www.rsc.org/materials



Synthesis and characterization of a novel poly(arylene ether sulfone) containing pendent imidazole groups for high temperature proton exchange membranes

Jing Wang,^{ab} Jifu Zheng,^a Zhuo Zhao^{ab} and Suobo Zhang^{*a}

Received 7th July 2012, Accepted 7th September 2012 DOI: 10.1039/c2jm34417c

A series of poly(arylene ether sulfone) containing pendent imidazole groups (PSf-Im-*x*) have been successfully synthesized based on a novel monomer 2,2'-bis-(2-methyl-imidazol-1-yl-methyl)-biphenyl-4,4'-diol (MIPO). The pendent imidazole groups along the polymer chain were expected to provide functional sites for the acid–base interaction with the doping phosphoric acid (PA) when they are used as polymer electrolyte membranes for high temperature fuel cell applications. The PA content of the linear PSf-Im-*x* membranes is about 172.3–235.8% in 85 wt% H₃PO₄ at room temperature. The volume swelling of these membranes is 114.4–194.0%, lower than that of polybenzimidazole (PBI) with similar PA content. The proton conductivities of the membranes are 0.021–0.053 S cm⁻¹ at 140 °C under absolutely dehydrated state. The low volume swelling and good proton conductivity may be attributed to the "side-chain-type" structures of pendent imidazole groups, which facilitate ion transport. To obtain higher acid doping while maintaining mechanical properties, cross-linked membranes were prepared by the reaction of the imidazole group of the polymer and *p*-xylene dichloride. The PA content of the membranes with 20% cross-linking is 313.2% in 85 wt% H₃PO₄ at 80 °C. The stress at breaking and the proton conductivity of the membrane is 3.2 MPa at room temperature and 0.063 S cm⁻¹ at 140 °C in an absolutely dehydrated state.

Introduction

Proton exchange membrane fuel cells (PEMFCs), which have been recognized as one of the most promising power generation technologies, could provide clean and efficient energy for stationary, transportation and portable electronics.^{1,2} Proton exchange membranes (PEM), key components for PEMFCs, have undergone much research in the past decades.³ Current commercial PEMs based on perfluorosulfonic acid (PSFA), such as Nafion, have good mechanical properties, excellent chemical stability and exhibit high proton conductivities only when hydrated (about 0.09 S cm⁻¹ at 25 °C), therefore, they are limited to operating temperatures up to around 80 °C.4 Several challenges for the PEMFC power technology are associated with low operating temperatures, including CO poisoning of the electrode Pt/catalyst, complexity of the heat and water management systems and limiting reaction kinetics.⁴ Development of high temperature PEMs would be an effective approach to overcome the technical challenges of the proton exchange membrane fuel cells (PEMFCs) arising at operational temperatures below 100 $^{\circ}\mathrm{C}.$

Acid-base polymer membranes, typically a basic polymer doped with a non-volatile inorganic acid or blended with a polymeric acid, have been considered for use as PEMs in elevated temperature fuel cell applications.⁵ In 1995, Wainright et al. successfully developed a high temperature polymer electrolyte by doping H₃PO₄ (PA) into polybenzimidazole (PBI), thereby creating polymers that function as PEMFCs at high temperatures and low humidity.⁶ Since that time, comprehensive investigations of the acid doped PBI for use in PEMFCs have been reported.7-10 To optimize membrane properties, high molecular weight PBIs are desired to achieve mechanically stable membranes with high PA content and therefore high proton conductivities. However, high molecular weight PBI has poor solubility and processability for membrane casting, and, the 3,3',4,4'-tetraaminobiphenyl (TAB) monomer commonly used for the synthesis of PBI is toxic.⁵ Alternative polymeric materials for high temperature PEM include polymers bearing basic sites such as aromatic polyether containing main chain pyridine,¹¹ aromatic poly(ether sulfone)s containing triazine groups,12 poly(arylene ether ketone) containing pendent quaternary ammonium groups¹³ and polysulfone containing imidazolium groups.14

In the PA doped membranes, a higher PA content leads to higher proton conductivities. The PA content can be increased at

^aKey Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. E-mail: sbzhang@ciac.jl.cn; Fax: +86 431 85262117; Tel: +86 431 85262118

