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Synthesis and Properties of Anion Conductive Ionomers Containing Tetraphenyl Methane Moieties

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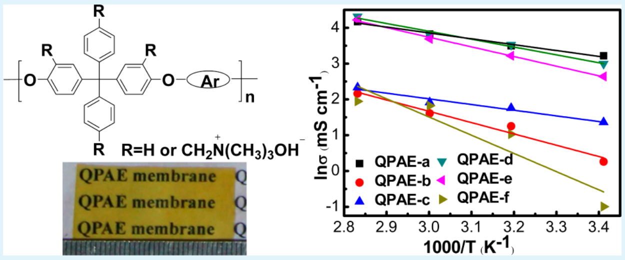

ABSTRACT: A series of anion conductive aromatic ionomers, poly(arylene ether)s containing various polymer backbones and quaternary ammonium basic group functioned tetraphenyl methane moieties, were synthesized via nucleophilic substitution polycondensation, chloromethylation, quaternization, and the subsequent alkalization reactions. The structures of poly(arylene ether)s (PAEs), chloromethylated poly(arylene ether)s (CMPAEs), and quaternized poly(arylene ether)s (QPAEs) ionomers were confirmed by ^{1}H NMR technique. Their thermal stabilities were evaluated by thermo gravimetric analysis (TGA). The water uptakes, ion exchange capacities (IEC), hydroxide ion conductivities, mechanical properties, and chemical stabilities of the membranes derived from the synthesized ionomers were assessed as anion exchange membranes. The QPAEs membranes were tough and thermally stable up to 170 °C. The IEC of the ionomers varied from 0.21 to 2.38 meq g^{-1} which can be controlled by chloromethylation reaction conditions. The ion conductivities of QPAEs membranes increase dramatically with increasing temperature. The hydroxide ion transport activation energy, E_a, of the QPAEs membranes varied from 13.18 to 42.30 kJ mol^{-1}. The QPAE-d membrane with lower IEC value of 1.04 meq g^{-1}, derived from copolymer CMPAE-d bearing sulfone/ketone structure, displayed the highest hydroxide ion conductivity of 75 mS cm^{-1} at 80 °C and showed strong tensile strength (29.2 MPa) at 25 °C. The QPAE-e membrane with IEC value of 1.09 meq g^{-1}, derived from copolymer CMPAE-e bearing sulfone/ketone−ketone structure, demonstrated 68 mS cm^{-1} at 80 °C. The QPAE-d membrane kept 90% of mechanical properties and 82% of hydroxide ion conductivity after being conditioned with 1 M NaOH at 60 °C for 170 h. These properties of the ionomers membranes show their potential as an anion exchange membrane of alkaline fuel cells.

KEYWORDS: *Poly(arylene ether)s, ionomers, chloromethylation, quaternization, alkaline anion exchange membrane, polymer electrolyte*

1. INTRODUCTION

In recent years, fuel cells have attracted extensive attention due to their high energy efficiency and low environmental pollution levels.[1−4] Among the several types of fuel cells, proton exchange membrane fuel cells (PEMFCs) have been well developed.[5] Perfluorinated ionomers such as Nafion (Dupont) are state-of-the-art polymer electrolyte membrane materials for PEMFCs. The PEMFCs demonstrate high proton conductivities and excellent stabilities. However several significant disadvantages such as high cost of membrane, slow electrode-kinetics, platinum group metal electrocatalysts, and low methanol barriers have limited their further development.[6−8]

Anion exchange membrane fuel cells (AEMFCs) can combine the advantages of proton exchange membrane fuel cells and traditional alkaline fuel cells and solve the problems of PEMFCs. Under basic conditions, the kinetics of oxygen reduction reaction is enhanced substantially, resulting in high fuel cell efficiency. Non-noble metals such as Ag, Co, or Ni can be used as catalysts in AEMFCs because of the facile electrochemical reactions in alkaline medium, thus reducing the cost of the fuel cells significantly. Furthermore, the direction of hydroxide anion motion opposes that of the methanol flux through the membrane and can reduce the methanol permeation greatly.[9,10] Since the existing anion exchange membranes (AEMs) are not as conductive and stable as proton exchange membranes (PEMs), a variety of AEMs materials with improving overall properties have been currently developed. Several approaches have been examined to prepare new AEMs materials. The AEMs based on poly(ether ketone),[11,12] polyethersulfones,[13−15] poly(ether imide) (PAEI),[16] or poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)[17] were typically prepared by chloromethylation of the pristine polymers and followed by exposure to trimethylamine to form benzyltrimethylammonio groups. The AEMs constructed from fluoro-olefin polymers[18−20] were synthesized by radiation-graft of vinylbenzyl group to the pristine polymers and followed by

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quaternization and alkalization reactions to form anion exchange groups. Poly(arylene ether sulfone)s and poly(arylene ether ketone)s, a class of aromatic polymers demonstrating good solubility in organic solvents, have been widely used as a backbone of hydrocarbon PEMs.[21−23] Therefore many research groups have attempted to use poly(arylene ether)s as AEMs by introducing quaternized ammonio groups. For example, poly(arylene ether)s with various backbones bearing quaternized ammonio groups were recently reported as AEMs.[24,25]

