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Novel side-chain-type sulfonated hydroxynaphthalene-based Poly(aryl ether ketone) with H-bonded for proton exchange membranes

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ABSTRACT

A series of novel side-chain-type sulfonated hydroxynaphthalene poly(aryl ether ketone)s (SHNPAEKs) containing hydroxyl groups was synthesized by post grafted method and the sulfonated degree (Ds) of the polymers could be well controlled. The resulting polymers were characterized by ^{1}H NMR, FT-IR and thermogravimetric analysis (TGA). Meanwhile, the membrane properties for fuel cell applications such as water uptake, proton conductivity and methanol transport have been studied. The influence of pendent structure and inter-/intramolecular H-bonded to the properties of SHNPAEKs has been investigated. The proton conductivities of SHNPAEK membranes showed a range of 0.020–0.197 S/cm and the highest conductivity of 0.197 S/cm was obtained for SHNPAEK-90 (IEC $= 2.08$ meq./g) at 80 °C. The methanol permeability of SHNPAEK membranes was in the range from 2.65×10^{-7} to 11.9×10^{-7} cm^2/s, which was much lower than that of Nafion 117.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs), electrochemical devices converting chemical energy into electric energy via redox reaction, have attracted more and more attention in the ubiquitous energy-dependent world due to low power-source emissions and high conversion efficiency [1–3]. In particular, proton exchange membranes (PEMs) which act as an electrolyte to transport protons from the anode to the cathode play a dominant role in this system. Perfluorosulfonic acid membranes such as Nafion (DuPont) have been recognized as the current choice for PEMs because of their high proton conductivity and excellent stability [4]. However, their disadvantages of high cost, low operation temperatures, and high methanol permeability have stimulated extensive research into the investigation of promising alternatives [5,6]. There is a great demand for fluorine-free materials with properties comparable to Nafion.

In recent years, many kinds of sulfonated aromatic polymers have been studied as the promising candidates for PEMs because of their low methanol permeability, excellent thermal and chemical stabilities [7–10]. However most of these sulfonated aromatic polymers formed bonds with sulfonic acid groups directly to the main chain, which showed less pronounced nanophase separation and more dead-end channels than that of Nafion [11]. It has been found that the nanophase separation between hydrophilic and hydrophobic domains could be improved, if the sulfonic acid groups were located onto the flexible pendant side chains, which made the hydrophilic sulfonic acid group regions separated from the hydrophobic polymer main chain [12–15]. And the microscopic phase separation is responsible for proton conduction and morphological stability. A variety of side-chain-type sulfonated polymers has been prepared by chemical grafting or direct copolymerization with novel monomers. Jannasch and co-workers have successfully attached flexible sulfoalkyl side chains to polysulfones, which carried 0.9 sulfopropyl chains per repeating unit and showed good proton conductivity at 70 °C under humidifying conditions [16]. Guiver's group synthesized comb-shaped poly(arylene ether sulfone)s containing two or four sulfonic acid groups on side-chain grafting units, resulting in effective water management and excellent proton conductivity in the range of 0.034–0.147 and 0.063–0.125 S/cm, respectively [17]. Watanabe et al. reported that a series of polyimide electrolytes with long pedant sulfonated groups showed improved oxidative and hydrolytic stability and high proton conductivity [18]. These polymers displayed advantageous conductivity and membrane hydrodynamic properties compared to most of main-chain-type sulfonated polymers.

Hydrogen bonded is a critical factor in determining the physical and mechanical properties of many polymeric materials [19]. It has

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been reported that inter- and intramolecular hydrogen-bonding interactions between sulfonic acid and hydroxyl groups have been used to improve the properties of PEMs [20–23]. In our previous report, a series of SPEEK/PHR (phenoxy resin) composite membranes, the SPEEK with hydroxyl group, was prepared. These composite membranes displayed an improvement of the mechanical and methanol resistant properties resulting from the interaction of hydrogen bonded [24].

In this study, we reported a novel sulfonated hydroxynaphthalene poly(aryl ether ketone)s (SHNPAEKs) containing both sulfonic acid on the side chain and hydroxyl groups in the structure. Dimethoxylnaphthalene poly(aryl ether ketone) (MNPAEKs) were first prepared via the nucleophilic aromatic substitution reactions, and then the dihydroxynaphthalene poly(aryl ether ketone)s (HNPAEKs) were obtained from the demethylation reactions. The different sulfonated degree (Ds) of SHNPAEKs was obtained by changing the ratio of 1,4-butane sultone which reacted with hydroxyl groups of HNPAEKs by the nucleophilic ring-opening reactions. Then, the properties of the side-chain-type sulfonated polymers were investigated as PEMs in detail, such as water uptake, proton conductivity, methanol permeability and mechanical properties. All the results demonstrated that SHNPAEKs is a promising candidate material for PEMFCs.