^bGraduate School of the Chinese Academy of Sciences, Beijing 100039, China

elevated temperatures to obtain membranes with a higher amount of PA. However, under high PA content, although the proton conductivities of the PA doped membranes are high, the mechanical stability deteriorates because the membranes swell in H_3PO_4 . As found in the PEM with sulfonic acid groups and AEM (anion exchange membrane) with quaternary ammonium groups, if the polymer structure contains flexible pendent side chains linking the polymer main chain and the sulfonic acid groups or quaternary ammonium groups, nanophase separation between hydrophilic and hydrophobic domains may be improved, which would enhance conductivity and decrease swelling in water.^{15–18} The strategy of utilizing a "side-chaintype" structure is also expected to be useful in the PA doped high temperature PEMs.

The covalent cross-linking of membranes may be another reasonable method for improving dimensional stability without impairing proton conductivity. Covalent cross-linking of PBIs has been achieved by thermal treatment,¹⁹ chemical reaction between PBI and the cross-linker *p*-xylene chloride,²⁰ *p*-xylene dibromide²¹ or epoxy resin.²² Lee *et al.*^{23,24} recently reported development of new H₃PO₄-doped cross-linked benzoxazine–benzimidazole copolymer membranes with interpenetrating network structures for use in fuel cells at elevated temperatures. These cross-linked membranes show enhanced mechanical properties and very high proton conductivity. Kallitsis *et al.*^{25,26} also improved the performance of the polyether containing main chain pyridine by covalent cross-linking.

In this paper, we report the synthesis of poly(arylene ether sulfone) containing pendent imidazole units (PSf-Im) based on a 2,2'-bis-(2-methyl-imidazol-1-yl-methyl)novel monomer biphenyl-4,4'-diol (MIPO). The pendent imidazole groups along the polymer chain were expected to provide functional sites for the acid-base interaction with the doping phosphoric acid. Use of this novel monomer affords precise control of the imidazole concentration in the final polymer, which leads to highly reproducible materials. The PSf-Im copolymer is a thermally stable polymer and with excellent solubility in polar solvents. The linear membranes are directly cast from the PSf-Im polymer. The crosslinked membranes are obtained by using p-xylene chloride as a cross-linker that reacts with the imidazole groups of PSf-Im. The solubility, swelling in the PA solution, mechanical properties, proton conductivity and oxidation stability of both linear and cross-linked membranes were studied.

Experimental section

Materials

2,2'-Bimethylaminemethylene-4,4'-biphenol was synthesized as reported in our previous paper.²⁷ 4,4'-Biphenol (BP), 4,4'bifluorodiphenylsulfone, 2-methylimidazole and *p*-xylylene dichloride were purchased from Aldrich. Polybenzimidazole (PBI) powder was kindly provided by Polymics ITP Co. Ltd., China. Formaldehyde solution (37%), dimethylamine solution (33%), potassium carbonate (K₂CO₃), *N*,*N*-dimethylacetamide (DMAc), dimethylbenzene and LiCl were purchased from Sinopharm Group Chemical Reagent Co., Ltd. All other reagents were obtained from commercial sources and used as received. ¹H NMR spectra were measured at 300 MHz on an AV300 spectrometer. The inherent viscosities were determined with an Ubbelohde capillary viscometer at 30 ± 0.1 °C on 0.5 g dL⁻¹ concentrations of polymer in CHCl₃ or DMAc. Molecular weights were also determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector operating at a wavelength of 260 nm. DMF was used as the eluent. Tensile measurements were carried out with an Instron-1211 mechanical testing instrument at a speed of 1 mm min⁻¹.

Synthesis of monomer 2,2'-bis-(2-methyl-imidazol-1-yl-methyl)biphenyl-4,4'-diol (MIPO)

To a 250 mL round-bottomed flask, 2,2'-bis-dimethylaminomethyl-biphenyl-4,4'-diol (30.0 g, 0.10 mol) was dissolved in dimethylbenzene and 2-methylimidazole (0.30 mol, 24.0 g) was added. The solution was stirred at 140 °C with a nitrogen inlet for 12 h. The precipitated solid was collected by filtration, washed with ethanol several times and was dried under vacuum at 80 °C for 24 h to produce the final product. The yield was 90%; the melting point was 298 °C. ¹H NMR (DMSO-d₆, ppm): δ 7.20– 7.24 (2H, dd), 7.05–7.06 (2H, d), 6.89 (2H, s), 6.86 (2H, s), 6.74– 6.75 (2H, d), 5.05 (4H, s) and 3.42 (6H, s). ¹³C NMR (DMSOd6): δ 153.5, 143.9, 131.1, 126.4, 126.2, 126.1, 123.8, 120.0, 115.4, 44.0, 12.9. Anal. calcd for C₂₂H₂₂N₄O₂ (374.4): C, 70.57%; H, 5.92%; N, 14.96%. Found: C, 70.62%; H, 5.89%; N, 14.91%.