Various types of poly(arylene ether)s have been investigated for the AEMs, however, the AEM polymers that have tetraphenyl methane moieties in the backbone have received little attention. For the past few years, we have synthesized a series of sulfonated poly(arylene ether)s containing tetraphenyl methane moieties as PEMs.[26,27] Since sulfonation takes place only at the specific position of tetraphenyl methane groups and sulfonic acid groups on tetraphenyl methane moieties distanced from the polymer backbone, the PEMs have high local concentration of ionic groups resulting in high proton conductivity and reduced hydrolytic and/or oxidative degradation caused by sulfonic acid groups. Chloromethylation has a reaction mechanism similar to that of sulfonation. Our idea is that tetraphenyl methane groups should function in the AEMs as well as PEMs. Herein, we report advanced novel quarterary ammonium basic poly(arylene ether)s containing tetraphenyl methane groups with precisely designed chemical structures as AEMs. Designed backbone group consisting of sulfone, ketone, ketone−ketone, sulfone/ketone, sulfone/ketone−ketone, and ketone/ketone−ketone have been investigated. Chloromethyl groups, the precursors of quaternized ammonio groups, were successfully introduced at the specific positions of tetraphenyl methane groups of the poly(arylene ether)s (PAEs) via Friedel−Crafts reaction. The chloromethylation reaction was well controlled by optimizing the reaction conditions. The obtained quaternized poly(arylene ether)s (QPAEs) were evaluated as AEMs in terms of water uptakes, ion conductivities, thermal properties, mechanical properties, and chemical stabilities.

2. EXPERIMENTAL SECTION

2.1. Materials. All the chemicals used were reagent grade and purified by standard methods. Bis(4-fluorophenyl) sulfone (FPS), 4,4-difluorobenzophenone, and 1,4-bis(4-fluorobenzoyl) benzene were obtained from Aldrich Chemical Co. Bis(4-hydroxylphenyl)diphenyl methane was synthesized as outlined in the previous work.[26] Dimethyl sulfoxide (DMSO), chloromethyl methyl ether (CMME), zinc chloride, trimethylamine aqueous solution (33 wt %), potassium carbonate, sodium hydroxide, toluene, methanol, and chloroform were obtained from commercial sources and used as received. *N,N'*-dimethylacetamide (DMAc) was dried over 4 Å molecular sieves. Toluene was dried over sodium wire prior to being used.

2.2. Polymerization. A series of poly (arylene ether)s (PAEs) containing tetraphenyl methane moieties (PAE-a to PAE-f) were synthesized by nucleophilic aromatic substitution with a stoichiometric ratio of various monomers, 1.5 equiv of potassium carbonate, DMAc as the solvent, and toluene as the azeotropic agent. A typical polymerization procedure for PAE-a was as follows: To a 25-mL, three-neck, round-bottomed flask equipped with Dean−Stark trap FPS (0.254 g, 1.0 mmol), bis(4-hydroxylphenyl)diphenyl methane (0.352 g, 1.0 mmol), potassium carbonate (0.208 g, 1.5 mmol), DMAc (2.0 mL), and toluene (4.0 mL) were added. The reaction was carried out at 150 °C for 4 h under nitrogen protection. After the Dean−Stark trap was removed, the temperature was elevated to 170 °C and kept for 4 h. After cooling, the mixture was poured into 100 mL of methanol containing 2 mL of concentrated HCl. The crude product was washed with water and methanol several times. After drying, it was dissolved in 50 mL of chloroform and filtered through a sintered glass funnel and then poured into 100 mL of methanol with stirring to precipitate out the polymer. Finally, the light yellow polymer was dried at 80 °C under vacuum for 24 h to give PAE-a (0.548 g, yield = 92%).

2.3. Chloromethylation. A typical procedure of chloromethylation reaction of poly(arylene ether)s is as follows: PAE-a (0.596 g, 1 mmol) was dissolved in 1,1,2,2-tetrachloroethane (20 mL) in a 50-mL, round-bottomed flask, then zinc chloride (0.136 g, 1 mmol) was added to the flask. After stirring the mixture for 10 min at room temperature, the chloromethyl methyl ether was dropwise added to the mixture and stirred at 40 °C for 48 h. The obtained chloromethylated polymer CMPAE-a was precipitated in methanol to remove the catalyst, excess chemicals, and solvent. The precipitates were washed with methanol several times, and then dried in a vacuum at 80 °C for 24 h to get the white polymer.

2.4. Membrane Preparation. CMPAE (0.3 g) was dissolved in 1,1,2,2-tetrachloroethane (6 mL) to make a 3 wt % solution and filtered via a 0.45-μm membrane filter. The filtrate was cast on a flat glass plate, dried in oven at 80 °C for 48 h to get a 100-μm thick, transparent and tough membrane, and then further dried in a vacuum oven at 80 °C for 24 h to remove the solvent completely.

2.5. Quaternization and Alkalization. The chloromethylated polymer membrane was immersed in a 33 wt % trimethylamine solution at room temperature for 48 h and then washed with deionized water several times. The obtained quaternized polymer membrane was soaked in a 1 M sodium hydroxide aqueous solution at room temperature for 48 h to convert the counteranion from chloride to hydroxide anion. The obtained quaternized poly(arylene ether) (QPAE) membrane was washed with deionized water several times and soaked in deionized water in a closed vessel at least 24 h prior to analysis.

2.6. Characterization. ^{1}H NMR spectra were measured at Bruker AVANCE 400S with deutrated chloroform ($CDCl_3$) or deutrated dimethyl sulfoxide (DMSO-d_6) as a solvent and tetramethylsilane (TMS) as an internal reference. Thermogravimetric analysis (TGA) was carried out using a TAINC SDT Q600 thermogravimetric analyzer at a heating rate of 20 °C per minute from 30 to 700 °C under a protective nitrogen atmosphere (100 mL min^{-1}). 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 polystyrenes as standards. The mechanical properties of membranes were measured by using a SANS power test at 25 °C and 100% RH at a stretching speed of 50 mm min^{-1}.

