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ARTICLE TYPE

Novel Side-chain-type Sulfonated Diphenyl-based Poly(arylene ether sulfone)s with Hydrogen-bonded Network as Proton Exchange Membranes

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A new bisphenol monomer, 3,3',5,5'-tetramethoxy -4,4`-dihydroxybiphenyl, was synthesized and copolymerized to prepare diphenyl-based poly(arylene ether sulfone) copolymers containing tetra-methoxy groups (MOPAES). After converting the methoxy group to the reactive hydroxyl group, the resulting side-chain-type sulfonated copolymers (SOPAES) with hydrogen bonded network were obtained by a sulfobutylation reaction. The copolymers were characterized and confirmed by ^{1}H NMR, FT-IR, thermogravimetric analysis (TGA) and small-angle X-ray scattering. The water uptake, proton and methanol transport properties of the resulted membranes were also determined for fuel cell applications. These SOPAES series membranes showed high proton conductivity in the range of 0.032-0.054 and 0.084-0.142 S/cm at 25 and 80 °C under hydrated conditions, respectively. SOPAES-40 (IEC = 1.38mequiv/g) showed comparable proton conductivity with Nafion 117 in the hydrated state. The methanol permeability of these membranes was in the range of $1.58 - 4.29\times10^{-7}$ cm^2/s, which is much lower than Nafion (1.55×10^{-6} cm^2/s). It should be noted that the intra/inter hydrogen bonds formed between sulfonic acid and hydroxyl groups or between hydroxyl and hydroxyl groups improved the mechanical properties and reduced the methanol permeability of the membranes effectively. A combination of suitable proton conductivities, low water uptake, and low methanol crossover for selected SOPAES indicates that they are good candidates as the proton exchange membrane materials for fuel cells.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs), especially direct methanol fuel cells (DMFCs) are considered as the ideal power sources for mobile and portable devices due to their high energy density, conversion efficiency, convenient fuel supply, quick start times and zero emissions levels.[1-4] As a solid electrolyte, PEMs not only conduct protons from the anode to the cathode, but also provide a barrier to the fuel cross-leaks between the electrodes. Currently, perfluorinated sulfonic acid (PFSA) copolymers such as Nafion (produced by Dupont) are the commercial PEM materials in DMFCs due to their high proton conductivities, excellent mechanical and chemical properties.[5-6] However, the low glass-transition temperature (ca. 110 °C) of these ionomers limited their operating temperature (below 80 °C). Furthermore, their high methanol/gas crossover, difficult synthesis procedures and high cost are perceived as critical drawbacks for commercial applications. Hence, aromatic hydrocarbon polymers have been developed as alternative PEM materials.[7-9]

The most widely reported aromatic PEMs materials, such as sulfonated derivatives of poly(arylene ether ketone),[10, 11] poly(arylene ether sulfone) (PAES),[12, 13] polyethersulfone,[14–15] polyimides [16, 17] and polybenzimidazoles, [18, 19] are a class of high-performance engineering thermoplastic materials. Generally, when the temperatures are higher than the percolation threshold, most of these sulfonated polymers suffer from excessive swelling, high methanol permeability, and couldn't afford enough mechanical strength.[20–22] *Kreuer* has reported that the main-chain-type sulfonated polymers show less nano-phase separation between hydrophilic sulfonic acid groups and hydrophobic polymer main chains than Nafion membrane.[21] Compared to the main-chain-type polymers, the side-chain-type sulfonated polymers have structural similarities to Nafion and it has been proved that the nano-scale separation morphology of the hydrophobic/hydrophilic domains is favourable for PEMs to achieve high conductivity at low ionic exchange capacity (IEC).[23-25] *Guiver et al.* reported fluorine-based poly(aryl ether sulfone)s containing four alkylsulfonic acid groups in each hydrophilic unit. The highest conductivity of 0.365 S/cm was obtained for these copolymers in the hydrated state at 80 °C.[26] In our previous report, a series of sulfonated naphthalene-based poly(aryl ether ketone)s (SNPAEKs) containing two pendant sulfoalkyl groups in each hydrophilic unit were prepared. The highest conductivity of 0.179 S/cm was obtained for these copolymers (IEC = 1.82 mequiv/g) in a hydrated state at 80 °C, which is higher than that of Nafion 117 (0.146 S/cm).[27]

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Unfortunately, these side-chain-type sulfonated PEMs become more swollen and gradually lose mechanical strength with the increasing number of acidic groups. To overcome this problem, cross-linking has attracted much attention due to the formation of dense cross-linking network structure. Especially, cross-linking by hydrogen bonding was recognized as one of the most effective strategies.[28, 29] Hydrogen bonding plays an important role in determining the physical and mechanical properties of many polymeric materials [30]. It has been reported that inter/intra hydrogen bonding interactions between sulfonic acid and hydroxyl groups show great potential to improve the properties of PEMs.[31, 32] In our previous work, a series of sulfonated poly (arylene ether ketone) bearing both sulfonic acids on the side chain and residual hydroxyl groups on the main chain were prepared. The flexible long alkyl sulfonated side chains are responsible for the high proton conductivity, while the hydrogen-bonded networks formed by inter- and intra-molecular hydrogen-bonding interactions are accountable for the excellent dimensional stability and methanol resistant properties. Therefore, the resulted membranes with hydrogen bonds showed low methanol permeability, lower water swelling, and high proton conductivity, which is advantageous to be used as a PEM in a DMFC. However, the synthesis process to achieve such polymers with a unique naphthalene moiety is complicated and difficult. The molecular design for the sulfonated polymers is still a big challenge for PEMs with optimized performances.