2. Experimental

2.1. Materials

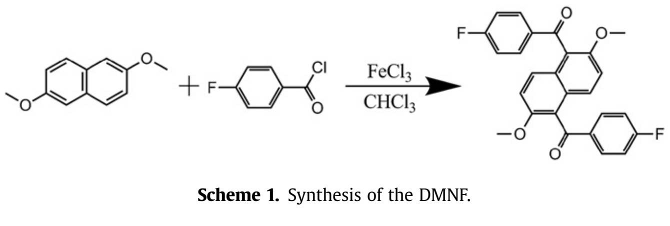
2,6-dimethoxylnaphthalene was obtained from Dalian Jinzhou Chemical. 4-fluorobenzoyl Chloride and 1,4-butane sultone were purchased from Sigma–Aldrich Ltd. Boron tribromide (BBr_3) and Bisphenol A were obtained from Beijing Chemical Reagents. *N*,*N*-dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), Dimethylacetamide (DMAc) 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-dimethoxynaphthalene (DMNF)

As shown in Scheme 1, the monomer DMNF was prepared following the procedure in our previously report [25]. A mixture of 2,6-dimethoxylnaphthalene (9.4 g, 0.05 mol) and 4-fluorobenzoyl chloride (17.4 g, 0.11 mol) in chloroform (300 mL) was stirred at 0–5 °C. Then 1.65 g anhydrous ferric chloride (0.01 mol) was added in small portions to the cold solution. The reaction was conducted at this temperature for 24 h. The resulting mixture was poured into cold hydrochloric acid and stirred for another 1 h. The product was removed by decantation and the brown solid was precipitated in methanol. The result precipitate was recrystallized twice from *N*,*N*-dimethylformamide (DMF)/water mixture (10:1 v/v).

Yield: 82%. ^1H NMR and ^{13}C NMR analyses (^1H NMR (500 MHz, DMSO-d_6): δ(ppm): 3.79 (m, 6H), 7.12 (t, $J = 8.56, 8.56$ Hz, 4H), 7.27 (d, $J = 8.77$ Hz, 2H), 7.63 (d, $J = 9.27$ Hz, 2H), 7.89 (dd, $J = 5.51, 8.66$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 57.04, 115.39, 116.33, 123.34, 127.41, 127.70, 132.77, 134.74, 153.17, 167.59, 196.23) confirmed the formation of monomer DMNF. Anal. Calcd for $C_{26}H_{18}F_2O_4$: C, 72.22; H, 4.20. Found: C, 72.25; H, 4.28. Mp (DSC): 262 °C.



Scheme 1. Synthesis of the DMNF.

2.3. Polymer synthesis

2.3.1. Polymerization of dimethoxylnaphthalene poly(aryl ether ketone) (MNPAEKs)

A 250 mL three-neck flask equipped with a mechanical stirrer, a Dean-Stark trap and a nitrogen inlet was charged with DMNF (8.65 g, 0.02 mol), Bisphenol A (4.56 g, 0.02 mol), K_2CO_3 (3.036 g, 0.022 mol), NMP (52 mL) and toluene (20 mL). The mixture was heated at 140 °C for about 3 h to remove water by azeotropic distillation with toluene, then slowly heated to 180 °C and maintained at that temperature for 6 h. When the increase of solution viscosity became obvious, the mixture was coagulated into a large excess of deionized water with vigorous stirring. The resulting fibrous polymer was washed thoroughly with water several times and dried under vacuum at 100 °C for 24 h.

2.3.2. Demethylation of MNPAEKs to dihydroxynaphthalene poly (aryl ether ketone)s (HNPAEKs)

MNPAEKs (1 g, 3.23 mmol methoxy groups) was dissolved in dry 10 mL CH_2Cl_2, and the solution was maintained at 0 °C (ice bath). A threefold excess (0.87 mL, 9.69 mmol) BBr_3 dissolved in 5 mL CH_2Cl_2 was added dropwise. The reaction mixture was stirred at room temperature under nitrogen for 12 h. When the temperature increased to reflux, the reaction proceeded for another 6 h. The mixture was poured into ice-water to hydrolyze the BBr_3 and the boron complexes, and then washed with methanol and deionized water thoroughly. The resulting polymers (HNPAEKs) dried under vacuum at 100 °C for 24 h.

2.3.3. Sulfobutylation of HNPAEKs to sulfonated hydroxynaphthalene Poly(aryl ether ketone) (SHNPAEK-xx)

The sulfobutylation experiment was illustrated by preparation of SHNPAEK-80. And herein, the sulfonation degree was defined as the molar ratio (%) of sulfonic acid converted from hydroxyl groups. In a three-neck flask, HNPAEK (1 g, 3.38 mmol hydroxy groups) was dissolved in 20 mL DMSO and NaOH (0.2 g, 5 mmol) was used to convert –OH groups into –ONa groups. The reaction mixture was stirred at room temperature for 6 h. 1,4-butane sultone (0.37 g, 2.704 mmol) was added dropwise and the reaction mixture was heated to 160 °C, stirred at this temperature for 12 h. The resulting sulfonated polymers were precipitated in acetone and washed by boiling water several times. The obtained polymer was immersed in a large excess of HCl (5 wt.%) solution over 24 h to make the salt form converted into the acid form. The product (SHNPAEK-80) was finally dried in a vacuum at 80 °C. For comparison, we also synthesized the SNPAEK-100 which converted all the –OH into $-SO_3H$.