For water uptake (WU), the QPAE membrane was vacuum-dried at 60 °C for 24 h to obtain a constant dry weight (W_{dry}). The dry membrane was immersed into deionized water at a given temperature for 24 h. Then the membrane was taken out, surface water was wiped out with tissue paper, and the membrane was weighed quickly to get wet weight (W_{wet}). The water uptake of the membrane was calculated according to the following:

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

Ion exchange capacity (IEC) of the QPAE membrane was determined by using the back-titration method. At first, the membrane was vacuum-dried at 60 °C for 24 h to obtain a constant weight, after which the membrane was immersed in 50 mL of HCl (0.01 M) standard for 48 h. Back titration was then accomplished with a standardized NaOH (0.01 M) solution to titrate the HCl solution using phenolphthalein as an indicator. The IEC values were calculated by

$$\text{IEC} = (M_1V_1 - M_2V_2)/W_{\text{dry}}$$

where M_1 (M) and V_1 (mL) are the concentration and volume of the initial HCl solution. M_2 (M) and V_2 (mL) are the concentration and volume of the standardized NaOH solution used to titration. W_{dry} (g) is the weight of dry QPAE membrane.

The hydroxide conductivities of the QPAE membranes were measured at 20, 40, 60, and 80 °C in a vessel filled with deionized water with a Solartron 1255B and 1287 frequency response analyzer at an oscillating voltage of 10 mV, using a two probe method at frequency ranging from 1 MHz to 1 kHz. The ionic conductivity was calculated as

$$\sigma = L/AR$$

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

3. RESULTS AND DICUSSION

3.1. Synthesis of Parent poly(Arylene ether)s (PAEs) and Chloromethylated poly(Arylene ether)s (CMPAEs).

Parent poly(arylene ether)s (PAEs) were synthesized via polycondensation reaction as shown in Scheme 1a. The polymerization of bis(4-hydroxylphenyl)diphenyl methane and difluoro monomers were carried out in anhydrous DMAc solution in a nitrogen ambient. The reaction mixture was first controlled at 135−140 °C for 3−4 h to azeotrope off water with toluene and then was heated to 160−180 °C for a long time to afford a high-molecular-weight polymer. The molecular weights of the PAEs were measured by GPC, in which the elution curves were unimodal. As summarized in Table 1, Mn and M_w of the PAEs were higher than 59 and 95 kg mol^{-1}, respectively. The PAEs were soluble in some organic solvents such as chloroform, dichloromethane, 1,1,2,2-tetrachloroethane, *N*,*N*-dimethylformamide (DMF), DMAc, and dimethylsulfoxide (DMSO). Transparent, ductile membranes were obtained by solution casting.

Scheme 1. Schematic diagram of synthesis: (a) polymerization; (b) chlorormethylation; (c) quaternization; and (d) alkalization

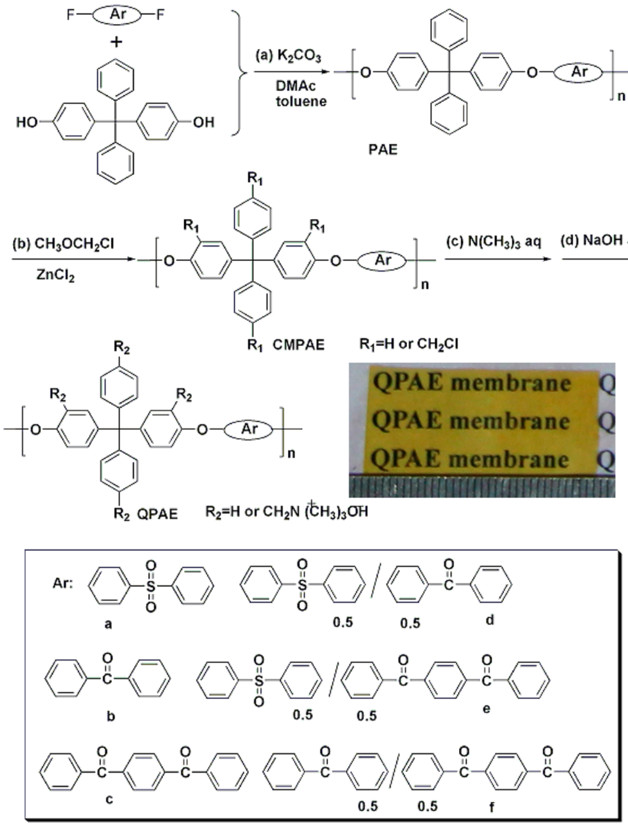

Table 1. Synthesis of Parent poly(Arylene ether)s (PAEs)

PAE	Mn/kg mol^{-1}	M_w/kg mol^{-1}	M_w/Mn
PAE-a	97	137	1.41
PAE-b	87	144	1.66
PAE-c	59	95	1.58
PAE-d	101	325	3.21
PAE-e	41	66	1.61
PAE-f	35	59	1.68

Chloromethylation is one of the most important steps in fabricating poly(arylene ether)s AEMs. The reason is that chloromethylation controls the amount of chloromethyl groups attached to the polymer and the reactivity of the tethered chloromethyl groups. Because of the high reactivity of the tethered chloromethyl groups, the chloromethylated polymer can be readily further modified.[9,28] After subsequent quaternization and alkalization, chloromethyl groups convert to quaternized ammonio groups which determine the ionic conductivity and mechanical strength of the fabricated ionomer membrane. Friedel−Craft chloromethylation occurs via electrophilic attack of chloromethylmethyl ether (CMME) on the phenyl rings. The published work revealed that the accompanying Friedel−Craft alkylation between the benzyl group ($ArCH_2Cl$) and the phenyl ring belonging to different PAE chains resulted in undesirable cross-linking gelation.[29] To avoid or reduce the alkylation, the effects of both reaction temperature and time were investigated. The chloromethylation results of PAEs are summarized in Table 2. The degree of chloromethylation (DCM), denoted as the average number of chloromethyl groups per repeating unit of PAEs, was determined by ^{1}H NMR technique. In all cases, 1 equiv catalyst of $ZnCl_2$ and 40 equiv of CMME were used (Scheme 1b). The results demonstrated that increasing temperature resulted in high DCM. It should be noted that the gelation happened at temperature higher than 60 °C. Figure 1 indicates that extended reaction time led to higher DCMs of CMPAE-c, CMPAE-e, and CMPAE-f compared to CMPAE-a, CMPAE-b, and CMPAE-d. The reason DCM is higher is that easier chloromethylation takes place for the first group of polymers containing 1,4-bis(4-fluorobenzoyl) benzene moieties with the dense carbonyl groups. The dense carbonyl groups enhanced