Herein, we present a study of novel poly(arylene ether sulfone) copolymers containing both two pendent butylsulfonic groups and two hydroxyl groups per repeat unit along the main chain. Poly (arylene ether sulfone) copolymers containing four methoxy groups per repeat unit were firstly prepared from on a novel diphenyl-based bisphenol monomer (Scheme 1), and then the methoxy groups were converted to reactive hydroxyl groups, which partial reacted with 1,4-butanesultone to achieve sulfonated copolymers bearing sulfobutyl side chains and residual hydroxyl groups. The hydrogen-bonded network could be formed between the sulfonic acid and hydroxyl groups or between the hydroxyl and hydroxyl groups. The small angle X-ray scattering (SAXS) demonstrated the existence of hydrophilic/hydrophobic microphase separation morphology in the membranes, thus resulting in a suitable proton conductivity at moderate IEC. Moreover, the intra/inter hydrogen-bonded network effectively reduce the water uptake and swelling ratio and improve the mechanical stability of the membranes. All the properties tested of these membranes showed that they are suitable for DMFC applications.

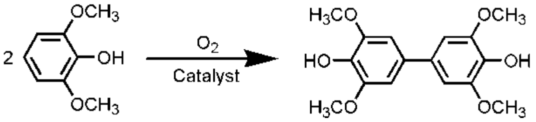
Experimental

Materials

2,6-Dimethoxyphenol, sodium dodecyl sulphate (SDS), hydrochloric acid (5 mol/L), 2,2-bis(4-hydroxyphenyl) propane (BPA), 1,4-butanesultone, and bis(4-fluorophenyl) sulfone were purchased from Sigma-Aldrich. *N*-Methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), ethyl alcohol absolute and boron tribromide (BBr_3) were purchase from TCI chemical company. All other solvents and reagents were reagent grade and were used as received.

Synthesis of 3,3',5,5'-tetramethoxy -4,4`-dihydroxybiphenyl (TMOBP)

SDS (0.20 g), 2,6- dimethoxyphenol (15.42 g ,0.1 mol), copper(I) chloride and H_2O (80 mL) were introduced into a 250 mL three-necked round-bottom flask, equipped with a reflux condenser, a magnetic stirrer, an oxygen inlet and a thermometer. The reaction mixture was stirred at 70 °C for 30 min and then let oxygen in. The temperate was kept at 70 °C and the oxygen rate was set at 10 mL/min for 4~6 h. When the mixture became reddish-brown oily droplets, a portion of 10 mL of 5 mol/L hydrochloric acid was added dropwise in 10 min, and then the reaction mixture became solid. When it was cooled down and transferred into cold water, the red solid product was obtained by filtration and washed with deionized water several times. The obtained red solid was dried and the crude product was recrystallized from absolute ethanol twice to afford 10.54 g (*yield: 78%*) of pure light-yellow crystalline 3,3',5,5'-tetramethoxy - 4,4`-dihydroxybiphenyl , mp: 189-192 °C. ^1H NMR (*500MHz, DMSO-d_6; ppm*): 8.34 (*2H, -OH*), 6.83 (*a, 4H, H_a*), 3.53 (*12H, -OCH_3*).



Scheme 1 Synthesis of the Monomer TMOBP.

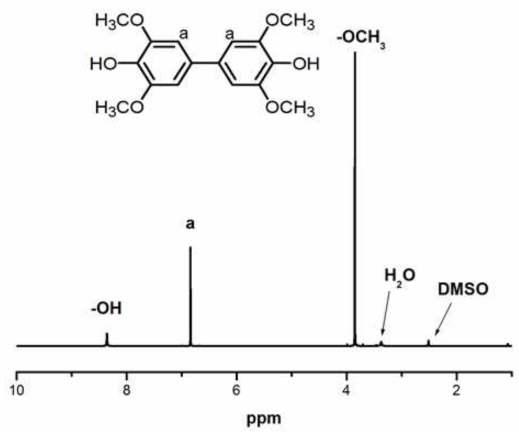


Fig. 1 ^1H NMR spectrum of bisphenol monomer TMOBP.

Synthesis of Poly(arylene ether sulfone)s Containing Methoxy Groups (MOPAES-xx)

A typical synthetic procedure, illustrated by the preparation of MOPAES-35 copolymer (TMOBP/ BPA = 35:65), is described as follows (Scheme 2). Samples of TMOBP (4.60 g ,9.9 mmol), BPA(3.42 g, 20.1 mmol), bis(4-fluorophenyl) sulfone (7.63 g ,30 mmol), K_2CO_3 (4.56 g, 33 mmol), DMSO (40 mL) and toluene (18 mL) were added into a 250 mL three-neck flask equipped with a mechanical stirrer, a dean stark trap, and a nitrogen inlet/outlet. The solution was allowed to reflux at 140 °C, while the water was azeotropically removed from the reaction mixture. After 4 h, the toluene was removed from the reaction by slowly

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increasing the temperature to 170 °C, and then the reaction was allowed to continue for another 2~3 h. When the viscosity was observed to increase dramatically, the mixture was slowly poured into 1000 mL deionized water. The resulting fibrous copolymer was washed with hot water several times and dried under vacuum at 80 °C for 24 h to give MOPAES-35.

