observed for water uptakes for QPFES-60 AEMs. Due to the high content of hydrophobic domains, it was difficult to get adequate connection between hydrophilic domains even when IEC was high. For a given IEC, the water uptake of three series of AEMs followed the trend of QPFES-100 > QPFES-80 > QPFES-60, which can be explained in terms of the more isolated hydrophilic domains in copolymers. The swelling ratios of QPFES AEMs were also measured in the in-plane direction at room temperature. Generally, the swelling ratios of QPFES showed similar behaviour to that of bulk water uptake. QPFES-60 AEMs showed the best dimensional stability for a given IEC, which is desired for fuel cell applications.

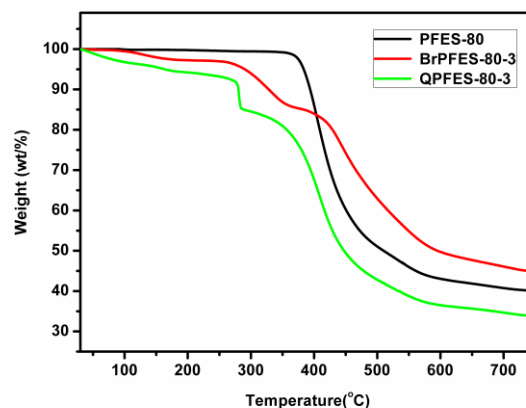


Figure 3. TGA traces of PFES-80, BrPFES-80-3 and QPFES-80-3.

The water uptakes for QPFES-based AEMs were measured at different temperatures, and the results are listed in Table 3. Figure 5 shows the temperature dependence of water uptakes

for QPFES-60-based AEMs. The water uptakes for all AEMs increased linearly with the increasing temperatures. The slopes strongly correlated with IEC and the hydrophobicity of the backbones. The high fraction of hydrophobic segments and low ion exchange content suppressed the swelling of AEMs at high temperatures, which led to lower increasing rate of water uptakes.

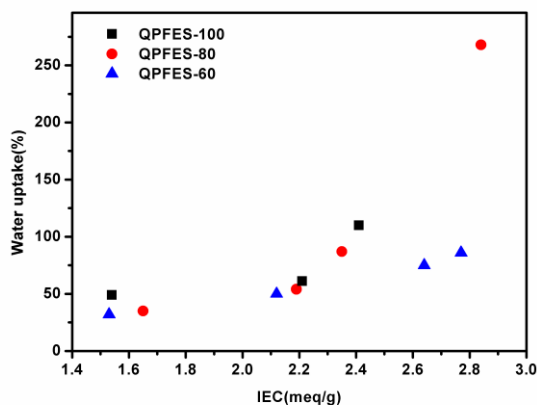


Figure 4. Water uptakes as a function of ion exchange capacity (IEC) for PFES-based AEMs

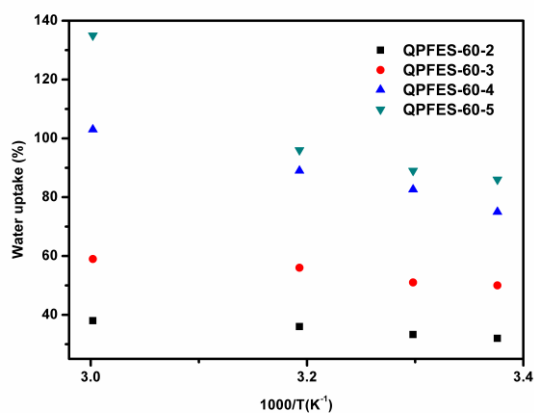


Figure 5. Water uptakes of AEMs based on QPFES-60 as a function of $1000/T$.

3.4 Conductivity

The conductivities of QPFES-based AEMs were measured at various temperatures in bicarbonate form. For a given polymer backbone, the conductivity increased with increasing IEC. For AEMs with similar IEC but different backbone composition, the bicarbonate conductivity followed the trend of $QPFES-100 > QPFES-80 > QPFES-60$. Generally, the trend of conductivity for all AEMs was similar to that of water uptake, which indicated that the bicarbonate conduction in these AEMs was strongly correlated to the bulk water uptakes. This observation agreed with the results in the literature.¹⁸ AEM QPFES-100-4 shows the highest conductivity among all the AEMs in this study. Meanwhile, their water uptakes were also higher than other AEMs. QPFES-60-5 and QPFES-80-4

