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Naphthalene-based poly(arylene ether ketone) anion exchange membranes

Zhuang Liu^a, Xiaobai Li^a, Kunzhi Shen^a, Pengju Feng^a, Yinan Zhang^a, Xu Xu^a, Wei Hu^a, Zhenhua Jiang^a, Baijun Liu^{a,*}, Michael D. Guiver^{b,c}

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Naphthalene-based poly(arylene ether ketone)s were obtained through a three-step process involving polymerization of methylated polymers, followed by bromination and derivatization with a diquaternary-ammonium group. The hydroxide conductivities of the anion exchange membranes were above 10^{-2} S cm^{-1} at room temperature and the membrane with an IEC = 1.46 mequiv. g^{-1} attained an ion conductivity of 7.4×10^{-2} S cm^{-1} at 100 °C, which is higher than many reported results. The membrane series had low water uptake and excellent dimensional stability, even at the highest IEC values. In addition, the membranes were insoluble in organic solvent and concentrated alkaline solution for many days, even under heating, suggesting their excellent stability. These combined data suggest that the membranes have potential for anion exchange membranes for fuel cells applications.

Introduction

Fuel cells are expected to play an important role as power devices in the economy of the 21st century and for the foreseeable future, because of features such as high energy density, high efficiency and environmental friendliness. Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFC) have attracted considerable attention for a variety of power generation applications, such as automotive transportation. The PEMFC is an energy system that can convert hydrogen fuel (or CH_3OH) and oxygen (or air) directly to electricity, with water as the primary byproduct.

However, the requirement for high cost precious metal (Pt) electrodes has limited their commercialization to some extent. There is renewed interest in alkaline fuel cells (AFCs), which are also capable of producing high power densities at low temperatures. AFCs can operate with a wide range of less expensive non-noble metal catalysts, due to their facile oxygen reduction electrokinetics in basic environments.^{6,7} However, the typical electrolytes used in AFC are concentrated alkaline solutions such as KOH solution, which can be extensively polluted by ambient CO_2 , resulting in much lower ionic conductivity and leading to leakage of the electrolyte solution. An effective solution for the carbonation issue is to utilize anion exchange polymeric electrolyte membranes as a substitute for alkaline solutions. A key feature of alkaline polymeric electrolyte membrane fuel cells is a positively charged polymer membrane with dissociated anions acting as the charge carrier for ionic conductance. Most commercial anion exchange membranes (AEMs) are polystyrenes containing quaternary ammonium groups, which having been employed in water processing. However, utilization of these AEMs for fuel cells is unsuitable

because of their low chemical and thermal stability, with the degradation temperature of the quaternary-ammonia functional group in polystyrene being about 40-60 °C.⁸⁻¹¹

Recently, a number of new polymers functionalized with quaternary ammonium groups, based on poly(phenylene),¹² poly(styrene)s,^{13, 14} poly(ether sulfone),¹⁵⁻¹⁹ poly(arylene ether)s²⁰ and poly(ether ether ketone)s (PEEKs),²¹ were synthesized from monomers or by polymer modifications. These materials have shown some promising results for use in anion exchange membranes fuel cells (AEMFCs).

Naphthalene has a fused bicyclic conjugated aromatic planar structure, which has a higher reactivity and more reactive sites compared with benzene. Naphthalene rings are increasingly being introduced into poly(aryl ether)s, because they are easier to functionalize and often show improvements in properties, but achieving high molecular weight is sometimes difficult.²²⁻²⁶ Naphthalene rings increase the hydrophobicity and stiffness of the polymer chain, and also improve the dimensional stability and mechanical property of films in water.^{27,28} However, research about quaternized poly(aryl ether ketone)s containing naphthalene has not been reported.

The present work reports the synthesis and properties of quaternized ammonium poly(aryl ether ketone) containing rigid naphthalene structures in the main chain. In order to obtain a structurally rigid AEM with a high ion exchange capacity (IEC) for high hydroxide ion conductivity, a bisphenol monomer containing naphthalene units substituted symmetrically with two methyl groups was prepared according to the literature.²⁹ From this monomer, a series of PEEKs containing methyl groups was synthesized by nucleophilic aromatic substitution polycondensation; the methyl content was controlled by the monomer feed ratio. The methyl sites of the resulting polymers

were brominated and then converted to quaternized ammonium groups. The *IEC* values, ion conductivity and dimensional stability were controlled by the monomer ratio in the copolymer structure. The study was to elucidate the structure-property relationships of these new types of PEEK for AEMs.

Experimental section

Chemicals and Materials

2,6-Dimethoxynaphthalene (Dalian Jinzhou Chemical Reagent), 4,4-difluorobenzophenone (Yanji Chemical Plant), 3-methylbenzoyl chloride and 1,1,2,2-tetrachloroethane were purchased from Aladdin Reagent. N-bromosuccinimide (NBS) and benzoyl peroxide (BPO) were purchased from Sigma-Aldrich Ltd. Zinc chloride, boron tribromide (BBr₃) and hydroquinone (HQ) were purchased from Beijing Chemical Reagent. Anhydrous potassium carbonate (K₂CO₃, Beijing Chemical Reagent) was ground into fine powder and dried at 120 °C for 24 h before use. Other chemical reagents and organic solvents were purchased from Beijing Chemical Reagent and purified by conventional methods.