Conversion of Methoxy Groups (MOPAES-xx) to Hydroxyl Groups (HOPAES-xx)

The methoxy groups in the copolymers were converted into hydroxyl functionalities according to a similar procedure previously reported.[27] A sample of MOPAES-35 (2.0 g) was dissolved into $CHCl_3$ (50 mL) in a 100 mL three-neck flask equipped with a mechanical stirrer and a nitrogen inlet. BBr_3 (2 mL) was mixed with CH_2Cl_2 (20 mL), and the resulting solution was added dropwise to the MOPAES-35 solution at 0°C (ice bath). After 24 h, the resulting copolymer (HOPAES-35) was filtered, washed with boiling water, recovered, and then dried under vacuum at 80 °C for 24 h.

Preparation of Sulfonated Copolymer (SOPAES-xx)

Samples of HOPAES-35 (2.0 g) and NaOH (0.42 g) were dissolved into 30 mL of DMSO at room temperature and stirred for 10 min under nitrogen atmosphere. Then 2mL of 1,4-butanesultone was added, and the reaction was heated to 100 °C for another 10 h. The viscous solution was precipitated into 200 mL of acetone and washed with boiling water several times. The polymer was dried in vacuum at 50 °C for 12 h to obtain SOPAES-35.

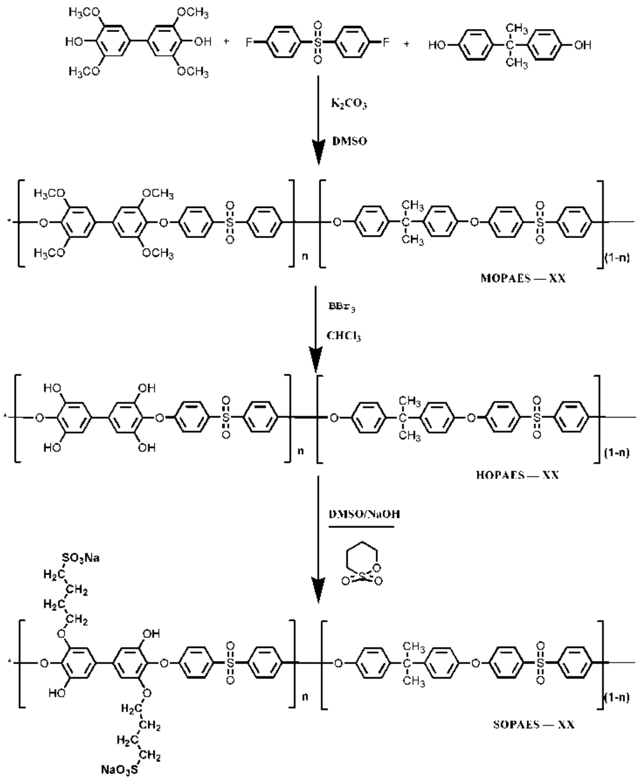
Membrane preparation

The membranes were prepared by casting from a 10 wt.% sulfonated copolymer solution in NMP onto glass plates and dried at 60 °C for 10 h. To remove any excess of the solvent, the membranes were dried under vacuum at 80 °C for 24 h. The acidification of the membranes was performed by immersing the membranes into 1 M HCl solution for 24 h and washed with deionized water to remove residual acid. The dry acid form membranes were obtained by drying at 80 °C for 12 h and the thickness was in the range of 70–90 µm.

Characterization and measurements

Chemical structure, thermal and mechanical properties of the membranes

^1H NMR spectrum was conducted with a 500MHz Bruker Avance 510 spectrometer using DMSO-d_6 as solvent and tetramethylsilane (TMS) as standard. The thermogravimetric analysis (TGA) measurements were performed on Perkin–Elmer in a nitrogen atmosphere using a heating rate of 10 °C/min from 80 °C to 700 °C. 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 Fourier-transform infrared spectrometer at a resolution of 4 cm^{-1}. The solubility of the SOPAES-xx membranes was evaluated by immersing the membranes into several organic solvents at room temperature for 1 h. The mechanical properties of the dry membranes were measured at room temperature on SHIMADZU AG-I 1 KN at a strain rate of 2 mm/min. At least five samples (15 mm×4 mm) were used for each measurement and their average values were calculated.



Scheme 2 Synthesis of copolymers MOPAES-xx, HOPAES-xx, and SOPAES-xx.

Ionic exchange capacity

The IEC values of these membranes were determined by classical acid–base titration. The dried membrane (acid form) was weighed and immersed in 1 M NaCl solutions for 24 h to replace the protons of sulfonic acid groups with sodium ions. The H^+ ions in solution were then titrated with 0.01 M NaOH using phenolphthalein as indicator. The IEC (mequiv/g) values were calculated from the titration results:

$$\mathrm{IEC} = \frac{\text{consumed NaOH(ml)}\times\text{molarity NaOH}}{\text{weight of dry membrane}} \qquad (1)$$

where V_{NaOH} (mL) is the consumed volume of NaOH, C_{NaOH} (mol/L) is the molarity of NaOH and W_{dry} (g) is the weight of dry membranes.

