



Cross-linked tri-side chains poly(arylene ether ketone)s containing pendant alkylsulfonic acid groups for proton exchange membranes

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ABSTRACT

In order to enhance the ion exchange capacity (IEC) in the proton exchange membrane materials, a novel sulfonated poly(arylene ether ketone) (SQNPAEK) containing tri-side chains in one unit is synthesized by direct polymerization. The SQNPAEK membrane shows excellent proton conductivity up to 0.102 S cm^{-1} at 80°C , which are superior to previous side-chain-type and main-chain-type sulfonated polymer membranes at similar IEC. Cross-linked membranes are then obtained by a heating reaction at 190°C , using 4,4'-diglycidyl (3,3',5,5'-tetramethylbiphenyl) epoxy resin (TMBP) as the cross-linker. As expected, the water uptake and the methanol permeability of the cross-linked membranes decrease with increasing the content of TMBP. Compared to Nafion 117, the cross-linked membranes show comparable proton conductivities and much higher selectivities, which are in the range of 5.18×10^5 – $1.46 \times 10^6 \text{ S s}^{-1} \text{ cm}^3$. Other properties of the cross-linked membranes, such as mechanical properties, thermal properties, are also investigated. All the results indicated that the cross-linked membranes based on SQNPAEKs and TMBP are promising candidate for direct methanol fuel cells.

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1. Introduction

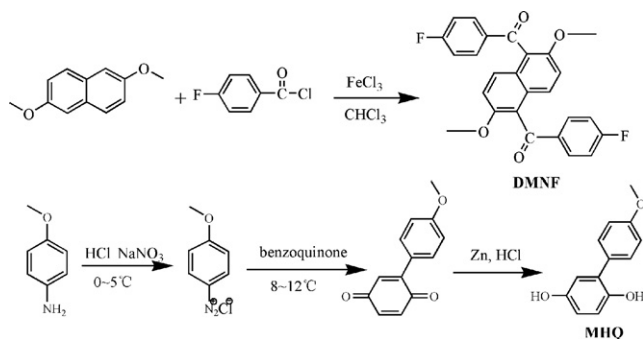
Over the past decade, proton exchange membranes (PEMs) have attracted extensive attention due to their applications in proton exchange membrane fuel cells (PEMFCs) [1]. As a solid electrolyte, PEMs not only conduct protons from the anode to the cathode, but also provide a barrier to the fuel crossleaks between the electrodes [2,3]. Therefore, a successful PEM should possess high proton conductivity, good thermal, dimensional stability and good mechanical strength [4]. Perfluorosulfonic acid polymers, such as Nafion (DuPont), are commercially available because of their outstanding properties. However, some drawbacks hinder widespread commercial use in PEMFCs, such as high methanol crossover and high cost. Meanwhile, due to the loss of water, the proton conductivity of Nafion decreases drastically when the operation temperature is higher than 80°C .

Up to now, great efforts have been made to develop the alternative materials to Nafion. Sulfonated aromatic polymers, such as sulfonated multiblock copolymers [5,6], sulfonated poly(arylene ether ketone) [7], sulfonated polyimides [8,9], sulfonated poly(arylene ether nitrile) [10,11], sulfonated poly(arylene

ether sulfone) [12,13], and sulfonated poly(benzimidazole) [14], have been considered as promising candidates for PEMs because of their well-known high proton conductivity, low cost and proper methanol permeability. However, the non-fluorinated sulfonated aromatic polymer membranes should possess a high level of ion exchange capacity (IEC) in order to achieve sufficient proton conductivity because of lower acidity of sulfonic acid groups, less flexibility and less distinct phase separation between hydrophilic and hydrophobic domains when compared to Nafion [15]. But high IEC usually results in significant swelling in water, thus leading to the loss of the mechanical properties as well as high methanol crossover [1,2]. There are several approaches to overcome these problems: grafted and cross-linked membranes, hybrid and/or composite membranes, and pore-filling electrolyte membranes.

According to the attachment site of the sulfonic acid groups, sulfonated aromatic polymers can be divided into two types, main-chain-type [15,16] and side-chain-type [17–19]. Compared with the main-chain-type polymers, the side-chain-type sulfonated polymers indicated several advantages: (1) structural similarities to Nafion, which achieve high conductivity at low IEC; (2) distinct nano-phases separation between hydrophilic and hydrophobic domains, which could get proper water uptake and swelling ratio; (3) continuous ion-conducting pathway, which is benefit to the proton conductivity. Naoki Asano and Kenji Miyatake et al. recently reported that side-chain-type sulfonated polymers showed high

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Scheme 1. Synthesis of monomer DMNF and MHQ.

proton conductivity with a low swelling ratio at 80 °C [18,19]. However, most of those polymers only have one pendant sulfonic group in one repeat unit, because it is difficult to design side-chain-type monomer with more sulfonic groups.

In our previous work, we have prepared naphthalene-based poly(arylene ether ketone) bearing two sulfobutyl groups within one repeat unit [17]. These side-chain-type PEMs exhibited improved dimensional stability, low methanol permeability and appropriate proton conductivity. In this study, we designed and synthesized a novel side-chain-type sulfonated poly(arylene ether ketone) with tri-side pendent sulfonic acid groups in one repeat unit for the first time. It showed high proton conductivity at moderate IEC and desirable mechanical strength. Furthermore, we reported a series of cross-linked membranes based on the novel SQNPAEK polymers through the thermal curing reaction between the hydroxyl groups in the sulfonated polymers and the epoxy groups in 4,4'-diglycidyl (3,3',5,5'-tetramethylbiphenyl) epoxy resin (TMBP). To the best of our knowledge, very few researches have been done to develop cross-linked membranes with side-chain-type matrix. Covalent cross-linking can effectively reduce water swelling, methanol permeability and improve the mechanical stability of the membranes [20,21]. The properties of the cross-linked membranes were studied in details for the future application in direct methanol fuel cells (DMFCs).

2. Experimental

2.1. Materials

2,6-Dimethoxynaphthalene, 1,4-butane-sultone, 4-Methoxyaniline, 4,4'-diglycidyl (3,3',5,5'-tetramethylbiphenyl) epoxy resin (TMBP), 1,4-benzoquinone, and 4-fluorobenzoyl chloride were purchased from Sigma-Aldrich Ltd. Boron tribromide (BBr_3) and Bisphenol A were obtained from Beijing Chemical Reagents. Potassium carbonate (K_2CO_3) was dried at 120 °C for 24 h before used. N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP) were vacuum-distilled prior to use. Other reagents were commercially available grade and used without further purification.

2.2. Monomer synthesis

2.2.1. Synthesis of

1,5-bis(4-fluorobenzoyl)-2,6-dimethoxy-naphthalene (DMNF)

The synthetic procedure of monomer DMNF has been described in our previous work [17] (Scheme 1). In brief, anhydrous ferric chloride (1.65 g, 0.01 mol) was added in small portions to a cold solution (0–5 °C) with a mixture of 2,6-dimethoxynaphthalene (9.4 g, 0.05 mol) and 4-fluorobenzoyl chloride (17.4 g, 0.11 mol) dissolved in chloroform. And the reaction was then kept at this temperature for 24 h. The resulting mixture was poured into

hydrochloric acid. The product was removed by decantation and the brown solid was precipitated in methanol. The crude product was then recrystallized twice from DMF/water mixture (10:1, v/v).