Synthesis of poly(arylene ether sulfone) containing pendent imidazole groups (PSf-Im-*x*)

The DF values of the copolymers, where DF represents the degree of functionalization (the number of imidazole groups/ repeat unit), were controlled by adjusting the molar ratio of MIPO to BP (4,4'-biphenol monomer). A typical synthesis procedure of PSf-Im-60, where 60 refers to the feed percent of MIPO, was as follows. A flame-dried 100 mL three-necked flask equipped with a nitrogen inlet and overhead stirrer was charged with MIPO (2.2464 g, 6 mmol), BP (0.7448 g, 4 mmol), 4,4'bifluorodiphenylsulfone (2.5425 g, 10 mmol), K₂CO₃ (2.90 g, 21 mmol) and dry DMAc (50 mL; 10% solids). The mixture was kept at room temperature for a few minutes and then slowly heated at 120 °C for 12 h. After cooling to room temperature, an additional 30 mL of DMAc was added so as to dilute the highly viscous solution, after which the solution was filtered and dropped into stirred deionized water. The fiber-like precipitate was filtered off and washed with hot water three times prior to being dried under vacuum to produce the final product.

Membrane casting of linear PSf-Im-x and cross-linked C-PSf-Im-70-n

For linear membrane casting, the polymer PSf-Im-x was dissolved in DMAc at 80 °C under stirring to form a 5% solution. The resulting solution was then filtered and degassed and transferred to a preheated glass dish where the cross-linked reaction occurred, followed by solvent evaporation yielding the clear, thin membrane.

The following represents a typical procedure for the synthesis of C-PSf-Im-70-30. PSf-Im-70 (1.10 g, 2 mmol) was dissolved in 20 mL of dimethylacetamide (DMAc), and then 0.42 mmol *p*-xylylene dichloride was added to the solution. After 10 min of vigorous stirring, the homogeneous solution was degassed and transferred to a preheated glass dish where the cross-linking reaction occurred, followed by solvent evaporation yielding the clear, thin membrane.

Membrane casting of PBI

The PBI membrane was obtained by dissolving PBI powder (5 wt %) and LiCl (1 wt%) in dimethylacetamide at 120 °C and casting the solution at 120 °C for 12 h. Acid-doped PBI was obtained by immersion of the PBI membrane in phosphoric acid (85 wt%) at room temperature for 48 h, blotting with filter paper and then drying at 110 °C for 24 h.

Acid doping

The thoroughly dried membrane was cut into pieces of $4 \text{ cm} \times 5 \text{ cm}$ and immersed into $85 \text{ wt}\% \text{ H}_3\text{PO}_4$ solutions at room, or elevated temperatures, for 48 h in order to obtain the desired PA content (wt %). The PA content (wt%) of a membrane is defined as the mass changes of the membrane sample before and after doping:

PA content (wt%) =
$$(m_{\rm A} - m_{\rm B})/m_{\rm B} \times 100$$
 (1)

where m_A is the mass of the membrane after the doping and blotting with filter paper and then drying at 110 °C for 24 h, and m_B is the mass of the membrane before the doping, respectively.

The area and volume swellings of a membrane sample in an acid solution were determined by measuring the membrane dimension before (D_B) and after (D_A) immersion of the sample for 48 h and drying with blotting paper and then drying at 110 °C for 24 h, and calculated using eqn (2).

Swelling (%) =
$$(D_{\rm A} - D_{\rm B})/D_{\rm B} \times 100$$
 (2)

Solubility test

The cross-linking was characterized by measuring the solubility of the membranes in DMSO. 0.1 g of membrane was immersed in 20 mL DMSO 80 °C under stirring for 48 h. Then the remaining, not dissolved membrane samples were collected, dried and weighed. The solubility of the membranes was then obtained from the weight losses observed.