Water uptake and swelling ratio

Before the equilibrium water uptake and swelling ratio was measured, the membranes were vacuum-dried at 100 °C until constant weights were obtained. The weight (W_{dry}) and length (L_{dry}) of dry membranes were measured and immersed the dried

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samples in deionized water for 24 h at different temperatures. After that, the samples were took out and wiped out the surface water immediately and then measured the weight (W_{wet}) and the length (L_{wet}). The water uptake was calculated using the expression:

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (2)$$

where W_{wet} and W_{dry} are the weights of the membrane in wet and dry state. The swelling ratio was calculated from the change of membrane thickness by:

$$SW(\%) = \frac{D_{wet} - D_{dry}}{D_{dry}} \times 100\% \qquad (3)$$

where D_{wet} and D_{dry} are the thicknesses of the wet and dry membranes respectively.

Proton Conductivity

The proton conductivity was measured by a four-electrode AC impedance method from 0.1 Hz to 100 KHz with 10 mV AC perturbations and 0.0 V DC rest voltage using a Princeton Applied Research 2273 potentiostat/galvanostat/FRA. The membranes (4 cm × 1 cm) were dipped in deionized water 24 h before analysis. A sheet of membrane was placed in the test cell, which was immersed in water with 100% relative humidity at desired temperature ranging from 25 ^{o}C to 80 ^{o}C. The proton conductivity was calculated by the following equation:

$$\sigma = \frac{L}{RS} \qquad (4)$$

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

Methanol permeability

The methanol permeability was determined by using a two-chamber glass diffusion cell, which was consisted of two identical compartments separated by the test membranes. 10 M methanol solution was placed on one side of the diffusion 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 measured by using SHIMADZU GC-8A chromatograph. The methanol permeability was calculated as follows:

$$C_B(t) = \frac{A}{V_R}\frac{DK}{L}C_A(t-t_0) \qquad (5)$$

where A (cm^2) and L (cm) are the effective area and the thickness of membrane, respectively. V_R (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.

Small-angle X-ray scattering

SAXS measurements were carried out on the membranes ion-exchanged to the Ag$^+$ form by immersion in a 1 wt.% aqueous solution of silver nitrate.[34] The Small-angle X-ray scattering system was equipped with sealed tube X-ray generator (SAXSess mc^2) and the wavelength (λ) is 0.1542 nm. Hydrated membranes were analyzed in a solid sample holder at room temperature. The scattering vector q (nm^{-1}) was calculated by the following equation:

$$q = \frac{4\pi \sin\theta}{\lambda} \qquad (6)$$

where θ is the scattering angle, the characteristic separation length d (nm), the Bragg spacing was calculated using:

$$d = \frac{2\pi}{q} \qquad (7)$$

Results and discussion

Synthesis and Characterization of Monomer and Copolymers

The monomer TMOBP was prepared by CuCl$_2$ solution catalyzed oxidative-coupling reaction of 2,6-dimethoxyphenol with O$_2$. The reaction procedure is depicted in Scheme 1. The structure of TMOBP was confirmed by ^{1}H NMR spectroscopy in DMSO-d_6. As shown in Fig.1, the -OH signal appeared at 8.34 *ppm*, and the proton peak at 3.78 *ppm* was assigned to the proton in methoxy groups ($-OCH_3$). The clear peak of aromatic protons H_a confirmed the diphenyl structure of the new monomer TMOBP.

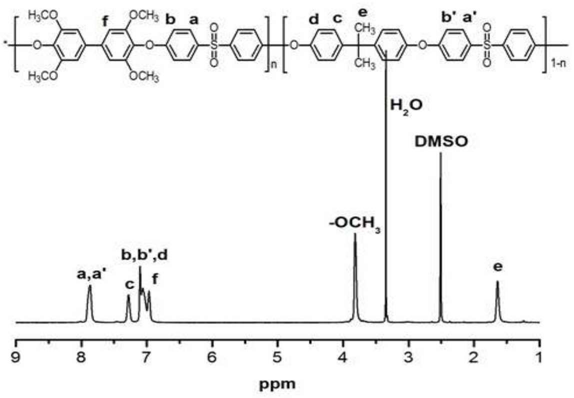

Fig. 2 ^{1}H NMR spectrum of the MOPAES-35 (-OCH$_3$).

Also, as shown in Scheme 2, the diphenyl-based poly(arylene ether sulfone) copolymers containing methoxy groups (MOPAES-xx, xx: mole ratio of TMOBP) were synthesized by polycondensation using various feed ratios of TMOBP/BPA. The polymerization reactions took place smoothly as no evident cross-linking found even at >180 ^{o}C. Then, the demethylation of MOPAES-xx to the reactive hydroxyl-containing HOPAES-xx for chemical grafting was conducted at room temperature in dichloromethane using BBr$_3$. Although the MOPAES-xx copolymers were readily soluble in chloroform, the resulting HOPAES copolymers were insoluble and precipitated during the reaction due to the polar nature of phenolic hydroxyl groups. Fig.2 and Fig.3 provide the representative ^{1}H NMR spectra of MOPAES-35 and HOPAES-35. The proton peaks at 3.78 *ppm* attributing to the hydrogen atom of -OCH$_3$ groups disappeared,

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while the proton peaks for the proton of -OH groups were observed in the spectrum of HOPAES-35 at about 9.8 *ppm*. The results indicated that the demethylation reaction was completely preceded.

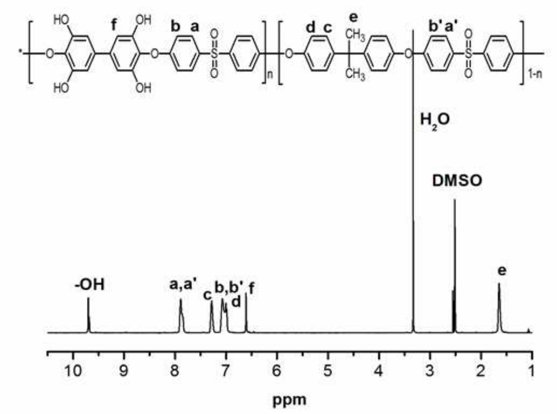

Fig.3 The ^{1}H NMR spectrum of the HOPAES-35 (-OH) copolymer.