2.2.2. Synthesis of (4-methoxy) phenyl hydroquinone (MHQ)

A brief procedure for synthesizing the monomer MHQ was as follows. 4-Methoxyaniline (61.5 g, 0.5 mol) and hydrochloric acid (169.5 mL, 11.8 M) were dissolved in DI water (200 mL) to get a solution at 0–5 °C. Then a concentrated water solution of sodium nitrite (34.5 g, 0.5 mol) was added with stirring. The obtained solution was added dropwise into an aqueous solution of 1,4-benzoquinone (43.2 g, 0.4 mol), sodium bicarbonate (168 g, 2 mol) and was stirred for 2 h at 8–10 °C. The resulting mixture was filtered and washed with DI water. The obtained deep red solid was dried at 60 °C in the vacuum oven for 24 h.

The above product (64 g, 0.3 mol) and Zn powder (58.9 g, 0.9 mol), and deionized water (500 mL) were added into a three-necked flask equipped with a mechanical stirrer, a condenser and a dropping funnel. 72 mL HCl (11.8 M) was added dropwise into the mixture when it was heated to 90 °C. The mixture was refluxed for another 2 h and then was filtered. The obtained precipitate was recrystallized twice from toluene (Scheme 1).

2.3. Polymer synthesis

2.3.1. Synthesis of naphthalene-based poly(arylene ether ketone) polymers containing tri-methoxy groups (TMQNPAEK)

DMNF (8.65 g, 0.02 mol), MHQ (4.32 g, 0.02 mol), K_2CO_3 (2.764 g, 0.02 mol), NMP (40 mL) and toluene (15 mL) were added into a 250 mL round-bottomed three-neck flask equipped with a mechanical stirrer, a Dean-Stark trap and a nitrogen inlet/outlet. The mixture was heated at 140 °C for about 2 h to remove water caused from alkaline-neutralising by azeotropic distillation with toluene, and then slowly heated to 180 °C and maintained at this temperature until a highly viscous mixture was obtained. Then the high viscous reaction mixture was poured into DI water to precipitate a white fibrous polymer. The obtained polymer was washed thoroughly with DI water several times and dried in vacuum at 100 °C for 24 h (Scheme 2).

^1H NMR (500 MHz, DMSO-d_6 , δ , ppm): 3.64 (10H, $-\text{OCH}_3$), 6.84 (8H, 9H, ArH ortho to ether, ArH), 7.05 (1H, ArH ortho to ether), 7.21 (5H, 6H, 7H, ArH ortho to ether), 7.36 (3H, 4H, Naphthalene β -H, Naphthalene α -H), 7.59–7.70 (2H, ArH ortho to carbonyl).

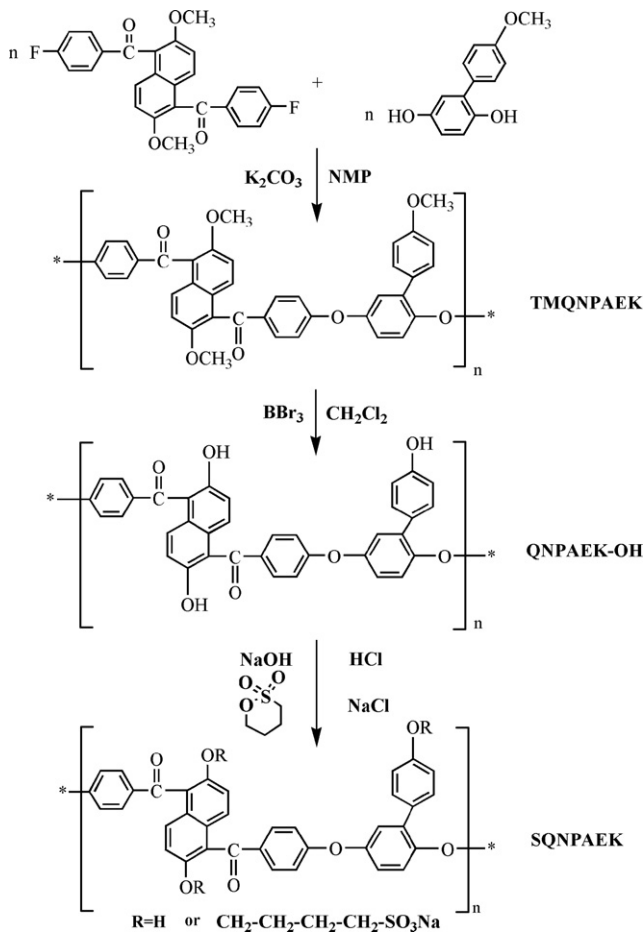
2.3.2. Synthesis of naphthalene-based poly(arylene ether ketone) polymers bearing tri-hydroxyl groups (QNPAEK-OH)

Demethylation reaction was described as follow: 1.0 g TMQNPAEK was dissolved into 25 mL anhydrous CH_2Cl_2 in a 100 mL three-neck flask equipped with a magnetic stirrer and a nitrogen inlet/outlet. The solution was cooled down to 0–5 °C (ice bath) and 1 M solution of BBr_3 in CH_2Cl_2 was added dropwise. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 6 h. The mixture was poured into 100 mL ice-water to quench excess BBr_3 , and then washed with methanol and DI water. The resulting polymer (QNPAEK-OH) was dried under vacuum at 100 °C for 24 h.

^1H NMR (500 MHz, DMSO-d_6 , δ , ppm): 6.74 (9H, ArH), 6.94 (8H, ArH ortho to hydroxyl), 7.13 (1H, ArH ortho to ether), 7.23 (3H, Naphthalene β -H), 7.31 (4H, 5H, 6H, 7H, Naphthalene α -H, ArH ortho to ether), 7.70–7.79 (2H, ArH ortho to carbonyl), 9.56, 9.82 (10H, 11H, $-\text{OH}$).

2.3.3. Synthesis of naphthalene-based tri-side chain poly(arylene ether ketone) with pendant alkylsulfonic acid groups (SQNPAEK)

8 mL toluene and 0.5 g NaOH were added into the solution of QNPAEK-OH (1 g) in DMSO (20 mL). The mixture was magnetically



stirred at room temperature for half an hour, and then heated at 140 °C for 2 h to remove water. Then 1,4-butanediol (1.997 g, 1.5 mL) was added dropwise into the reaction system, and the reaction was slowly heated to 150 °C and kept for 12 h. The resulting sulfonated polymers were precipitated in 150 mL acetone and collected by suction filtration, washed by distilled water several times and dried in a vacuum at 80 °C.

¹H NMR (500 MHz, DMSO-d₆, δ, ppm): 1.47 (11H, 12H, -CH₂CH₂-), 2.45 (13H, -CH₂SO₃H), 3.97 (10H, -OCH₂-), 4.28–5.57 (14H, -SO₃H), 6.73 (9H, ArH), 7.14 (1H, ArH ortho to ether), 6.93 (8H, ArH), 7.25 (3H, Naphthalene β-H), 7.31 (5H, 6H, 7H, ArH), 7.48 (4H, Naphthalene α-H), 7.66–7.77 (2H, ArH ortho to carbonyl).

