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Synthesis of novel sulfonated polybenzimidazole and preparation of cross-linked membranes for fuel cell application

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Abstract

A novel sulfonated polybenzimidazole, sulfonated poly[2,2′-(*p*-oxydiphenylene)-5,5′-bibenzimidazole] (SOPBI), was successfully prepared by post-sulfonation reaction of the parent polymer, poly[2,2′-(*p*-oxydiphenylene)-5,5′-bibenzimidazole] (OPBI), using concentrated and fuming sulfuric acid as the sulfonating reagent at 80 °C, and the degree of sulfonation (DS) could be regulated by controlling the reaction conditions. No significant polymer degradation was observed in the post-sulfonation processes. Direct polymerization of 4,4′-dicarboxydiphenyl ether-2,2′-disulfonic acid disodium salt (DCDPEDS) and 3,3′-diaminobenzidine (DABz), however, resulted in insoluble gels either in polyphosphoric acid (PPA) or in phosphorus pentoxide/methanesulfonic acid (PPMA) in a ratio of 1:10 by weight reaction medium. The SOPBIs prepared by the post-sulfonation method showed good solubility in dimethyl sulfoxide (DMSO), high thermal stability, good film forming ability and excellent mechanical properties. Cross-linked SOPBI membranes were successfully prepared by thermal treatment of phosphoric acid-doped SOPBI membranes at 180 °C in vacuo for 20 h and the resulting cross-linked membranes showed much improved water stability and radical oxidative stability in comparison with the corresponding uncross-linked ones, while the proton conductivity did not change largely. Highly proton conductive (150 mS cm^{-1}, 120 °C in water) and water stable SOPBI membrane was developed.

Keywords: Sulfonated polybenzimidazole; Synthesis; Cross-linking

1. Introduction

Polybenzimidazoles (PBIs) have attracted much attention in the past decade because of their potential important application in polymer electrolyte membrane fuel cells (PEMFCs) [1–16]. One of the most important features of phosphoric acid-doped PBI membranes is that at high doping levels (>300%) they show high proton conductivities even in completely anhydrous state and the conductivity increases with an increase in temperature up to 200 °C, which make them the most promising membrane materials for medium temperature (150–200 °C) PEMFC application. This is quite different from the case of sulfonated polymer membranes whose proton conductivity strongly depends on the dissociation of sulfonic acid and the amount of water molecules (carrier) for proton transport leading to drastic reduction in proton conductivity as the relative humidity decreases to low levels (<30%). The proton conductivity of phosphoric acid-doped PBI membranes is closely dependent on the doping level and higher doping level generally results in larger proton conductivity. The widely studied PBIs for PEMFC use are poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (a commercial PBI) and poly(2,5-benzimidazole) (ABPBI). Recently sulfonated polybenzimidazoles (SPBIs) have attracted particular attention and it has been reported that phosphoric acid-doped SPBI membranes generally showed higher proton conductivities than the corresponding phosphoric acid-doped non-sulfonated PBI membranes [10–18]. The synthesis of SPBIs can be

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achieved by three approaches. The first approach is chemical modification of the commercial PBI with lithium hydride followed by reaction with sulfonating reagents such as 4-bromomethylbenzene sulfonic acid sodium salt [10] and alkanesultone [11]. The second approach is direct polymerization from the sulfonated dicarboxylic acid monomers [12–14]. The third approach is post-sulfonation of PBI or ABPBI by heat treatment of sulfuric acid-doped membranes at high temperatures (450–475 °C) [15–18]. Direct polymerization method can give SPBIs with exactly desired structure and precisely controlled degree of sulfonation, but almost all the sulfonated monomers are not commercially available and needed to be synthesized. Post-sulfonation method is quite simple, however, it is reported that cross-linked and/or fragile membranes with low degree of sulfonation were often obtained because of the too high reaction temperature which is essential for sulfonation due to the rather low reactivity of both the commercial PBI and ABPBI. If the reactivity of PBIs is enhanced, sulfonation reaction might be carried out under relatively mild conditions. Incorporation of activated phenyl rings into PBI structure is expected to be an efficient way to achieve this goal. In this paper, we report on the synthesis and properties of a new sulfonated polybenzimidazole, sulfonated poly[2,2′-(*p*-oxydiphenylene)-5,5′-bibenzimidazole] (SOPBI), via both direct polymerization method and post-sulfonation method. A new and facile cross-linking method is also proposed to prepare cross-linked sulfonated polybenzimidazole membranes.

2. Experimental

2.1. Materials

3,3′-Diaminobenzidine (DABz) was purchased from Acros Organics and used without further purification. 4,4′-Dicarboxydiphenyl ether (DCDPE) was kindly supplied by Peakchem (Shanghai) and vacuum dried at 80 °C prior to use. Methanesulfonic acid (MSA), phosphorus pentoxide, polyphosphoric acid (PPA), fuming sulfuric acid, 96% concentrated sulfuric acid, dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) were purchased from SCRC. DMSO, NMP, DMAc and DMF were distilled under reduced pressure and dried over 4A molecular sieves before use. Other materials were used as received. Poly[2,2′-(*p*-oxydiphenylene)-5,5′-bibenzimidazole] (OPBI) was synthesized by condensation polymerization of DCDPE and DABz in PPMA at 140 °C for 160 min with total monomer concentration of 10 wt% [19].

2.2. Post-sulfonation

To a 100 mL dry flask were added 1.0 g of OPBI and 10 mL of 96 wt% concentrated sulfuric acid or fuming sulfuric acid containing 10% or 20% sulfur trioxide. The mixture was magnetically stirred and slowly heated to 80 °C and kept at this temperature for a given time. The homogeneous solution was slowly poured into ice water and the resulting fiber-like precipitate was soaked in 5% sodium bicarbonate solution at room temperature for two days. The solid was collected by filtration, thoroughly washed with deionized water and dried in vacuo at 150 °C for 10 h.