The hydrogen bond is one of the important factors that affect the mechanical properties of polymer materials. Researchers have blended Nafion and other sulfonated polymer containing the hydroxyl groups to prepare the composite proton exchange membranes. It was observed that the intra/inter hydrogen-bond formed by sulfonic acid / hydroxyl or hydroxyl / hydroxyl improved the mechanical properties of the membranes and reduced the methanol permeability effectively.[29] In the present work, the sulfobutyl side chains were proposed to graft onto HOPAES copolymers by a nucleophilic ring opening reaction with 1,4-butanesultone in the presence of NaOH. However, because the steric hindrance of the diphenyl ring would prevent the rotational freedom of the bulky sulfobutyl groups, only one of the two hydroxyl groups on the benzene-ring has the ability of nucleophilic ring-opening reaction with 1,4-butanesultone.

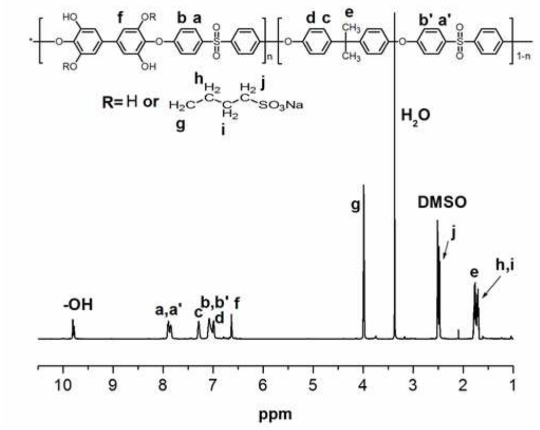

Fig.4 The ^{1}H NMR spectrum of SOPAES-35.

A series of SOPAES copolymers containing both sulfobutyl groups and residual hydroxyl groups were obtained by tuning the -OH contents in HOPAES-xx copolymers. The chemical structures of SOPAES-xx were confirmed by ^{1}H NMR spectra. As expected, the ^{1}H NMR spectrum showed the proton of the four middle methylene groups (peaks H_g, H_h, H_i, and H_j) from sulfobutylation appeared at lower frequencies (Fig. 4). Due to the steric hindrance of the diphenyl ring, the proton of –OH (9.8 *ppm*) was still observed as a broad multiple. Furthermore, the integrated area ratio of –OH to H_j was calculated as 1:2, which demonstrated that only two of the four hydroxyl groups in the diphenyl structure has the ability of nucleophilic ring-opening reaction with 1,4-butanesultone.

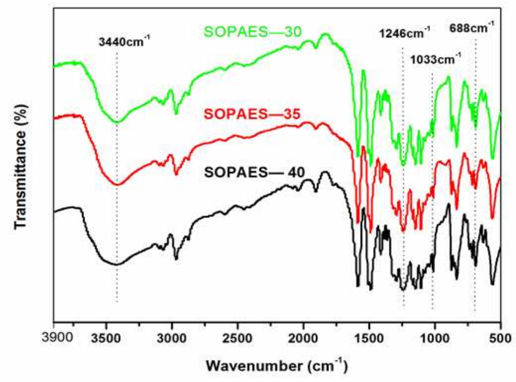

Fig. 5 FT-IR spectra of SOPAES-xx.

Fig.5 shows the FT-IR spectra of SOPAES-xx with different sulfonated degrees. The observed bands at 1246 and 1033 cm^{-1} were assigned to the symmetric and asymmetric stretching vibrations of O=S=O. The infrared band at about 688 cm^{-1} was assigned to the S-O stretching of sulfonated groups. The infrared band located at 3440 cm^{-1} for SOPAES-xx corresponded to the hydroxyl groups which interact with the sulfonic group of the polymer. 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 [35, 36]. For the SOPAES-xx, the broad band around 3440 cm^{-1} increased in its intensity, which can be attributed to the H-bond associated between the sulfonic acid groups and the residual hydroxyl groups.

3.2 Thermal and Mechanical Properties

The thermal stabilities of the polymers were investigated by TGA, and their 5 wt.% weight loss temperatures are listed in Table 2. Fig.6 shows the TGA curves of SOPAES-xx in the sulfonic acid form, which appear to have two distinct degradation steps. The initial degradation step observed at around 284–325 ^{o}C is likely associated with the thermal degradation of the sulfobutyl groups, while the second steps starting at about 450 ^{o}C correspond to the remainder of the polymer. The results showed that the thermal behavior of both MOPAES-30 and HOPAES-30 copolymers was mainly affected by hydroxyl content as the T_d increased with increasing hydroxyl content of copolymers. Both MOPAES-30 and HOPAES-30 copolymers showed excellent thermal stability (decomposition temperatures > 400 ^{o}C). After tethering the sulfo-butyl side chain, the thermal decomposition temperatures (T_d) decreased from 324.46 ^{o}C to 283.68 ^{o}C with the content of TMOBP increasing from 0.30 to 0.40, but it didn't exhibit a dramatic change because of the existence of –OH groups and biphenyl moiety in the main chain as shown in Fig. 4. First, as shown in Table 1, the –OH level of SOPAES-xx

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increased from 1.06 mequiv/g to 1.36 mequiv/g with the content of TMOBP increasing from 0.30 to 0.40. These –OH groups provided sufficient hydrogen-bonded cross-linking network to improve their thermal stabilities. Second, the biphenyl moiety content of SOPAES-xx also increased the rigidity of copolymer chains. These two factors improved the thermal stabilities of the SOPAES.

