

PREPARATION AND CHARACTERIZATION OF SOLUBLE SULFONATED POLYBENZIMIDAZOLE FOR PROTON EXCHANGE MEMBRANE MATERIALS*

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Abstract A series of sulfonated polybenzimidazoles (sPBI-SF) were prepared from 2,2-bis(4-carboxyphenyl)hexafluoropropane (BIS-B-AF), 3,3'-disulfonyl-4,4'-dicarboxydiphenylsulfone (DSDCDPS) and 3,3'-diaminobenzidine (DAB) at various stoichiometric ratio by solution copolycondensation in poly(phosphoric acid). The chemical structure of the resulting sPBI-SF was confirmed by FTIR and ¹H-NMR. The sPBI-SFs with high molecular-weights ($M_n = 39400\text{--}65500$) were soluble in DMF, DMSO or DMAc. Therefore, they could form some transparent and flexible membranes easily by solution casting. The glass-transition temperatures of the acidic form sPBI-SF were in the range from 222°C to 269°C. The extrapolated onset decomposition temperatures were up to 440°C. The sulfonic groups grafted in the PBI chain had higher initial thermal degradation activation energy and exhibited excellent thermal stability. In addition, these membranes with good mechanical properties presented the swelling degree below 12% and the water uptake about 16%. The proton conductivities of sPBI-SF membranes measured by alternating-current impedance spectroscopy attained to 1.64×10^{-3} S/cm at 70°C.

Keywords: High performance polymers; Heteroatom-containing polymers; Membranes; Polyelectrolytes; Thermogravimetric analysis.

INTRODUCTION

The environment-friendly and high power density generators have been investigated as the promising technology to relieve the global environmental and energy crisis. Polymer electrolyte membrane fuel cell (PEMFC) has recently attracted much attention due to its pollution-free and high energy-conversion efficiency^[1, 2]. Polymer exchange membrane (PEM) plays a key role in PEMFC system. It is not only an electrolyte transporting protons produced at anode to cathode but also a separator between fuel and oxygen. Up to now, the crucial drawbacks of commercial Nafion[®] membranes were high cost and poor performance at elevated temperatures due to dehydration. Lately, it has been reported that PEMFC operated above 100°C has some prominent advantages, for example, increasing the CO tolerance of the catalyst and enhancing the fuel efficiency^[3]. Thus the new proton-conducting membranes such as sulfonated polysulfone, sulfonated polyetheretherketone and sulfonated polyimide have been rapidly developed^[4–8]. It is observed that these membranes possess high proton conductivity, good mechanical strength, high thermochemical stability and less cost.

The poly[(2,2'-*m*-phenylene)-5,5'-bibenzimidazole] (PBI) is one aromatic heterocyclic polymer with

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excellent thermochemical stability and mechanical properties^[9, 10]. The phosphoric acid doped PBI membranes were suggested for application as PEM, attributable to their potential properties, for example, high proton conductivity, almost zero electro-osmotic drag number, much lower permeability for hydrogen and methanol, and good mechanical flexibility at elevated temperature (*ca.* 150–200°C)^[11–14]. Aside from phosphoric acid and sulfonic acid, solid inorganic compounds including oxides (*e.g.*, amorphous silica) and inorganic proton conductors such as phosphotungstic acid, silicotungstic acid and zirconium phosphate were incorporated with PBI to develop the high performance electrolyte^[15–18]. Recently, the acid-base blend membranes based on PBI with sulfonated poly(ethersulfone) or sulfonated poly(etheretherketone) have also been investigated^[19–23].