Table 2. Reaction Conditions and the Results of Chloromethylation of PAEs

				DCM		
run	PAE	chloromethylation temperature (°C)	chloromethylation time (h)	main chains	pendant groups	total
1	PAE-a	60	24		gelation	
2		50	48	2.04	0.80	2.84
3		50	24	1.90	0.44	2.34
4		40	48	2.00	0.50	2.50
5		40	24	1.50	0.28	1.78
6		40	12	0.52	0.11	0.63
7		40	6	0.35	0.09	0.44
8	PAE-b	50	48	3.00	1.00	4.00
9		40	48	2.26	0.74	3.00
10		40	24	1.51	0.43	1.94
11	PAE-c	40	24	1.70	0.55	2.25
12	PAE-d	40	24			1.70[a]
13	PAE-e	40	12			3.10
14	PAE-f	40	12			3.74

[a] The peaks of chloromethylene protons assigned to main chains and pendant groups are overlapped in the ^{1}H NMR spectra in the cases of copolymers CMPAE-d, CMPAE-e, and CMPAE-f.

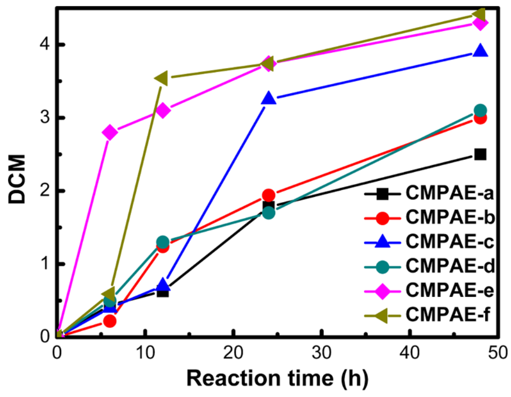

Figure 1. Effect of reaction time on DCM.

the molecular interaction between the macromolecules and chloromethylation reagent and provided more opportunities to the chloromethylation reagent to attack electron-rich active centers in homogeneous reaction systems.

Parent poly(arylene ether)s (PAEs) and chloromethylated poly(arylene ether)s (CMPAEs) were characterized by ^{1}H NMR. ^{1}H NMR spectra of PAE-a and CMPAE-a (example of homopolymers) are shown in Figure 2. ^{1}H NMR spectra of PAE-d and CMPAE-d (example of copolymers) are demonstrated in Figure 3a and Figure 3b. Compared with ^{1}H NMR spectrum of PAE-a (Figure 2a), two new characteristic peaks at 4.48 and 4.57 ppm assigned to chloromethyl groups were observed in ^{1}H NMR spectrum of CMPAE-a (Figure 2b). The introduction of chloromethyl groups onto the polymer chains altered several peaks' shifts between 6.8 and 7.4 ppm, which were derived from tetraphenyl methyl moieties protons. The integration of the new peak m at 4.48 ppm was in good agreement with the decreasing integration of peaks corresponding to protons of the tetraphenyl methane moieties ortho to ether bonds. It confirmed that the peak m was attributed to the chloromethyl groups on the polymer backbone and the peak n was assigned to the chloromethyl groups on the pendant phenyl ring of tetraphenyl methyl moieties (Figure 2b). DCM was calculated from the integral ratio of the peaks m and n to peak b attributed to the ortho-positional protons in biphenyl sulfone moiety, which are intact during the chloromethylation.

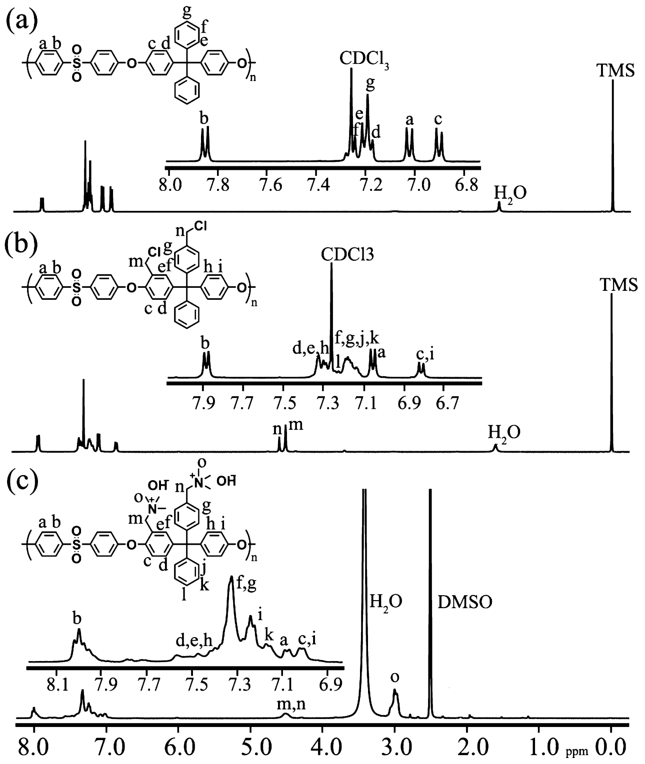

Figure 2. ^{1}H NMR spectra of (a) PAE-a, (b) CMPAE-a, and (c) QPAE-a.