Synthesis of 1,5-bis(3-methyl)-2,6-dimethoxynaphthalene (DMN-Me)

Following a procedure similar to that reported in ref. 29, anhydrous zinc chloride (2.72 g, 0.02 mol) was added to a stirred solution of 3-methylbenzoyl chloride (46.38 g, 0.30 mol) and 2,6-dimethoxynaphthalene (18.82 g, 0.10 mol) in 1,1,2,2-tetrachloroethane (200 mL). The mixture was stirred 40 °C for 4 h and at 80 °C for another 8 h. The resulting mixture was poured into cold hydrochloric acid and stirred for 1 h. The lower organic layer was collected and washed with water several times. Then, the solid was precipitated with the addition of cyclohexane and washed with acetone to afford 1,5-bis(3-methyl)-2,6-dimethoxynaphthalene (yield: 85%; mp: 262 °C). FTIR (KBr, cm⁻¹): 1659 (C=O), 2830 (–OCH₃). ¹H NMR (300 MHz, CDCl₃; ppm): 7.715 (s, 2H, H₁), 7.639 (d, *J* = 2.4, 2H, H₃), 7.607 (d, *J* = 2.4, 2H, H₂), 7.421 (d, *J* = 7.5, 2H, H₆), 7.350 (m, 2H, H₅), 7.269 (d, *J* = 2.4, 2H, H₄), 3.768 (s, 6H, –OCH₃), 2.383 (s, 6H, –CH₃).

Synthesis of 1,5-bis(3-methyl)-2,6-dihydroxynaphthalene (DMN-OH)

Following a procedure similar to that reported in ref. 29, DMN-Me (20 g) was dissolved in 600 mL dry CH₂Cl₂. The reaction mixture was kept in an ice salt bath and BBr₃ dissolved in CH₂Cl₂ (282 mL) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 12 h, and then was poured into 500 mL ice-water to hydrolyze any excess BBr₃ and other impurities. The organic layer was extracted by 500 mL water three times. The solvent CH₂Cl₂ was evaporated by rotary evaporation. The monomer, 1,5-bis(3-methyl)-2,6-dihydroxynaphthalene was obtained and dried at 60 °C in a vacuum oven for 24 h (yield: 97%. mp: 297 °C). IR (KBr, cm⁻¹): 1633 (C=O), 3270 (–OH). ¹H NMR (300 MHz, DMSO-d₆; ppm): 9.828 (s, 2H, –OH), 7.628 (s, 2H, H₁), 7.553 (d, *J* = 7.2, 2H, H₃), 7.497 (d, *J* = 7.2, 2H, H₂), 7.427 (m, 2H, H₅), 7.347 (d, *J* = 8.4, 2H, H₄), 7.156 (d, *J* = 8.4, 2H, H₆), 2.383 (s, 6H, –CH₃).

Copolymerization of naphthalene-based poly(arylene ether ketone) copolymers containing methyl groups (NAPAEK-Me-X)

A typical preparation procedure of naphthalene-based poly(arylene ether ketone) copolymer based on DMN-OH, NAPAEK-Me-90 (DMN-OH/HQ=9/1), is described as follows: Into a 100 mL round-bottomed flask, 3.568g (9 mmol) of DMN-OH, 0.110 g (1 mmol) of HQ, 2.182 g (10 mmol) of 4,4-difluorobenzophenone, 1.518 g (11 mmol) of K₂CO₃, 18 mL of tetramethylenesulfolane (TMS) and 10 mL of toluene were added. First, the mixture was heated to 140 °C with mechanical stirring under nitrogen atmosphere for 2 h to remove the produced water by azeotropic distillation with toluene, and then the temperature was raised up to 190–200 °C for 4–6 h. The high viscosity mixture was coagulated into a large excess of deionized water with stirring. The resulting fibrous copolymer was pulverized into powder using a blender. The polymer powder (NAPAEK-Me-90) was washed several times with boiling ethanol and water and dried in a vacuum oven.

The other polymers, NAPAEK-Me-80 and NAPAEK-Me-100, were synthesized using the similar procedures, but with different monomer feed ratios.

Synthesis of bromomethylated naphthalene-based poly(arylene ether ketone)s (NAPAEK-Br-X)

A typical procedure for preparing bromomethylated copolymer NAPAEK-Br-90 was as follows. PEEK-Me-90 (2.0 g, the amount of –CH₃ was 6.596 mmol) was completely dissolved in 40 mL of 1,1,2,2-tetrachloroethane at room temperature with a 50 mL three-necked flask, magnetic stirrer, nitrogen inlet and condenser. The bromination agent NBS (1.291 g, 7.256 mmol) was added at the same time as the initiator BPO (0.117 g, 0.363 mmol). The reaction system was slowly heated to 85 °C for 7 h under nitrogen atmosphere, and then cooled down to room temperature. The mixture was coagulated in methanol with vigorous stirring. The resulting fiber-like polymer was washed with acetone several times and dried under vacuum for 24 h at 60 °C before used. The other polymers, NAPAEK-Br-80 and NAPAEK-Br-100, were bromomethylated using similar procedures.