2.3. Synthesis of 4,4′-dicarboxydiphenyl ether-2,2′-disulfonic acid disodium salt (DCDPEDS)

To a 100 mL dry three-neck flask were added 5.16 g (20.0 mmol) of DCDPE and 20 mL of fuming sulfuric acid (30% SO_3). The reaction mixture was stirred at 80 °C for 12 h. Upon cooling to room temperature, the mixture was poured into crushed ice. Sodium chloride was added to salt out the product. The resulting precipitate was filtered off, washed with saturated sodium chloride solution and dried in vacuo. The crude product was added to 200 mL of DMSO with stirring and the insoluble solid was filtered off. The filtrate was distilled under reduced pressure and the residual was thoroughly washed with acetone and dried in vacuo at 120 °C for 20 h. A white solid weighing 5.75 g was obtained, yield: 62%. ^{1}H NMR (DMSO-d_6):$\delta = 13.02$ (2H, −COOH), 8.371 (s, 2H), 7.885 (d, 2H), 6.809 (d, 2H). Melting point: 250 °C (DSC, no decomposition peak was observed up to 350 °C).

2.4. Polymerization

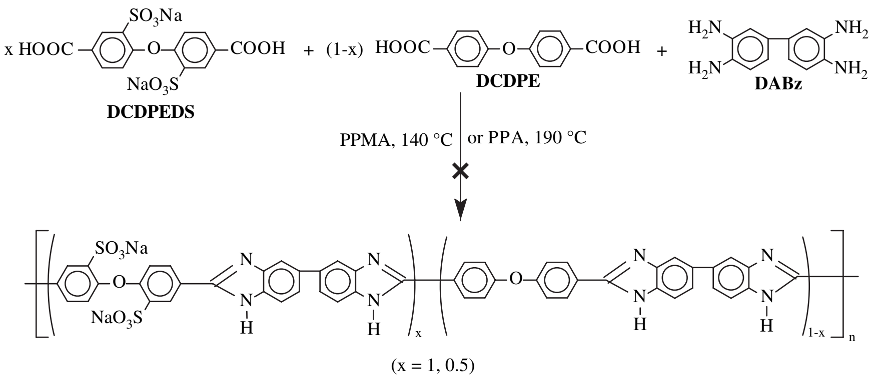
Two procedures were employed for polymerization of DCDPEDS and DABz and the experimental details are described as follows using the homopolymer as an example.

Procedure 1. To a 100 mL dry three-neck flask were added 0.6428 g (3.0 mmol) of DABz, 1.386 g (3.0 mmol) of DCDPEDS and 20 mL of PPMA under nitrogen flow. The reaction mixture was magnetically stirred and slowly heated to 140 °C for 20 h. Upon cooling, the gel-like mixture was transferred to ice water with stirring and the precipitate was filtered off. The solid was soaked in 5% sodium bicarbonate solution for two days, then filtered, thoroughly washed with deionized water and dried in vacuo at 120 °C for 10 h.

Procedure 2. To a 100 mL dry three-neck flask equipped with a mechanical stirring device were added 25 g of PPA and 5.5 g of phosphorus pentoxide under nitrogen flow. The mixture was heated and stirred until phosphorus pentoxide was completely dissolved. After cooling to room temperature, 0.6428 g (3.0 mmol) of DABz and 1.386 g (3.0 mmol) of DCDPEDS were added to the reaction flask. The reaction mixture was stirred and heated at 150 °C for 4 h and 190 °C for 20 h, respectively. Upon cooling, the gel-like mixture was transferred to ice water with stirring and the precipitate was filtered off. The solid was soaked in 5% sodium bicarbonate solution for two days, then filtered, thoroughly washed with deionized water and dried in vacuo at 120 °C for 10 h.

2.5. Membrane formation

Polymer solution of 5–10 wt% in DMSO was cast onto glass plates and dried in an air oven at 80 °C for 5 h. The films were peeled off from glass plate and dried in vacuo at 120 °C



Scheme 1. Direct polymerization method.

for 10 h. The resulting SOPBI membranes are in their sodium salt form and were converted to their proton form by soaking in 1.0 M sulfuric acid solution at 80 °C for 10 h followed by thorough washing with deionized water and drying in vacuo at 120 °C for 10 h.

2.6. Cross-linking treatment

SOPBI membranes were immersed into 85 wt% phosphoric acid at room temperature for 36 h. The membranes were taken out, whipped with tissue paper, and dried in vacuo at 80 °C for 2 h and 180 °C for 20 h successively. After cooling to room temperature, the membranes were thoroughly rinsed with deionized water (immersed into deionized water for 10 h and this process was repeated three times) and dried in vacuo.

2.7. Measurements

FT-IR spectra of the polymer membranes (for organo-soluble polymers) or powder (for organo-insoluble polymers) with thickness of about 10–30 μm were recorded on a Perkin–Elmer Paragon 1000PC spectrometer. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 400 MHz instrument. Thermogravimetric analysis (TGA) was performed in air with a TGA 2050 instrument at a heating rate of 10 °C/min. For each measurement the sample cell was maintained at 100 °C for half an hour to evaporate the absorbed water in the sample before test. The inherent viscosities (η_{inh}) were measured in DMSO with an Ubbelohde viscometer at 30 °C. Tensile measurements were performed with an Instron 4456 instrument in ambient atmosphere at a crosshead speed of 1 mm/min. Dynamic mechanical analysis (DMA) was performed with a TA Instruments DMA 2980 mechanical spectrometer under nitrogen flow in tension mode at a frequency of 1.0 Hz at temperatures ranging from room temperature to 400 °C and a heating rate of 10 °C/min. The initial static force was set to be 1.0 N.

Water uptake measurements were carried out by immersing the membranes (0.1–0.2 g per sheet) into deionized water at 30 °C for 24 h. Then the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake S was calculated from

$$S = \frac{(W_s - W_d)}{W_d} \times 100\,(\%) \tag{1}$$

where W_d and W_s refer to the weight of dry (before immersion in water) and wet membranes, respectively.

Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 kHz (Hioki 3552) [20]. A sheet of SOPBI membrane (proton form) and two pairs of blackened platinum plate electrodes were set in a Teflon cell. The cell was placed in either a thermo-controlled humid chamber for measurement at relative humidity (RH) lower than 100% or distilled deionized water for measurement in liquid water. The resistance value was determined from high frequency intercept of the impedance with the real axis. Proton conductivity was calculated from the following equation:

$$\sigma = d/(t_s\, w_s\, R) \tag{2}$$

where d is the distance between the two electrodes, t_s and w_s are the thickness and width of the membrane at 70% RH (for the conductivity measurement at RH below 100%) or in water (for the conductivity measurement in water), respectively, and R is the resistance value measured. For measurement in liquid water, the dimensions in fully hydrated state were used.

3. Results and discussion

3.1. Polymer synthesis

We primarily synthesized the SOPBI by direct polymerization of DCDPEDS and DABz in PPMA at 140 °C (procedure 1) and in PPA at 190 °C (procedure 2), respectively (Scheme 1). In procedure 1, because of the low reactivity of DCDPEDS resulting from the strong electron-withdrawing effect of the sulfonic acid group (electron-withdrawing substituents *meta* to the carboxylic groups have been reported to be unfavorable for the formation of the active intermediate acylium ions, leading to low reactivity of the carboxylic acid monomer [19]), the

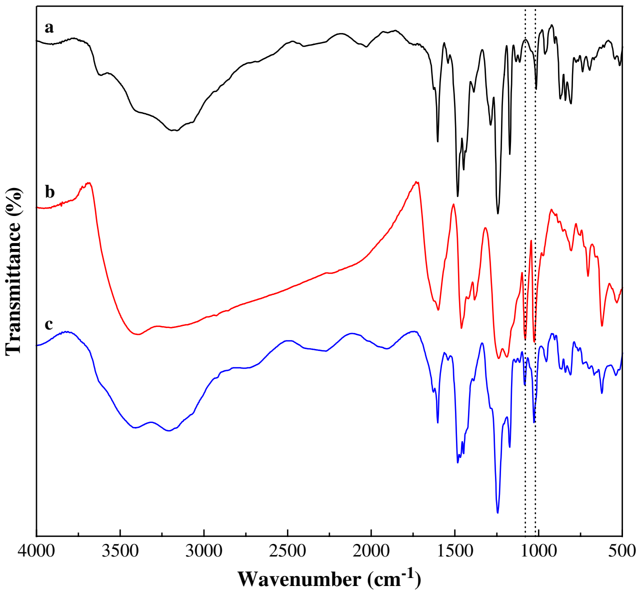
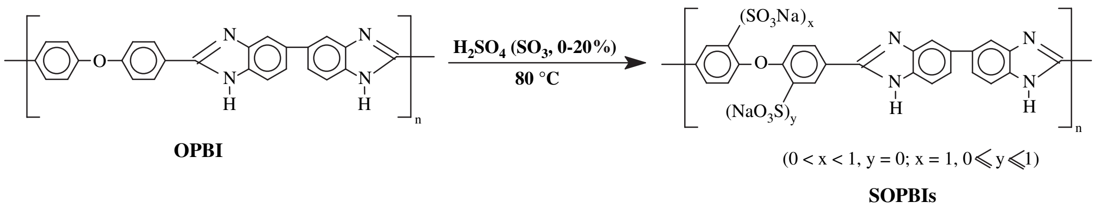


Fig. 1. FT-IR spectra of (a) OPBI, (b) the sulfonated homo-polybenzimidazole prepared by direct polymerization method in PPMA, and (c) SOPBI prepared by post-sulfonation in concentrated sulfuric acid at 80 °C for 5 h.

polymerization was carried out at 140 °C for a prolonged time (20 h). In procedure 2, to protect DABz from any possible oxidation, DCDPEDS and DABz were allowed to react first at 150 °C for 4 h under nitrogen flow to form poly(*o*-aminoamide) precursor which underwent cyclization at high temperature (e.g. 190 °C) to yield SOPBI. With both procedure 1 and procedure 2, however, insoluble gels were always obtained in each polymerization system. The resulting gels are insoluble either in pure methanesulfonic acid or in any other solvents such as DMSO, DMAc and concentrated (85%) phosphoric acid which are good solvents for some other PBIs. It is even insoluble in hot water in spite of its very high content of sulfonic acid groups. Copolymerization of DCDPEDS, DCDPE and DABz (DCDPEDS/DCDPE = 1/1) via either procedure 1 or 2 gave similar results. This is different from the case reported in the literature that many soluble sulfonated PBIs (homopolymers and copolymers) have been successfully synthesized by direct polymerization of sulfonated aromatic dicarboxylic monomers and DABz in PPA [17,18]. Fig. 1 shows the FT-IR spectra of OPBI and the sulfonated homo-polybenzimidazole synthesized in PPMA. The characteristic absorption bands around 3500–2500 cm^{-1} (–NH/protonated nitrogen), 1630 cm^{-1} (–C=N), 1460 cm^{-1} (in-plane deformation of imidazole rings) in both spectra suggest the formation of imidazole rings [9,12], while the absorption bands around 1240 cm^{-1} and 1030 cm^{-1} in Fig. 1(b) are attributed to the symmetric and asymmetric S–O stretching of sulfonate groups [10,12–14]. The broad absorption bands in the region of 3000–2500 cm^{-1} is related to the protonated nitrogen of imidazole rings [9] and the existence of residual acid in the polymer indicating that it is difficult to completely remove the acid even if the sample was thoroughly rinsed with deionized water due to cross-linking. The absorption band around 1600 cm^{-1} is assigned to the stretch vibration of phenyl ring backbone and the band around 623 cm^{-1} is due to C–S stretch vibration. The FT-IR spectrum suggests the formation of sulfonated PBI structure. The insolubility of the sulfonated polymers indicates that cross-linking occurred in the polymerization processes because, as discussed below, organo-soluble SOPBIs were obtained by post-sulfonation method (Scheme 2).

