Investigation on Structure and Properties of Anion Exchange Membranes Based on Tetramethylbiphenol Moieties Containing Copoly(arylene ether)s

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ABSTRACT: Quaternary ammonium functionalized poly(arylene ether)s (QPAEs) containing 2,2′,6,6′-tetramethylbiphenol moieties were designed and successfully synthesized via nucleophilic substitution polycondensation, bromination, quaternization and alkalization. The structure, water uptake, ion exchange capacities (IECs), hydroxide ion conductivities, and mechanical properties, as well as thermal and chemical stabilities of obtained QPAEs membranes were investigated. The QPAE-a membrane with IEC value of 0.98 meq g^{-1} demonstrated the highest ion conductivity (47.4 mS cm^{-1}) at 80°C. The ion transport activation energy (E_a) of QPAEs membranes varied from 8.57 to 19.95 kJ mol^{-1}. After chemical stability test conditioned in 1M NaOH at 60°C for 7 days, the QPAEs membranes except QPAE-c (IEC = 0.88 meq g^{-1}) still exhibited high hydroxide ion conductivities (over 15 mS cm^{-1}) and acceptable tensile strength (~10 MPa). These properties indicate that the ionomers membranes are potential candidates for anion exchange membranes in anion exchange membrane fuel cells. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2015, 132, 41525.

INTRODUCTION

Fuel cells have been regarded as a superior alternative of traditional energies due to their high energy efficiency and low pollution levels.[1–3] In terms of the nature of the electrolytes, fuel cells are divided into five categories: alkaline fuel cells (AFCs), solid oxide fuel cells (SOFCs), phosphoric acid fuel cells (PACFs), molten carbonate fuel cells (MCFCs), and polymer electrolyte membrane fuel cells, which include proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs).[4,5] High methanol permeability of proton exchange membranes and high cost of both membranes and catalysts have drawn back the mass commercialization of PEMFCs. Meanwhile, AEMFCs have attracted enormous attention with advantages as follows: (1) faster oxygen reaction kinetics, (2) extended selective range of catalysts, such as non-noble-metal catalysts (Ag, Ni, or Ru) and metal-free catalysts, (3) low fuel permeability due to the opposite direction of fuel and hydroxide ion (OH$^-$) migration, (4) ameliorative radical oxidation stability of membranes in alkaline medium, (5) excellent corrosion resistance of metal materials under basic circumstance and so on.[6–9]

Anion exchange membrane (AEM) is one of the key components in AEMFCs. Scientists have designed new kinds of AEMs by changing the chemistry of the polymers and functionalization techniques, and the processing of the membranes. The researches on AEM have been mushrooming in recent years. Alkaline doped polymers such as poly(vinyl alcohol) (PVA)/KOH, PVA/layered double hydroxide, and polybenzimidazole/KOH,[10–12] hybrid membranes (e.g., PPO-SiO$_2$),[13] (semi)interpenetrated polymer networks (sIPN) (e.g., poly(vinyl alcohol)-poly(1,3-diethyl-1-vinylimidazolium bromide)),[14] AEMs-based chemical modified aliphatic ethers,[15,16] poly(phenylene),[17] poly(benzimidazole),[18] poly(aromatic ether)s,[19–24] poly(ether imide),[25] and fluorinated polymers[26,27] have been reported. Owing to the outstanding chemical and thermal stabilities, poly(arylene ether)s (PAEs), especially poly(arylene ether sulfone) and poly(arylene ether ketone), are the choices of many investigations. Polycondensation, followed by halogen methylation, quaternization, and alkalization is the general preparation process of quaternized poly(arylene ether)s (QPAEs). Tanaka et al. reported QPAEs membranes with ion exchange capacity (IEC) value of 2.54 meq g^{-1}, which were synthesized by chloromethylation method, showed high hydroxide ion conductivity up to 50 mS cm^{-1} at 30°C.[28] As chloromethyl methyl ether is acutely toxic and carcinogenic, safer synthesis route is needed. Yan and

Hickner published a safe and quick way to get AEMs by bromination of tetramethyl bisphenol A-based poly(sulfone)s.[29] In the previous work, we reported an interesting phenomenon that the QPAE based on the copolymer containing sulfone-ketone structure displayed the highest hydroxide ion conductivity of 75 mS cm^{-1} at 80°C in a lower IEC value of 1.04 meq g^{-1}.[30] Herein, we constructed a series of AEMs from quarterary ammonium functionalized PAEs containing tetramethylbiphenol moieties with tuned sulfone-ketone structures. The structure, water uptake, swelling ration, hydroxide ion conductivities, and mechanical properties, as well as thermal and chemical stabilities of the obtained QPAEs were investigated.

EXPERIMENTAL

Materials
Bis(4-fluorophenyl)sulfone (FPS) and 4,4′-difluorodiphenylmethanone (DFDPM) were purchased from TCI, Tokyo, Japan. 2,2′,6,6′-Tetramethylbiphenol (TMBP) was synthesized according to the published reference.[31] N,N′-Dimethylacetamide (DMAc), potassium carbonate, toluene, N-bromosuccinimide (NBS), azodiisobutyronitrile (AIBN), methanol, 1,1,2,2-tetrachloroethane (TCE), chloroform, trimethylamine aqueous solution (33 wt %), and sodium hydroxide were obtained from commercial sources and used as received.