2.4. Membrane preparation

Membranes were prepared by dissolving 1.0 g SHNPAEK-xx in DMAc (10 wt.%) casting the solution on glass plate and drying at 60 °C for 24 h. The membranes were then peeled off the substrates. To remove any excess of the solvent, the membranes were dried under vacuum at 80 °C for 48 h.

2.5. Polymer characterization

2.5.1. Measurements

^1H NMR spectra were conducted with a 500 MHz Bruker Avance 510 spectrometer at 298 K with deuterated dimethyl sulfoxide

(DMSO-d_6) as the solvent and tetramethylsilane (TMS) as the standard. FT-IR spectroscopy of dry membrane samples was recorded on the power samples dispersed in dry KBr in form of disks, using a BRUKER Vector 22 spectrometer at a resolution of 4 cm^{-1} min^{-1} from 4000 to 400 cm^{-1}. The TGA measurements were performed on a Pyris 1TGA (PerkinElmer) under a nitrogen atmosphere using a heating rate of 10 °C/min from 80 to 700 °C. The mechanical properties of the membranes were measured using SHIMADZU AG-I 1 KN at the speed of 2 mm/min. At least five samples (15 mm × 4 mm) were used for each measurement and their average value was calculated.

2.5.2. *Degree of sulfobutylation (Ds)*

The low-field signals (6.71–7.86 ppm) were characteristic resonances of the aromatic hydrogen atoms (H_{Ar}). The signal at 3.99 ppm was assigned to the hydrogen atoms (H_9) of the methylene groups ortho to the ether groups from the sulfobutylation. The Ds of the polymer was estimated by ^{1}H NMR [26,27] and calculated by the following equation:

$$\mathrm{Ds} = \frac{5\,A_{\mathrm{H9}}}{A_{\mathrm{HAr}}} \times 100\% \tag{1}$$

where A_{H9} is the peak area of H_9, A_{HAr} is the integral peak area of the signals corresponding to the aromatic hydrogen of the polymers.

2.5.3. *Ionic exchange capacity (IEC)*

IEC was measured as reported previously [28]. The theoretical IEC can be calculated from Ds with Eq. (2):

$$\mathrm{IEC} = \frac{2\,\mathrm{Ds} \times 1000}{592 + 2\,\mathrm{Ds} \times 136} \tag{2}$$

2.5.4. *Water uptake and swelling ratio*

Before testing water uptake and swelling ratio, the membranes were vacuum-dried at 100 °C until constant weight was obtained. The dried weight (W_{dry}) and length (L_{dry}) of membranes were measured. Then the dried samples were immersed in deionized water for 24 h at different temperatures. Then the samples were taken out and immediately measured (W_{wet}) and (L_{wet}) after wiping out the surface water. The water uptake was calculated using the expression:

$$\text{water uptake(WU)(\%)} = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \times 100\% \tag{3}$$

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

Swelling ratio of membranes was calculated with the following formula:

$$\text{swelling ratio(\%)} = \frac{L_{\mathrm{wet}} - L_{\mathrm{dry}}}{L_{\mathrm{dry}}} \times 100\% \tag{4}$$

where L_{dry} is the length of dried membrane and L_{wet} is the length of fully hydrated membranes.

2.5.5. *Proton conductivity*

The proton conductivity in water-equilibrated membranes was determined by a four-point probe alternating current impedance spectroscopy using an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287). A single cell with two pairs of gold-plate electrodes was mounted on a Teflon plate and immersed in distilled deionized water where the temperatures were controlled. The proton conductivity was calculated by the following equation:

$$\sigma = \frac{L}{R \times S} \tag{5}$$

where σ is the proton conductivity (S/cm), L is the distant between the two electrodes ($L = 1$ cm), R is the resistance value of the membrane and S is the cross-section area of the membrane (cm^2).

2.5.6. *Methanol permeability*

The Methanol permeability was measured by using a two-chamber glass diffusion cell, which was consisted of two identical compartments separated by the test membranes placed on a screw clamp. 10 M methanol solution was placed on one side of the cell and water was placed on the other side. Each chamber was stirred by a magnetic stirrer to ensure uniformity. The concentration of methanol was determined by using SHIMADZU GC-8A chromatograph. The methanol permeability was calculated as follows:

$$C_{\mathrm{B}}(t) = \frac{A}{V_{\mathrm{B}}}\frac{\mathrm{DK}}{L}C_{\mathrm{A}}(t - t_{\mathrm{o}}) \tag{6}$$

where A (cm^2) and L (cm) are the effective area and the thickness of membrane, respectively. V_{B} (mL) is the volume of diffusion reservoir. C_{A} and C_{B} (mol/L) are the methanol concentration in feed and in diffusion reservoir, respectively. DK (cm^2/s) is the methanol permeability.