In recent years, a particularly attractive way to functionalize polybenzimidazole into proton conducting materials was the introduction of sulfonic groups into PBI main chain. Three approaches for PBI sulfonation have been developed as below: (a) direct sulfonation of the PBI backbone^[24, 25]; (b) chemical grafting of functional monomers such as propanesultone, butanesultone, and sodium (4-bromomethyl)benzenesulfonate onto the PBI backbone^[26–28]; and (c) co-polycondensation of a sulfonated aromatic diacid and a non-sulfonated aromatic diacid with an aromatic tetraamine^[29–32]. The last synthesis route is the most appropriate method, and it can effectively control the sulfonation degree and avoid side reactions during polycondensation. However, only few sulfonated aromatic diacids such as 5-sulfoisophthalic acid, 2-sulfoterephthalic acid and disulfodifluoroterephthalic acid are available to prepare various sulfonated polybenzimidazoles. Recently, two new sulfonated diacid monomers, 4,8-disulfonyl-2,6-naphthalenedicarboxylic acid, 3,3'-disulfonyl-4,4'-dicarboxydiphenyl sulfone (DSDCDPS) were synthesized to prepare some new sulfonated PBIs^[33, 34]. In this study, some soluble sulfonated polybenzimidazoles were prepared successfully to form some transparent and more flexible films. They are promising to be used for proton exchange membranes.

EXPERIMENTAL

Materials

BIS-B-AF, DAB and 4,4'-dimethyldiphenylsulfone (DMDPS) were used directly as received from Aldrich Chemical Co. Other reagents and solvents were purchased from Shanghai Chemical Reagents Co. and used as received. The sulfonated diacid monomer of DSDCDPS, was prepared from DMDPS through sulfonation and subsequent oxidation according to the Ref. [32].

Synthesis of the Sulfonated Polybenzimidazole (sPBI)

The numbers in abbreviation of the resulting polymers (sPBI-SF0, sPBI-SF20, sPBI-SF30, sPBI-SF40 and sPBI-SF50) mean the mole ratio of monomers DSDCDPS to BIS-B-AF, which were 0, 20/80, 30/70, 40/60 and 50/50 respectively. They were synthesized by the solution copolycondensation in poly(phosphoric acid) according to Ref. [32]. In addition, sPBI-SF40 with $-\text{SO}_3\text{H}$ or $-\text{SO}_3\text{Na}$ was named as sPBI-SF40H or sPBI-SF40Na, respectively.

Membrane Preparation

The resulting sodium form polymer was dissolved in DMAc. Then the polymer solution was cast on a square glass substrate (14 cm $\times$ 14 cm) and dried to form a membrane at 100°C for 16 h. The membranes were peeled off from the substrate by immersion in water. A series of transparent and flexible membranes were thus obtained with thickness in the range of 30–45 μm . All sulfonated membranes were acidified with 1 mol/L HCl solution overnight and then rinsed repeatedly with deionized water. Finally, all membranes were dried in a vacuum oven at 110°C for 30 h. In addition, some thinner membranes with a thickness of about 15 μm were also prepared by the similar method for FTIR study.

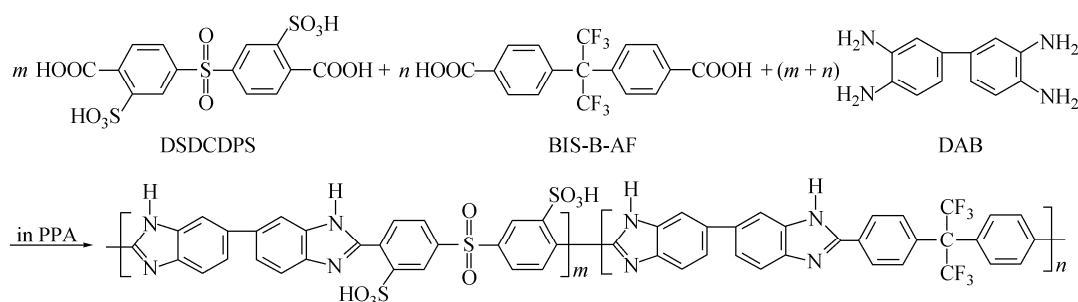
Measurements

FTIR spectra of the thin membranes were recorded on a Paragon 1000 IR spectrometer (Perkin-Elmer Co., USA). ^1H -NMR spectra were performed on a Varian Mercury Plus 400 MHz NMR spectrometer using $\text{DMSO-}d_6$ as solvents and tetramethylsilane as the internal standard. Gel permeation chromatography (GPC) was conducted on a PE 200 apparatus installing a mixed 10 μm PS column with a length of 750 mm. DMF