Proton conductivity

The proton conductivities (σ , S cm⁻¹) of the membranes were obtained using $\sigma = d/L_s W_s R$ (*d* is the distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). Here, ohmic resistance (*R*) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected to an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of goldplate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. 1 cm \times 5 cm membranes were introduced to the conductivity cell and heated to 140 °C and held for 60 min. Measurements were taken as the cell then cooled to 100 °C in 10 °C steps.

Fenton test

To test membrane degradation by oxidative radicals the produced membranes were immersed in a Fenton solution containing 3% H₂O₂ and 4 ppm Fe²⁺ (added as FeSO₄). In this solution hydroxyl radicals were produced resulting in oxidative attack of the membranes, mimicking possible operating conditions during use in fuel cells. The membrane samples were immersed in the Fenton solution at 80 °C. The stability was evaluated by the time when the membrane broke into pieces after being shaken vigorously.

Results and discussion

Synthesis of monomers and copolymers containing pendent imidazole groups (PSf-Im-*x*)

Scheme 1 shows the two-step synthesis of 2,2'-bis-(2-methylimidazol-1-yl-methyl)-biphenyl-4,4'-diol (MIPO). In step one, 2,2'-bis-dimethylaminomethyl-biphenyl-4,4'-diol is synthesized according to the method we reported previously.²⁷ In step two, DABP, which decomposes to an *o*-quinone methide intermediate at 140 °C, ^{28,29} reacts with 2-methylimidazole to yield the product, MIPO, as shown in Scheme 2. The structure of MIPO was confirmed by the ¹H NMR and ¹³C NMR spectrum (Fig. 1).

The poly(arylene ether sulfone) with pendent imidazole groups (PSf-Im-*x*) was obtained from MIPO, BP and 4,4'-bifluorodiphenylsulfone by nucleophilic substitution polycondensation (Scheme 1). The use of a monomer containing pendent imidazole groups eliminates the need for post polymerization modifications and ensures reproducibility of the imidazole content. The imidazole content of the copolymers was readily controlled through the feed ratio of the monomers MIPO and BP. The



Scheme 1 Sythentic procedure of 2,2'-bis-(2-methyl-imidazol-1-ylmethyl)-biphenyl-4,4'-diol (MIPO) and copolymer poly(arylene ether sulfone) containing pendent imidazole groups (PSf-Im-*x*). *Reagents and conditions*: (i) formaldehyde solution (37%), dimethylamine solution (33%), 24 h, 25 °C; (ii) 2-methylimidazole, dimethylbenzene, 12 h, 140 °C.



Scheme 2 Reaction mechanism of preparing 2,2'-bis-(2-methyl-imidazol-1-yl-methyl)-biphenyl-4,4'-diol (MIPO).



Fig. 1 ¹H NMR and ¹³C NMR spectra of 2,2'-bis-(2-methyl-imidazol-1-yl-methyl)-biphenyl-4,4'-diol (MIPO).

polycondensation reaction was completed in a few hours (12 h) at 120 °C in the presence of 2.1 equivalents of K₂CO₃. These mild reaction conditions yielded high molecular weight polymers as shown by their inherent viscosities and GPC (Table 1). Typical average molecular weights and polydispersities ranged from 74 000 to 86 000 and 2.1 to 2.3, respectively. Fig. 2 shows the ${}^{1}\text{H}$ NMR spectrum of PSf-Im-70, -100 in CDCl₃. The synthesized polymer exhibited good solubility in CDCl₃ and polar aprotic solvents such as DMF, DMAc, DMSO and NMP. Fig. 3 shows the TGA (thermo-gravimetric analysis) curves for the PSf-Im-70 membranes, which were recorded under a nitrogen atmosphere from 40 °C to 800 °C. Two decomposition steps were observed for PSf-Im-70. The first decomposition step, at a temperature range from 270 to 450 °C, was attributed to the loss of imidazole groups, whereas the second step corresponded to the degradation of the PSf backbone.

PA content, mechanical properties and conductivity of linear PSf-Im-*x* membranes

Fig. 4 shows the variations of PA content of linear PSf-Im-x membranes as a function of time immersing the membranes in 85 wt% PA solutions at 25 °C. The PA content of the membranes increased during the first 10 h, and then levelled off with time.