3. Results and discussion

3.1. *Synthesis and characterization of the monomer and polymers*

The monomer DMNF was prepared via Friedel–Crafts acylation of 2,6-dimethoxylnaphthalene with 4-fluorobenzoyl chloride catalyzed by anhydrous ferric chloride. The synthetic route of DMNF is shown in Scheme 1. The molecular structure of DMNF was confirmed by ^{1}H NMR spectroscopy in DMSO-d_6. As shown in Fig. 1, the proton peak at 3.78 ppm (H_3) was assigned to the proton in methoxy groups. The proton peak in phenyl ring ortho to carbonyl group appeared at 7.89 ppm (H_2) which was attributed to the chemical shift by electron withdrawing effect. The ^{1}H NMR

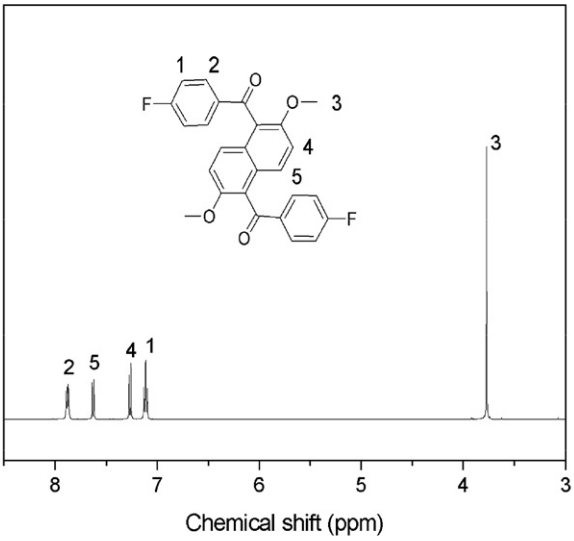
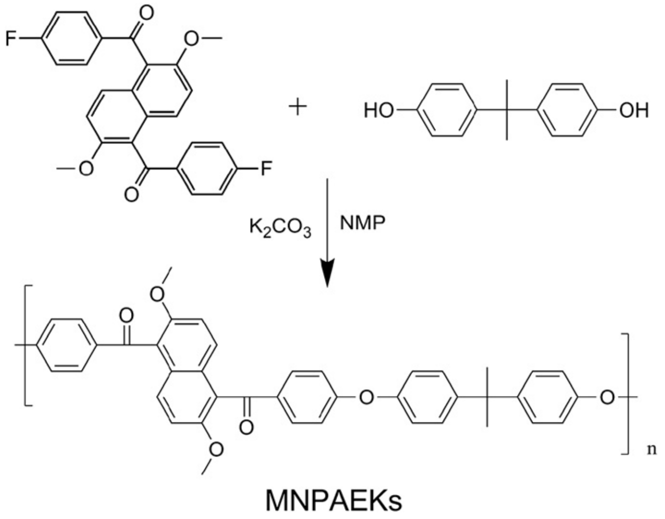


Fig. 1. ^{1}H NMR spectra of DMNF.

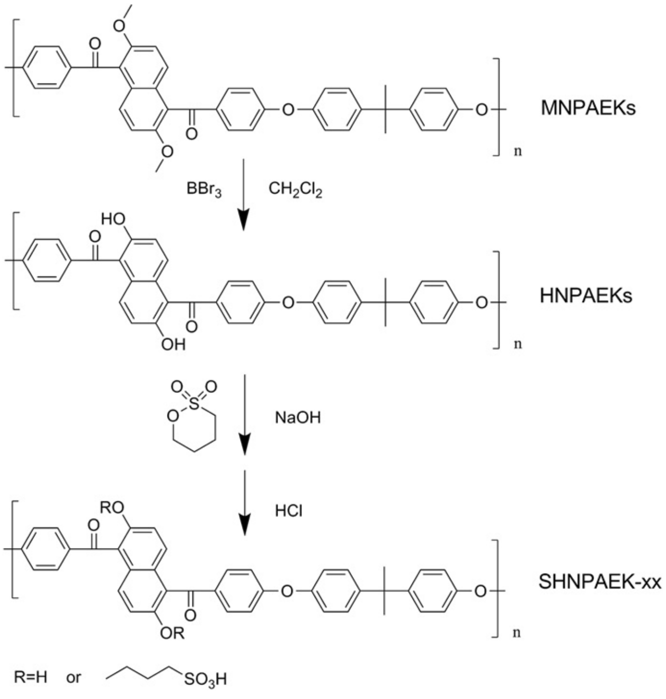


Scheme 2. Synthesis of the MNPAEK.

spectrum confirmed that dibenzoylation regioselectively occurred at lst- and 5th-positions of the naphthalene ring.

The MNPAEK were synthesized via polycondensation reactions (Scheme 2). The polymerization reactions took place smoothly as no evident cross-linking found even at >180 °C. The conversion of MNPAEKs to HNPAEKs was conducted in CH_2Cl_2 using BBr_3 and the resulted polymer precipitated from CH_2Cl_2 solvent due to the polar nature of $-OH$ group (Scheme 3). Fig. 2 provides the ^1H NMR spectra of MNPAEKs and HNPAEKs. The proton peaks at 3.78 ppm attributed to the hydrogen atom of $-OCH_3$ groups disappeared, while the proton peaks for the proton of $-OH$ groups were observed in the spectrum at about 9.8 ppm.