Polymerization
A series of tetramethylbiphenyl-bearing PAEs (PAE-a to PAE-e) were synthesized by nucleophilic aromatic substitution. A typical polymerization procedure for PAE-a was as follows: TMBP (2.4231 g, 10 mmol), DFDPM (2.1805 g, 10 mmol), potassium carbonate (2.0729 g, 15 mmol), DMAc (16 mL), and toluene (20 mL) were introduced into a 100-mL three neck round-bottomed flask equipped with Dean-Stark trap and a mechanical stirrer. The reaction was carried out at 150°C for 4 h under nitrogen flow, and then toluene was removed. The temperature was elevated to 170°C and kept for 12 h to obtain a light yellow, viscous mixture. After cooling down, the mixture was poured into 400 mL of methanol containing 2 mL of concentrated HCl. The crude product was washed with deionized water until pH 7 was reached and then dried at 80°C. The dried crude polymer was dissolved in 50 mL of chloroform and filtered with diatomite to remove inorganic salts. The filtrate was poured into 400 mL of methanol. The precipitated polymer was dried at 80°C under vacuum for 24 h to give PAE-a (3.740 g, yield = 88.9%). Using 10 mmol of the mixtures with certain molar ratios of DFDPM to FPS or FPS to replace DFDPM to run the polymerization, PAE-b–e have been synthesized with high yields.

Bromination
The brominations of the PAEs ran in TCE, using NBS as the bromination agent and AIBN as the radical initiator. A typical procedure of brominations of PAEs was as follows: PAE-a (1.8263 g, 4 mmol) was dissolved in TCE (40 mL) in a 100-mL round-bottomed flask, then NBS (1.0679 g, 6 mmol) and AIBN (0.0657 g, 0.9 mmol) were added. The reaction underwent at 80°C for 2 h. The mixture was precipitated in 200 mL of methanol, washed with methanol several times and dried at 80°C under vacuum to obtain the brominated polymer BMPAE-a. BMPAE-b–e were obtained following the similar procedure.

Membrane Preparation, Quaternization, and Alkalization
The brominated polymers BMPAEs were dissolved in TCE to form 6 wt % solutions. The solutions were filtrated, cast on flat glass plates, deposited for 12 h at room temperature to evaporate TCE and dried in oven at 80°C for 24 h to get 50–80-μm thick, transparent and tough membranes. The membranes were immersed in 33 wt % aqueous trimethylamine at room temperature for 48 h and then washed with deionized water several times to get the quaternized membranes. Afterward, the membranes were immersed in 1M NaOH at room temperature for 48 h to convert the anion from bromide to hydroxide, and then the obtained quaternized membranes were washed with deionized water several times and soaked in deionized water in closed vessels at least 24 h prior to analysis.

Characterization
^{1}H-NMR spectra were recorded at Bruker AVANCE 400S with deuterated chloroform (CDCl$_3$) or deuterated dimethyl sulfoxide (DMSO-d_6) as a solvent and tetramethylsilane (TMS) as an internal reference. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere with a TAINC SDT Q600 thermogravimetric analyzer at a heating rate of 10 °C per minute from room temperature to 700°C. The QPAE membrane samples were vacuum dried at 60°C for 24 h before the testing. Gel permeation chromatography (GPC) analyses were carried out on a Waters 510 HPLC equipped with 5 μm phenol gel columns (linear, 4 × 500 Å) arranged in series with chloroform as a solvent, a UV detector at 254 nm, and standard polystyrene Shodex STANDARD SM-105 as a standard. Mechanical properties of the membranes were determined with a SANS power testing machine at 25°C and 100% RH at a stretching speed of 10 mm min^{-1}. The QPAE membrane samples with size of 50 mm × 5 mm were soaked in deionized water at 25°C for 24 h before the testing.

The water uptakes of the QPAEs membranes were determined by the method as the following. A QPAE membrane was immersed into deionized water under a given temperature for 24 h. Then the membrane was taken out, surface water was wiped away with tissue paper, and the membrane was weighed quickly to get wet weight (W_{wet}). The wet membrane was vacuum dried at 60°C for 24 h to obtain a constant dry weight (W_{dry}). The water uptake of the membrane was calculated according to the following:

$$WU(\%) = (W_{wet} - W_{dry}) / W_{dry} \times 100 \qquad (1)$$

The swelling ratio (SR) of the QPAEs membranes was characterized by linear expansion ratio, which was determined by the dimension change between the wet membrane and the dry membrane. It was calculated according to the equation:

$$SR(\%) = (L_{wet} - L_{dry}) / L_{dry} \times 100 \qquad (2)$$

where L_{wet} was the length of the wet sample in deionized water at given temperature for 24 h, L_{dry} was the length of the dry membrane.