It is interesting that the post-sulfonation reaction of the precursor polymer OPBI, can be performed under mild conditions, i.e., it can be readily sulfonated in concentrated (96%) sulfuric acid at 80 °C which is much lower than that reported in the literature for sulfonation of ABPBI (450 °C) and commercial PBI (475 °C) [11,14,15]. This is because of the high reactivity of the ether bond-linked phenyl rings of OPBI in comparison with that of commercial PBI and ABPBI. The sulfonation sites occurred in the acid moiety (DCDPE) not in the tetramine moiety (DABz) because the nitrogen atoms were protonated in sulfuric acid leading to great deactivation effect on the phenyl rings of DABz, whereas the electron-donating effect of ether bond activated the phenyl rings of DCDPE. Fig. 1(c) shows the FT-IR spectrum of the SOPBI prepared in sulfuric acid at 80 °C for 5 h. The characteristic absorption bands assigned to both imidazole rings and sulfonic acid groups were observed indicating that the sulfonation reaction occurred and the post-sulfonation treatment did not cause any damage to the imidazole structure. ^{1}H NMR spectra of SOPBIs also confirmed the occurrence of sulfonation. Fig. 2 shows the ^{1}H NMR spectra of OPBI and SOPBI synthesized in concentrated sulfuric acid at 80 °C for 10 h. The peak at 8.74 ppm is assigned to the protons adjacent to the sulfonic acid group, and the degree of sulfonation (DS) is estimated to be 83% from the integration ratio of the peak at 8.74 ppm over the peaks at 7.1–8.2 ppm (other protons of the aromatic protons). Here, DS is defined as the number (percentage) of sulfonic acid groups per repeat unit. Fig. 3 shows the variation of DS as a function of reaction time at 80 °C. DS increased rapidly in the primary stage, then slowly and tended to level off. DS reached 100% when the sulfonation reaction time was prolonged to 20 h. The sulfonation reaction was more



Scheme 2. Post-sulfonation of OPBI.

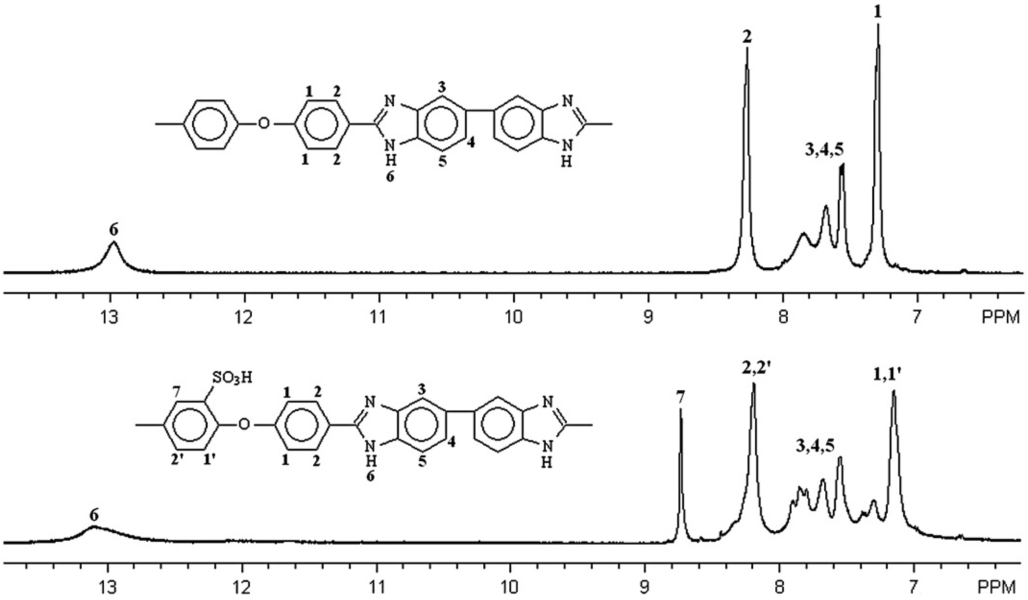


Fig. 2. ^{1}H NMR spectra of OPBI (top) and SOPBI prepared by post-sulfonation in concentrated sulfuric acid at 80 °C for 10 h.

significantly accelerated by using fuming sulfuric acid as the sulfonating reagent (Fig. 4). A high DS of 154% was obtained by reaction in fuming sulfuric acid containing 20% sulfur trioxide at 80 °C for 5 h.

Table 1 lists the solubility behaviors and inherent viscosities of OPBI and the SOPBIs prepared by post-sulfonation reaction under different conditions. OPBI is well soluble in DMSO, NMP, DMAc and methanesulfonic acid but insoluble in DMF and concentrated (85%) phosphoric acid. SOPBIs in their sodium salt form are also readily dissolved in DMSO, but the solubility in NMP and DMAc reduced drastically as the DS increased. In 85% phosphoric acid, the solubility of SOPBIs strongly depends on the DS level. SOPBI with the highest DS (154%) is soluble in 85% phosphoric acid on slight heating, whereas at low DS level SOPBIs are insoluble. The good solubility of SOPBIs in DMSO clearly indicates that the foregoing mentioned insoluble gels produced in the direct polymerization processes is not because of the poor solubility of sulfonated polymers but due to the occurrence of cross-linking. To confirm the formation of cross-linking, we redissolved the SOPBI of DS = 60% in PPMA and then heated the solution mixture to 140 °C. It was observed that gelation occurred after about 4 h and the resulting polymer became completely insoluble in DMSO and pure methanesulfonic acid in which the SOPBI was well soluble before this treatment. Similar phenomenon was observed by treating the polymer in PPA at 170 °C. These results clearly demonstrated that cross-linking did occur in the direct polymerization processes. Ueda has reported that many diaryl sulfones could be readily synthesized by condensation reaction of arenesulfonic acids and activated (electron-rich) aromatic hydrocarbons in PPMA, and 4-phenoxybenzenesulfonic sodium salt could even undergo

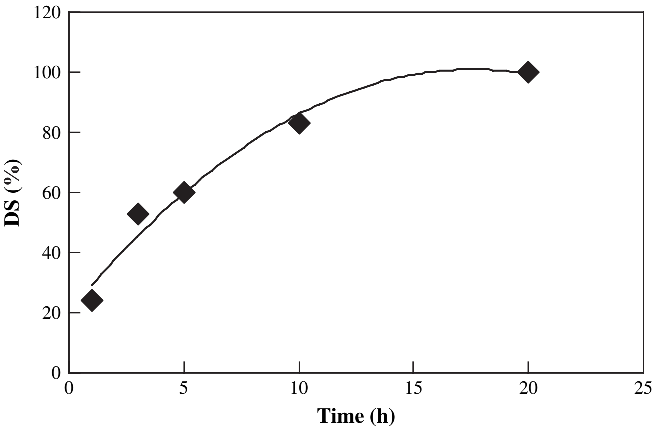


Fig. 3. Effect of reaction time on DS (concentrated sulfuric acid, 80 °C).