 Table 1
 Inherent viscosity, molecular weight and DF values of PSf-Im-x

Sample	$\eta_{\rm inh}^{a}_{(\rm dL~g^{-1})}$	DF^b	$\frac{M_{\rm n}}{(10^4 {\rm g mol}^{-1})}$	$\frac{M_{\rm w}}{(10^4 {\rm g mol}^{-1})}$	PDI ^c
PSf-Im-50	0.43	1.20	8.2	17.6	2.1
PSf-Im-60	0.42	1.40	8.3	16.0	1.9
PSf-Im-70	0.40	1.59	8.6	17.7	2.1
PSf-Im-80	0.41	1.81	7.9	16.8	2.1
PSf-Im-100	0.42	2.00	7.4	16.5	2.2

^{*a*} Inherent viscosity measured at a concentration of 0.5 dL g⁻¹ in DMAc at 30 °C. ^{*b*} Degree of functionalization = (number of the imidazole groups/repeat unit). ^{*c*} Polydispersity.



Fig. 2 ¹H NMR spectra of PSf-Im-70, -100 in CDCl₃.

The membranes with a higher imidazole content absorbed more phosphoric acid. The PA content of the PSf-Im-70 membrane was 235.8%, which is similar to that found for PBI membranes (239.7% in 85 wt% PA at room temperature). The swelling of the PSf-Im-70 membranes in 85 wt% PA, however, was less than that of PBI membranes. For example, the swelling of the PSf-Im-70 membrane in H₃PO₄ was 110.0% in area and 194.0% in volume, whereas the swelling of the PBI membrane in H₃PO₄ was 146.7% in area and 237.5% in volume (Table 2). When the membranes are doped in H₃PO₄, the imidazole groups are protonated, which then react with the phosphoric acid anion to create sites on the polymer chain in which free phosphoric acid molecules can immobilize. Separating the imidazole groups from the polymer main chain, e.g., localizing the imidazole groups on side chains grafted onto the polymer main chain, decreases the interaction between H₃PO₄ and the polymer main chain, and decreases membrane swelling in H₃PO₄. The imidazole groups for PBI, are located in the polymer main chain, while for PSf-Im-x they are located on side chains grafted onto the polymer main chain.



Fig. 3 TGA curves for PSf-Im-70 and C-PSf-Im-70-40.



Fig. 4 PA content of PSf-Im-x membranes as a function of time immersed in 85 wt% phosphoric acid at room temperature.

The mechanical properties of acid doped PSf-Im-*x* membranes are shown in Table 2. The doping PA molecules reduced the tensile strength but increased the elongation of the membranes, a common observation in the acid doped PBI.^{30,31} Before doping, the PSf-Im-50, 60, and 70 membranes had tensile strengths of 40.2–70.5 MPa and elongated by 20–70%. After doping, the tensile strength of the acid doped PSf-Im-50, 60, 70 membranes decreased to 11.1, 7.8, and 4.2 MPa, and elongation increased to 56.0, 89.2, and 180.0%, respectively.

Fig. 5 shows the proton conductivity of PA doped PSf-Im-*x* membranes as a function of temperature under anhydrous conditions. Conductivities of these membranes were all above 0.01 S cm⁻¹. Conductivity increased linearly with increasing temperature. In addition, conductivities increased with increased PA content at the same temperature. The PSf-Im-70 membranes with PA content of 235.8% displayed a conductivity of 0.048 S cm⁻¹ at 130 °C, whereas the PBI membrane with a PA content of 239.7% exhibited a conductivity of 0.041 S cm⁻¹ at 130 °C as seen in Table 2. The higher conductivity of PSf-Im-70 was due to the "side-chain-type" structures that facilitate ion transport.