In the case of homopolymer, peaks m and n are separate. The chloromethylation contribution of the polymer backbone and the side pendant groups is tabulated in Table 2. The DCM values of the polymer backbone are higher than those of the side pendant groups because the electron donating conjugation of saturated oxygen atom activates the chloromethylation centers in the polymer backbone. There were three new peaks ranging from 4.45 to 4.60 ppm appearing in the ^{1}H NMR spectrum of the copolymer CMPAE-d (Figure 3b), which were assigned to chloromethyl groups attached to phenyl ring of tetraphenyl methyl moieties and polymer chain, respectively. The copolymers backbones consisting of two kinds of repeat

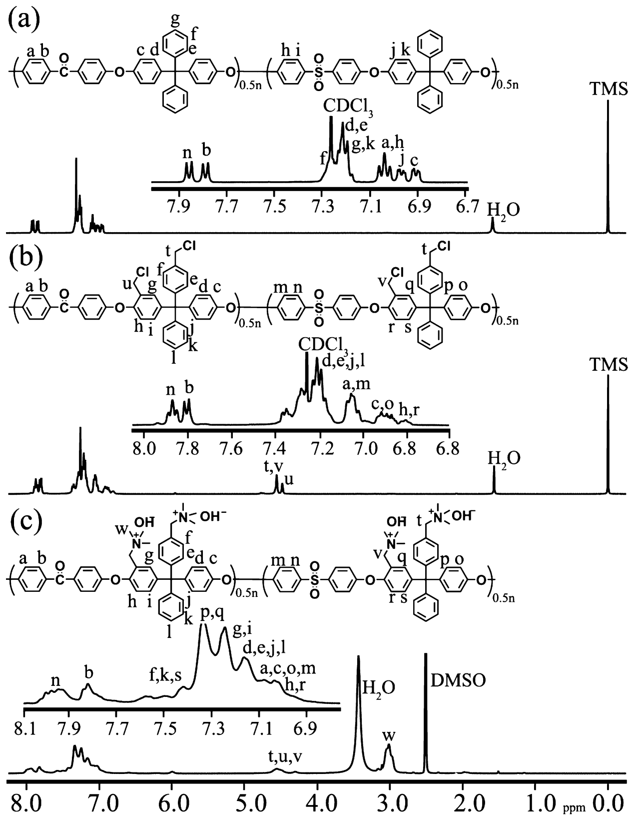

Figure 3. ^{1}H NMR spectra of (a) PAE-d, (b) CMPAE-d, and (c) QPAE-d.

units messed the chemical circumstance of chloromethyl groups. The peaks assigned to various chloromethyl groups were overlapped. However the base peaks assigned to intact protons were well separated. The total chloromethylation contributions of the polymer backbone and the side pendant groups of copolymers are listed in Table 2.

3.2. Preparation of Quaternized poly(Arylene ether)s (QPAEs) Membranes. The membranes of CMPAEs were fabricated by dissolving CMPAEs in 1,1,2,2-tetrachloroethane followed by casting on a flat glass plate, then dried under vacuum to remove residual solvent. The obtained membranes were colorless, transparent, and flexible. These membranes were then immersed in trimethylamine aqueous solution to form quaternized membranes (Scheme 1c). Subsequently the quaternized membranes were immersed in 1 M sodium hydroxide solution to convert chloride ion to hydroxide ion (Scheme 1d) and the quaternized membranes became hydrophilic and swelling. DCM was an important factor to affect the fabrication of quaternized membranes. When DCM was too high, the quaternized membranes exhibited considerable swelling even dissolved in solution. QPAEs membranes with suitable hydrophilicity were obtained by controlling the DCM value of CMPAEs. The final QPAEs membranes appeared to be light yellow, tough, and less soluble compared with CMPAEs. The chemical structure of QPAEs was characterized by ^{1}H NMR technique. ^{1}H NMR spectra of QPAE-a and QPAE-d, the examples of homopolymers and copolymers, are shown as Figures 2c and 3c, respectively. The sharp peaks of methylene protons at 4.57 and 4.48 ppm in ^{1}H NMR spectrum of CMPAE-a (Figure 2b) shifted to 4.52 ppm as a broad peak in ^{1}H NMR spectrum of QPAE-a (Figure 2c). A new multisplit peak at 3.02 appeared in Figure 2c, which was assigned to methyl groups on the quaternized ammonio groups. Compared with Figure 3b, the peaks assigned to the methylene groups and methyl groups in copolymer exhibited characteristics similar to those in Figure 3c.

3.3. Thermal Stabilities of the QPAEs Membranes. Since AEMFCs usually work at elevated temperature and some AEMs based on quaternary ammonium salts are not stable under basic condition at elevated temperature,[30,31] thermal stability is an important criteria of AEMs. Figure 4 shows the TGA curves for PAE-a, CMPAE-a, QPAE-a, and QPAE-d in turn, which ran from room temperature to 700 °C to examine their thermal stability. There was only one weight loss stage for PAE-a contributed by the main-chain decomposition and its 5% weight loss temperature was above 480 °C because of its rigid aromatic backbone. Two stages of weight loss behavior were observed for CMPAE-a. The first stage from 100 to 400 °C with a weight loss less than 5% was assigned to the decomposition of chloromethyl groups. The second stage started from 350 °C contributed by the decomposition of the polymer backbone. There were three major stages of weight loss for QPAE-a. The first weight loss stage commenced from below 100 °C corresponding to the removal of residual water from the membrane. The second weight loss stage around 170 °C was assigned to the degradation of quaternary ammonio groups according to Tanaka's work.[3] The third stage of weight loss was ascribed to the polymer backbone decomposition commencing from around 350 °C. The TGA curve of QPAE-d showed decomposing behavior similar to that of QPAE-a. Due to its higher IEC value, the weight loss of second stage was more than that of QPAE-a.