Preparation of the anion exchange membranes

The brominated membranes were prepared by dissolving 0.8 g NAPAEK-Br-X in dimethylacetamide (DMAc, 10 wt.%), casting the solution on a glass plate and drying at 60 °C for 12 h, at 80 °C for 12 h, and finally in a vacuum oven at 100 °C. The membranes were removed from the glass by immersion in water. In order to obtain a quaternized ammonium membrane, the brominated membranes were immersed into a 33% aqueous solution of trimethylamine (TMA) for 48 h at room temperature. The membranes were placed in 1 M KOH for 48 h, thoroughly washed with deionized water, and then stored in deionized water before use.

Measurements

¹H NMR experiments were carried out on a Bruker 510 spectrometer (300 MHz for ¹H) using DMSO-d₆ and CDCl₃ as solvent. The gel permeation chromatographic (GPC) analysis was carried out with a Waters 410 instrument with tetrahydrofuran (THF) as the eluent and polystyrene as the standard. Thermo

gravimetric analysis (TGA) was employed to assess thermal stability of membranes with a Netzch Sta 449c thermal analyzer system. Before analysis, the films were dried and kept in the TGA furnace at 120 °C in a nitrogen atmosphere for 15 min. The samples were cooled to 100 °C and then reheated to 800 °C at 10 °C min⁻¹, and the temperatures at 5% and 10% weight loss were recorded for each sample.

The mechanical properties of dry membranes were measured at room temperature on SHIMADIU AG-I 1KN at a strain rate of 2 mm min⁻¹. The size of samples was 18 mm × 4 mm. The samples of NAPAEEK-Me-X and NAPAEEK-Br-X in a dry state were obtained by placing them in a vacuum oven at 120 °C for 24 h. The samples of NAPAEEK-Q-X in a wet state were obtained by immersing them in water for at least 24 h.

The ion-exchange capacity (IEC) values of copolymer membranes were determined by a standard back-titration method. Membrane samples were immersed in about 100 mL of HCl solution (0.01 M) for at least one week for an ionic exchange process (the OH⁻ ions in the membranes were consumed by H⁺ ions). The residual protons within the solutions were titrated with standardized NaOH aqueous solution by using phenolphthalein as an indicator. For each sample, at least three measurements were carried out until the titration reached to a constant value. The IEC value was calculated from the titration result via the following formula:

$$IEC \text{ (mequiv. g}^{-1}\text{)} = [0.001 - (V_{\text{NaOH}} \times M_{\text{NaOH}})] / W_{\text{dry}}$$

where V_{NaOH} is the consumed volume of NaOH, M_{NaOH} is the molarity of NaOH, and W_{dry} is the weight of dry membranes.

The water uptake and dimensional swelling were measured as follows: the sample films (1 cm × 5 cm) were dried at 100 °C for 24 h prior to the measurements. After measuring the lengths and weights of dry membranes, the sample films were soaked in deionized water at the desired temperature to reach equilibrium. Before measuring the lengths and weights of hydrated membranes, water was removed from the membrane surfaces by blotting with a paper towel until a constant weight and length was obtained. The water uptake was calculated by the following equation:

$$\text{Water uptake (\%)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100\%$$

where W_{dry} and W_{wet} are the weights of dried and wet samples, respectively.

Dimensional swelling of the copolymer membranes was investigated by immersing the samples in deionized water at the desired temperature to reach equilibrium. The change of film length was calculated from

$$\text{Dimensional swelling (\%)} = [(L_{\text{wet}} - L_{\text{dry}}) / L_{\text{dry}}] \times 100\%$$

where L_{dry} and L_{wet} is the length of the dry and wet membranes, respectively.

The hydroxide conductivity was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&GPC, Princeton, NJ). The samples were soaked in deionized water for at least 24 h prior to the test.

Hydroxide conductivity measurements of fully hydrated NAPAEEK-Q-X membranes in the alkali form were carried out with a cell immersed in water, and measured in the longitudinal direction. The hydroxide conductivity was calculated by the

following equation:

$$\sigma = L/RA$$

Where L is the distance between the electrodes, R is the membrane resistance and A is the cross-sectional area of the membrane.