PA content, mechanical properties and conductivity of a crosslinked C-PSf-Im-70-*n* membrane

In the PA doped membranes, higher doping temperatures enhanced PA doping levels, which in turn lead to higher proton conductivities. However, at a high PA content, although proton



Fig. 5 Conductivities of acid doped PSf-Im-*x* membranes as a function of temperature.

conductivities are high, the mechanical stabilities of the PA doped membranes deteriorate. For example, the PSf-Im-70 membrane swells to yield a gel with 85 wt% PA at 80 °C. To overcome this problem, we used *p*-xylylene dichloride to make a cross-linked membrane. The chemical structure of the cross-linked polymer is shown in Scheme 3. Assuming complete reaction of each mole of the *p*-xylylene dichloride with 2 equivalents of PSf-Im-70 imidazole groups, the extent of cross-linking would be 10, 20, 30 and 40%, of the total imidazole groups, respectively. Virgin PSf-Im-70 is thermally stable at temperatures up to 270 °C while cross-linked PSf-Im-70-40 (C-PSf-Im-70-40) could be thermally stable up to 340 °C, as shown in Fig. 3. The weight loss observed for C-PSf-Im-70-40 at temperatures below 340 °C is due to removal of the residual water bound with the hydrophilic imidazolium moieties. Membranes with 10–40% cross-linking are



Scheme 3 Chemical structures of the cross-linked polymers.

Table 2 Variations and mechanical properties of linear and cross-linked membranes in 85 wt% of phosphoric acid solutions at 25 $^{\circ}$ C and conductivities at 130 $^{\circ}$ C

Sample	Mass (%)	Area (%)	Volume (%)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Conductivity (S cm ^{-1})
PSf-Im-50	172.3	50.0	114.4	11.1	12.9	56	0.019
PSf-Im-60	202.4	72.3	141.2	7.8	7.19	89	0.034
PSf-Im-70	235.8	110.0	194.0	4.2	2.49	180	0.048
C-PSf-Im-70-10	213.5	36.5	118.4	5.9	28.5	120	0.043
C-PSf-Im-70-20	199.2	30.9	102.8	6.6	23.8	100	0.034
C-PSf-Im-70-30	170.4	23.8	86.8	8.2	16.0	71	0.019
C-PSf-Im-70-40	148.6	15.5	65.0	10.9	64.8	44	0.009
PBI	239.7	146.7	237.5	4.8	3.14	110	0.041



Fig. 6 Conductivities of C-PSf-Im-70-*n* membranes doping in 85 wt% H_3PO_4 at 25 °C (top) or 80 °C (bottom) as a function of temperature.

homogeneous, transparent membranes with a light yellow color. The solubility of these membranes in DMSO was measured at 80 $^{\circ}$ C by determining their residual weight after 48 h of immersion. Membrane samples of linear PSf-Im-70 with no cross-linker dissolved in DMSO at 80 $^{\circ}$ C within one-half hour. The 10–40% cross-linked membranes were more stable since only 3–5 wt% was soluble during 48 h of immersion in DMSO.

The doping ability of the cross-linked membranes in phosphoric acid at 25 °C is depicted in Table 2 and for comparison the doping ability of the linear polymers is also presented. The crosslinked membrane C-PSf-Im-70-*n* possessed a PA content of 148.4–213.5%, which was lower than that of linear PSf-Im-70 under the same conditions. This is because cross-linking leads to more compact chemical structures that decrease the doping ability. The volume swelling of the cross-linked membranes is also lower than that of the linear PSf-Im-70 membrane. For example, after 2 days of immersion in the 85 wt% PA solution at 25 °C, the linear PSf-Im-70 membrane showed a volume swelling of 194.0%, while the C-PSf-Im-70-10, 20, 30, 40 membranes showed lower volume swellings: 118.4, 102.8, 86.8, 65.0%, respectively.

In Fig. 6 is depicted the temperature dependence of the ionic conductivity of the cross-linked membranes, and the linear PSf-Im-70 membrane. The conductivity of membranes is highly dependent on the PA content. Compared with the linear PSf-Im-70 membrane, immersing the cross-linked membranes in phosphoric acid solution at 25 $^{\circ}$ C gave a lower PA content. As a result, the conductivity of the cross-linked membrane is lower compared to the neat polymer, and decreased with the increasing extent of cross-linking.

Increasing the doping temperature can enhance the mobility of polymer chains and the free volume for the acid doping, which leads to the increased PA content of the membranes. Thus, the cross-linked membranes were doped in 85% H₃PO₄ at temperatures up to 80 °C in order to achieve high PA content. By immersing the membrane samples in 85% phosphoric acid at 80 °C for 48 h, as an example, the linear PSf-Im-70 membrane swelled to a gel. As a comparison, the cross-linked membranes had a PA content of 385.2, 313.2, 209.1 and 178.7%, respectively, corresponding to volume swellings of 170.8, 150.0, 105.2 and 84.8% for cross-linking degrees of 10, 20, 30 and 40%, respectively, as shown in Table 3.