The IEC of the QPAEs membranes was measured by titration. A QPAE membrane was immersed in 50 mL of HCl standard (0.01M) for 4 h. Then the HCl solution mixture was titrated
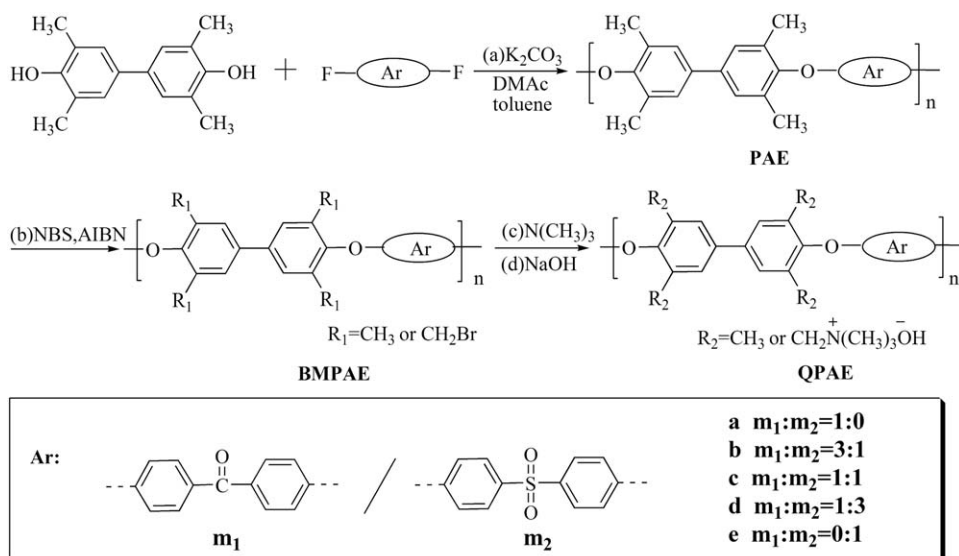
Scheme 1. Schematic diagram of synthesis of QPAEs: (a) polymerization; (b) bromination; (c) quaternization; (d) alkalization.

with a standardized NaOH (0.01M) solution using phenolphthalein as an indicator. The IEC values were calculated according to:

$$IEC = (M_{HCl}V_{HCl} - M_{NaOH}V_{NaOH})/W_{dry} \qquad (3)$$

where M_{HCl} (M) and V_{HCl} (mL) are the concentration and volume of the initial HCl solution. M_{NaOH} (M) and V_{NaOH} (mL) are the concentration and volume of the standardized NaOH solution used for titration. W_{dry} (g) is the weight of the dry QPAE membrane.

The hydroxide ion conductivity of the QPAEs membranes were measured at 30, 40, 60, and 80°C in a vessel filled with deionized water with a IviumStat at an oscillating voltage of 10 mV, and the frequency ranging from 1 MHz to 1 kHz. The hydroxide ion conductivity was calculated according to:

$$\sigma = L/(AR) \qquad (4)$$

where L (cm) and A (cm^2) are the membrane thickness and the electrode area respectively, R (Ω) is the resistance of the membrane.

The chemical stability of the QPAE membranes were explored by immersing the membranes in a 1M NaOH at 60°C for 168 h and then assessing their hydroxide ion conductivity at 60°C, mechanical properties, and IEC after thoroughly washed with deionized water.

Table I. Synthesis of Parent Poly(arylene ether)s (PAEs)

PAE	M_n (kg mol^{-1})	M_w (kg mol^{-1})	M_w/M_n
PAE-a	42	73	1.73
PAE-b	100	267	2.67
PAE-c	47	83	1.74
PAE-d	35	61	1.76
PAE-e	61	107	1.74

RESULTS AND DICUSSION

Synthesis of Parent Poly(arylene ether)s and Brominated Poly(arylene ether)s

Parent PAEs were synthesized via nucleophilic substitution polycondensation as shown in Scheme 1(a). The polymerizations of TMBP and difluoro monomers were performed in anhydrous DMAc under nitrogen atmosphere. The reaction mixtures were maintained at 140–155°C for 3–4 h to distill off the toluene-water azeotrope and then were heated to 160–170°C for a long time to obtain high molecular weight polymers. GPC was used to measure the molecular weights of the PAEs. All the GPC elution curves are unimodal and the results are summarized in Table I. M_n and M_w of the PAEs are 35–100 kg mol^{-1} and 61–267 kg mol^{-1}, respectively. PAEs except PAE-b show similar distribution indexes at the values about 1.73–1.76. All the PAEs display good solubility in some organic solvents such as chloroform, TCE, N,N-dimethylformamide (DMF), DMAc, and dimethylsulfoxide (DMSO). Transparent, tough membranes can be obtained by solution casting.