The methanol diffusion coefficient was measured by using a cell made up of two half-cells separated by the membrane, which was fixed between two rubber rings. Aqueous methanol (10 M) was placed on one side (A) of the diffusion cell, and deionized water was placed on the other side (B). The liquids in both compartments were stirred magnetically continuously. The methanol concentrations in B cell were periodically surveyed by using a SHIMADZU GC-14C gas chromatograph. The methanol permeability coefficient was calculated using the following equation:

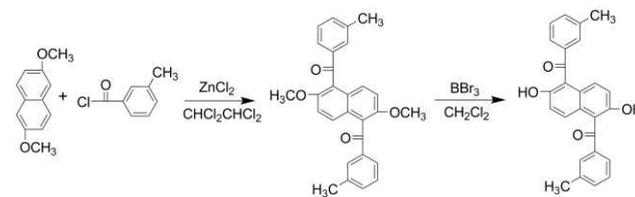
$$C_B(t) = A \times DK \times C_A(t - t_0) / (V_B \times L)$$

where DK is the methanol diffusion coefficient (cm² s⁻¹), $C_B(t)$ is concentration of methanol in cell B (mol L⁻¹), C_A is concentration of methanol in cell A (mol L⁻¹). A , L and V_B are the effective area, membrane thickness and the volume of the diffusion reservoirs, respectively.

The alkaline stability of NAPAEEK-Q-X membranes was measured by immersing the samples in NaOH solution (4.0 M) at room temperature and 80 °C for a certain time. The shape of the test sample was observed after being shaken.

Results and discussion

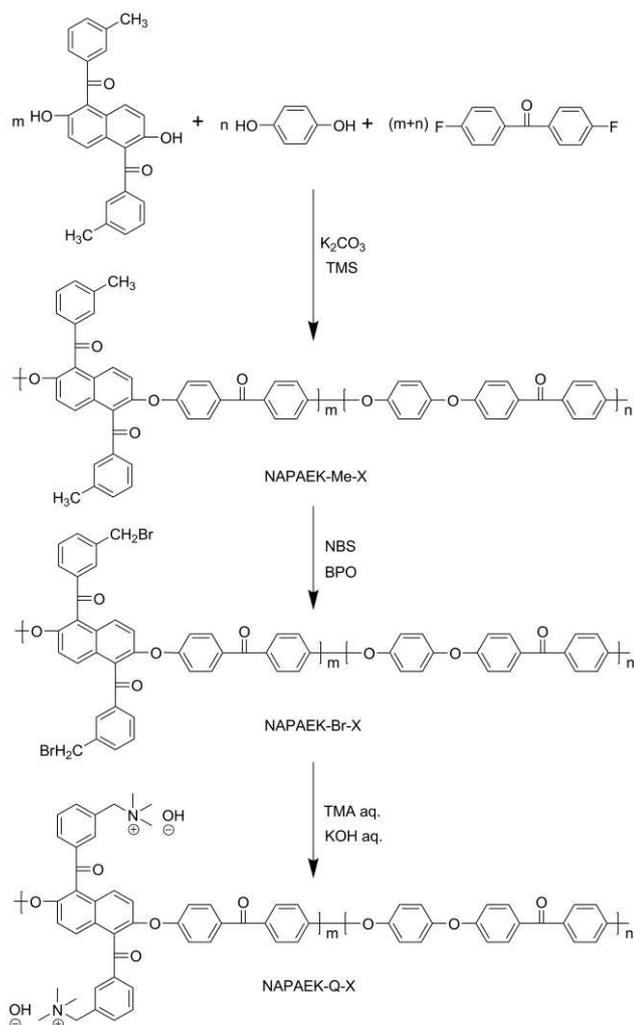
Synthesis and characterization of the monomer and copolymers



Scheme 1 Synthesis of the monomer DMN-OH.

Since naphthalene-containing units incorporated into polymers provide some beneficial properties for ion exchange membranes, the incorporation of them into aromatic polymers is attractive. However, synthesis of the naphthalene-based monomers with high purity and high reactivity is vital.²² As shown in Scheme 1, the symmetrical monomer DMN-OH was successfully synthesized in high purity and high yield via a two-step reaction route. DMN-OMe was prepared by an anhydrous zinc chloride-catalyzed Friedel-Crafts acylation of 2,6-dimethoxynaphthalene with 3-methylbenzoyl chloride at 80 °C. Then, the unpurified DMN-OMe intermediate was demethylated to DMN-OH using BBr₃ solution. The crude product was obtained quite pure and the yield without further purification was nearly 100%. The molecular structures of DMN-OMe and DMN-OH were confirmed by ¹H NMR spectra in CDCl₃ and DMSO-d₆, respectively. As shown in Fig. 1, the singlets at 3.77 ppm and 2.38 ppm corresponded to protons -OCH₃ and -CH₃, respectively. When -OCH₃ groups were transformed to -OH groups, the singlet at 3.77 ppm disappeared completely in DMN-OH, while an additional strong signal at 9.82 ppm was observed,

corresponding to $-\text{OH}$ protons. The ^1H NMR spectra also supported the dibenzoylation reaction occurring regioselectively at 1,5-positions on the naphthalene ring.



Scheme 2 The polymerization of poly(aryl ether ketone)s bearing pendant quaternary ammonium groups (NAPAEEK-Q-X).