The mechanical properties of the linear and cross-linked membranes are listed in Tables 2 and 3 for different PA contents. When cross-linked, the membranes show a much improved mechanical strength. As seen from Table 3, the cross-linked membrane C-PSf-Im-70-20 with PA content of 313.2% exhibited a similar tensile strength and young modulus as those for linear PSf-Im-70 with PA content of 235.8%. It should be noticed that the two membranes have similar mechanical properties and the measured conductivity was very different, as shown in Fig. 6 (bottom). A higher conductivity is observed for the cross-linked membranes with a PA content of 313.2%. As expected, higher PA contents are effective in achieving higher conductivity. The cross-linked membranes make this possible to some extent without deteriorating the mechanical strength.

Oxidation stability

Fenton test treatment was performed in order to evaluate whether the membranes were able to withstand a strong oxidizing environment during the fuel cell operation. The resistance to oxidation of the membranes was examined by observing the dissolving behavior. The PSf-Im-70 started to break into pieces after 36 h, while the PSf-Im-50 kept its shape for 240 h.

Table 3 Variations and mechanical properties of cross-linked membranes in 85 wt% of phosphoric acid solutions at 80 °C and conductivities at 130 °C

Sample	Mass (%)	Area (%)	Volume (%)	Tensile strength (MPa)	Tensile strength (MPa)	Elongation at breaking (%)	Conductivity (S cm^{-1})
C-PSf-Im-70-10	385.2	62.5	170.8	1.7	3.2	100	0.075
C-PSf-Im-70-20	313.2	35.0	150.0	3.2	3.7	46	0.056
C-PSf-Im-70-30	209.1	28.3	105.2	5.4	4.6	33	0.031
C-PSf-Im-70-40	178.7	23.2	84.8	6.0	10.9	31	0.023

For the covalently cross-linked membranes, the cross-linking structure indeed enhanced the free radical oxidative stability. The cross-linked membranes with 10-40% cross-linking degree could keep its shape for more than 360 h.

Conclusions

High molecular weight poly(arylene ether sulfone) with pendent imidazole groups (PSf-Im-x) was successfully synthesized using a novel monomer 2,2'-bis-(2-methyl-imidazol-1-yl-methyl)biphenyl-4,4'-diol (MIPO) and its ability to absorb phosphoric acid was characterized. With a PA content of 172.3% to 235.8%, the membranes showed a volume swelling of 114.4-194.0%, a proton conductivity of 0.021-0.053 S cm⁻¹ at 140 °C, and a tensile strength of 4.2-11.1 MPa. The low volume swelling and good proton conductivity are attributed to the "side-chain-type" structures of the pendent imidazole groups. Using p-xylylene dichloride, cross-linked membranes PSf-Im-70 membranes (C-PSf-Im-70-n) were prepared. Higher doping temperatures increased the PA of the cross-linked membranes. C-PSf-Im-70-20 membrane had a PA content of 313.2% in 85 wt% H₃PO₄ solution at 80 °C and exhibited a proton conductivity of 0.063 S cm⁻¹ at 140 °C. Compared to linear membranes, cross-linked membranes result in increased chemical stability towards oxidation by peroxide radicals in the Fenton test.

Acknowledgements

We thank the National Basic Research Program of China (no. 2009CB623401, 2012CB932802) and the National Science Foundation of China (no. 51133008, 50825302 and 51021003).

Notes and references

- 1 M. Winter and R. J. Brodd, Chem. Rev., 2004, 104, 4245.
- 2 M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla and J. E. McGrath, *Chem. Rev.*, 2004, **104**, 4587.
- 3 B. C. H. Steele and A. Heinzel, Nature, 2001, 414, 345.
- 4 Q. Li, R. He, J. O. Jensen and N. J. Bjerrum, *Chem. Mater.*, 2003, **15**, 4896.
- 5 Q. Li, J. O. Jensen, R. F. Savinell and N. J. Bjerrum, *Prog. Polym. Sci.*, 2009, **34**, 449.