Compared with chloromethylation, bromination is a more quantitative, rapid, and green procedure to fabricate AEM.[29] The degree of bromination (DBM), denoted as the average number of bromomethyl groups per repeating unit of PAEs, is a direct parameter of bromination and can be determined by ^{1}H-NMR. Figure 1 demonstrates ^{1}H-NMR spectra of parent PAE-e and brominated BMPAE-e (DBM = 1.06). In ^{1}H-NMR spectrum of PAE-e [Figure 1(a)], signal a is attributed to the methyl moieties protons and signals b, c, d between 6.88 and 8.00 are assigned to the protons in the aromatic rings. The calculated integral ratio of the characterized peaks is a : b : c : d = 11.73 : 3.91 : 4.00 : 3.99 agreeing well with the configuration. Compared with PAE-a, a new signal e around 4.40 ppm assigned to the protons in the bromomethyl groups is observed, signal b splits into three separate signals (signal b, signal b′, and signal b″) owing to the position effect of the new bromomethyl groups, and the signal of methyl moieties protons decreases in
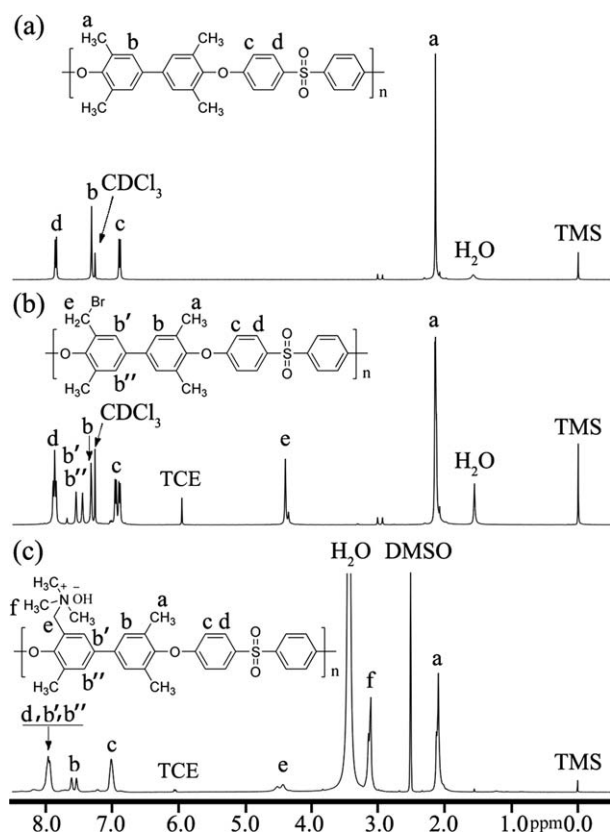
Figure 1. ^{1}H-NMR spectra of (a) PAE-e, (b) BMPAE-e (DBM = 1.06), and (c) QPAE-e (IEC = 1.00 meq g^{-1}).
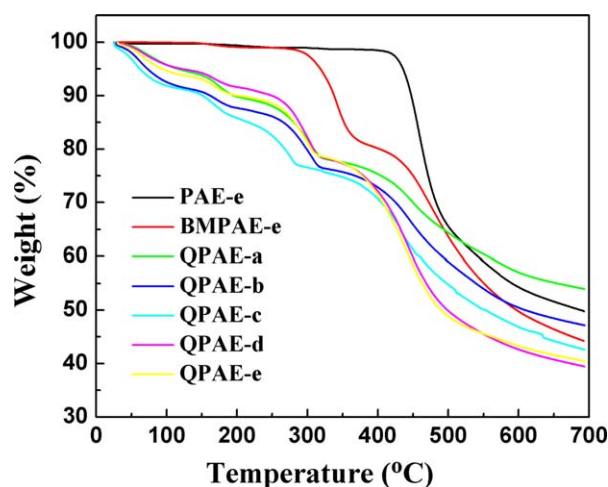

Figure 2. TGA curves for PAE-e, BMPAE-e (DBM = 1.06), QPAE-a (IEC = 0.98 meq g^{-1}), QPAE-b (IEC = 0.88 meq g^{-1}), QPAE-c (IEC = 0.96 meq g^{-1}), QPAE-d (IEC = 0.96 meq g^{-1}), and QPAE-e (IEC = 1.00 meq g^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chain. The integral ratio of (b + b′ + b″) : c : d (3.88 :4.00 : 3.99) is very close to that of PAE-e confirming the high stability of the backbone in the bromination. DBM of BMPAE-e was calculated with the integral ratio of signal a to signal e (8.87 : 2.14) according to the published method.[32] The value of DBM of the polymer is 1.06, which is listed in Table II. DBMs of other BMPAEs were calculated by the same method and also shown in Table II. The amount of NBS and the reaction time of bromination reactions were investigated at a feed ratio of NBS/ AIBN of 15/1 at 80°C. The bromination results of PAE-a indicate DBM of the brominated polymer increases with the extended reaction time at the first 2 h and then levels off. Generally, DBM depends on the ratio of NBS to PAE and increases when increasing the feed ratios and reaction time. At 2 h, the brominations for the other types of PAEs are considered complete. The complete of bromination within 2 h is superior to the chloromethylation with reaction time of one day or more. The bromomethylated PAEs (BMPAEs) with varying DBMs were synthesized by tuning the ratios of NBS to PAEs. The bromination degrees of PAEs show no obvious difference under the same reaction conditions. This indicates that the bromination process provides a repeatable and more convenient method to control the structure of QPAEs.