Generally, it is difficult to obtain high-molecular-weight PAEEKs containing rigid and bulky naphthyl units because of limited reactivity and possible side reactions of naphthene-containing monomers. In this study, a three-step reaction was adopted to synthesize the quaternized poly(aryl ether ketone)s as anion exchange membrane materials. The starting polymers (NAPAEEK-Me-X), were readily synthesized with molecular weights of ~ 31000 – 40000 g mol^{-1} using nucleophilic aromatic polycondensation of DMN-OH monomer, despite its bulky and rigid structure (Scheme 2). Bromination of the soluble starting polymers occurred readily using NBS and BPO, converting the $-\text{CH}_3$ groups to $-\text{CH}_2\text{Br}$ groups. The conversion of NAPAEEK-Me-80 and NAPAEEK-Br-80 was monitored by ^1H NMR spectroscopy, which confirmed the formation of bromomethylated polymer from the precursor starting polymer. A new singlet at 4.46 ppm corresponded to the $-\text{CH}_2\text{Br}$ proton and a sharp decrease in the $-\text{CH}_3$ singlet at 2.35 ppm was observed. The final step was amination of the brominated polymers was conducted in the membrane form. The aminated polymers had poor solubility in organic solvents, and consequently, no NMR

results can be presented.

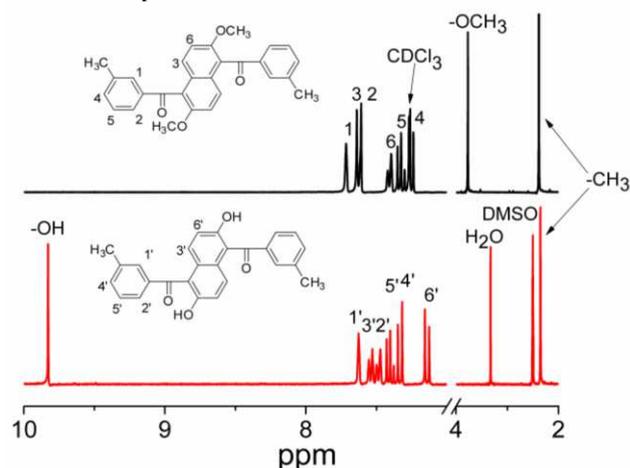


Fig. 1 ^1H NMR spectra of DMN-OMe and DMN-OH.

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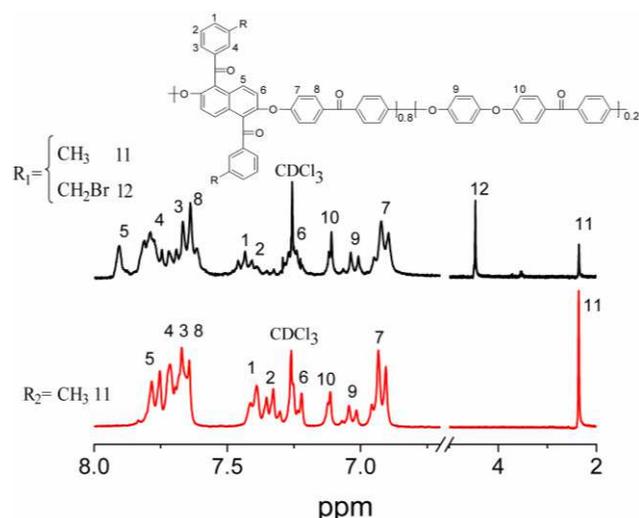


Fig. 2 ^1H NMR spectra of NAPAEEK-Me-80 and NAPAEEK-Br-80.

Thermal stability and mechanical properties

Elevated temperatures enhance the reaction kinetics and reduce the thermodynamic voltage losses of AEMFCs. Therefore, it is important to prepare membrane materials having good thermal stability, capable of operating at elevated temperatures. As expected, the starting polymers exhibited the best thermal stability, as investigated by TGA, and the results are listed in Table 1. The 5% and 10% weight loss temperatures of NAPAEEK-Me polymers were in the range of 458 – 460 $^{\circ}\text{C}$ and 480 – 482 $^{\circ}\text{C}$, respectively. Significant changes in the TGA curves were observed for the polymers containing bromomethyl and quaternary ammonium groups. The TGA curves of NAPAEEK-Me-100, NAPAEEK-Br-100 and NAPAEEK-Q-100 are compared in Fig. 3. All the polymers had similar major weight loss profiles for temperatures above 440 $^{\circ}\text{C}$, which indicated degradation of the main-chain. NAPAEEK-Me-100 had a single stage weight loss at around 440 $^{\circ}\text{C}$, while NAPAEEK-Br-100 and NAPAEEK-Q-100 exhibited two stage weight losses; the first stages at around 200 $^{\circ}\text{C}$ corresponded to degradation of the bromomethyl and quaternary ammonium groups.