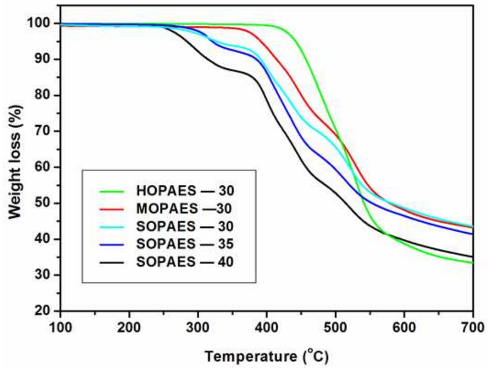

Fig. 6 TGA curves of membranes from a measurement run at 10 °C/min in N_2.

The mechanical properties of membranes were evaluated and the results are listed in Table 1. After the sulfobultylation, SOPAES-xx membranes in dry state still showed good mechanical properties with tensile strength, elongation at break and Young's modulus in the ranges of 39-53MPa, 15.34–26.75% and 1.01–1.25 GPa respectively. The tensile strength of these membranes decreased due to the introduction of strong polar -SO_3H groups in the side chains, which damaged the ordering of aggregative state. However, with the increasing of intra/inter hydrogen-bond and the content of diphenyl moiety in the polymer, Young's modulus and elongation at break didn't show a dramatic change. These results indicate that these side-chain-type SOPAES membranes with hydrogen-boned network were sufficiently tough and ductile for potential use as PEM materials in a fuel cell.

3.3 Membrane Properties: IEC, Water Uptake, and swelling ratio

Table 2 summaries the IEC, water uptake, and swelling ratio of the SOPAES-xx membranes. IEC represents the amount of exchangeable protons in ionomer membranes. The IEC values were determined by a titration method and the measured IEC values of SOPAES-xx are in the range of 1.06 – 1.38 mequiv/g, which are close to the theoretical value. It further demonstrated that the sulfonic acid groups were quantitatively introduced to the copolymers by a sulfobutylation reaction.

Membranes	Young's modulus (MPa)	Tensile modulus (MPa)	Maximum elongation (%)	T_d^a (°C)	-OH level [b] (mequiv/g)
SOPAES-30	1004.27	39.83	29.43	324.46	1.06
SOPAES-35	1132.78	45.15	18.48	320.62	1.22
SOPAES-40	1238.67	52.39	19.82	283.68	1.36

Table 1. Thermal and mechanical properties.

Td[a] : 5% weight loss temperature in N_2 gas (acid form membrane).

-OH level[b]: Calculated by H NMR integral area.

Water uptake is an important parameter for PEMs because its critical influence on the proton conductivity, dimensional stability and membrane-electrode compatibility. According to "vehicle mechanism" of proton conduction, protons within PEM could not be conducted unless they are hydrated by water.[30, 31] However, excessive water uptake would deteriorate the dimensional stability, which leads to the loss of mechanical properties. The water uptake and swelling ratio of SOPAES membranes were evaluated by comparing their hydrated state with dry state membranes at different temperatures.

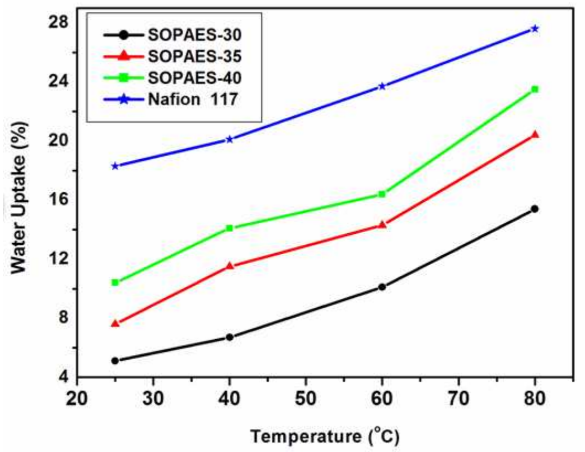

Fig. 7 Water uptake of SOPAES-xx membranes and Nafion 117.

Fig.7 shows the water uptake of SOPAES membranes at different temperatures. The water uptake of SOPAES-xx increased with IEC at a given temperature, due to the increased hydrophilicity. However, at a given temperature, the water uptake increased much slowly with the copolymerization ratio increasing from SOPAES-30 to SOPAES-40 and the values were much lower than that of Nafion at the same temperature. This phenomenon could be due to the flexible pendant sulfonic acid groups and –OH groups in SOPAES-xx copolymers. It formed hydrogen-bonded network obviously, which could restricted the water absorption even at relatively high temperature. The morphology transform of hydrophilic ionic clusters from segregated to continuous, resulted in the increase of water uptake.[37]

Similarly, the swelling ratio in length and thickness also increased with IEC increasing. As shown in Fig. 8, the SOPAES-xx membranes showed much lower swelling ratio than those of other main-chain-type sulfonated poly(arylene ether)s and Nafion membranes.[13]

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The side-chain-type sulfonated polymers located the sulfonic acid groups on the flexible side chains are helpful to separate the hydrophobic and hydrophilic domains, which would suppress the swelling behavior of the polymer films. Besides, biphenyl-based and hydrogen bonded SOPAES-xx also restricted the anisotropic membrane swelling, no matter in thickness direction or in plane. It was noteworthy that the high rigidity of the biphenyl groups in main chains and hydrogen bonded network in the copolymers made the orientation of polymer chains in plane direction difficult, which was helpful to maintain the dimensional shapes.