containing 0.01 mol/L of LiBr was applied as eluant at a flow rate of 1.0 mL/min at 70°C. The obtained polymer solution was filtered through a 0.45 µm PTFE filter before it was injected into the column. Calibration was made by polystyrene as the standard. Thermogravimetric data of the resulting polymers were collected on a TGA 2050 instrument under nitrogen at a heating rate of 20 K/min. Additionally, TGA of sPBI-SF40H were performed at other three heating rates of 3, 10 and 40 K/min under N₂ to calculate its thermal degradation activation energy. All samples were preheated from room temperature to 200°C and held for 10 min in order to remove moisture from them, and then they were cooled to *ca.* 90°C *in situ* and finally reheated to 800°C. Dynamic mechanical analysis was performed on a DMA 2980 apparatus at 10 Hz frequency in dry nitrogen atmosphere. The sample was fixed in a clamp holder and then the temperature scan was completed in the range from 40°C to 450°C at a heating rate of 10 K/min. Tensile measurement was conducted on an Instron 4465 instrument at 22°C at an elongation rate of 5 mm/min. The sample dimensions for DMA and tensile measurements were about 40 mm × 5 mm. Swelling degree and water uptake were measured at 80°C *via* the experiments proposed in Reference^[4]. The proton conductivity of the sPBI-SF membrane was evaluated in the frequency range of 10² to 10⁷ Hz with oscillating voltage 10 mV, using a Solartron 1260 frequency analyzer and 1287 electrochemical interface. The sample (10 mm × 20 mm) was clamped in a two-probe conductivity cell^[4]. After soaked in deionized water for 12 h, the measurements were made in the temperature range from 30°C to 90°C.

RESULTS AND DISCUSSION

The sPBI-SF polymers with different sulfonation degrees (SD) were prepared from various stoichiometric mixtures of BIS-B-AF, DSDCDPS and DAB in PPA. The procedure was presented in Scheme 1.



Scheme 1 Synthesis of sPBI-SF

The solubility of the resulting polymers is better than that of other PBIs from SDBA, DSDCDPS and DAB in polar aprotic solvents^[32]. The hexafluoropropane groups, which were introduced into the polymer main chain, are more effective to improve the solubility of sulfonated PBI. The flexible membranes with SD up to 100% were easily prepared by the solution of sPBI-SF in DMSO, DMAc or DMF.

FTIR of sPBI-SF

The chemical structure of the resulting sPBI-SF was analyzed by FTIR spectroscopy. The representative FTIR spectra of sPBI-SF0 and sPBI-SF50H were shown in Fig. 1. The benzimidazole characteristic absorption peaks were detected at 1630, 1590, 1448 and 807 cm⁻¹^[22]. The absorption bands at 838 and 1022 cm⁻¹ in Fig. 1(a) were assigned to the *para*-substituted benzene rings. The band at 1022 cm⁻¹ blue-shifted to 1026 cm⁻¹, as presented in Fig. 1(b). It is ascribable to the electrophilic effect of the sulfones in main chain and the side sulfonic groups. After introducing the monomer of DSDCDPS, the peak at 1139 cm⁻¹ due to the stretching vibration of —CF₃ distinctly decreased in intensity. However, the absorption bands at 1175 cm⁻¹ attributable to the asymmetric vibration of —SO₃H increased. In addition, the novel peak due to the symmetric vibration of —SO₃H was clearly observed at 1069 cm⁻¹ in Fig. 1(b), and the peak owing to the stretching vibration of C—S was also detected at 619 cm⁻¹. It has been proved that the —SO₃H groups were successfully incorporated into the sPBI-SF main chain by copolycondensation.