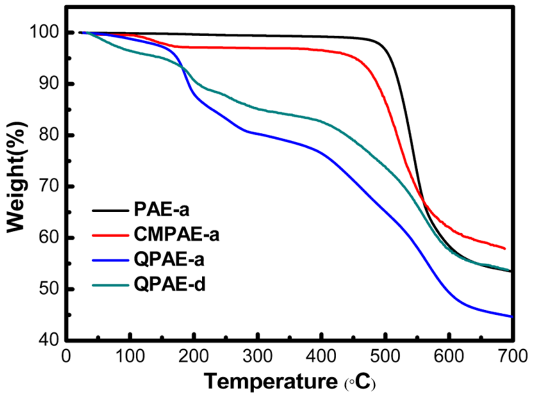

Figure 4. TGA curves for PAE-a, CMPAE-a, QPAE-a (IEC = 0.72 meq g^{-1}), and QPAE-d (IEC = 1.04 meq g^{-1}).

3.4. Ion Exchange Capacity (IEC), Water Uptake, and Hydroxide Conductivity of the QPAEs Membranes. As shown in Table 3, the experimental IEC values were all lower than the theoretical IEC values calculated from ^{1}H NMR data of CMPAEs based on the assumption of complete quaternization and alkalization. One of the reasonable explanations for the results is that the quaternization process was carried out in solid membrane rather than in solutions, chloromethyl groups inside of the membrane can hardly contact with trimethylamine and result in incomplete functionalization. The ^{1}H NMR spectra determination results of QPAE supported the conjecture. Based on the assumption of complete quaternization and alkalization, the theoretical integral ratio of ammonium methyl groups protons to methylene moieties protons should be 9:2.

Table 3. DCM, IEC, Water Uptake, and Hydroxide Conductivity of QPAEs Membranes

		IEC (meq g^{-1})		water uptake (%)		conductivity (mS cm^{-1})	
sample	DCM	theoretical[a]	experimental[b]	20 °C	80 °C	20 °C	80 °C
QPAE-a	1.78	2.56	2.38	19	63	25.0 ± 1.5	64.7 ± 1.8
	0.63	0.90	0.72	9	15	4.5 ± 0.7	23.0 ± 2.3
	0.44	0.63	0.41	5	12	1.2 ± 0.3	10.0 ± 0.4
QPAE-b	1.02	1.55	0.78	9	26	1.3 ± 0.2	8.7 ± 0.5
QPAE-c	0.70	0.91	0.52	8	23	3.9 ± 0.5	10.3 ± 0.4
QPAE-d	1.70	1.28	1.04	10	52	20.0 ± 2.8	75.0 ± 1.4
QPAE-e	1.66	1.16	1.09	6	40	14.0 ± 0.3	68.0 ± 2.9
QPAE-f	0.59	0.42	0.21	5	14	0.37 ± 0.04	7.0 ± 0.6

[a]Calculated from NMR. [b]Determined by titration.

Table 4. IEC, Water Uptake, and Hydroxide Conductivity Reported in the Literature for Different AEMs

membrane	ionic group	IEC (meq g^{-1})	water uptake (%)	conductivity (mS cm^{-1})
QBPES-40[35]	QATMA[a]	1.62	20 °C 27	20 °C 29
PSQN-50[34]	QATMA	1.85	20 °C 12	20 °C 32
QPMBV[36]	QATMA	0.66−1.25	80 °C 2.8−239	80 °C 5.2−13.5
QPSU/20%ZrO_2[37]	QATMA	0.921	rt 19	rt 15.1
PVDF-G-PVBC[18]	QATMA	0.72	20 °C 70	20 °C 25
QPEK-C[12]	QATMA	0.11	20 °C 3.11	20 °C 1.6
QPE-b[3]	QATMA	1.31	30 °C 61	30 °C 12
ETFE-AAEM[20]	QATMA	1.03 ± 0.11	20 °C 40 ± 4	20 °C 27 ± 5
QSEBS[38]	QATMA	0.3	not reported	30 °C 5
QAPVA[39]	QATMA	not reported	not reported	30 °C 2.76−7.34
poly(ether-imide)[40]	QATMA	0.983	25 °C 43.1	25 °C 2.28−3.51
PPO/silica[41]	QATEA[b]	2−2.3	25 °C 9−26	30−90 °C 12−35
QAPSEBS[42]	QATEA	0.578	30 °C 5.74	30 °C 0.69
PSf135-ImOH[43]	imidazolium	2.46 ± 0.25	20 °C 92.8 ± 2.8	20 °C 20.7 ± 0.6
polyfluorene ionomer[44]	imidazolium	0.98	30 °C 17.26	30 °C 23.5
DABCO-cellulose[45]	DABCO[c]	2.43	rt 102	rt 4.3
PES-G-OH[46]	guanidinium	1.39	60 °C 35.8	60 °C 42
pyridinium-type polymer/fibrous woven cloth[47]	pyridinium	not reported	not reported	25 °C 8

[a]QATMA, TMA based quaternary ammonium. [b]QATEA, TEA based quaternary ammonium. [c]DABCO, Diazobicycloocate (triethylenediamine).

However, the calculated integral ratio of characterized peaks was 7.3:2 (Figure 2c). Another effect that must be taken into account is the neutralization contributed by carbon dioxide. During the titration, hydroxide ions were open to carbon dioxide in the air and easily transformed to carbonate and/or bicarbonate ions. These reactions also increased the disparity of experimental IEC values and theoretical values.

Water uptake is known to have a significant effect on ion conductivity and mechanical properties of AEMs.[32] A membrane with adequate water can offer more transport channels for anions and indicates high ion conductivity. However, excess water uptake will lead to membrane swelling and uncontrollable deformation. Table 3 shows that the water uptakes of the QPAEs membranes increased with increasing temperature and IEC values. Overall, the water uptakes of the QPAEs membranes with controlled DCM were moderate under the test conditions.