As shown in Scheme 3, the sulfobutyl groups can be grafted onto HNPAEKs by nucleophilic ring-opening reaction with the 1,4-butane sultone. A series of SHNPAEK-xx with different sulfonate and hydroxyl groups content was prepared by tuning up the amount of 1,4-butane sultone. The chemical structures of SHNPAEK-xx were confirmed by ^1H NMR and FT-IR. The ^1H NMR shows proton of $-OH$ group at 9.8 ppm (H_9) diminished, while the signals for the four middle methylene groups (peak H_9, H_{10}, H_{11}, and H_{12}) from sulfobutylation appear at lower frequencies (Fig. 3).



Scheme 3. Preparation of HNPAEK and SHNPAEK-xx.

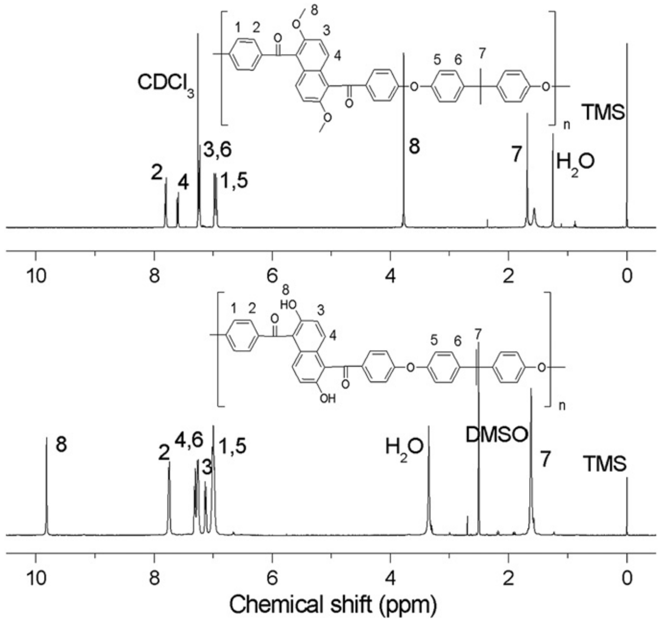


Fig. 2. ^1H NMR spectra of MNPAEK and HNPAEK.

Ds of the SHNPAEK-xx were quantitatively determined by the ^1H NMR spectrum and the results are listed in Table 2. The calculated Ds values from ^1H NMR spectra were almost the same as the expected Ds derived from the feed ratio. This result indicated that the sulfonic acid group was introduced to polymer by sulfobutylation reaction and the Ds values could be well controlled by adjusting the amount of 1,4-butane sultone.

Fig. 4 shows the FT-IR spectra of SNPAEK-100 and SHNPAEK-xx. Observed bands at 1246 and 1033 cm^{-1} were assigned to symmetric and asymmetric stretching vibrations of O=S=O. The infrared band at about 688 cm^{-1} can be assigned to the S–O stretching of sulfonated groups. The infrared band located at

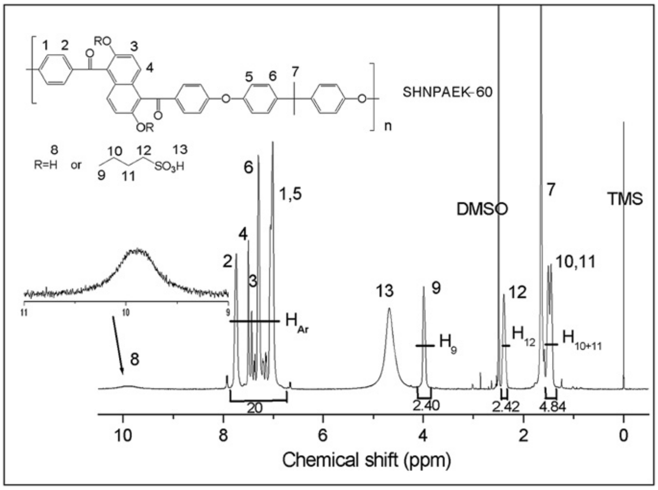


Fig. 3. ^1H NMR spectra of SHNPAEK-60.

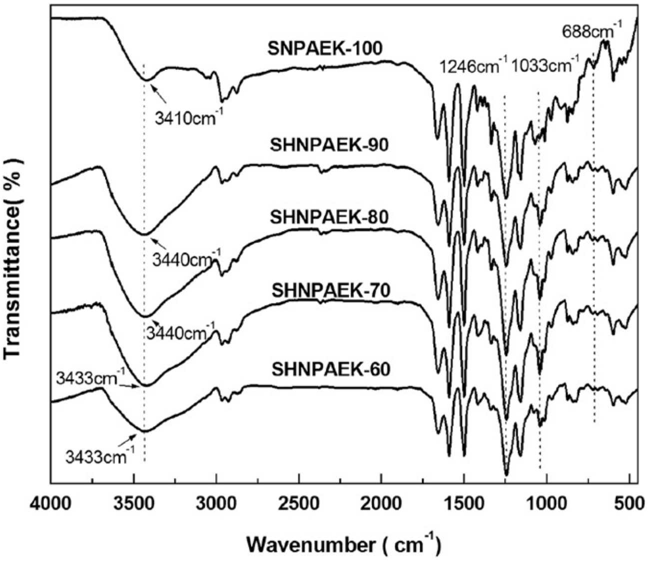


Fig. 4. FT-IR spectra of SHNPAEK-xx.