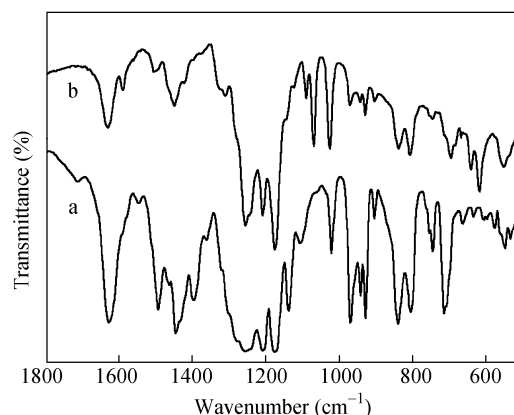


Fig. 1 FTIR spectra for sPBI-SF0 (a) and sPBI-SF50H (b)

¹H-NMR of sPBI-SF

Figure 2 showed the ¹H-NMR spectra from $\delta = 14$ to 7 for sPBI-SF 50 Na and sPBI-SF0. A strong signal peak ascribable to the imidazole protons (H_1) of sPBI-SF0 was detected at $\delta = 13.14$ in Fig. 2(a). However, the imidazole protons ($H_{1'}$ and H_1) of sPBI-SF 50 Na presented only a broad and weak peak attributing to the electron-withdrawing effect of the $-\text{SO}_3\text{H}$ groups. Comparing the ¹H-NMR spectrum of sPBI-SF 50 Na with that of sPBI-SF0, three novel peaks of H_3 , H_4 and H_5 were detected in lower field because of the distinct electrophilic difference between hexafluoropropane and sulfone. In addition, three new signal peaks attributable to H_7 , H_8 and H_9 were respectively observed at $\delta = 8.58$, 8.62 and 8.15 in Fig. 2(b), and the ratio of three signal integrals is approximately 1:1:1, in good accordance with the chemical structure of the sPBI-SF 50 Na repeating units. It is recognized that the SD value of the sulfonated polymer can be calculated by the ¹H-NMR method. The sPBI-SF 50 Na's SD defined as the molar ratio of twice sulfonated units to the total repeating units is about 90%, approximating to the theoretical value (100%). Therefore, the ¹H-NMR spectra confirmed the proposed structure of the resulting sPBI-SF as shown in Fig. 2, and the sPBI-SF's SD is controllable by the molar ratio of DSDCDPS to BIS-B-AF.

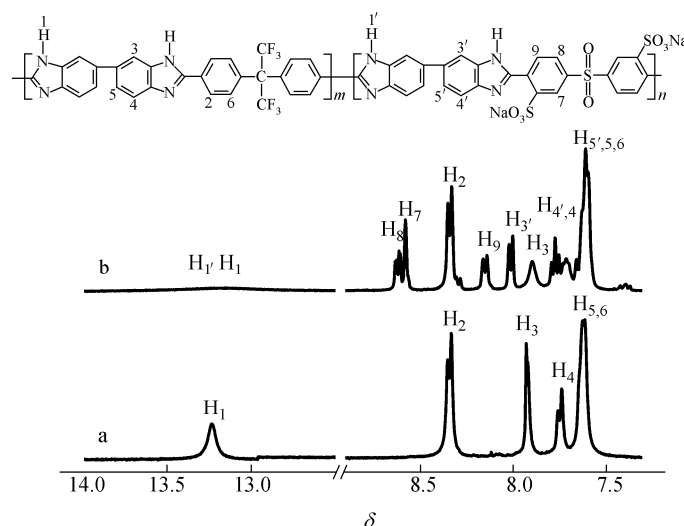


Fig. 2 ¹H-NMR spectra of sPBI-SF0 (a) and sPBI-SF50Na (b)

GPC of sPBI-SF

The molecular weights of the resulting polymers were measured by GPC using DMF as eluant. The data of the molecular weights were summarized in Table 1. The number-average molecular weights (M_n) ranged from 39400 to 65500. The polydispersity indices (PDI) were in the range of 1.98–2.25. It indicates that the synthesis of high molecular weight sPBI was successful.