2.3.4. Preparation of cross-linked membranes

The cross-linked membranes were prepared using a solution casting method. First, 1 g SQNPAEK and TMBP with different TMBP amounts (2.5, 5, 10, 15 wt.%) were dissolved in 10 mL DMSO and stirred for about 12 h. Then the membranes were formed after the heating of solution at 50 °C for 24 h to evaporate the solvent. The samples were cured by raising the temperature slowly to 190 °C and holding for 6 h in a vacuum to induce cross-linking. And then, all the membranes were immersed in 1 M sulfuric acid (H₂SO₄) solution at room temperature for 24 h to obtain the cross-linked membranes in acid form. The cross-linked membranes were described as SQNPAEK/TMBP-xx, where “xx” represents the content of epoxy resin in the cross-linked membranes by weight percent. For comparison, we also prepared a blending membrane with 15 wt.% content of TMBP without a thermal curing procedure, which is marked with SQNPAEK + TMBP (15 wt.%).

2.4. Measurements

2.4.1. Structural characterization

The ¹H NMR spectrum was measured on a 500 MHz Bruker Avance 510 spectrometer at 298 K using DMSO-d₆ as solvent and tetramethylsilane (TMS) as the standard.

FT-IR measurements were performed with a Nicolet Impact 410 Fourier transform infrared spectrometer using KBr disc. The grafting degree (DG) of these side-chain-type SQNPAEK polymers can be determined by ¹H NMR spectra. The signals around 3.97 ppm were attributed to the hydrogen atoms (H10) of aliphatic side chain (-OCH₂-), and the signals around 7.77–6.73 ppm were assigned to the hydrogen atoms (H1–H9) in phenyl ring. The DG was calculated by the following formula (1):

$$DG = \frac{9.5A(10)}{3A(1-9)} \quad (1)$$

where A(10) is the peak area of H10, A(1–9) is the integral peak area of the signals corresponding to the aromatic hydrogen of the polymers.

2.4.2. Ion exchange capacity, water uptake and swelling ratio measurements

The IEC of the membranes was determined by a classical titration method [22]. The theoretical IEC can be calculated from DG with formula (2):

$$IEC = \frac{DG \times 1000}{566 + 137 \times DG} \quad (2)$$

The water uptake was determined by the same method as previously reported [23]. It was calculated using the formula (3):

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (3)$$

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

The dimensional change of the membranes was measured in the length direction, which was calculated with the following formula (4):

$$\text{Swelling ratio (\%)} = \frac{l_w - l_d}{l_d} \times 100 \quad (4)$$

where l_w and l_d are the lengths of the wet membrane and dry membrane, respectively.

2.4.3. Thermal properties of membranes

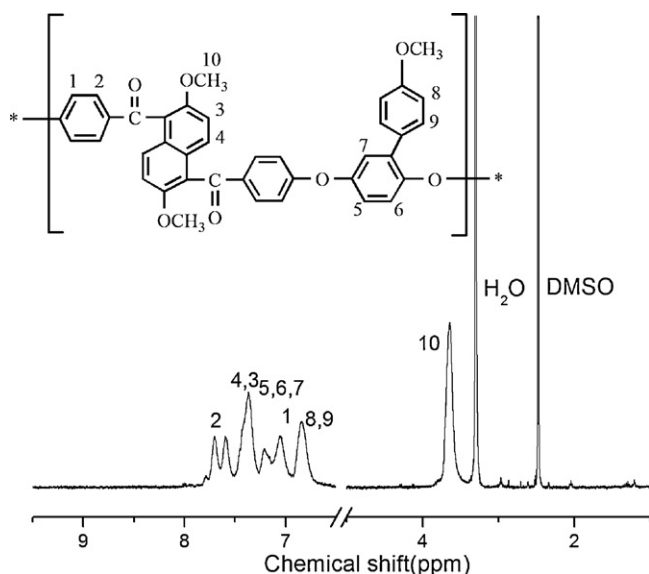
The thermogravimetric analyses (TGA) measurements were performed on a Perkin-Elmer TGA-2 thermogravimetric analyzer from 80 to 700 °C at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. Before the heating scan, all the samples were pre-dried under N₂ at 150 °C for 20 min to remove water.

2.4.4. Proton conductivity and methanol permeability

The proton conductivities of all the membranes were measured by a four-probe AC impedance method from 10⁻¹ Hz to 10⁷ Hz, using a Princeton Applied Research Model 2273A Potentiostat in DI water [22]. The membranes (4 cm × 1 cm) were dipped in DI water for 48 h before analysis. A sheet of membrane was placed in the test cell, which was immersed in water at desired temperature. The proton conductivity σ (S cm⁻¹) was calculated by the following formula (5):

$$\sigma = \frac{L}{RS} \quad (5)$$

where L (cm) is the distance between the electrodes, R (Ω) is the membrane resistance, and S (cm²) is the cross-sectional area of membrane.

Fig. 1. ^1H NMR spectrum of TMQNPAEK.

The methanol permeability was determined by using a common method with a diffusion cell described in the literatures [22,24,25]. The concentration of methanol was determined by using SHIMADZU GC-8A chromatograph. The methanol permeability was calculated with the following formula (6):

$$C_{B(t)} = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (6)$$

where A (cm^2) and L (cm) are the effective area and the thickness of the membrane, respectively. V_B (mL) is the volume of diffusion reservoir. C_A and C_B (mol L^{-1}) are the methanol concentration in feed and in diffusion reservoir, respectively. DK is the methanol permeability ($\text{cm}^2 \text{s}^{-1}$).

2.4.5. Mechanical properties

The mechanical properties of the thin dry membranes were evaluated at room temperature on SHIMADZU AG-I 1KN at a speed of 2 mm min^{-1} . The size of the samples was $15 \text{ mm} \times 4 \text{ mm}$. Before testing, all the membranes were dried in the oven at 80°C for 4 h.

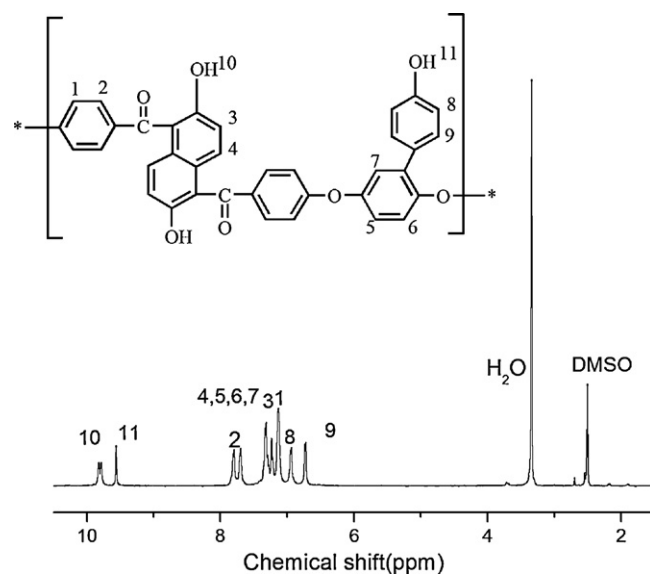
2.4.6. Transmission electron microscope (TEM) observations

TEM images were determined by JME-2000EX. Before testing, the membranes were first converted into Ag^+ form by immersing the samples in AgNO_3 solutions for 48 h. The SQNPAEK-Ag in NMP solution doping of different contents of TMBP was then cast onto copper grids. After evaporating the solvent, the temperature was raised to 190°C for 6 h in a vacuum to obtain a cross-linked membrane for TEM used.