3440 cm^{-1} for SNPAEK-100 corresponded to the hydroxyl groups in water and hydronium ions that interact with the sulfonic group of the polymer less than 100% RH. It has reported that the infrared absorbance band corresponding to the O–H stretch broadens and strengthens in its intensity upon formation of the hydrogen bond [29]. For the SHNPAEK-xx, the broad band around 3440 cm^{-1} increased in its intensity, which can be attributed to the H-bond associated between the sulfonated acid groups and the residual hydroxyl groups (Fig. 5).

3.2. Thermal and mechanical properties

The thermal stabilities of the polymers were investigated by TGA measurement. Fig. 6 shows the TGA curves of SHNPAEK-xx. All the SHNPAEK-xx in acid form contained two step degradation patterns. The first degradation step observed around 228–300 °C was attributed to the splitting-off by sulfonic acid groups, located on the sulfobutylate groups. The second step started at about 460 °C corresponded to the main chain decomposition.

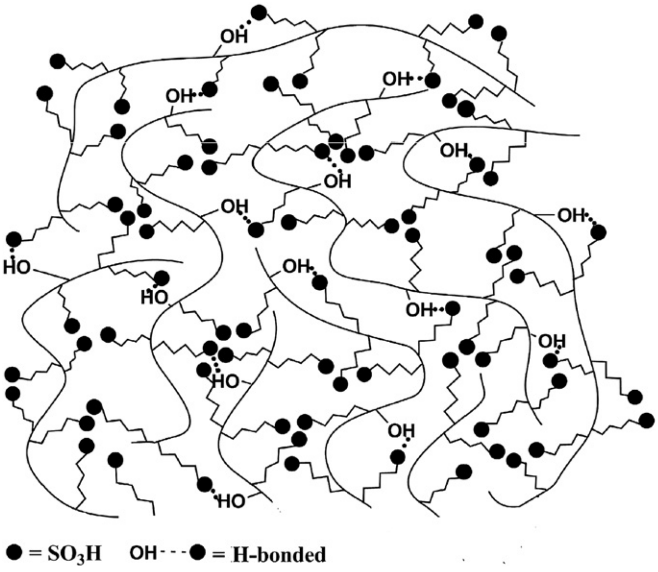


Fig. 5. Schematic illustration of the inter-/intramolecular H-bonded interactions.

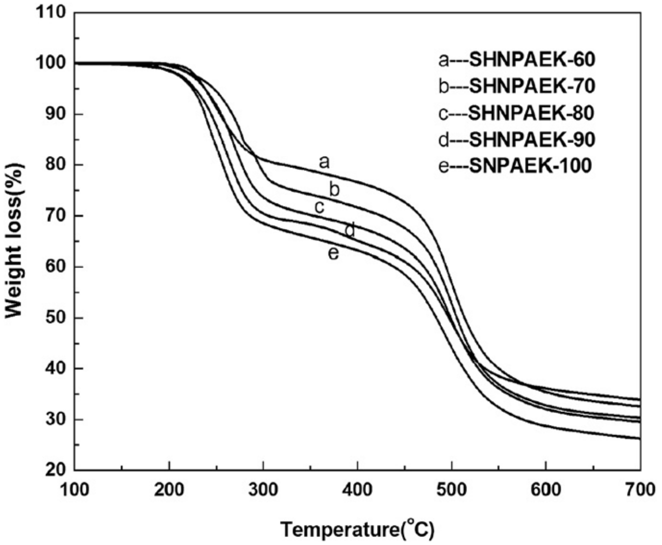


Fig. 6. TGA curves of SHNPAEK-xx polymers.

The mechanical properties of membranes were evaluated and listed in Table 1. The SHNPAEK series membranes had the tensile modules of 0.76–1.47 GPa, elongations at break of 10.13–17.07%, and tensile strength of 38.57–61.41 Mpa. These results indicated that the SHNPAEKs membranes were tough and ductile enough for potential use as PEMs materials.

3.3. IEC, water uptake and swelling of the SHNPAEKs membranes

The inoic exchange capacity (IEC), water uptake and swelling ratio of the SHNPAEK series films are summarized in Table 2.

It is constant for IEC which represented the amount of the exchangeable protons in ionomer membranes. The IEC values of these acid-form membranes were determined by classical acid–base titration. The experimental IEC values were in the range of 1.51–2.08 meq./g, which were in good agreement with the calculated IEC.

For most proton conductive polymers, proton can be transported in hydrogen bonded ionic channels, along with cationic mixtures in the water medium, such as H_3O^+, $H_5O_2^+$, and $H_9O_4^+$ [30,31]. Accordingly, suitable water content should be maintained in sulfonated polymer membranes to ensure high proton conductivity. However, excessively high levels of water in the membrane can result in unacceptable dimensional change or loss of dimensional shape, which will incur a dimensional mismatch or weakness between the electrode and the membrane in a membrane electrode assembly (MEA). Fig. 7 shows the water uptake of the SHNPAEK-xx membranes as a function of temperature. As expected, the water uptake of SHNPAEK-xx membranes had an increasing

Table 1
Thermal and mechanical properties.