^{1}H-NMR spectrum of BMPAE-e (DBM = 1.06) [Figure 1(b)]. The signals c and d of the protons in the aromatic rings of biphenyl sulfone moieties of BMPAE-e have also been altered due to the introduction of bromomethyl groups onto the main

Preparation of Quaternized Poly(arylene ether)s Membranes
The QPAEs membranes were fabricated by heterogeneous quaternization. The membranes were initially cast in nonionic form and subsequently introduced the quaternary ammonium into the solid membrane to get ionic form [Scheme 1(c)]. After washed with water, the quaternized membranes were immersed in 1M sodium hydroxide solution for 48 h to change bromide ion to hydroxide ion [Scheme 1(d)]. As the quaternized membranes are hydrophilic and swelling, over high DBM of the precursor polymer leads to high hydrophilic swelling and extreme dissolving in the aqueous trimethyl amine solutions during the quaternization. DBM of the precursor polymer should be

Table II. The Results of Bromination of PAEs at the Reaction Temperature of 80°C

Starting polymer	n (PAE) : n (NBS)	Time (h)	DBM
PAE-a	1 : 1.5	1	1.27
	1 : 1.5	2	1.35
	1 : 1.5	4	1.30
	1 : 1.5	6	1.34
	1 : 1.2	2	1.05
	1 : 1.7	2	1.50
PAE-b	1 : 1.2	2	1.06
	1 : 1.5	2	1.37
PAE-c	1 : 1.2	2	1.06
	1 : 1.5	2	1.37
PAE-d	1 : 1.2	2	1.07
	1 : 1.5	2	1.37
PAE-e	1 : 1.2	2	1.06
	1 : 1.5	2	1.36

Table III. DBM, IEC, Water Uptake, λ, Swelling Ratio, and Hydroxide Conductivity of QPAEs Membranes

QPAEs	DBM	IEC (meq g⁻¹) Theo.[a]	IEC (meq g⁻¹) Exp.[b]	WU (%) 30°C	WU (%) 80°C	λ[c] 30°C	λ[c] 80°C	SR (%) 30°C	SR (%) 80°C	δ (mS cm⁻¹) 30°C	δ (mS cm⁻¹) 80°C
QPAE-a	1.05	2.10	0.98 ± 0.01	53.3 ± 2.4	67.8±5.1	29.9	38.0	13.4 ± 1.3	19.7 ± 3.2	22.5 ± 0.1	47.4 ± 0.6
	1.34	2.57	1.34 ± 0.02	494.2 ± 66.8	–	202.6	–	63.3 ± 13.4	–	17.8 ± 0.4	38.4 ± 0.0
QPAE-b	1.06	2.08	0.88 ± 0.04	48.5 ± 1.2	57.1 ± 1.1	30.3	35.7	12.8 ± 0.4	14.5 ± 2.1	17.5 ± 0.1	31.8 ± 0.2
	1.37	2.57	1.26 ± 0.00	129.0 ± 19.0	604.3 ± 47.6	56.3	263.5	22.7 ± 7.5	–	10.3 ± 0.1	20.7 ± 0.1
QPAE-c	1.06	2.05	0.96 ± 0.10	43.2 ± 5.8	56.3 ± 1.0	24.7	32.2	8.4 ± 1.0	16.2 ± 2.8	14.1 ± 0.1	28.1 ± 0.1
	1.37	2.53	1.39 ± 0.03	116.3 ± 8.0	–	46.0	–	25.4 ± 2.6	–	17.3 ± 0.0	35.1 ± 0.3
QPAE-d	1.07	2.03	0.96 ± 0.11	49.8 ± 1.2	56.3 ± 0.3	28.5	32.2	10.4 ± 4.6	15.4 ± 2.2	16.0 ± 0.1	36.4 ± 0.1
	1.37	2.49	1.25 ± 0.12	80.7 ± 4.8	–	35.5	–	20.5 ± 0.7	–	10.8 ± 0.2	17.4 ± 0.0
QPAE-e	1.06	1.98	1.00 ± 0.00	50.1 ± 5.2	58.9 ± 2.9	27.5	32.4	12.9 ± 0.6	14.5 ± 0.2	12.6 ± 0.2	45.6 ± 0.0
	1.36	2.43	1.30 ± 0.00	91.4 ± 1.5	424.9 ± 35.1	38.6	179.6	24.9 ± 2.0	50.0 ± 6.4	14.6 ± 0.1	28.1 ± 0.1
TMPAEK-NOH[32]	2	–	0.96	22.3 (20°C)	32.6 (60°C)	–	–	2.7 (20°C)	7.8 (60°C)	8(rt)	–
TMPAES-80-NOH[33]	1.7	–	1.03	21.2 (20°C)	27.9 (70°C)	–	–	6.4 (20°C)	9.7 (70°C)	–	16 (70°C)
TMPAES-140-NOH[33]	1.7	–	1.37	28.2 (20°C)	42.0 (70°C)	–	–	10.5 (20°C)	20.4 (70°C)	–	54 (70°C)