3. Results and discussion

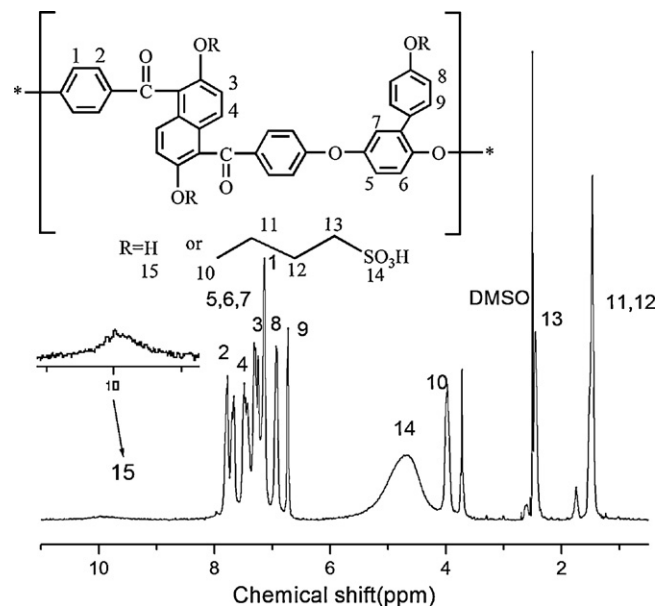
3.1. Synthesis and characterization of TMQNPAEK, QNPAEK-OH and SQNPAEK

Scheme 2 shows the synthesis of naphthalene-based poly(arylene ether ketone) polymer containing tri-methoxy groups (TMQNPAEK) by aromatic nucleophilic substitution reaction. Fig. 1 shows the ^1H NMR spectrum of TMQNPAEK. The signal at 3.64 ppm could be contributed to the chemical shift of $-\text{OCH}_3$ protons (H10). The integration of all the aromatic protons signals (H1–H9) to the $-\text{OCH}_3$ protons was 2.0. The result indicated that the tri-methoxy side chain polymer was successfully synthesized and no by-product was observed during the reaction.

Fig. 2. ^1H NMR spectrum of QNPAEK-OH.

Scheme 2 also shows the synthesis of QNPAEK-OH by a demethylation reaction which converted the methoxyphenyl groups to the phenols using BBr_3 . The resulting polymers precipitated from CH_2Cl_2 solvent due to the polar nature of the hydroxyl groups. Fig. 2 shows the ^1H NMR of QNPAEK-OH. The proton peaks at 3.64 ppm attributed to the hydrogen atoms of $-\text{OCH}_3$ groups disappeared, while the new peaks corresponding to the $-\text{OH}$ groups were observed in the spectrum at about 9.8 ppm and 9.57 ppm.

Scheme 2 also shows the synthesis of SQNPAEK by a nucleophilic ring-opening reaction, in which the sulfoethyl groups were grafted to QNPAEK-OH. Fig. 3 shows the ^1H NMR spectrum of SQNPAEK. The proton signal of $-\text{OH}$ group at 9.8 ppm almost disappeared while the signals for the four middle methylene groups from sulfoethyl groups appeared at lower frequencies. In addition, the broad peak at 4.5 ppm (H12) was ascribed to the proton of $-\text{SO}_3\text{H}$ group deriving from the sulfoethyl groups [26]. The ^{13}C NMR spectrum was used to further determine the structure of SQNPAEK. The signals from 21.77 ppm, 28.54 ppm, 51.53 ppm, 69.53 ppm assigning to the

Fig. 3. ^1H NMR spectrum of SQNPAEK.

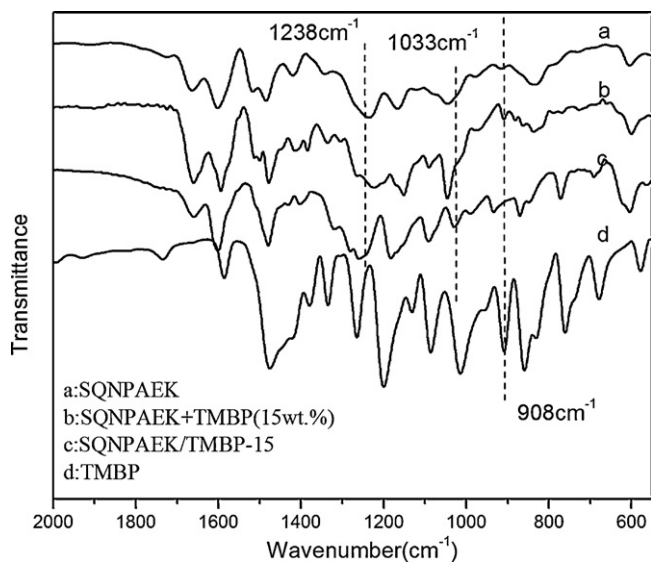


Fig. 4. FT-IR spectra of polymers.

sulfobutyl group indicated that the sulfobutyl groups were successfully grafted onto the polymer main chain. In this case, we used SQNPAEK polymer with the DG of 0.42 as the original polymer for crosslinking.

The obtained polymers dissolved well in polar solvents, such as DMAc, NMP, and DMSO. SQNPAEK exhibited well solubility than the TMQNPAEK polymer. The attachment of alkylsulfonic acid side chain enhanced the inter-chain interactions than the original rigid polymer, resulting in the good solubility of the SQNPAEK.

3.2. Preparation and characterization of the cross-linked membranes (SQNPAEK/TMBP-xx)

The cross-linked membranes were obtained by the thermal curing reaction at 190 °C between the hydroxy and epoxy groups (Scheme 3) [27]. The SQNPAEK membrane could be easily dissolved in common organic polar solvents, such as NMP, DMSO and DMF, while the cross-linked membranes could not. Fig. 4 shows the FT-IR spectra of SQNPAEK, TMBP, SQNPAEK/TMBP-15 and SQNPAEK + TMBP (15 wt.%), respectively. The typical absorption bands around 1238 and 1033 cm^{-1} were assigned to the symmetric and asymmetric stretching vibrations of sulfonic acid groups [28]. Compared to SQNPAEK + TMBP (15 wt.%), the disappearance of the characteristic absorption peak of epoxy group at 908 cm^{-1} indicated that the cross-linked membrane had been successfully prepared.

3.3. Thermal and mechanical properties

The thermal stability of polymers was evaluated by TGA analysis. Fig. 5 shows the TGA curves of TMQNPAEK, QNPAEK-OH, SQNPAEK and the cross-linked membranes. The original TMQNPAEK showed excellent thermal stability and the temperature for 5% weight loss was observed at 442 °C. As shown in Table 1, after sulfobutylation, the polymer bearing pendant sulfonic acid groups showed lower thermal decomposition temperature.