Samples	$T_{d5\%}$[a] (°C)	$T_{d10\%}$[b] (°C)	Tensile strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)
SHNPAEK-60	240	254	61.41	1.47	12.52
SHNPAEK-70	249	267	49.68	1.07	10.13
SHNPAEK-80	240	254	43.12	0.89	17.07
SHNPAEK-90	228	244	38.57	0.76	11.03
SNPAEK-100	226	239	31.28	0.31	19.35

[a] Temperature of 5% weight loss.

[b] Temperature of 10% weight loss.

Table 2
Properties of the SHNPAEK-xx Membranes.

Samples	Ds[a]	Cal.IEC (meq./g)[b]	Exp.IEC (meq./g)[c]	Methanol permeability (cm^2/s) × 10^{-7}	Proton conductivity (S/cm)		Water uptake (%)		Swelling ratio (%)	
					25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
SHNPAEK-60	0.60	1.59	1.51	2.65	0.020	0.054	21.52	28.52	5.15	8.71
SHNPAEK-70	0.71	1.81	1.75	7.51	0.044	0.128	31.14	49.14	7.39	12.77
SHNPAEK-80	0.81	1.99	1.94	9.03	0.057	0.161	44.65	68.83	8.71	16.45
SHNPAEK-90	0.89	2.13	2.08	11.9	0.067	0.197	53.32	86.41	10.12	21.22
SNPAEK-100	0.99	2.30	2.28	17.2	0.123	0.270	79.15	104.42	21.23	36.92

[a] Determined from equation (1).
[b] Determined from equation (2).
[c] Determined by titration.

tendency with increasing of sulfonate contents at a given temperature. For example, SHNPAEK-80 and SHNPAEK-90 exhibited the value of water uptake with 68.83% and 86.41% at 80 °C, respectively. The comparatively high water uptake of the membranes, due to their high Ds, could be responsible for bringing hydrophilic ionic clusters from segregated to continuous.

The swelling of SHNPAEK-xx membranes are displayed in Fig. 8. We can see that the swelling of ionomer membranes increased along with the increment of IEC. Though the SHNPAEKs hold high Ds, the swelling of the membranes are still acceptable, which are in the range of 5.15–21.22%. SHNPAEK-90 with the IEC of 2.08 meq./g, showed the swelling ratio of 21.22% at 80 °C, which was much lower than the other kinds of SPAEKs with similar or even low IEC values. For instance, the IEC of SPAEEKK-B90 was 1.59 meq./g but the swelling ratio reached 46.50% [32]. SHNPAEK-xx membranes show excellent resistance to swelling which could result from the unique morphological structure of the side-chain-type sulfonated polymer locating the sulfonic acid units on the flexible side chains which would be helpful to separate the hydrophobic and hydrophilic domain. This separation could serve to maintain both the structure and dimensional stability of the material [25]. Also the highly rigidity of the naphthalene groups in main chain made the orientation of polymer chain difficult, which was helpful to maintain the dimensional shapes [33,34]. Besides, the inter-/intramolecular hydrogen bonded could restrict the mobility of the ionic clusters, which could help to maintain the dimensional stability [35]. Compared with SHNPAEK-xx, the SNPAEK-100 without remained -OH showed much bigger swelling ratio. For instance, the swelling ratio of SNPAEK-100 and SHNPAEK-90 were 21.23% and 10.12% at 25 °C, respectively. It worth noticed that the swelling ratio of SHNPAEK-xx increased rapidly when temperature rose above 60 °C. This may due to the weakening or even disassociation of the H-bonded at elevated temperature [29,36].

3.4. Proton conductivities and methanol permeability

The proton conductivities of SHNPAEK-xx polymers were measured at 100% RH and plotted as functions of temperature in Fig. 9. Compared to the main-chain-type SPAEKs, SHNPAEKs attaching the sulfonic groups on pendants could lead the hydrophilic/hydrophobic separation more obvious thus enhancing the proton conductivity of the ionomers. When IEC value increased from 1.51 to 2.08 meq./g, the proton conductivity increased from 0.054 to 0.197 S/cm at 80 °C, which was suitable for practical application as PEMs in fuel cell. It has been found that SHNKAEK-60 exhibited proton conductivity of 0.054 S/cm at 80 °C but SHNPAEK-90 reached 0.197 S/cm at the same temperature. It resulted from that the higher sulfonate content was, the bigger the hydrophilic ionic cluster became in size. At the same time, with the decreasing of the −OH group content, the sulfonate groups bound by hydrogen bonding were released to help forming the ionic network.