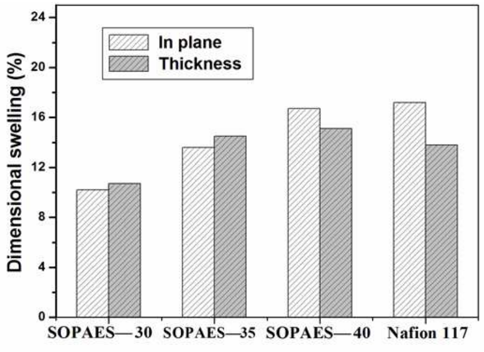

Fig. 8 Swelling ratio of SOPAES-xx membranes and Nafion 117.

3.4 Proton Conductivity and Methanol permeability

In order to explore the comprehensive performance of the proton conductivity and the alcohol resistance, we adopt the concept of selectivity (membrane conductivity and methanol permeability coefficient ratio) for evaluating membrane performance. Normally, a high selectivity often means a good performance of the battery. Fig. 9 shows the relative selectivity of the SOPAES-xx membranes to Nafion 117 membrane. The methanol permeability displayed a slight increase with increasing SOPAES- xx content. The relative selectivity of SOPAES-xx membrane is ranging from 3.31×10^5 S/cm^3 to 5.32×10^5 S/cm^3, much higher than that of Nafion 117 (0.96×10^5 S/cm^3). The selectivity shows that the SOPAES-xx membranes could be potentially used for DMFC applications

As shown in Table 2, with an increase in IEC values of SOPAES-xx from 1.06 to 1.38 mequiv/g, proton conductivity increased from 0.084 to 0.142 S/cm at 80 °C. The proton conductivity of the SOPAES membranes at 100% RH was plotted as a function of temperature and the results are displayed in Fig. 10.

Table 2. IEC, Proton Conductivity, Methanol permeability, Swelling Ratio, and Water Uptake of the SPAES-xx and Nafion Membranes

Membranes	IEC (mequiv.g^{-1})		Proton Conductivity (S cm^{-1})		Water Uptake (%)		Swelling Ratio (%) In thickness (Δd)		Swelling Ratio (%) In plane (Δl)		Methanol permeability
	IEC[a]	IEC[b]	25°C	80°C	25°C	80°C	25°C	80 °C	25°C	80°C	(10^{-7} cm^2/s)
SOPAES-0.30	1.06	1.02	0.032	0.084	4.9	19.3	4.1	10.7	6.3	10.2	1.58
SOPAES-0.35	1.20	1.17	0.043	0.103	7.6	20.2	5.1	14.5	8.9	13.6	2.61
SOPAES-0.40	1.38	1.33	0.054	0.142	10.8	26.5	6.9	15.1	10.2	16.7	4.29
Nafion 117	--	0.90	0.075	0.149	18.3	27.9	4.8	13.8	10.6	17.2	15.50

IEC[a] : Theoretical value. IEC[b]: Calculated by titration.

In the SOPAES-xx membranes, the introduction of highly rigid diphenyl groups into polymers backbone and hydrogen bonded network could restrict the free volume and reduce the mobility of ionic segments. Meanwhile, the sulfonic acid groups on the flexible aliphatic side chains would beneficial to aggregate the ionic clusters, which would lead to more obvious hydrophilic/hydrophobic separation. When the content of the sulfonic groups increased to a certain value, the ionic clusters would interconnect strongly to form the ionic network, and thus, the proton conductivity of the copolymers also enhanced. In case of SOPAES-40 membranes, the proton conductivity reached up to 0.116 S/cm and 0.142 S/cm at 60 °C and 80 °C, which are slightly lower than those of Nafion 117, and are suitable for practical applications as PEMs in fuel cell.

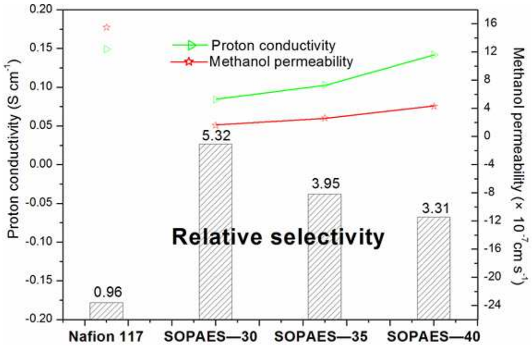

Fig. 9 The relative selectivity of the hydrogen-bond cross-linked SOPAES-xx membranes and Nafion 117.

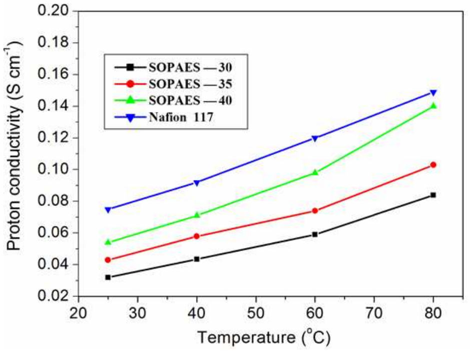

Fig.10 Proton conductivity of SOPAES-xx and Nafion membranes.