The ion conductivities of QPAEs membranes listed in Table 3 increased dramatically with increasing examining temperature and IEC values. It shows a tendency similar to that of water uptakes. The QPAE-d (IEC = 1.04 meq g^{-1}) and QPAE-e (IEC = 1.09 meq g^{-1}) membranes exhibited higher ion conductivities of 75 and 68 mS cm^{-1}, respectively, at 80 °C when compared to that of QPAE-a membrane with higher IEC value (IEC = 2.38 meq g^{-1}) at the same temperature. The possible reason is that QPAE-d (IEC = 1.04 meq g^{-1}) and QPAE-e (IEC = 1.09 meq g^{-1}) were synthesized by random co-condensations of various dihalides with the molar ratios of 1:1 and bis(4-hydroxylphenyl)diphenyl methane. Bulky repeat units containing sulfone moieties disordered the uniformed sequenced ketone backbones and widened the ionic pathways enhancing the exchange ability contributed by repeating units containing carbonyl moieties. It agreed well with results of the conductivities of homopolymers QPAE-a (IEC = 0.72 meq g^{-1}) and QPAE-b (IEC = 0.78 meq g^{-1}) in Table 3. The narrow ionic pathways provided by sequenced ketone backbone confine the migration of aqueous hydroxyl ions. The conductivities of QPAE-b (IEC = 0.78 meq g^{-1}) under various temperatures were less than 40% of those of QPAE-a (IEC = 0.72 meq g^{-1}). Table 4 lists the IEC, water uptake, and hydroxide conductivity results of various membranes, based on different polymeric materials attached with varying anion exchange groups in typical published works. It is obvious that the conductivities of QPAEs rank among good conductive aromatic group membranes taking account of IEC and water uptakes. In the function group consisting of QATMA with the close IEC, the lower the water uptakes the membranes have, the higher the dimension stabilities the membranes exhibit. The QPAEs membranes demonstrated the significantly improved dimension stabilities and the good conductivities simultaneously. Compared with other function groups such as imidazolium and diazobicyclooctate (triethylenediamine), the improvements of QPAEs are more apparent.

Figure 5 indicates the dependence of the ion conductivities of QPAEs on testing temperature. It is obvious that the relationship between ln*σ* (*σ* is the ion conductivity) and 1000/*T* (*T* is the absolute temperature) follows an Arrhenius behavior. Thus the ion transport activation energy E_a of the membranes can be calculated using the following equation:

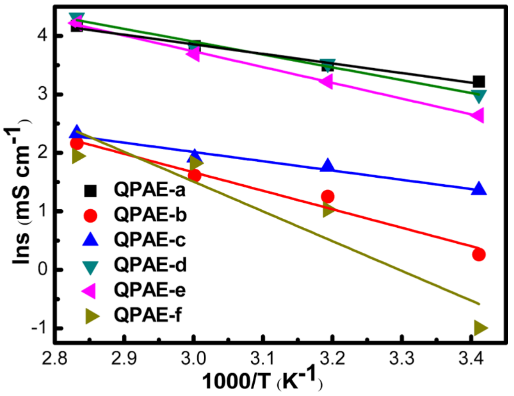

Figure 5. Arrhenius plots of QPAE-a (IEC = 2.38 meq g^{-1}), QPAE-b (IEC = 0.78 meq g^{-1}), QPAE-c (IEC = 0.52 meq g^{-1}), QPAE-d (IEC = 1.04 meq g^{-1}), QPAE-e (IEC = 1.09 meq g^{-1}), and QPAE-f (IEC = 0.19 meq g^{-1}) membranes at different temperatures.

$$E_a = -b \times R$$

where *b* is the slope of the regressed linear ln*σ*−1000/*T* plots, and *R* is the gas constant (8.314 J $(\text{mol K})^{-1}$). The calculated ion transport activation energy E_a of the various QPAEs membranes varied from 13.18 to 42.30 kJ mol^{-1} is listed in Table 5. The E_a values of QPAE-a, QPAE-c, and QPAE-d were similar to that of Nafion-117 (12.75 kJ mol^{-1})[33] and a reported quaternary ammonia poly(arylene ether) (13.3 kJ mol^{-1}).[30] The E_a values of other QPAEs were much higher than Nafion-117. The results indicate that the hydroxide ion mobility in the QPAE membranes was more sensitive to temperature than that of proton in Nafion-117. The distinctness of the E_a values depends on the difference of their polymer chain structure.

Table 5. Ion Transport Activation Energy, E_a, of QPAEs Membranes

QPAE	E_a (kJ/mol)
QPAE-a	13.62
QPAE-b	26.25
QPAE-c	13.18
QPAE-d	18.24
QPAE-e	22.4
QPAE-f	42.30

3.5. Mechanical Properties of the QPAEs Membranes.

Mechanical properties of QPAE-d (IEC = 1.04meq g^{-1}), QPAE-e (IEC = 0.24meq g^{-1}), and QPAE-f (IEC = 0.21meq g^{-1}) membranes are summarized in Table 6. All the membranes showed higher tensile strength (29−50 MPa), which was much higher than that of Nafion-117 and some reported AEMs. These results indicated that these membranes are strong enough to be used as anion exchange membranes for fuel cells.