- 6 J. S. Wainright, J.-T. Wang, D. Weng, R. F. Savinell and M. Litt, J. Electrochem. Soc., 1995, 142, L121.
- 7 D. Mecerreyes, H. Grande, O. Miguel, E. Ochoteco, R. Marcilla and I. Cantero, *Chem. Mater.*, 2004, **16**, 604.
- 8 L. Xiao, H. Zhang, E. Scanlon, L. S. Ramanathan, E.-W. Choe, D. Rogers, T. Apple and B. C. Benicewicz, *Chem. Mater.*, 2005, 17, 5328.
- 9 J. Weber, K.-D. Kreuer, J. Maier and A. Thomas, *Adv. Mater.*, 2008, 20, 2595.
- 10 J. A. Asensio, E. M. Sanchez and P. Gomez-Romero, *Chem. Soc. Rev.*, 2010, **39**, 3210.
- 11 N. Gourdoupi, A. K. Andreopoulou, V. Deimede and J. K. Kallitsis, *Chem. Mater.*, 2003, 15, 5044.
- 12 D. M. Tigelaar, A. E. Palker, C. M. Jackson, K. M. Anderson, J. Wainright and R. F. Savinell, *Macromolecules*, 2009, 42, 1888.
- 13 W. Ma, C. Zhao, H. Lin, G. Zhang, J. Ni, J. Wang, S. Wang and H. Na, J. Power Sources, 2011, 196, 9331.
- 14 J. Yang, Q. Li, J. O. Jensen, C. Pan, L. N. Cleemann, N. J. Bjerrum and R. He, J. Power Sources, 2012, 205, 114.
- 15 N. Li, Q. Zhang, C. Wang, Y. M. Lee and M. D. Guiver, *Macromolecules*, 2012, 45, 2411.
- 16 S. Xu, G. Zhang, Y. Zhang, C. Zhao, W. Ma, H. Sun, N. Zhang, L. Zhang, H. Jiang and H. Na, *J. Power Sources*, 2012, **209**, 228.
- 17 N. Gao, F. Zhang, S. Zhang and J. Liu, J. Membr. Sci., 2011, 372, 49.
- 18 K. Nakabayashi, T. Higashihara and M. Ueda, Macromolecules, 2011, 44, 1603.
- 19 J. K. Gillham, Science, 1963, 139, 459.
- 20 K. Wang, Y. Xiao and T. Chung, Chem. Eng. Sci., 2006, 61, 5807.
- 21 Q. Li, C. Pan, J. O. Jensen, P. Noyé and N. J. Bjerrum, *Chem. Mater.*, 2007, **19**, 350.
- 22 M. Han, G. Zhang, Z. Liu, S. Wang, M. Li, J. Zhu, H. Li, Y. Zhang, C. M. Lew and H. Na, J. Mater. Chem., 2011, 21, 2187.
- 23 S.-K. Kim, S.-W. Choi, W. S. Jeon, J. O. Park, T. Ko, H. Chang and J.-C. Lee, *Macromolecules*, 2012, **45**, 1438.
- 24 S.-K. Kim, T. Ko, S.-W. Choi, J. O. Park, K.-H. Kim, C. Pak, H. Chang and J.-C. Lee, *J. Mater. Chem.*, 2012, **22**, 7194.
- 25 K. D. Papadimitriou, F. Paloukis, S. G. Neophytides and J. K. Kallitsis, *Macromolecules*, 2011, 44, 4942.
- 26 A. Vöge, V. A. Deimede and J. K. Kallitsis, J. Polym. Sci., Part A: Polym. Chem., 2012, 50, 207.
- 27 J. Wang, Z. Zhao, F. Gong, S. Li and S. Zhang, *Macromolecules*, 2009, **42**, 8711.
- 28 P. Wang, R. Liu, X. Wu, H. Ma, X. Cao, P. Zhou, J. Zhang, X. Weng, X.-L. Zhang, J. Qi, X. Zhou and L. Weng, *J. Am. Chem. Soc.*, 2003, **125**, 1116.
- 29 Y. Song, T. Tian, P. Wang, H. He, W. Liu, X. Zhou, X. Cao, X.-L. Zhang and X. Zhou, Org. Biomol. Chem., 2006, 4, 3358.
- 30 J. Yang and R. He, Polym. Adv. Technol., 2010, 21, 874.
- 31 R. He, Q. Li, A. Bach, J. O. Jensen and N. J. Bjerrum, J. Membr. Sci., 2006, 277, 38.