Table 1 Molecular weight, mechanical properties and thermal stability of polymers

Polymer	M_n^a (g mol ⁻¹)	PDI ^b	Tensile modulus (GPa)	Tensile strength (MPa)	Maximum elongation (%)	T_{d5} (°C) ^c	T_{d10} (°C) ^d	Char yield (%) ^e
NAPAEK-Me-80	39700	2.22	3.47	83.08	16.51	460	480	63
NAPAEK-Me-90	36900	2.64	2.03	84.93	10.91	458	481	67
NAPAEK-Me-100	31400	2.66	1.50	82.57	10.64	459	482	67
NAPAEK-Br-80	44400	2.56	2.52	103.9	10.30	305	341	47
NAPAEK-Br-90	43300	2.24	1.84	90.63	9.59	304	338	47
NAPAEK-Br-100	41300	2.82	2.12	79.48	10.31	292	332	48
NAPAEK-Q-80	--	--	2.63	61.92	8.12	311	416	65
NAPAEK-Q-90	--	--	2.72	52.45	7.33	318	432	64
NAPAEK-Q-100	--	--	2.01	44.43	6.39	316	427	59

^a Number-average molecular weight obtained by GPC. ^b The polydispersity index. ^c Temperature at 5% weight loss. ^d Temperature at 10% weight loss. ^e Residual weight (%) at 800 °C in nitrogen.

The mechanical properties of the polymer membranes are summarized in Table 1. The samples of NAPAEK-Me-X and NAPAEK-Br-X were measured under a dry state. The AEMs were used in wet conditions, so the NAPAEK-Q-X membranes were immersed in water for 24 h before test. All the NAPAEK-Q-X membranes exhibited good tensile properties, with tensile strengths in the range of 44.43–61.92 MPa, elongation at break of 6.39–8.12%, and Young's moduli of 2.01–2.72 GPa. They showed good toughness and strength, which could fulfill the requirements of mechanical properties in AEMFCs.

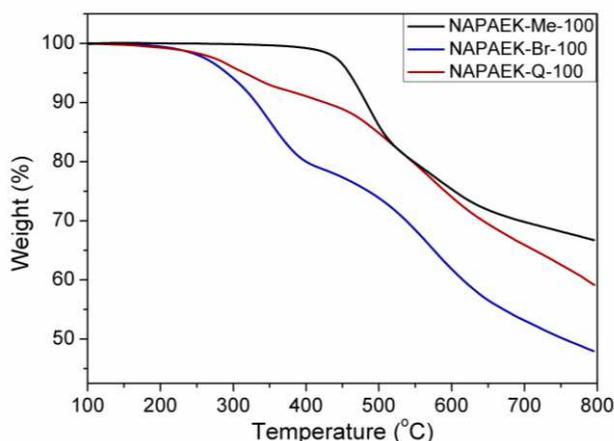


Fig. 3 The TGA curves of NAPAEK-Me-100, NAPAEK-Br-100 and NAPAEK-Q-100.

IEC, water uptake and dimensional swelling

Water uptake and dimensional swelling of AEMs are closely related to IEC, proton conductivity, dimensional stability, which are particularly important properties for fuel cell applications. In this study, both theoretical IEC values that were deduced from the ¹H NMR of PAEK-Br-X and the IEC values that were determined using the standard back-titration technique are given in Table 2. In order to make a wider comparison with other reported work, we also list a series of data of mono-functionalized quaternized non-naphthalene-based PEEK AEMs (PEEK-Q-X).²¹ NAPAEK-Q-X membranes could have obviously higher IEC values than those of PEEK-Q-X, because of their higher content of quaternary ammonium groups. This would result in higher ionic conductivity, which is useful providing the dimensional swelling and water uptake are controlled.

It is well-known that excessive water uptake leads to unacceptable dimensional change or loss of dimensional shape of the membrane, which increases the likelihood of mechanical weakness and dimensional mismatch when incorporated into a membrane electrode assembly.³⁰⁻³² In the present work, a very significant result is that water uptake and swelling ratio are well controlled through molecular design. The water uptake and dimensional swelling (Figs. 4 and 5) of the series NAPAEK-Q-80 to NAPAEK-Q-100 increased only slowly with increasing temperature, even at 100 °C, without an obvious upward trend. Despite of their high IEC values, NAPAEK-Q-X membranes exhibited excellent dimensional stability in comparison with PEEK-Q-X membranes. For example, NAPAEK-Q-X dimensional swelling values were lower than 26%, even at 100 °C. This attractive characteristic can be explained by the structural design. There is a good delineation between the hydrophilic ion-conducting phase and the hydrophobic naphthalene-containing main chain, because quaternization occurs in the side chain. The hydrophobic structures are confined to the main chain, allowing easier formation of a hydrophobic phase. The rigid and planar structure of the hydrophobic naphthyl segments favors self-association and reduce the flexibility of the main chain, which can help to maintain the dimensional stability of the polymers at elevated temperature.^{26,33}