[a] Calculated from the polymer composition and DBM.
[b] Determined by titration.
[c] λ = [water uptake(g/g)/18.02 (g/mol)] × [1000/IEC (mmol g⁻¹)].
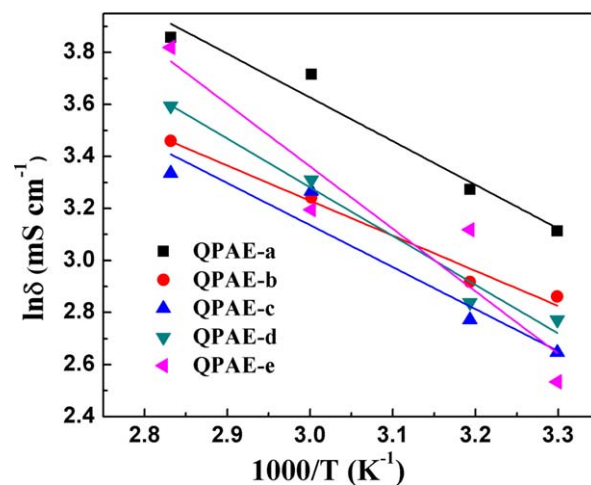
Figure 3. Arrhenius plots of QPAE-a (IEC = 0.98 meq g⁻¹), QPAE-b (IEC = 0.88 meq g⁻¹), QPAE-c (IEC = 0.96 meq g⁻¹), QPAE-d (IEC = 0.96 meq g⁻¹), QPAE-e (IEC = 1.00 meq g⁻¹) membranes at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

controlled in reasonable scope. ¹H-NMR spectrum of QPAE-e (IEC = 1.00 meq g⁻¹), which is derived from BMPAE-e (DBM = 1.06), is shown in Figure 1(c). The integral ratio of signal a to signal e in the spectrum of QPAE-e is 8.50 : 2 agreeing well with that of BMPAE-e (DBM = 1.06). A new multisplit signal f at 3.11 ppm was assigned to methyl protons in the quaternized ammonium groups. The integral ratio of signal e to signal f (2 : 8.42) in the spectrum is obviously smaller than the theoretical value of 2 : 9. This indicates the occurrence of side reactions of the functionalization, which are hydrolysis reactions of the benzyl bromide groups in the aqueous trimethyl amine solution and 1M sodium hydroxide solution. The shoulder of signal f results from the hydroxyl protons of hydrolysis product benzyl alcohol. The methylene protons of benzyl alcohol lead the spilt of signal e, which results from the methylene protons of the quaternized ammonium groups. The signals b, b′, b″, c, and d of the protons in the aromatic rings of QPAE-e have also been altered due to the changed solvent of DMSO-d_6 and the introduction of strong electron withdrawing quaternized ammonium groups. However, the integral ratio of signal e to aromatic signals agrees well with that of BMPAE-e (DBM = 1.06).

Thermal Stabilities

The thermal stability of the synthesized PAEs, BMPAEs, and QPAEs were investigated by TGA analyses. Figure 2 shows the TGA curves of PAE-e, BMPAE-e (DBM = 1.06), QPAE-a (IEC = 0.98 meq g⁻¹), QPAE-b (IEC = 0.88 meq g⁻¹), QPAE-c (IEC = 0.96 meq g⁻¹), QPAE-d (IEC = 0.96 meq g⁻¹), and QPAE-e (IEC = 1.00 meq g⁻¹). PAE-e is thermally stable and its 5% loss temperature is up to 430°C, due to its rigid aromatic structure. Two major stages of weight loss behavior are observed in the TGA curve of BMPAE-e. The first stage between 260°C and 380°C with a weight loss of 18.0% is assigned to the decomposition of —CH₂Br side groups. This result agrees well with the theoretical weight percentage of bromomethylene groups (18.4%) calculated from the corresponding DBM value

Table IV. Ion Transport Activation Energy, E_a, of QPAEs Membranes

Membrane	IEC (meq g^{-1})	E_a (kJ mol^{-1})	IEC (meq g^{-1})	E_a (kJ mol^{-1})
QPAE-a	0.98 ± 0.01	13.99	1.34 ± 0.02	13.27
QPAE-b	0.88 ± 0.04	11.21	1.26 ± 0.00	12.13
QPAE-c	0.96 ± 0.10	13.42	1.39 ± 0.03	12.53
QPAE-d	0.96 ± 0.11	15.57	1.25 ± 0.12	8.57
QPAE-e	1.00 ± 0.00	19.95	1.30 ± 0.00	11.46

(1.06) of the BMPAE-e. The second stage starting at 380°C is attributed to the degradation of polymer main chain. There are four stages of weight loss of QPAEs. The first stage starts from 30°C to 150°C corresponding to the evaporation of absorbed water. The second stage observed between 150°C and 220°C is contributed by the decomposition of quaternary ammonium groups according to Tanaka's work.[28] The third stage of weight loss starting at 220°C is ascribed to the decompositions of the nonvolatile residual of second stage and the unquaternized bromomethylene groups. The incomplete quaternization has been confirmed by the deviation of the determined IEC values from the theoretical ones in Table III. The last stage commencing around 350°C is ascribed to the degradation of polymer main chain. These results confirm that the QPAEs membranes are thermally stable to satisfy the requirement of thermal stability for the use in AEMFCs.