A two-step weight loss was observed for all cross-linked membranes in their acid form. The first weight loss observed from 232 °C to 350 °C was attributed to the decomposition of the pendant sulfonic acid groups [29,30]. The second decomposition stage around 490 °C was ascribed to the degradation of main and side chains. Table 1 lists 5% weight loss temperatures ($T_{d5\%}$) of SQNPAEK and the cross-linked membranes. Benefiting from the addition of the

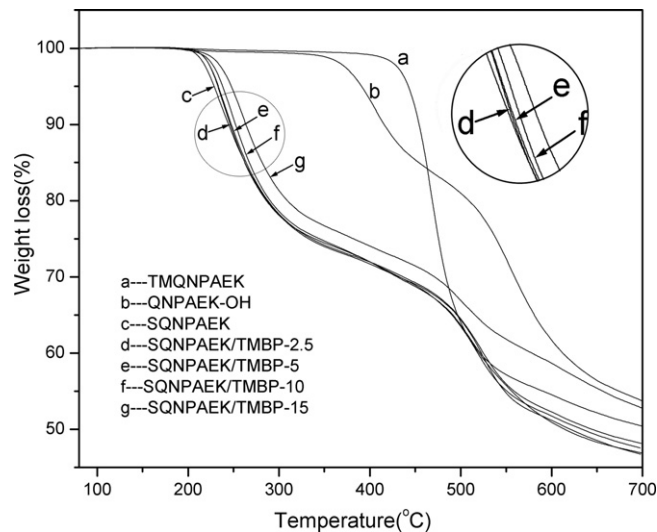


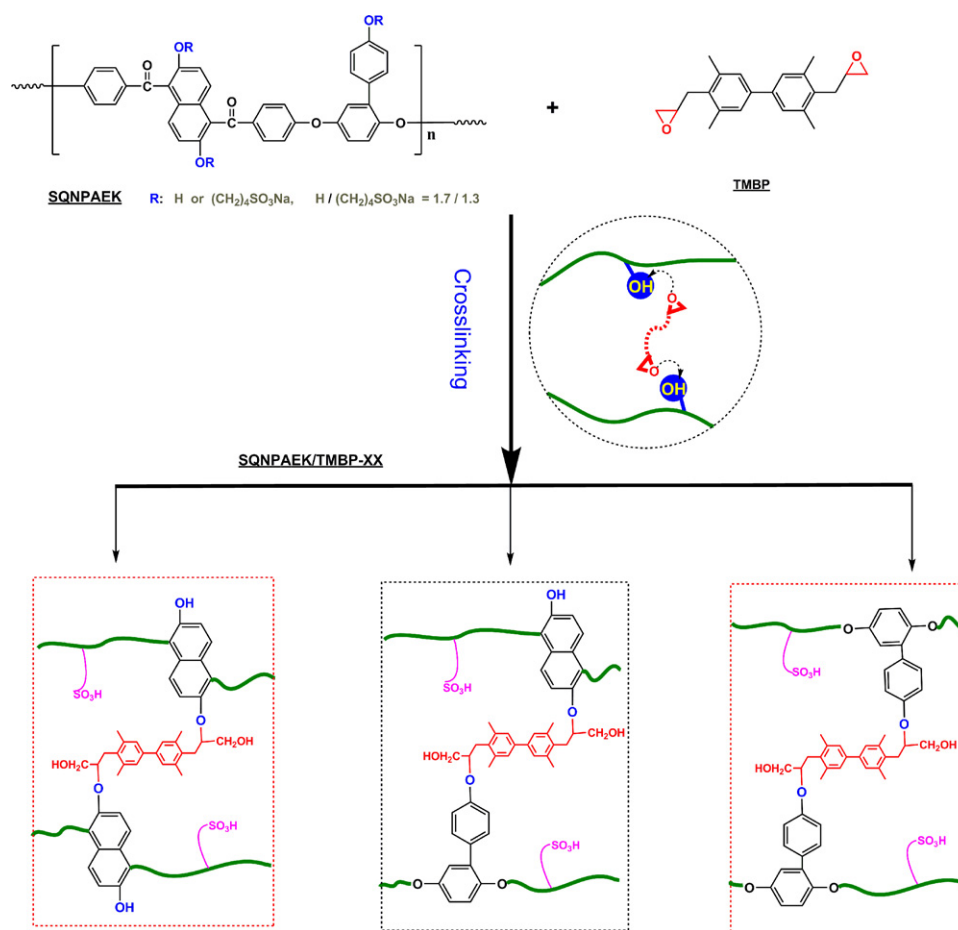
Fig. 5. TGA curves of the polymers.

TMBP, the thermal curing made the membrane more compact, which resulted in poor segmental activity. Thus, the values of $T_{d5\%}$ increased with increasing the content of TMBP.

Table 1 lists the mechanical properties of all the membranes tested in the dry state. All the cross-linked membranes showed higher Young's modulus and tensile strengths than those of the pristine membrane. The maximum load were in the range of 55–74 MPa, the Young's modulus were in 1.24–1.36 GPa, and the elongation at break were 9.08–10.24%. These results indicated that the cross-linked network structure restricted the molecule motion of the polymer chains and the cross-linking methods could efficiently improve the mechanical properties of the membranes.

3.4. IEC, water uptake, and swelling ratio measurements

The IEC value, which indicates the quantity of exchangeable ions in the polymer membranes, has a closer relationship to water uptake and swelling ratio. As shown in Table 2, with increasing the content of the cross-linker, the IEC value decreased from 1.710 to 1.180 mequiv. g^{-1} due to the addition of TMBP, which diluted the ion concentration. In DMFCs, water molecules act as the carrier for proton transportation through the PEMs. However, excessive water uptake would destroy the dimensional stability and mechanical properties of the polymer films. A lower water uptake and swelling ratio are desired for PEMs. Figs. 6 and 7 and Table 2 show the water uptake and swelling ratio of all membranes, respectively. As shown in Figs. 6 and 7, the SQNPAEK membrane showed the water uptake of 61.23% and the swelling ratio of 13.86% in length and 12.73% in thickness at 80 °C, respectively, which were much lower than the main-chain-type membranes under the same conditions. SQNPAEK/TMBP-15 showed the lowest water uptake of 35.00% and swelling ratio of 8.07% in length, which were much lower than the pristine membrane. Both of the water uptake and the swelling ratio increased with increasing temperatures and all the cross-linked membranes maintained good dimensional stability. It was also observed that the water uptake and swelling ratio of the cross-linked membranes decreased to a great extent with increasing the content of TMBP. This was due to the decrease of IEC and the formation of cross-linking network structure. The results indicated that cross-linking could effectively limit the motion of polymer chains, leading to the good dimensional stability.



Scheme 3. The mechanism of the cross-linking reaction of the membranes.

Table 1
Thermal and mechanical properties of the membranes.