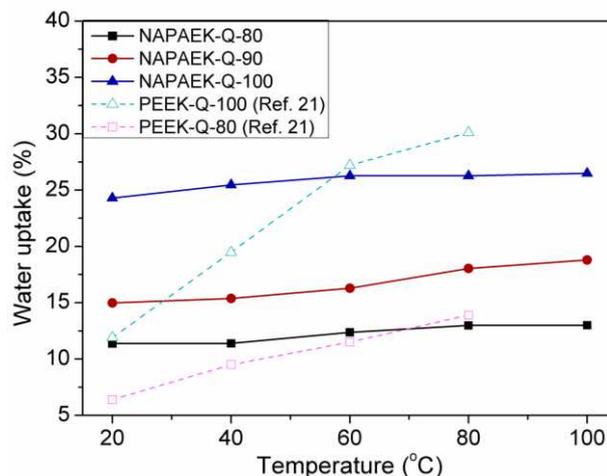
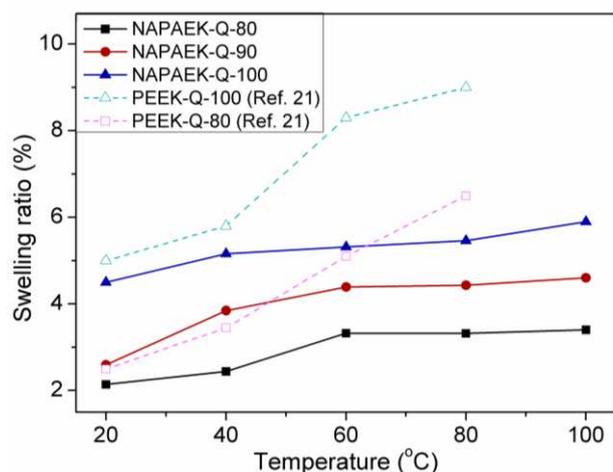
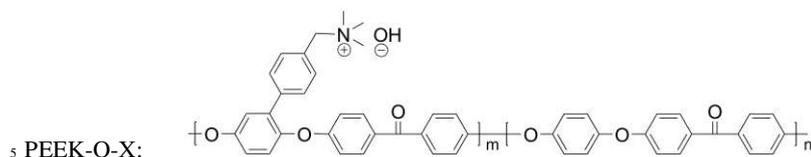


Fig. 4 The water uptake of the membranes.

Table 2 The IEC, water uptake, dimensional swelling, hydroxide conductivity and methanol permeability of membranes.

Polymer	IEC (mequiv. g ⁻¹)		Methanol Permeability (10 ⁷ cm ² s ⁻¹)	Conductivity (S cm ⁻¹)		Water uptake (%)		Dimensional swelling (%)	
	T ^a	E ^b		20 °C	80 °C	20 °C	80 °C	20 °C	80 °C
NAPAEEK-Q-80	1.61	1.32	0.2303	0.012	0.040	11.4	12.9	2.1	3.3
NAPAEEK-Q-90	1.70	1.40	0.4024	0.016	0.043	15.0	18.0	2.6	4.4
NAPAEEK-Q-100	1.79	1.46	0.8378	0.023	0.049	24.3	26.3	4.5	5.4
PEEK-Q-80 ^c	--	0.80	0.3180	0.007	0.022	6.4	13.9	2.5	6.5
PEEK-Q-100 ^c	--	0.90	1.4270	0.011	0.031	11.9	30.1	5.0	9.0

^a The IEC values were deduced from the ¹H NMR of NAPAEEK-Br-X. ^b The IEC values were determined using a standard back-titration technique. ^c Values taken from Ref. 21.

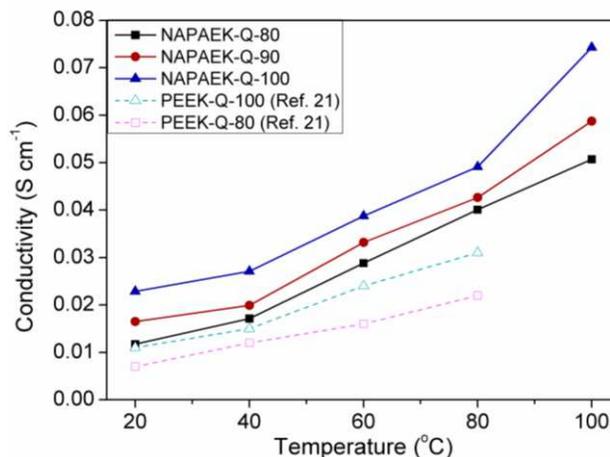
**Fig. 5** Dimensional swelling of the membranes.

Hydroxide conductivity and methanol permeability

The hydroxide ion conductivity of the NAPAEEK-Q-X membranes in alkali form was measured on samples immersed in water and plotted as a function of temperature in Fig. 6. The conductivities of the AEMs increased with in tandem with IEC and temperature, which was similar to the trend of water uptake. All the samples showed room temperature hydroxide conductivities higher than 10⁻² S cm⁻¹. The NAPAEEK-Q-100 membrane had the highest conductivity of 0.074 S cm⁻¹ at 100 °C. Similar to proton exchange membranes, NAPAEEK-Q-X AEMs with pendant quaternary ammonium groups can provide better hydrophilic/hydrophobic phase separation compared with polymers with functionalization directly on the main chain, which would enhance the conductivity of the ionomers. Table 2, compares two side-chain-type AEMs with the NAPAEEK-Q-X membranes; the former has a similar structure, but without naphthalene. The ion conductivities of NAPAEEK-Q-X are higher than those of PEEK-Q-X membranes, due to the higher IEC values.