Table 6. Mechanical Properties of the QPAE-d, QPAE-e, and QPAE-f Membranes

membrane	IEC (meq g^{-1})	tensile strength (Mpa)	tensile modulus (Mpa)	elongation at break (%)
QPAE-d	1.04	29.2 ± 0.5	210.8 ± 3.2	37.9 ± 1.2
QPAE-e	0.24	50.0 ± 12.7	790.4 ± 16.1	15.8 ± 1.5
QPAE-f	0.21	49.8 ± 10.2	670.1 ± 8.4	13.5 ± 0.7
Nafion-117[44]	0.91	21.1	6.60	370.6
QPE-b[3]	1.23	48.1	720	54
PSQNOH-80[34]	2.62	17.9	350	65.5

3.6. Chemical Stability of QPAEs Membranes.

Chemical stability is still a challenge for the application of AEMs in fuel cells, especially in strong basic and elevated temperature conditions. Herein, we examined the conductivity of the QPAE-a (IEC = 1.05 meq g^{-1}) at 40 °C after treatment with varying concentrations of NaOH at room temperature for 24 h. As shown in Figure 6, under a wide concentration range from 1 to 5 M NaOH the measured conductivities of the membranes were higher than 30.0 mS cm^{-1} and the highest conductivity of 33.6 mS cm^{-1} was obtained with 3 M NaOH. Elevating the conditioned concentration higher than 6 M, the measured conductivities were lower than 30.0 mS cm^{-1} (the conductivity of 1 M NaOH treated membrane) and exhibited lowest conductivity of 25.4 mS cm^{-1} after treatment of 8 M NaOH. The results indicated that the obtained membrane was very stable under a broad basic operation window at room temperature.

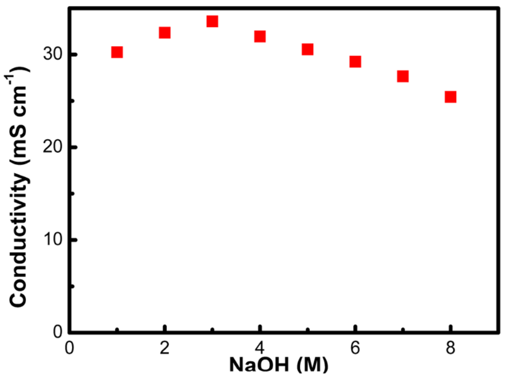

Figure 6. Effect of NaOH concentration on conductivity of the QPAE-a (IEC = 1.05 meq g^{-1}).

The alkaline stability of the QPAE membranes was further explored by measuring the conductivity and mechanical properties after conditioning with 1 M NaOH at 60 °C for 170 h. The membranes maintained their toughness and appearance. The mechanical properties comparisons of membranes before and after the stability test are listed in Table 7. The membranes kept 90% of the original mechanical properties. The variations in the hydroxide conductivities of the QPAEs membranes with alkaline stability test are shown in Table 8. It can be observed that the conductivity decrease amplitudes ranged from 9.5% to 25.0%, and especially QPEA-a, QPEA-c, QPEA-e, and QPEA-f have excellent long-term alkaline stability compared with some reported AEMs.[34]

Table 7. Variation in the Mechanical Properties of the Membranes with Alkaline Stability Test at 60 °C

		tensile strength (Mpa)		elongation at break (%)	
membrane	IEC	before stability test	after stability test	before stability test	after stability test
QPAE-a	1.05	32.3 ± 8.2	29.1 ± 5.1	28.3 ± 3.1	25.8 ± 4.3
QPAE-d	0.98	27.3 ± 6.3	24.5 ± 7.9	32.7 ± 5.7	29.7 ± 0.7

Table 8. Variation in the Hydroxide Conductivities of the QPAE-a (IEC = 1.05 meq g^{-1}), QPAE-b (IEC = 1.33 meq g^{-1}), QPAE-c (IEC = 0.83 meq g^{-1}), QPAE-d (IEC = 0.92 meq g^{-1}), QPAE-e (IEC = 0.24 meq g^{-1}), and QPAE-f (IEC = 0.21 meq g^{-1}) Membranes with Alkaline Stability Test at 60 °C

	stability test condition			conductivity at 60 °C (mS cm^{-1})		
membrane	concentration	temperature (°C)	time (h)	before stability test	after stability test	decrease amplitude (%)
QPAE-a	1 M NaOH	60	170	38.2 ± 1.5	33.4 ± 2.3	12.6
QPAE-b	1 M NaOH	60	170	21.6 ± 0.8	16.2 ± 1.8	25.0
QPAE-c	1 M NaOH	60	170	15.5 ± 2.3	13.4 ± 0.6	13.5
QPAE-d	1 M NaOH	60	170	45.6 ± 1.9	37.3 ± 2.1	18.2
QPAE-e	1 M NaOH	60	170	8.1 ± 0.9	7.3 ± 1.3	9.8
QPAE-f	1 M NaOH	60	170	18.9 ± 2.3	17.1 ± 0.3	9.5
O-PBI Me2731[48]	1 M KOH	60	120		breaks when handled	
FAA[49]	1 M KOH				not reported	15

4. CONCLUSION

In summary, novel anion exchange membranes based on poly(arylene ether)s containing tetraphenyl methane groups were successfully synthesized via polycondensation, chloromethylation, quaternization, and alkalization. Under the optimized conditions, the obtained CMPAEs had a DCM value up to 4 without obvious side reaction. The ion conductivities of QPAEs membranes increased dramatically with increasing test temperature. The calculated hydroxide ion transport activation energy E_a of the QPAE membranes was calculated to range from13.18 to 42.30 kJ mol^{-1}. The highest ion conductivities of QPAE-d membrane with IEC value of 1.04 meq g^{-1} were up to 20 mS cm^{-1} at 20 °C and 75 mS cm^{-1} at 80 °C. The water uptakes of the determined QPAE membranes can be adjusted by controlling their DCM values. Moreover, the QPAE membranes exhibited excellent thermal stabilities, mechanical properties, and chemical stabilities. These properties of the as-made membranes seem promising as an anion exchange membrane of alkaline fuel cells.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

PAEs = poly(arylene ether)s
CMPAEs = chloromethylated poly(arylene ether)s
QPAEs = quaternizated poly(arylene ether)s

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