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3.5 Morphology of SOPAES membranes

SAXS was applied to analyze the hydrophilic clusters of the PEMs. The morphology of the SOPAES-xx membranes was observed by an SAXS system under hydrated conditions, and the results are shown in Fig. 11. In general, the characteristic separation lengths between the ion-rich domains in the hydrophobic polymer-rich domains can be observed in terms of the values of *q* corresponding to the so-called ionomer peak. SOPAES-40 showed a distinct peak at 1.13 nm^{-1}, suggesting a longer-distance order and the lamellar microphase separation structure. The value of *d* for the SOAPES-40 membrane was 5.56 nm, which is larger than that of Nafion (3.16 nm)[37]. This large *d* and unique phase-separated morphology are likely originated from the chemical structure of SOPAES-xx copolymers, which facilitates phase separation between hydrophilic and hydrophobic to aggregate to form nano-channels for efficient proton-transport. The morphological characteristics were also contributed to the higher proton conductivity of side-chain-type SOPAES membranes than those of main-chain-type sulfonated poly(arylene ether)s at similar IEC.

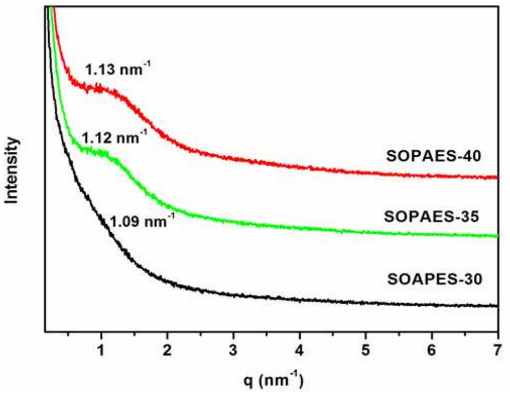

Fig. 11 SAXS profiles of SOPAES-xx membranes.

4. Conclusions

A novel biphenyl-based bisphenol monomer containing tetra-methoxy groups has been successfully synthesized in high yield by an oxidative-coupling reaction. Sulfonated poly(arylene ether sulfone)s with two pendant aliphatic sulfonic acid groups and two -OH groups per repeating unit were obtained by sequential polycondensation, demethylation and sulfobutylation. The IEC of the SOPAESs (1.06–1.38 mequiv/g) can be readily controlled by using different -OH content in HOPAES-xx copolymers with 1,4-butanesultone via sulfobutylation reactions. In comparison with Nafion membrane, these membranes exhibited very low water uptake and dimensional change, even at elevated temperatures (80 °C). The SOPAES-40 membranes displayed good proton conductivity, which are comparable to Nafion 117 at 100% RH. Moreover, the methanol permeability values of these SOPAES-xx membranes are much lower than Nafion and the relative selectivity are better. The SOPAES-xx membranes showed anisotropic membrane swelling in water with larger swelling in thickness than in plane, which was helpful to improve the dimensional stability. The SAXS profiles revealed that sulfonate groups aggregated into hydrophilic clusters to form a continuous network at 40% (SOPAES-40). The combination of facile synthetic routes for monomer and polymers, good relative proton to methanol transport, relatively low water uptake and swelling ratio makes these membranes attractive as PEM materials for further investigation in fuel cell applications.

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Notes and references

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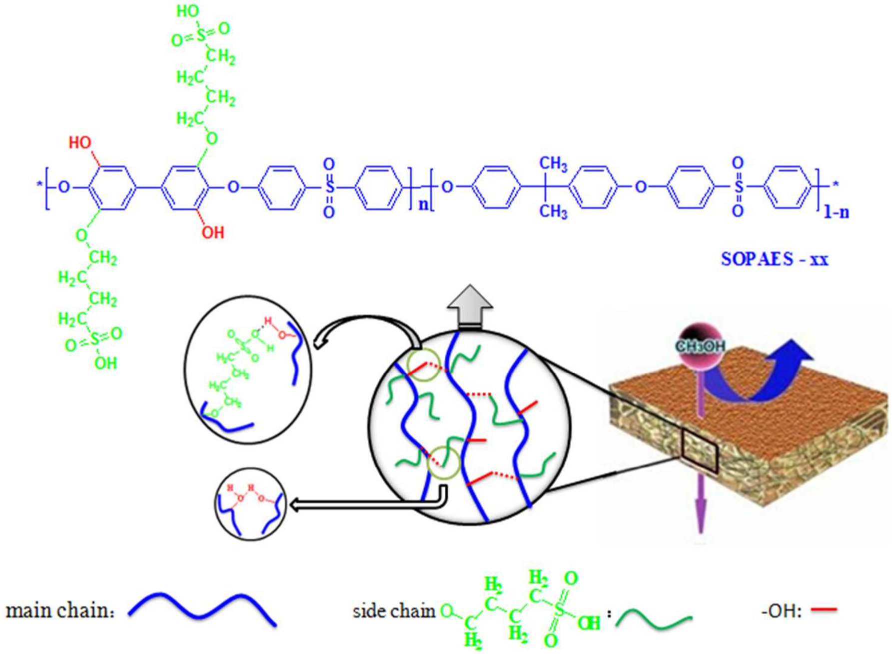

The diphenyl-based poly(arylene ether sulfone) membranes with side-chain-type architecture and hydrogen-bonded network were prepared.

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