Samples	$T_{d\ 5\%}^a$ (°C)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
SQNPAEK	228	53.50	1.07	9.45
SQNPAEK/TMBP-2.5	232	67.17	1.36	9.323
SQNPAEK/TMBP-5.0	233	71.54	1.25	10.24
SQNPAEK/TMBP-10	238	64.91	1.24	9.65
SQNPAEK/TMBP-15	247	70.02	1.35	9.08

^a SQNPAEK/TMBP-xx in acid form.

3.5. Proton conductivity

Proton conductivity is generally considered as an important property of the PEMs. There is a close connection between

the proton conductivity and the IEC. The higher the value of IEC is, the higher conductivity it has. Fig. 8 shows that the side-chain-type polymer can easily form continuous ion-conducting pathways which enable the membranes achieve high

Table 2
IEC, methanol permeability, water uptake, swelling ratio, relative selectivity and proton conductivity of the membranes.

Polymer membranes	IEC ^a (mequiv. g ⁻¹)	Methanol permeability (cm ² s ⁻¹) × 10 ⁻⁶	Proton conductivity (S cm ⁻¹)		Water uptake (%)		Swelling ratio (%)				Relative selectivity ^b
			25 °C	80 °C	25 °C	80 °C	Δl		Δd		
							25 °C	80 °C	25 °C	80 °C	
SQNPAEK	1.710	0.114	0.059	0.102	28.98	61.23	7.43	13.86	5.45	12.73	1
SQNPAEK/TMBP-2.5	1.435	0.101	0.055	0.096	27.48	51.53	7.14	12.24	5.00	11.1	1.05
SQNPAEK/TMBP-5.0	1.364	0.0636	0.054	0.088	27.46	48.36	6.49	12.12	3.77	9.43	1.64
SQNPAEK/TMBP-10	1.250	0.0528	0.051	0.079	20.76	37.50	5.69	10.50	2.83	7.55	1.86
SQNPAEK/TMBP-15	1.180	0.0309	0.045	0.066	19.75	35.00	5.13	8.07	2.08	4.26	2.81
Nafion 117	0.90	2.38	0.08	0.10	22	38	10.6	17.2	–	–	–

^a The IEC values were measured by titration method.

^b Relative selectivity = membrane selectivity/SQNPAEK selectivity at 25 °C (selectivity = [proton conductivity]/[methanol permeability]).

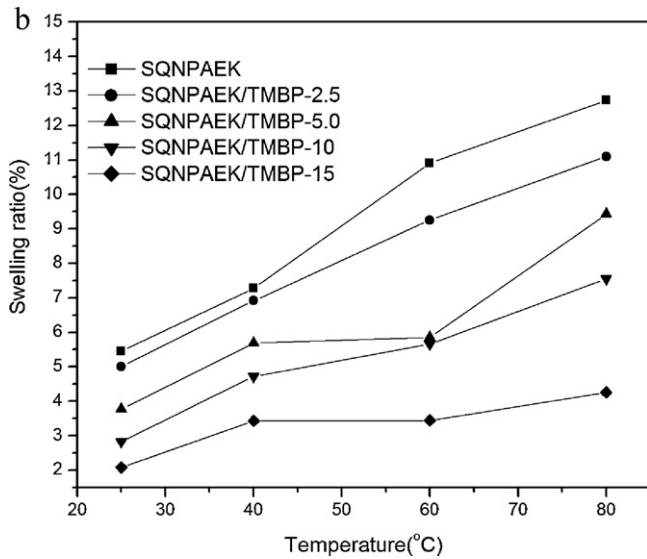
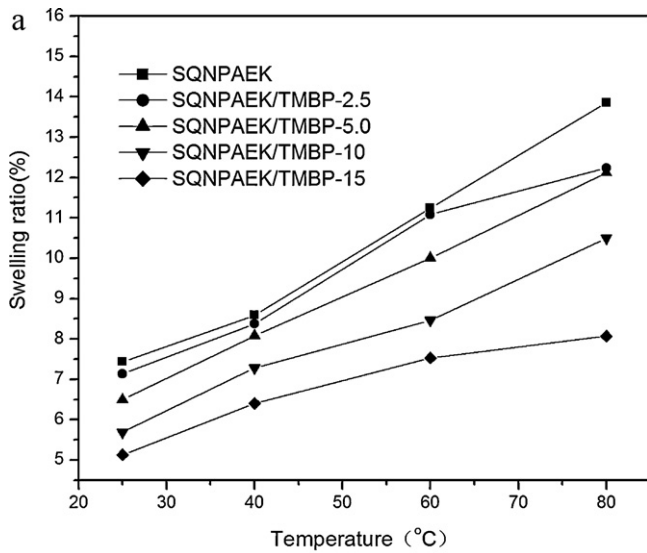


Fig. 6. Swelling ratio of SQNPAEK/TMBP-xx membranes; (a) swelling ratio in length, (b) swelling ratio in thickness.

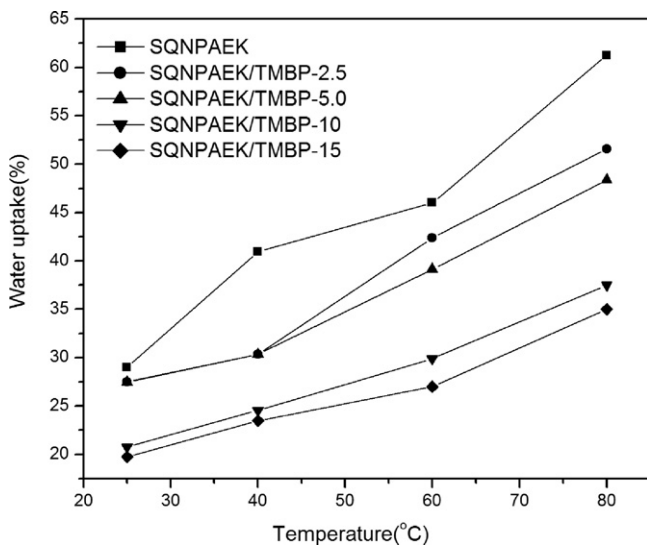


Fig. 7. Water uptake of SQNPAEK/TMBP-xx membranes.

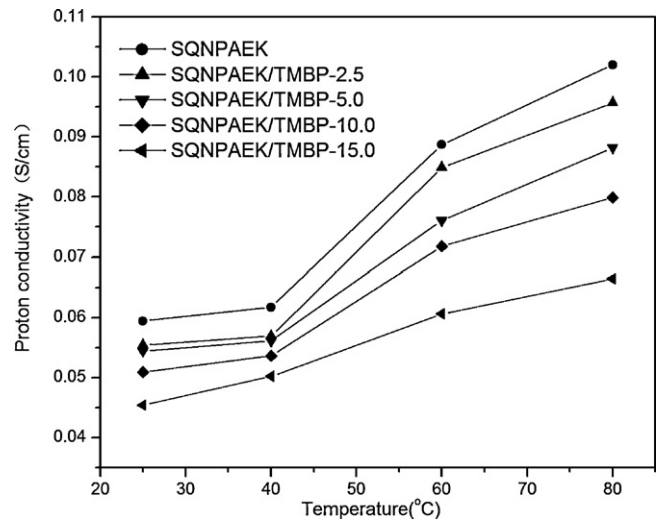


Fig. 8. Proton conductivity of all the membranes at different temperatures.