exhibited a combination of reasonably high conductivities and moderate water uptakes. The quaternary ammonium groups were randomly distributed along the polymer backbone in homo-polymers. With the increasing IEC, the hydrophilic domains became more and more connected. Consequently, the conductivity and water uptake simultaneously increased. In copolymers, 4, 4'-biphenol residue can't be functionalized over bromination and amination, and the quaternary ammonium groups were selectively located in the DMHPF segments. Therefore, 4, 4'-biphenol residue acted as hydrophobic segments in copolymers. The continuation of hydrophilic segments with quaternary ammonium groups was interrupted by the incorporation of hydrophobic 4, 4'-biphenol segments, which suppressed the swelling of AEMs. Meanwhile, the conductivity was still kept at a reasonable level due to the higher ionic concentration, for a given IEC. The properties of these AEMs could be tuned over a wide range of water uptakes and conductivities by varying IEC and the content of hydrophobic domains. AEMs based on copolymers are more suitable for alkaline fuel cell applications considering their reasonably high conductivities and moderate water uptakes.

As shown in Table 3 and Figure 7, the bicarbonate conductivities for QPFES-60-based AEMs increased gradually with increasing temperatures in an Arrhenius mechanism. The activation energies for bicarbonate conduction were around 20 KJ/mol, which is typical for AEMs in bicarbonate form.¹⁸

The hydroxide conductivities of QPFES-based AEMs were estimated by a method validated by Varcoe *et al.*:³⁰ multiplying bicarbonate conductivities with a factor of 3.8. This approach is based on the difference of ion mobility between hydroxide and bicarbonate. As listed in Table 3, the hydroxide conductivities ranged from 9.9 to 56.6 mS/cm. The reasonably high hydroxide conductivities further demonstrated the good potential of these AEMs for alkaline fuel cell applications.

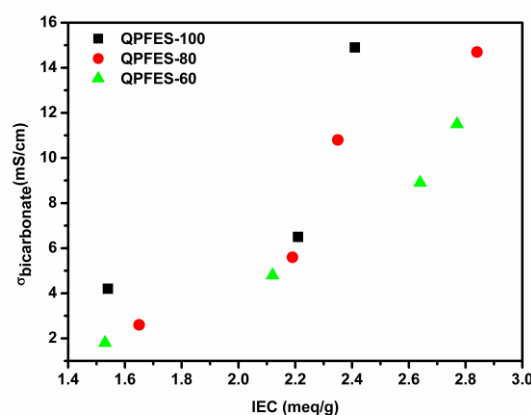


Figure 6. Bicarbonate conductivities as a function of ion exchange capacity (IEC) for PFES-based AEMs.

3.5 Mechanical property

The mechanical properties of PFES-based AEMs were evaluated in both wet and dry states, and the results are listed in

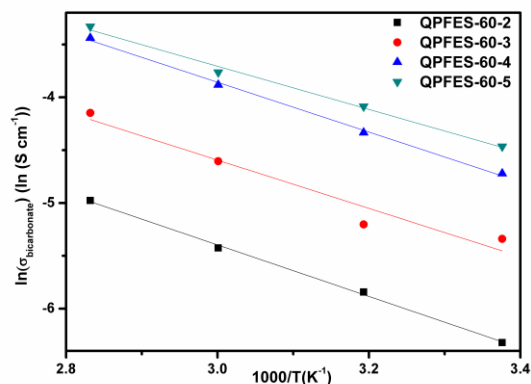


Figure 7. Arrhenius plot of bicarbonate conductivity for AEMs based on QPFES-60 in water.

Table 4. For a given polymer backbone, the tensile strength and modulus values for wet membranes decreased as the increase of IEC, which can be rationalized in terms of the plasticizing effect of absorbed water. Meanwhile, similar trend was observed for dry samples, which indicated that the introduction of quaternary ammonium groups lowered the mechanical properties of PFES-based AEMs. In general, the mechanical properties for PFES-based AEMs were acceptable for alkaline fuel cell applications.

Table 3. Properties of QPFES-based AEMs

Membrane ^a	IEC ^b	Water uptake (%)			Swelling ratio (%)	σ _{bicarbonate} (mS/cm) ^c				σ _{hydroxide} (mS/cm) ^d
		23 °C	40 °C	60 °C		23 °C	40 °C	60 °C	80 °C	
QPFES-100-2	1.54	49	59	61	10	4.2	6.6	9.4	12.0	16.0
QPFES-100-3	2.21	61	72	76	18	6.5	11.1	17.5	26.1	24.7
QPFES-100-4	2.41	110	117	143	31	14.9	20.8	29.7	46.9	56.6
QPFES-80-2	1.65	35	37	43	9	2.6	3.1	4.6	7.0	9.9
QPFES-80-3	2.19	54	57	64	15	5.6	8.3	11.0	21.1	21.3
QPFES-80-4	2.35	87	98	121	29	10.8	15.5	24.6	36.1	41.0
QPFES-80-5	2.84	268	296	- ^e	- ^f	14.7	21.9	31.1	68.7	55.9
QPFES-60-2	1.53	32	36	38	6	1.8	2.9	4.4	6.9	6.8
QPFES-60-3	2.12	50	56	59	15	4.8	5.5	10.0	15.8	18.2
QPFES-60-4	2.64	75	89	103	26	8.9	13.1	20.6	32.1	33.8
QPFES-60-5	2.77	86	96	135	- ^f	11.5	16.8	23.2	35.8	43.7