IEC, Water Uptake, Swelling Ratio, and Hydroxide Ion Conductivity of QPAEs Membranes

Table III shows the IEC, water uptake, λ, SR, and hydroxide ion conductivity of QPAEs membranes and some AEMs in the literature.[32,33] Theoretical IECs were calculated from the copolymers compositions and DBM values based on hypothesis that benzyl bromide completely converted to benzyltrimethyl ammonium groups and all the bromine ions exchanged into hydroxide ions. All the experimental IEC values are much lower than the theoretical ones because of the side reactions of the functionalization. This confirms the deductions obtained from the NMR

spectrum [Figure 1(c)]. The conversions of the functionalization are much lower than that in our previous work based on the configurations with bulky side groups.[34] The possible explanation is the designed molecular configurations form tight aggregations in the parent membranes, which is not favorable for undergoing quaternization in solid membranes under the most reported quaternization conditions.

Water uptakes and SRs of the QPAEs membranes with two levels of IEC were measured at 30°C and 80°C. It can be seen that the water uptake and SR increase with increasing IECs due to the augment of hydrophilic groups. Water uptake rises up with an elevation in temperature. With the increasing content of phenyl sulfone moieties, water uptakes of QPAEs with higher IEC level (1.25–1.39 meq g^{-1}) show decreasing tendency, while that of QPAEs with low IEC level (0.88–1.00 meq g^{-1}) demonstrates no significant change. The water uptakes and SRs of QPAEs membranes with higher IECs show stronger dependence on temperature than that of QPAEs membranes with lower IECs. In order to investigate the relationship of hydrophilicity and the structures of the QPAEs membranes, the number of bonded water per ammonium group (expressed as λ in Table III) of the QPAEs membranes with various molecular configurations was calculated. λ increases with increasing IEC and elevated temperature. A comparison among all the QPAEs membranes indicates that the QPAE-a with pure poly(aromatic ether ketone) structure bonds more water than other polymers with similar IEC. The possible reasons are the alkaline circumstance benefits the nucleophilic addition of the ketone group and the undergoing reaction changes the aggregations in the membrane. As an excessively high level of water uptake results in the losing of mechanical properties and disqualifies the membranes in fuel cells, the water uptake of the prepared membranes should be controlled in a reasonable range.

The QPAEs membranes exhibit hydroxide ion conductivities in the range of 10.3–22.5 mS cm^{-1} at 30°C and 17.4–47.4 mS cm^{-1} at 80°C, respectively. Taking IEC values into consideration, membranes based on homopolymer display higher hydroxide ion conductivities with lower IEC values than that has been

Table V. Mechanical Properties of the QPAEs Membranes

Membrane	IEC (meq g^{-1})	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
QPAE-a	0.98 ± 0.01	17.2 ± 1.1	68.7 ± 8.9	235.2 ± 2.1
	1.34 ± 0.02	–	–	–
QPAE-b	0.88 ± 0.04	13.1 ± 0.4	18.5 ± 4.7	214.8 ± 2.5
	1.26 ± 0.00	6.2 ± 1.1	35.6 ± 0.4	109.6 ± 4.9
QPAE-c	0.96 ± 0.10	15.9 ± 1.7	27.2 ± 9.6	223.2 ± 8.7
	1.39 ± 0.03	5.9 ± 0.1	12.1 ± 3.1	111.6 ± 5.1
QPAE-d	0.96 ± 0.11	14.9 ± 1.3	8.7 ± 0.1	256.3 ± 2.6
	1.25 ± 0.12	5.3 ± 0.4	2.0 ± 0.1	332.2 ± 19.5
QPAE-e	1.00 ± 0.00	14.4 ± 1.0	6.2 ± 0.9	248.0 ± 9.2
	1.30 ± 0.00	6.9 ± 0.3	6.3 ± 1.3	122.4 ± 3.5
TMPAES-80-NOH[33]	1.03	22.8	5.13	866.3
TMPAES-140-NOH[33]	1.37	2.1	1.09	164.9

Table VI. Changes in IEC, δ, and Mechanical Properties of the QPAEs Membranes with Alkaline Stability Test at 60°C for 7 Days

Membrane	IEC (meq g^{-1})		δ (mS cm^{-1})		Tensile strength (MPa)		Elongation at break (%)	
	AST[a]	Residual[b] (%)	AST[a]	Residual[b] (%)	AST[a]	Residual[b] (%)	AST[a]	Residual[b] (%)
QPAE-a	1.12 ± 0.14	114.3	17.7 ± 0.2	43.1	9.6 ± 0.2	55.8	4.6 ± 0.4	6.7
QPAE-b	1.14 ± 0.07	129.5	17.0 ± 0.1	66.4	13.0 ± 0.6	99.2	8.9 ± 0.7	48.1
QPAE-c	0.88 ± 0.19	91.7	9.8 ± 0.2	37.4	10.9 ± 0.2	68.6	6.2 ± 0.9	22.8
QPAE-d	1.15 ± 0.05	119.8	15.9 ± 0.2	58.0	9.8 ± 0.1	65.8	3.7 ± 0.7	42.5
QPAE-e	1.11 ± 0.02	111.0	15.1 ± 0.1	61.9	10.8 ± 1.4	75.0	5.1 ± 0.8	82.2

[a] AST means after stability test.
[b] Residual means the ratio of the parameter value of the treated membrane to that of the origin membrane.