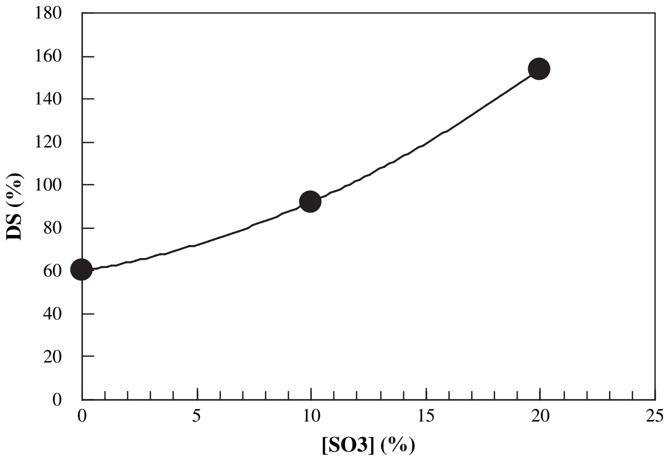


Fig. 4. Effect of sulfur trioxide concentration in fuming sulfuric acid on DS (80 °C, 5 h).

Table 1
Solubility and inherent viscosity (η) of sulfonated and non-sulfonated PBIs

Polymer	η[b] (dL/g)	Solubility					
		DMSO	NMP	DMAc	DMF	$MeSO_3H$	85% H_3PO_4
OPBI	4.7	+	+	+	±	+	−
SOPBI-60[a]	13.7	+	+	±	±	+	−
SOPBI-92[a]	12.2	+	±	±	±	+	−
SOPBI-154[a]	11.5	+	±	±	±	+	+

[a] The numeral refers to the degree of sulfonation (%) determined by ^1H NMR.

[b] Measured at a polymer concentration of 0.5 g/dL in DMSO at 30 °C.

self-condensation polymerization in PPMA to form high molecular weight poly(ether sulfone) [21,22]. In those reactions, sulfonic acid groups underwent reaction with activated phenyl rings to form aryl sulfones and water. We recently have also found that sulfonated polyimide membranes containing activated phenyl rings could be readily cross-linked by immersing them into PPMA at 80 °C [23]. In the present case, the cross-linking reaction might occur between the sulfonic acid groups and the dicarboxylic moiety of SOPBIs. To elucidate the detailed cross-linking mechanism, more work is needed.

It should be noted that the post-sulfonation treatment did not cause significant degradation of the polymer judging from the very high inherent viscosities which are about three times higher than that of OPBI as well as the high tensile strength of SOPBIs (Table 2). This indicates that OPBI has unusually high tolerance to oxidation even in fuming sulfuric acid containing 20% sulfur trioxide at 80 °C, which is superior to many other hydrocarbon polymers such as polystyrene and its derivatives, poly(ether sulfone)s and poly(ether ketone)s. SOPBI membranes could maintain very good flexibility even after being dried at 150 °C in vacuo for 20 h.

3.2. Thermal stability and dynamic mechanical analysis

The thermal stability of SOPBIs was determined by TGA. As shown in Fig. 5, for all the samples no polymer degradation was observed below 300 °C which is high enough for fuel cell application. Fig. 6 shows the DMA spectra of OPBI and SOPBIs. OPBI has a storage modulus of 5.3 GPa at room temperature and the glass transition temperature (T_g) is estimated to be 260 °C based on the peak of tangent delta. SOPBI membranes showed lower initial storage moduli because of the plasticization effect of the absorbed water. The storage moduli of SOPBI membranes increased with an increase in temperature up to 100 °C due to the evaporation of absorbed water. From 100 °C to 400 °C, the change of storage modulus is much smaller for SOPBIs (<20%) than for OPBI (70%) because of the strong interchain interaction of ions for the former. The high moduli and the high tensile strength suggest good mechanical properties of the SOPBIs.

Table 2
Tensile strength and elongation at break, and radical oxidative stability (Fenton reagent: 3% H_2O_2 containing 3 ppm $FeSO_4$ at 80 °C for 12 h) of OPBI and SOPBIs

Polymer	Tensile property		Fenton test
	Stress (MPa)	Strain (%)	Remaining weight[b] (%)
OPBI	129	14.9	94.0
SOPBI-60	98	15.2	90.9 (91.5)
SOPBI-92	90	11.6	37.9[c] (86.6)
SOPBI-154	81	12.3	Dissolved[d] (84.1)
PBI[a]	–	–	90.1

–: Not measured.

[a] Synthesized from isophthalic acid and DABz in PPA at 190 °C for 20 h.

[b] The data in parenthesis refer to cross-linked membranes.

[c] Broke into pieces.

[d] Elapsed time: <20 min.

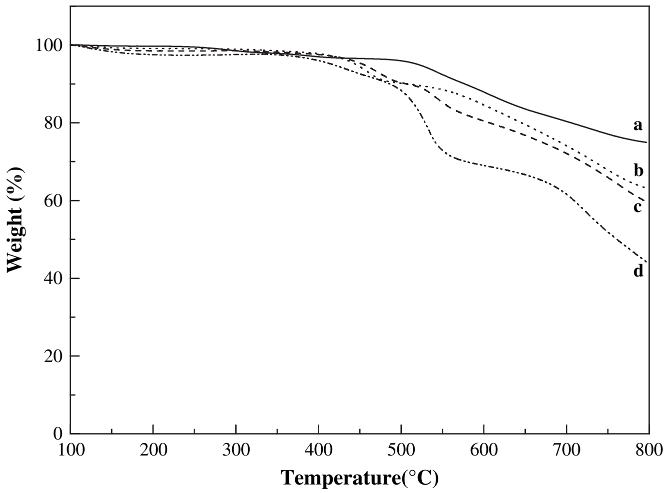


Fig. 5. Thermogravimetric curves of OPBI (a) and uncross-linked SOPBIs: (b) DS = 60%, (c) DS = 92%, (d) DS = 154%.