Membranes intending for direct methanol fuel cell (DMFC) must both possess high proton conductivity and be an effective barrier for methanol crossover from the anode to the cathode compartment. It has been reported that methanol is transported by diffusion in the membrane and by convection with the water flux [37]. So, the methanol permeability increases with increasing water

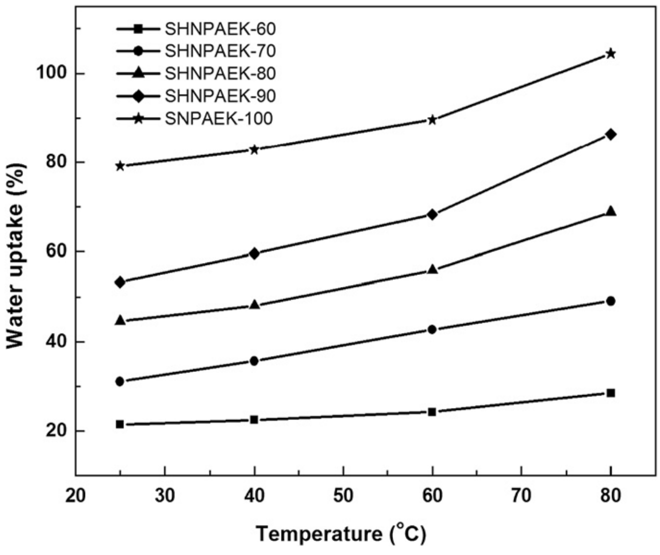


Fig. 7. Water uptake of SHNPAEK-xx membranes.

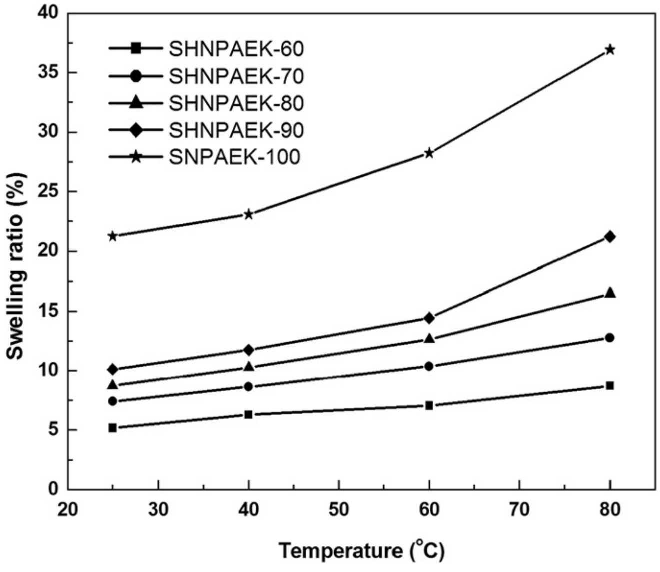


Fig. 8. Swelling ratio of SHNPAEK-xx membranes.

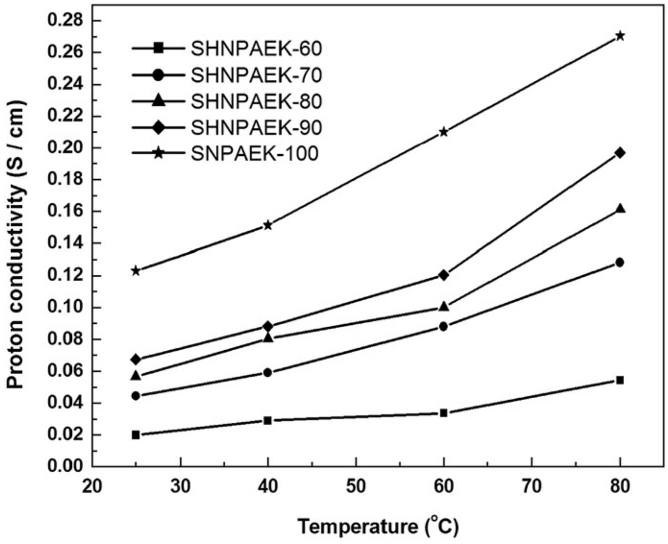


Fig. 9. Proton conductivity of SHNPAEK-xx membranes.

content, and therefore with the Ds. But the influence of the membrane dimensional stability on the methanol permeability should also be taken into account [38]. The methanol permeability of the SHNPAEK series membranes at room temperature is shown in Table 2. The methanol permeabilities of SHNPAEKs were in the range of 2.65×10^{-7} to 11.9×10^{-7} cm^2/s, which were lower than the value of Nafion 117 (1.61×10^{-6} cm^2/s). On the other hand, the methanol permeability of SNPAEK-100 was 17.2×10^{-7} cm^2/s. The high methanol permeability may due to the excess water uptake and swelling ratio.

4. Conclusions

A series of novel side-chain-type sulfonated hydroxynaphthalene-based poly(aryl ether ketone) (SHNPAEKs) with H-bonded was successfully synthesized. The side chain structures of the polymer were responsible for the high proton conductivity, while the H-bonded structures were accountable for excellent dimensional stability and methanol resistant properties. For example, SHNPAEK-80 and SHNPAEK-90 exhibited high proton conductivity of 0.161 S/cm and 0.197 S/cm at 80 °C, respectively. Also, the SHNPAEK-xx exhibited the good methanol resistant properties which were in the range of 2.65×10^{-7} to 11.9×10^{-7} cm^2/s. Therefore, the SHNPAEK-xx membranes exhibited low methanol permeability, lower water swelling, and high proton conductivity and could be the promising materials for DMFC applications.

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