conductivities. The proton conductivities of all the membranes were in the order of IEC values and increased with temperatures. The SQNPAEK (IEC = 1.710 mequiv. g⁻¹) membrane showed excellent proton conductivity of 0.102 S cm⁻¹ at 80 °C. Compared to the main-chain-type sulfonated poly(arylene ether ketone), SQNPAEK showed much lower water content but higher proton conductivity at similar IEC values [31]. The conductivity values were also higher than those of other side-chain type PEMs with similar IEC [17,19], despite that the DG of SQNPAEK was only 0.42. It could be explained that the tri-side sulfonic acid groups on the flexible aliphatic side chains would be beneficial to aggregate the ionic clusters and improve the nanophase separation between hydrophobic and hydrophilic domains. Fig. 8 also shows that the proton conductivity decreased with the increase of the TMBP content. The SQNPAEK/TMBP-2.5 membrane showed a comparable conductivity of 0.096 S cm⁻¹ at 80 °C. When the content of TMBP reached to 15%, the conductivity still remained at 0.066 S cm⁻¹ at 80 °C. Although the sulfonic acid group was diluted with the addition of the TMBP, spherical or bi-continuous structure still allowed the ions to transport [32]. This result indicates that hydrophilic/hydrophobic phase separation was the principal factor to achieve high conductivity, even though at low IEC. Furthermore, the structure of the membranes could be more compact after the cross-linking reaction, which supplemented the reduction of the conductivity caused by

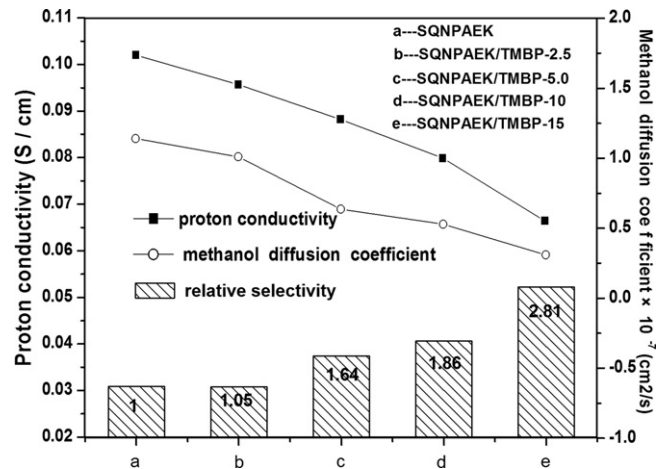


Fig. 9. The relative selectivity of cross-linked membranes (proton conductivity at 80 °C, methanol permeability at 25 °C).

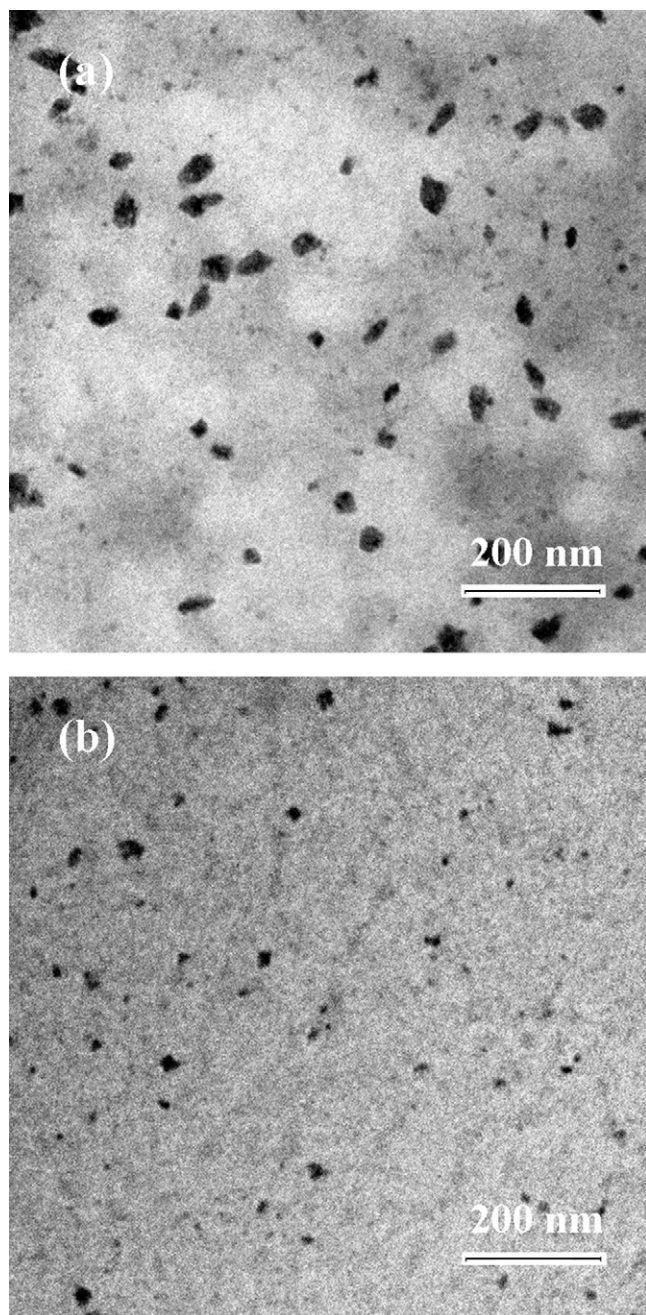


Fig. 10. TEM images of the membranes: (a) SQNPAEK; (b) SQNPAEK/TMBP-15.

adding the TMBP. The change of microstructure would be discussed by the study of TEM later.

3.6. Methanol permeability and relative selectivity

In DMFCs, PEMs must possess both high proton conductivity and low methanol permeability. Because the proton conduction and methanol permeation take place through the same hydrophilic cluster channels [22,25], SPAEK with high degree of sulfonation usually shows higher methanol permeability [15]. The methanol permeability of SQNPAEK/TMBP-xx membranes at room temperature is shown in Table 2. For comparison, the methanol permeability of Nafion 117 was also measured under the same conditions. The methanol permeability of the tri-side chainable membrane was $0.114 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which was much lower than Nafion 117 ($2.38 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). After cross-linking, the methanol

permeability rapidly decreased to $0.0309 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which was an order of magnitude lower than that of the pristine membrane. The cross-linked network structure induced a much compact structure and acted as an effective methanol barrier [33].

The high proton conductivity and low methanol permeability of SQNPAEK/TMBP-xx resulted in excellent selectivity, which was the combined factor to evaluate the membrane performances in DMFCs. The selectivity can be used as a parameter to develop better PEMs [23]. Fig. 9 shows the relative selectivity of the cross-linked membranes to the pristine membrane, which increased with the cross-linker content. All the cross-linked membranes showed that the relative selectivity was greater than 1. The SQNPAEK/TMBP-15 membrane showed that the highest relative selectivity with a value of 2.81. Although the cross-linked membranes showed slight lower proton conductivity compared with the pristine membrane, it was sufficient to achieve improved DMFC performance through their low methanol permeability and better selectivity.