3.3. Preparation of cross-linked membranes

By utilizing the cross-linking reaction discussed above, cross-linked SOPBI membranes were successfully prepared by thermal treatment of phosphoric acid-doped SOPBI membranes at 180 °C in vacuo for 20 h. During the thermal

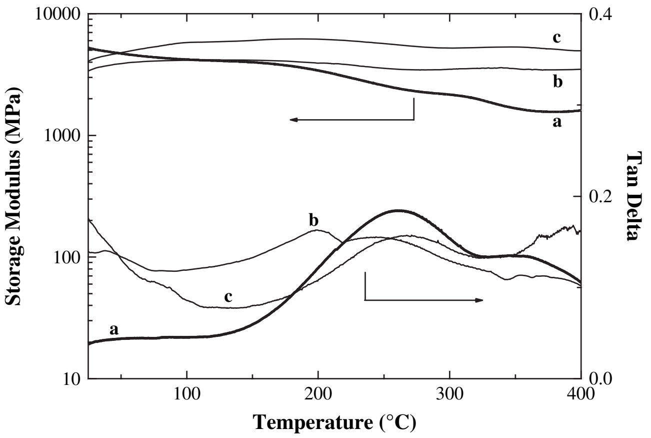


Fig. 6. DMA curves of OPBI (a) and uncross-linked SOPBIs: (b) DS = 60%, (c) DS =92%.

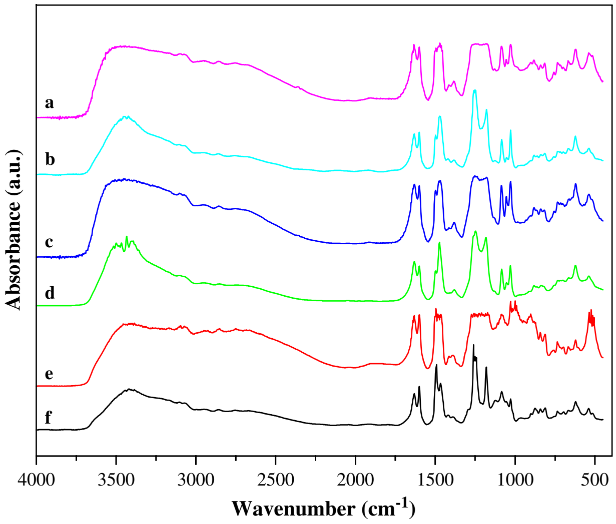


Fig. 7. FT-IR spectra of SOPBI membranes: (a) SOPBI-154, cross-linked; (b) SOPBI-154, uncross-linked; (c) SOPBI-92, cross-linked; (d) SOPBI-92, uncross-linked; (e) SOPBI-60, cross-linked; (f) SOPBI-60, uncross-linked.

treatment process, water was removed gradually and phosphoric acid was converted to polyphosphoric acid which catalyzed the cross-linking reaction. The resulting membranes were insoluble in DMSO (sodium bicarbonate was used to convert the polymer from acid form to sodium salt form before solubility test) or methanesulfonic acid indicating the occurrence of cross-linking. Fig. 7 shows the FT-IR spectra of the cross-linked and uncross-linked SOPBI membranes. For SOPBI-154 and SOPBI-92, the spectra of the cross-linked membranes are roughly similar to that of the corresponding uncross-linked ones. Cross-linked SOPBI-60, however, has very broad absorption bands in the range of 1300–800 cm^{-1} which is not observed with the uncross-linked SOPBI-60. Such broad absorption bands in this range can be assigned to phosphoric acid (overlapped with the absorption bands of sulfonic acid groups).

Table 3 lists the elemental analysis results for the cross-linked and uncross-linked SOPBIs. It can be seen that cross-linking did not cause large changes in the element content ratios of C/S, N/S and C/N. The data of hydrogen content are of less significance because the samples absorb water from air. It is interesting that for the cross-linked SOPBI-60, there is 8.02% phosphorus (=25.4% phosphoric acid) remained in the membrane. Note that the membrane has been rinsed with deionized water after the thermal cross-linking treatment. This indicates that some phosphoric acid can be blocked in the membrane by cross-linking which may provide a useful way to solve phosphoric acid leaking problem associated with phosphoric acid-doped PBI membranes. For the cross-linked SOPBI-92, the residual phosphorus is 2.05% (=6.48% phosphoric acid) which is much lower than that of the cross-linked SOPBI-60. This is probably because of the higher swelling degree (in water) of the former than that of the latter. Cross-linked SOPBI-154 could still significantly swell in water due to the high degree of sulfonation and therefore little phosphoric acid remained in the membrane.

3.4. Radical oxidative stability

Fenton reagent test was carried out with OPBI, SOPBIs and commercial PBI to examine the radical oxidative stability of these polymer membranes. The membranes (thickness: 10–30 μm) were soaked in 3% H_2O_2 containing 3 ppm $FeSO_4$ at 80 °C for 12 h and the stability was characterized by the remaining weight of the membranes. As shown in Table 2, OPBI, commercial PBI and SOPBI-60 showed more than 90% remaining weight after the Fenton reagent test and they were still very tough indicating excellent oxidative stability of these membranes. The highly sulfonated membranes, SOPBI-92 and SOPBI-154, however, displayed much poorer radical oxidative stability than SOPBI-60, OPBI and commercial PBI. SOPBI-154 dissolved within 20 min, while SOPBI-92 broke into pieces and partially dissolved within 5 h. It is interesting that cross-linking caused great improvement in the oxidative stability of SOPBIs. The remaining weight is larger than 84% for the cross-linked SOPBI-92 and SOPBI-154 indicating good radical oxidative stability due to cross-linking.