reported in the previous work.[30] However, the hydroxide ion conductivities of copolymers with various molar ratios of ketone to sulfone moieties, QPAE-b, QPAE-c, and QPAE-d, show no obvious change with the tuning backbones. The result is contrary to the reported work.[30] This illuminates that the bulky loosen backbones benefit high conductive ion channels and tight molecular configurations built low conductive ion channels. An abnormal phenomenon to the published works is that the hydroxide ion conductivities of all QPAEs membranes are inversely proportional to increasing IEC. As far as the designed molecular configurations are concerned, water uptakes increase dramatically with the increasing IECs. QPAE-c with IEC value of 0.96 meq g^{-1} displays higher ion conductivity than TMPAEK-NOH[32] and QMPAES-80-NOH[33] as an adequate amount of water is a prerequisite to obtain an efficient conductivity by hydrating and transporting the ions. However, extensive water inside the QPAEs membranes with higher IECs leads to the dilution of cation groups' concentration and results in the decline in ion conductivities.

Hydroxide ion conductivities of the QPAEs membranes exhibit an approximate Arrhenius-type temperature behavior (Figure 3). And the ion transport activation energy (E_a) is calculated according to $E_a = -b \times R$, where b is the slope of the regressed liner $\ln\sigma - 1000/T$ plots, and R is the gas constant (8.314 J (mol K)$^{-1}$). The E_a values of the various membranes varied from 8.57 to 19.95 kJ mol^{-1} are listed in Table IV. The values are similar to that of Nafion-117 (12.75 kJ mol^{-1})[35] and some reported FCAEM membranes (10.69–21.14 kJ mol^{-1}).[27] QPAE-e (IEC = 1.00 meq g^{-1}) has a highest E_a of 19.95 kJ mol^{-1} among the QPAEs group. This reveals that its hydroxide ion mobility is more sensitive to temperature than that of others.

Mechanical Properties
The mechanical properties of the QPAEs membranes were measured at 25°C and 100% RH. The results are listed in Table V, the QPAEs membranes with lower IEC showed tensile strengths at maximum load varying from 13.1 to 17.2 MPa, elongations at break varying from 6.2 to 68.7%, and tensile modulus ranging from 214.8 to 256.3 MPa. The QPAEs membranes with high IEC showed tensile strengths at maximum load ranging from 5.3 to 6.9 MPa. Tensile strengths of the QPAEs membranes decrease significantly with the increasing IECs due to the plasticizing effect

of the absorbed water. The analogous phenomenon has been observed in both PEM and AEM.[33,36,37] QPAE-a with a IEC of 1.34 meq g^{-1} cannot be measured because of excessive swelling. QPAEs of lower IEC are suitable to apply in AEMFC as they possess relative high tensile strength, which is higher or comparable to the tensile strength of the reported AEMs.[38,39]

Chemical Stability
Table VI shows the variations in IEC, hydroxide ion conductivity, and mechanical properties of the QPAEs membranes after treatment with 1M NaOH solution at 60°C for 7 days. The IEC values of QPAE-a, QPAE-b, QPAE-d, and QPAE-e increase after stability test. The possible reasons are that benzyl alcohol groups have been formed by the nucleophilic displacement of the ammonium group with the OH$^-$ anions[40] and the further hydrolysis of some of unfunctionalized benzylmethyl bromide groups under the strong alkaline circumstance. And hydroxyl groups of benzyl alcohol groups combine with sodium hydroxide via strong interactions such as dipole–dipole interactions and hydrogen bonds. Moreover, benzyl dimethyl t-amine groups, which are protonated at the end of the back titration for IEC determination, can also formed by the nucleophilic displacement of the ammonium group with the OH$^-$ anions.[40] These lead to the increase of IEC and result in the descent of ion conductivity because alkali doped AEMs display relatively weak ionic migration[10] and the benzyl dimethyl t-amine groups attached to the backbones have no ion conductivity. However even after 168 h chemical stability test, the QPAE membranes still exhibit high hydroxide ion conductivities approximate or higher than 10^{-2} S cm^{-1} and acceptable tensile strength. The results of chemical stability show that QPAEs membranes with lower IEC are promising for application in AFCs.

CONCLUSIONS

In summary, AEMs based on PAEs containing tetramethylbiphenol were designed and successfully synthesized via nucleophilic substitution polycondensation, bromination, quaternization and alkalization. BMPAEs with two levels of DBM (about 1.05 and 1.35) were obtained under the optimized conditions. The QPAE-a membrane with IEC value of 0.98 meq g^{-1} demonstrated the highest ion conductivity of 47.4 mS cm^{-1} at 80°C. The transport activation energy (E_a) of QPAEs membranes

varied from 8.57 to 19.95 kJ mol^{-1}. The hydroxide ion conductivities of QPAEs membranes increased dramatically with test temperature. Due to the reduction of fixed charge or fixed ion concentration by excessively high level of water uptake, ion conductivities of QPAEs membranes displayed a decline with elevated IEC. Moreover, the QPAEs membranes with IEC nearly 1.0 meq g^{-1} exhibited excellent thermal and chemical stabilities, as well as mechanical properties. These properties of the obtained membranes seem promising as AEM for fuel cell application.

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