3.7. TEM observations

Fig. 10 shows the TEM results of SQNPAEK and SQNPAEK/TMBP-15. The dark regions represented hydrophilic domain and bright regions represented the hydrophobic domain. In SQNPAEK membrane, the black clusters were randomly dispersed throughout polymer matrix. Similar TEM images have been also observed in other side-chain sulfonated polymers [34]. Compared with SQNPAEK membrane, the SQNPAEK/TMBP-15 had smaller hydrophilic domains, which indicated that the addition of the TMBP diluted the density of sulfonic acid groups. The TEM image suggests that the sulfonic acid groups might aggregate into hydrophilic clusters, which could provide proton transport pathways or ionic transport channels.

4. Conclusions

In summary, a novel cross-linked sulfonated naphthalene-based poly(arylene ether ketone) (SQNPAEK) membranes were obtained by a simple heating treatment method. Epoxy resin was introduced as the cross-linker. The SQNPAEK polymer containing pendant alkylsulfonic acid groups was successfully prepared by a direct polymerization and a nucleophilic ring-opening reaction. The obtained polymer containing tri-side chains within one repeat unit exhibited good solubility, and could be easily made into a flexible and tough membrane by casting from common organic solvents. All the cross-linked membranes showed drastically reduced water uptake, swelling ratio and methanol permeability. Furthermore, the cross-linked membranes showed higher selectivity and excellent mechanical properties compared to the pristine membrane. Compared to Nafion 117, the SQNPAEK/TMBP-15 membrane showed about half of the swelling ratio, 8.07%. The preliminary properties demonstrated the strategy to combine cross-linking and pendant alkylsulfonic acid groups is a promising way to achieve high performance PEM materials. Additionally, the research results will develop a new way to design superior membranes, e.g., the different cross-linker or multi-side chains groups to improve membrane performances.

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References

- [1] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, G.E. McGrath, *Chem. Rev.* 104 (2004) 4587–4612.
- [2] M.A. Hickner, B.S. Pivovar, *Fuel Cells* 5 (2005) 213–229.
- [3] J. Larminie, A. Dicks, *Fuel Cell Systems Explained*, John Wiley & Sons, Ltd., Chichester, 2002, pp. 188–199.
- [4] M. Winter, R.J. Brodd, *Chem. Rev.* 104 (2004) 4245–4269.
- [5] K. Nakabayashi, T. Higashihara, M. Ueda, *Macromolecules* 43 (2010) 5756–5761.
- [6] B. Bae, K. Miyatake, M. Watanabe, *Macromolecules* 43 (2010) 2684–2691.
- [7] T.W. Kim, M. Sahimi, T.T. Tsotsis, *Ind. Eng. Chem. Res.* 48 (2009) 9504–9513.
- [8] T. Suda, K. Yamazaki, H. Kawakami, *J. Power Sources* 195 (2010) 4641–4646.
- [9] K. Yaguchi, K. Chen, N. Endo, M. Higa, K. Okamoto, *J. Power Sources* 195 (2010) 4676–4684.
- [10] H.B. Zhang, J.H. Pang, D. Wang, A.Z. Li, Z.H. Jiang, *J. Membr. Sci.* 264 (2005) 56–64.
- [11] Y. Gao, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, X. Li, S. Kaliaguine, *Macromolecules* 38 (2005) 3237–3245.
- [12] S.J. Grunzinger, M. Watanabe, K. Fukagawa, R. Kikuchi, Y. Tominaga, T. Hayakawa, M. Kakimoto, *J. Power Sources* 175 (2008) 120–126.
- [13] K.B. Heo, H.J. Lee, H.J. Kim, B.S. Kim, S.Y. Lee, T.H. Lim, *J. Power Sources* 172 (2007) 215–219.
- [14] J.A. Mader, B.C. Benicewicz, *Fuel Cells* 11 (2010) 212–221.
- [15] S. Matsumura, A.R. Hlil, C. Lepiller, J. Gaudet, D. Guay, S. Holdcroft, A.S. Hay, *Macromolecules* 41 (2008) 281–284.
- [16] K. Yoshimura, K. Iwasaki, *Macromolecules* 42 (2009) 9302–9306.
- [17] K. Shao, J. Zhu, C.J. Zhao, X.F. Li, H. Na, *J. Polym. Sci. Part A: Polym. Chem.* 47 (2009) 5772–5783.
- [18] N. Asano, M. Aoki, S. Suzuki, K. Miyatake, H. Uchida, M. Watanabe, *J. Am. Chem. Soc.* 128 (2006) 1762–1769.
- [19] K. Miyatake, Y. Chikashige, E. Higuchi, M. Watanabe, *J. Am. Chem. Soc.* 129 (2007) 3879–3887.
- [20] L.Y. Jang, O.H. Kweon, K.E. Kim, G.J. Hwang, A.B. Moon, A.S. Kang, *J. Power Sources* 181 (2008) 127–134.
- [21] S.G. Feng, Y.M. Shang, Y.Z.W. Wang, X.F. Xie, V.K. Mathurb, J.M. Xua, *J. Power Sources* 195 (2010) 2541–2548.
- [22] Y. Zhang, Y. Wan, C.J. Zhao, K. Shao, G. Zhang, H. Na, *Polymer* 50 (2009) 4471–4478.
- [23] Y. Zhang, Z.M. Cui, C.J. Zhao, K. Shao, H.T. Fu, T.Z. Li, H. Na, W. Xing, *J. Power Sources* 191 (2009) 253–258.
- [24] B.J. Liu, W. Hu, G.P. Robertson, M.D. Guiver, *J. Mater. Chem.* 18 (2008) 4675–4682.
- [25] C.H. Lee, H.B. Park, Y.S. Chung, Y.M. Lee, B.D. Freeman, *Macromolecules* 39 (2006) 755–764.
- [26] P. Gode, A. Hult, P. Jannasch, M. Johansson, L.E. Karlsson, G. Lindbergh, E. Malmstrom, D. Sandquist, *Solid State Ionics* 177 (2006) 787–794.
- [27] Shaobing Wu, Jon D. Jorgensen, Allen D. Skaja, Jonathan P. Williams, Mark D. Soucek, *Prog. Org. Coat.* 36 (1999) 21–33.
- [28] K.D. Kreuer, S.J. Paddison, E. Spohr, M. Schuster, *Chem. Rev.* 104 (2004) 4637–4678.
- [29] K.S. Lee, J.S. Lee, *Chem. Mater.* 18 (2006) 4519–4525.
- [30] J.H. Pang, H.B. Zhang, X.F. Li, Z.H. Jiang, *Macromolecules* 40 (2007) 9435–9442.
- [31] W. Li, A. Manthirama, M.D. Guiver, *J. Membr. Sci.* 362 (2010) 289–297.
- [32] B.P. Tripathi, V.K. Shahi, *J. Phys. Chem. B* 112 (2008) 15678–15690.
- [33] S.L. Zhong, X.J. Cui, S. Dou, W.C. Liu, *J. Power Sources* 195 (2010) 3990–3995.
- [34] H.D. Moore, T. Saitoab, M.A. Hickner, *J. Mater. Chem.* 20 (2010) 6316–6321.