^a The first and second numbers stand for the molar percentage of DMHPF in the total of bisphenols, and the millimolar equivalents of NBS used per gram PFES, respectively.

^b Calculated from ¹H NMR.

^c Measured in DI water at 23, 40, 60, and 80 °C.

^d Estimated from bicarbonate conductivity according to the method in the literature.

^e Not measured because this membrane is too brittle at 60 °C.

^f Not measured because these membranes are too brittle in dry state

4. Conclusions

In this work, a series of fluorene-containing AEMs were prepared by bromination of benzylmethyl-containing poly(fluorene ether sulfone)s, followed by quaternization with trimethylamine, and ion exchange. Bromination showed several advantages over chloromethylation such as relatively shorter reaction time, higher efficiency, and higher selectivity. Consequently, the properties of QPFES-based AEMs, such as water uptake and conductivity, can be easily controlled by the amounts of bromination reagent and the ratios of 9, 9-bis (3, 5-dimethyl-4-hydroxyphenyl) fluorene to 4, 4'-biphenol. For a given polymer backbone, water uptakes and ion conductivities increased with the increasing IEC. Furthermore, a critical IEC around 2.2 meq/g was found for QPFES-100 and QPFES-80 based AEMs, while no critical ion content existed in AEMs based on QPFES-60. For a given IEC, copolymers, including QPFES-80 and QPFES-60-based AEMs, showed slightly lower conductivities but much lower water uptakes and swelling ratios than homo-polymers, which can be attributed to the interruption of the continuous hydrophilic domains by the hydrophilic 4, 4'-biphenol residues. AEMs based on copolymer showed better potentials for alkaline fuel cell applications due to a combination of reasonably high conductivities and improved dimensional stability. This report provided our community some insights on the structure-property relationships on fluorene-containing AEMs.

Table 4. Mechanical properties of QPFES-based AEMs in both wet and dry states

Membrane ^a	IEC ^b	Tensile strength (MPa)		Modulus (GPa)		Elongation at Break (%)	
		wet	dry	wet	dry	wet	dry
QPFES-100-2	1.54	38	58	1.1	1.7	30	15
QPFES-100-3	2.21	30	50	0.67	1.4	23	16
QPFES-100-4	2.41	16	41	0.46	1.2	13	5.5
QPFES-80-2	1.65	37	42	0.98	0.98	87	50
QPFES-80-3	2.19	23	39	0.48	0.94	75	60
QPFES-80-4	2.35	9	32	0.23	0.81	25	8.2
QPFES-80-5	2.84	5	- ^c	0.09	- ^c	24	- ^c
QPFES-60-2	1.53	44	54	0.99	1.85	127	27
QPFES-60-3	2.12	19	24	0.44	0.54	83	40
QPFES-60-4	2.64	11	20	0.22	0.45	44	17
QPFES-60-5	2.77	10	- ^c	0.19	- ^c	42	- ^c

^a The first and second numbers stand for the molar percentage of DMHPF in the total of bisphenols, and the millimolar equivalents of NBS used per gram PFES, respectively.

^b Calculated from ¹H NMR.

^c Not measured because these membranes are too brittle in dry state.

Acknowledgements

The authors express their thanks to the National Science Foundation of China (NO. 51173178 and 21304093) for their financial supports.

Notes and references

^a Laboratory of Polymer Composites Engineering, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun, 130022, China. Email: jyan@ciac.ac.cn. Phone: +86-431-85262682, Fax: +86-431-85262682.