Table 1. The molecular weight, thermal and mechanical properties of the resulting polymers

Sample ^a	$M_n \times 10^{-4}$	PDI	T_d^b (°C)	$T_{5\%}^c$ (°C)	$T_{10\%}^c$ (°C)	T_p^d (°C)	Break strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)	$\tan\delta_{\max}$	T_g^e (°C)
sPBI-SF0	6.40	2.17	532	539	558	566	98.9	94.5	6.0	0.154	269
sPBI-SF20	6.55	2.20	449	495	540	565	80.5	27.1	6.2	0.138	255
sPBI-SF30	4.72	2.25	447	481	523	566	89.4	26.2	5.8	0.111	222
sPBI-SF40	3.94	2.14	440	466	503	566	98.5	23.3	5.2	0.111	229
sPBI-SF50	3.97	1.98	440	460	492	570	77.5	17.0	4.9	0.102	233

^a The acid form sPBI-SF except that the sodium form one for GPC;

^b The extrapolated onset decomposition temperature for the first weight loss;

^c Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 20 K/min in nitrogen;

^d Temperature at which a maximum rate of weight loss was detected from the DTG curve;

^e Glass-transition temperature determined by DMA at a heating rate of 10 K/min in a frequency of 10 Hz

Thermal Stabilities of sPBI-SF

The acid form sPBI-SF samples and sPBI-SF0 were used in TGA measurement to characterize their thermal stabilities. On account of the hygroscopicity, these samples must be pretreated in-situ in the TGA instrument to exclude the absorbed water as much as possible. The data of thermal stabilities as listed in Table 1 were obtained on the assumption that absence of moisture in samples.

The TGA and DTG curves of sPBI-SF0, sPBI-SF20H and sPBI-SF50H were represented in Fig. 3. There is no significant weight loss below 400°C for all samples. It clarifies the nearly complete closure of the imidazole rings. The initial peak in the temperature range of 450–650°C was observed from the DTG curve of sPBI-SF0 due to the thermal degradation of $-\text{CF}_3$, and the second wider peak above 650°C attributable to the decomposition of the polymer chain. As shown in Fig. 3, the novel shoulder peaks in the range of 350–520°C increased with increasing SD in the DTG curves of sPBI-SF20H and sPBI-SF50H. It is ascribable to the degradation of the side sulfonic groups. The weight losses in the range of 450–650°C were attributed to the

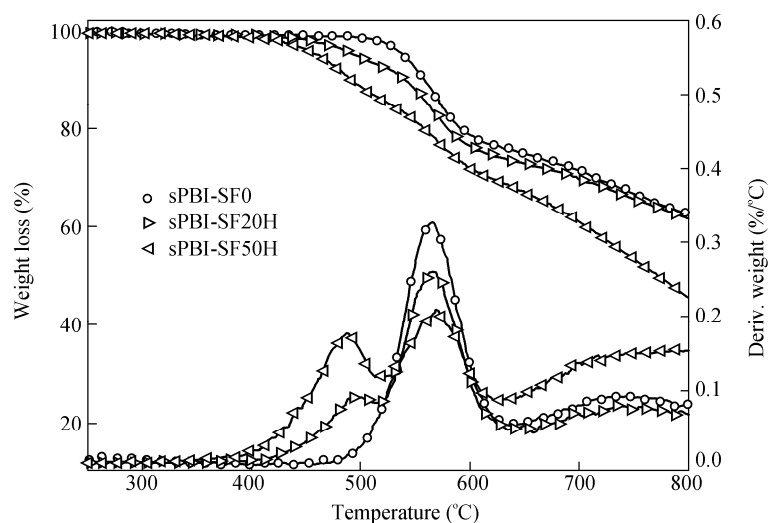


Fig. 3 TGA-DTG thermograms of sPBI-SF0, sPBI-SF20H and sPBI-SF50H

decomposition of $-\text{CF}_3$ and sulfone in the main chain. Therefore, the thermal stabilities of the acid form sPBI-SF samples were inferior to that of sPBI-SF0, after the introduction of the sulfonic groups into the polymer chain. As presented in Table 1, the temperature values of $T_{5\%}$ and $T_{10\%}$ respectively decreased from 495°C to 460°C and 540°C to 492°C with increasing the theoretical SD values from 40% to 100%. However, there was no distinct influence on T_d 's and T_p 's of the sulfonated samples with increasing SD. In a word, the sPBI-SF samples presented excellent thermal stabilities under N_2 , and their decomposition temperatures over 350°C could suffice for the fuel cell applications.