Membranes utilized for direct methanol fuel cell (DMFC) must both possess high ion conductivity and be effective barriers to limit methanol crossover. It has been reported that methanol is

transported by diffusion across the membrane and by electro-osmotic drag. The methanol permeability values for 10 M methanol of NAPAEEK-Q-X membranes at room temperature were in the range of 0.2303×10⁻⁷ to 0.8378×10⁻⁷ cm² s⁻¹, which shows the membranes have low methanol permeability (Table 2). In order to evaluate the combined performance of hydroxide conductivity and methanol permeability, the selectivity (calculated from the ratio of hydroxide conductivity and methanol permeability) was used and shown in Fig. 7. Clearly, NAPAEEK-Q-X membranes exhibited much higher selectivity than PEEK-Q-80 and PEEK-Q-100.

**Fig. 6** The hydroxide conductivity of membranes.

Alkaline stability

Alkaline stability is also an important factor for AEM because the membrane must withstand strong alkali in AEMFCs. The alkaline stability of membranes was determined by immersing the membranes in 4 M NaOH solution at room temperature for 30 days and at 80 °C for 7 days. The samples showed no visible change in shape after being shaken lightly and maintain their flexibility and toughness. Combined with other properties, these AEMs exhibit promising characteristics for fuel cell applications.

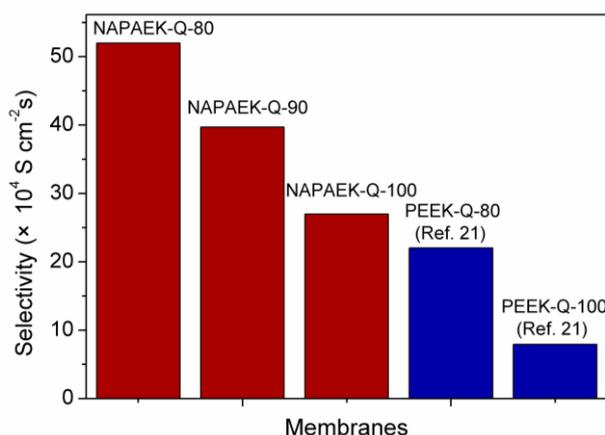


Fig. 7 The selectivity of membranes.

Conclusion

A series of novel naphthalene-based poly(arylene ether ketone)s bearing symmetric bifunctional pendant quaternary ammonium groups were prepared by bromination of methyl-containing starting NAPAEEK-Me-X polymers, followed by quaternization. The IEC values obtained in the range of 1.32–1.46 mequiv. g^{-1} were readily controlled by the methyl content in the starting polymers. The membranes possessed adequate mechanical and chemical stability and the pendant quaternary ammonium structures led to high proton conductivity, excellent dimensional stability and low methanol permeability. For example, NAPAEEK-Q-100 exhibited a hydroxide conductivity of 0.049 S cm^{-1} at 80°C and 0.074 at 100°C . Among currently reported AEMs, NAPAEEK-Q-X membranes possess an attractive combination of properties suitable for further evaluation in DMFCs.

Acknowledgements

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Notes and references

^a College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R. China

^b National Research Council, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada

^c Department of Energy Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, South Korea

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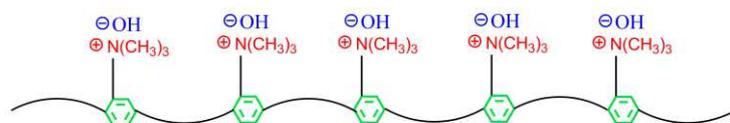
Graphical Abstract

Naphthalene-based poly(arylene ether ketone) anion exchange membranes

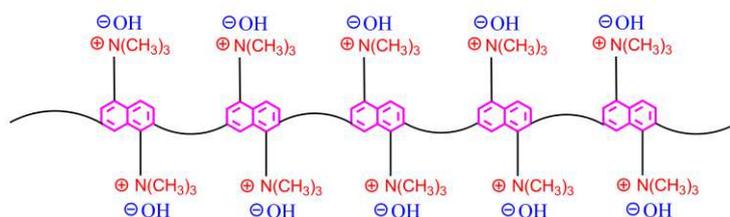
Zhuang Liu, Xiaobai Li, Kunzhi Shen, Pengju Feng, Yinan Zhang,

Xu Xu, Wei Hu, Zhenhua Jiang, Baijun Liu, Michael D. Guiver

Naphthalene-based poly(arylene ether ketone) membranes bearing symmetric bifunctional pendant quaternary ammonium groups were prepared for fuel cell applications.



Typical AEM structure:
asymmetric monosubstituted.



Naphthalenic AEM:
1 disubstituted and symmetric;
2 high *IEC* and conductivity;
3 higher chain rigidity;
4 excellent dimensional stability.