^b Institute of Chemistry, Northeast Normal University, Changchun 130024, China

- J. Weber, K. D. Kreuer, J. Maier and A. Thomas, *Adv. Mater.*, 2008, **20**, 2595.
- M. P. Nieh, M. D. Guiver, D. S. Kim, J. F. Ding and T. Norsten, *Macromolecules*, 2008, **41**, 6176.
- P. C. Su, C. C. Chao, J.H. Shim, R. Fasching and F. B. Prinz, *Nano Lett.*, 2008, **8**, 2289.
- N. Fujiwara, Z. Siroma, S. Yamazaki, T. Ioroi, H. Senoh and K. Yasuda, *J. Power Sources*, 2008, **185**, 621.
- K. Kordesch, V. Hacker, J. Gsellmann, M. Cifrain, G. Faleschini, P. Enzinger, R. Fankhauser, M. Ortner, M. Muhr and R. R. Aronson, *J. Power Sources*, 2000, **86**, 162.
- J. R. Varcoe and R. C. T. Slade, *Fuel Cells*, 2005, **5**, 187.
- J. R. Varcoe, R. C. T. Slade and E. L. H. Yee, *Chem. Commun.*, 2006, **13**, 1428.
- H. Liu, S. H. Yang, S. L. Wang, J. Fang, L. H. Jiang and G. Q. Sun, *J. Membr. Sci.*, 2011, **369**, 277.
- T. Sata, M. Tsujimoto, T. Yamaguchi and K. Matsusaki, *J. Membr. Sci.*, 1996, **112**, 161.
- L. Li and Y. X Wang, *J. Membr. Sci.*, 2005, **262**, 1.
- J. Pan, S. F. Lu, Y. Li, A. B. Huang, L. Zhuang and J. T. Lu, *Adv. Funct. Mater.*, 2010, **20**, 312.
- C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel and M. Pineri, *Polymer*, 2001, **42**, 359.
- J. Fang, X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita and K. Okamoto, *Macromolecules*, 2002, **35**, 9022.
- N. Li, T. Yan, Z. Li, T. Thurn-Albrecht and W. H. Binder, *Energy Environ. Sci.*, 2012, **5**, 7888.
- A. L. Ong, S. Saad, R. Lan, R. J. Goodfellow and S. Tao, *J. Power Sources*, 2011, **196**, 8272.
- T. J. Clark, N. J. Robertson, H. A. Kostalik, E. B. Lobkovsky, P.F. Mutolo, H. D. Abruna and G. W. Coates, *J. Am. Chem. Soc.*, 2009, **131**, 12888.
- M. R. Hibbs, C. H. Fujimoto and C. J. Cornelius, *Macromolecules*, 2009, **42**, 8316.
- J. Yan and M. A. Hickner, *Macromolecules*, 2010, **43**, 2349.
- M. R. Hibbs, *J. Polym. Sci., Part B: Polym. Phys.*, 2013, **51**, 1736.
- K. Miyatake, B. Baeb and M. Watanabe, *Polym. Chem.*, 2011, **2**, 1919.
- M. Tanaka, M. Koike, K. Miyatake and M. Watanabe, *Macromolecules*, 2010, **43**, 2657.
- M. Tanaka, K. Fukasawa, E. Nishino, S. Yamaguchi, K. Yamada, H. Tanaka, B. Bae, K. Miyatake and M. Watanabe, *J. Am. Chem. Soc.*, 2011, **133**, 10646.
- D. W. Seo, M. A. Hossain, D. H. Lee, Y. D. Lima, S. H. Lee, H. C. Lee, T. W. Hong, W. G. Kima, *Electrochimica Acta*, 2012, **86**, 360.
- M. Tanaka, M. Koike, K. Miyatake and M. Watanabe, *Polym. Chem.*, 2011, **2**, 99.

- 25 D. Chen, M. A. Hickner b, S. Wanga, J. Pan, M. Xiao and Y. Meng, *Int. J. Hydrogen Energy*, 2012, **37**, 16168.
- 26 D. Chen and M. A. Hickner, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5775.
- 27 P. Xu, K. Zhou, G. Han, Q. Zhang, A. Zhu and Q. Liu, *J. Membr. Sci.*, 2014, **457**, 29.
- 28 R. Vismanathan, B. C. Johnson, J. E. McGrath, *Polymer*, 1984, **25**, 1827.
- 29 H. Yanagi, K. Fukuta, *ECS Transactions*, 2008, **16**, 257.
- 30 O. I. Deavin, S. Murphy, A. L. Ong, S. D. Poynton, R. Zeng, H. Herman, and J. R. Varcoe, *Energy Environ. Sci.*, 2012, **5**, 8584.
- 31 J. Yan, H. D. Moore, M. R. Hibbs and M. A. Hickner, *J. Polym. Sci., Part B: Polym. Phys.*, 2013, **51**, 1790.

Fluorene-containing anion exchange membranes were synthesized via the bromination reaction of poly(sulfone)s, which exhibited reasonably high conductivities.