3.5. Proton conductivity

Table 4 shows the water uptake and the proton conductivities in deionized water at 60 °C of SOPBI membranes. For comparison purpose, the data of some other sulfonated polymer membranes from the literature [10,14,15,18,24–26] are also listed in this table. The SOPBI membranes showed much larger water uptake than other SPBIs. This is likely because SOPBIs had fairly flexible structure resulting from the flexible ether bond linkages, whereas the SPBIs and SABPBI reported in the literature had highly rigid structure. Flexible structure led to easy chain relaxation and thus high water

Table 3
Elemental analysis results of cross-linked and uncross-linked SOPBIs

Sample	Cross-linking	C (%)	H (%)	N (%)	S (%)	P (%)	C/S (–)	N/S (–)	C/N (–)
SOPBI-60	No	60.34	4.49	10.76	4.16	<0.5	14.5 (16.3)	2.59 (2.92)	5.61 (5.57)
	Yes	46.93	4.26	8.22	2.78	8.02	16.9	2.96	5.71
SOPBI-92	No	45.39	3.92	8.24	4.96	<0.5	9.15 (10.6)	1.66 (1.90)	5.51 (5.57)
	Yes	47.64	4.14	8.76	5.11	2.05	9.32	1.71	5.44
SOPBI-154	No	39.34	3.57	6.83	6.12	<0.5	6.43 (6.33)	1.12 (1.14)	5.76 (5.57)
	Yes	41.83	3.90	7.38	6.59	<0.5	6.34	1.12	5.69

The data in parenthesis were calculated from the degree of sulfonation determined by ^{1}H NMR.

Table 4
Water uptake and proton conductivities in liquid water at 60 °C of SOPBI and other membranes

Polymer	DS (%)	IEC (meq/g)	Water uptake (%w/w)	σ (mS cm^{-1})	Ref.
SOPBI-60	60	1.34[c]	70 (29.2[d])	6.9	[f]
SOPBI-92	92	1.94[c]	176 (51[d])	34	[f]
SOPBI-154	154	2.94[c]	397 (102[d])	185 (90[d])	[f]
OPBI	0	0	29		[f]
PBI (commercial)	0	0	19		[7]
SPBI	62–67	0.12	–	0.075[e]	[18]
Sulfobenzyl-grafting-PBI	150	2.66	35	10	[10]
SPBI-NF60H	120	2.12	26	2.7	[14]
SABPBI/4.6H_3PO_4	41	–	–	35	[15]
SPI[a]	100	1.95	87	120	[24]
	200	2.80	250	230	[25]
PBPS[b]	120	2.20	148	170	[26]

Key "–": not available from the literature.
[a] Sulfonated polyimide.
[b] Sulfonated poly(ether sulfone).
[c] Calculated from DS.
[d] Cross-linked membrane.
[e] 160 °C, 100% relative humidity.
[f] This study.

stability. The membrane swelling was greatly suppressed by cross-linking treatment. SOPBI of DS = 154%, for example, had a water uptake value of 102% after cross-linking which is about one fourth of the value before cross-linking.

The proton conductivity strongly depended on the DS and it increased from 6.9 mS cm^{-1} for the membrane of DS = 60% (uncross-linked) to 185 mS cm^{-1} for the one of DS = 154% (uncross-linked). The variation of proton conductivity of cross-linked and uncross-linked SOPBI (DS = 154% before cross-linking) as a function of relative humidity (RH) at 60 °C is shown in Fig. 8. For both cross-linked and uncross-linked membranes, the conductivity increased with an increase in RH. This is a common phenomenon which has been observed with many other sulfonated polymer membranes. Moreover, it can be seen that cross-linking did not cause large reduction in proton conductivity. At 100% RH the cross-linked membrane displayed somewhat lower conductivity than the uncross-linked one, whereas at RH of 30–80% the proton conductivity is similar or even slightly higher for the cross-linked membrane. The temperature dependence of proton conductivity of SOPBI (DS = 154%) in deionized water is shown in Fig. 9. For the uncross-linked membrane, the conductivity primarily increased with an increase in temperature up to 90 °C and dropped thereafter. The drop of conductivity at high temperatures (>90 °C) is because the membrane highly swelled and deformed. In contrast, the cross-linked membrane displayed much improved water stability and the conductivity increased with an increase in temperature in the whole temperature range. High proton conductivity of 150 mS cm^{-1} was obtained at 120 °C with the cross-linked membrane.

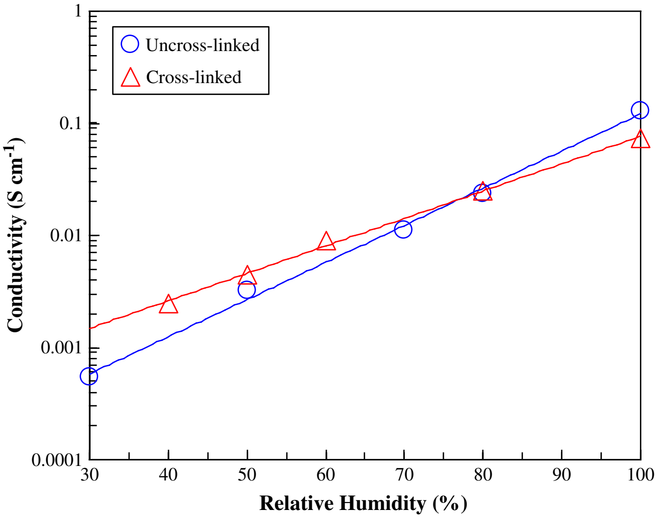


Fig. 8. Variation of proton conductivity of cross-linked and uncross-linked SOPBI membranes (DS = 154%) as a function of relative humidity (RH) at 60 °C.

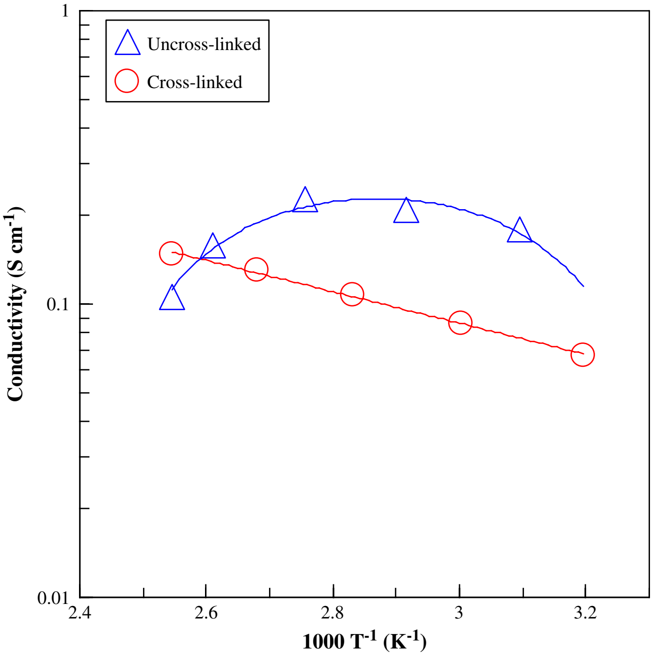


Fig. 9. Variation of proton conductivity in deionized water of cross-linked and uncross-linked SOPBI membranes (DS = 154%) as a function of temperature.

It has been reported that the undoped SPBI membranes generally showed rather low proton conductivities due to the reduced proton mobility resulting from the strong interactions between protons and the nitrogen atoms of imidazole rings (base) [14,17,18]. In this study, the proton conductivities of SOPBI membranes are lower than many other sulfonated polymers (e.g. sulfonated polysulfone and sulfonated polyimides). However, the effect of proton–nitrogen interaction on proton conductivity is much less significant than that observed with other SPBI membranes. We cannot give a proper explanation at present. The conductivity measurement of phosphoric acid-doped SOPBI membranes and the leaking rate of phosphoric acid from the cross-linked and uncross-linked membranes are in progress and will be reported elsewhere.

4. Conclusions

Direct polymerization method is not suitable for preparation of the desired sulfonated polybenzimidazoles (SOPBIs) because of gelation, whereas post-sulfonation method is very useful and facile for preparing SOPBIs with controlled degrees of sulfonation. No significant polymer degradation was observed in the post-sulfonation process even when fuming sulfuric acid containing 20% sulfur trioxide was used as the sulfonating reagent at 80 °C. The resulting SOPBIs showed good solubility, high thermal stability, and excellent mechanical properties. Cross-linked SOPBI membranes were successfully prepared by thermal treatment of phosphoric acid-doped SOPBI membranes at 180 °C in vacuo for 20 h and the resulting cross-linked membranes showed much improved water stability and radical oxidative stability in comparison with the corresponding uncross-linked ones, while the proton conductivity did not change largely. Highly proton conductive (150 mS cm^{-1}, 120 °C in water) and water stable SOPBI membrane was developed.

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References

[1] Wainright JS, Wang JT, Weng D, Savinell RF, Litt M. J Electrochem Soc 1995;142:L121–3.
[2] Wang JT, Savinell RF, Wainright JS, Litt M, Yu H. Electrochim Acta 1996;41:193–7.
[3] Wang JT, Wainright JS, Savinell RF, Litt M. J Appl Electrochem 1996;26:751–6.
[4] Savadogo O, Xing B. J New Mater Electrochem Syst 2000;3:345–9.
[5] Savadogo O, Xing B. Electrochem Commun 2000;2:697–702.
[6] He R, Li Q, Xiao G, Bjerrum NJ. J Membr Sci 2003;226:169–84.
[7] Li Q, He R, Jensen JO, Bjerrum NJ. Fuel Cells 2004;4:147–59.
[8] Asensio JA, Gomez-Romero P. Fuel Cells 2005;5:336–43.
[9] Bouchet R, Siebert E. Solid State Ionics 1999;118:287–99.
[10] Glipa X, Haddad ME, Jones DJ, Roziere J. Solid State Ionics 1997;97:323–31.
[11] Bae JM, Honma I, Murata M, Yamamoto T, Rikukawa M, Ogata N. Solid State Ionics 2002;147:189–94.
[12] Asensio JA, Borros S, Gomez-Romero P. J Polym Sci Part A Polym Chem 2002;40:3703–10.
[13] Qing S, Huang W, Yan D. Eur Polym J 2005;41:1589–95.
[14] Qing S, Huang W, Yan D. React Funct Polym 2006;66:219–27.
[15] Asensio JA, Borros S, Gomez-Romero P. Electrochim Acta 2004;49:4461–6.
[16] Asensio JA, Borros S, Gomez-Romero P. Electrochem Commun 2003;5:967–72.
[17] Ariza MJ, Jones DJ, Roziere J. Desalination 2002;147:183–9.
[18] Staiti P, Lufrano F, Arico AS, Passalacqua E, Antonucci V. J Membr Sci 2001;188:71–8.
[19] Ueda M, Sato M, Mochizuki A. Macromolecules 1985;18:2723–6.
[20] Guo X, Fang J, Watari T, Tanaka K, Kita H, Okamoto K. Macromolecules 2002;35:6707–13.
[21] Ueda M, Uchiyama K, Kano T. Synthesis 1984;323–5.
[22] Ueda M. Makromol Chem Rapid Commun 1985;6:271–4.
[23] Fang J, Zhai F, Guo X, Xu H, Okamoto K. J Mater Chem 2007;17:1102–8.
[24] Fang J, Guo X, Harada S, Watari T, Tanaka K, Kita H, et al. Macromolecules 2002;35:9022–8.
[25] Yin Y, Fang J, Watari T, Tanaka K, Kita H, Okamoto K. J Mater Chem 2004;14:1062–70.
[26] Wang F, Hickner M, Kim Y, Zawodzinski T, McGrath J. J Membr Sci 2002;197:231–42.