For further measuring the thermal degradation activation energy of the sulfonic groups, the thermal analyses of sPBI-SF40H were performed at four kinds of heating rates (β) under N_2 , respectively. The activation energy values computed by both Ozawa and Kissinger method, as applied in previous work^[32].

The linear relationship between $\lg\beta$ and $1/T$ was presented in Fig. 4. When the weight loss was lower than 62%, the isoconversional plots were two sets of parallel straight lines with the correlation coefficients in the range of 0.973–0.999. Therefore, two average values of the activation energy calculated by Ozawa method from the slopes of these parallel straight lines were 270.5 and 395.2 kJ/mol, respectively. The former corresponding to the degradation of the sulfonic groups was close to the activation energy of sPBI-SS40H^[32].

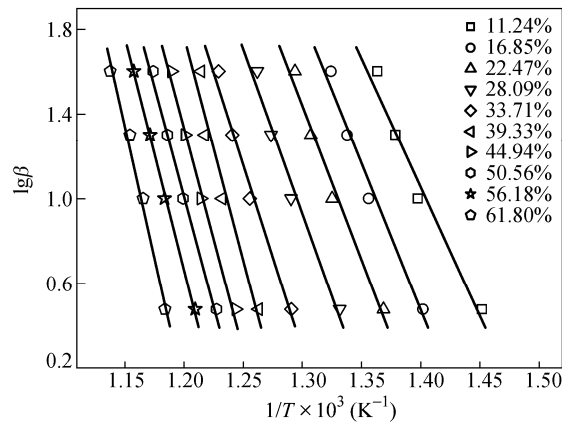


Fig. 4 Ozawa plots of $\lg\beta$ versus $1/T \times 10^3$ for sPBI-SF40H under N_2

Two peaks ($T_{\max 1}$ and $T_{\max 2}$) were observed in the temperature range of 400–650°C from the DTG curves of sPBI-SF40 H. Two linear relationships were obtained by Kissinger method for $\ln(\beta/T_{\max 1}^2)$ versus $1/T_{\max 1}$ and $\ln(\beta/T_{\max 2}^2)$ versus $1/T_{\max 2}$, as shown in Fig. 5. Their correlation coefficients were 0.993 and 0.989, respectively. Two thermal degradation activation energy values were determined respectively to be 280.4 and 378.6 kJ/mol for $T_{\max 1}$ and $T_{\max 2}$, in accordance with those from the Ozawa one.

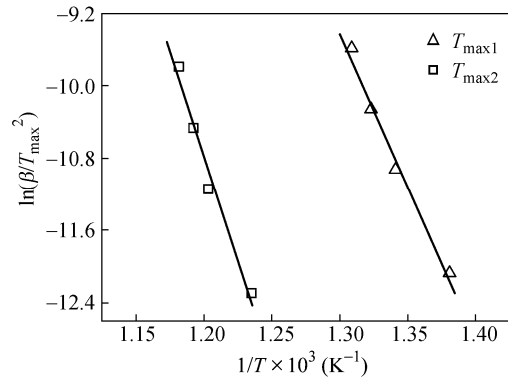


Fig. 5 Kissinger plots of $\ln(\beta/T_{\max}^2)$ versus $1/T_{\max} \times 10^3$ for sPBI-SF40H under N_2

Mechanical Properties of sPBI-SF

The dynamic mechanical analyses were conducted by DMA, as presented in Fig. 6. The storage moduli (E') of all the membranes were relatively high due to their rigid chain, even after their glass transitions. The E' of the sulfonated membrane had a distinct enhancement, comparing with that of the non-sulfonated membrane. For example, the E' values at 150°C were 3.05, 4.06, 2.98 and 5.04 GPa with increasing SD from 40% to 100% in contrast to 2.69 GPa of sPBI-SF0. In addition, the loss moduli (E'') of all the sulfonated membranes are remarkably higher than that of sPBI-SF0 at temperatures below 200°C. For instance, the E'' values at 150°C were 143, 269, 334, 255 and 416 MPa with an increase of SD from 0 to 100%. As a result, it is indicated that the sPBI-SF membranes hold excellent rigidity and tenacity.

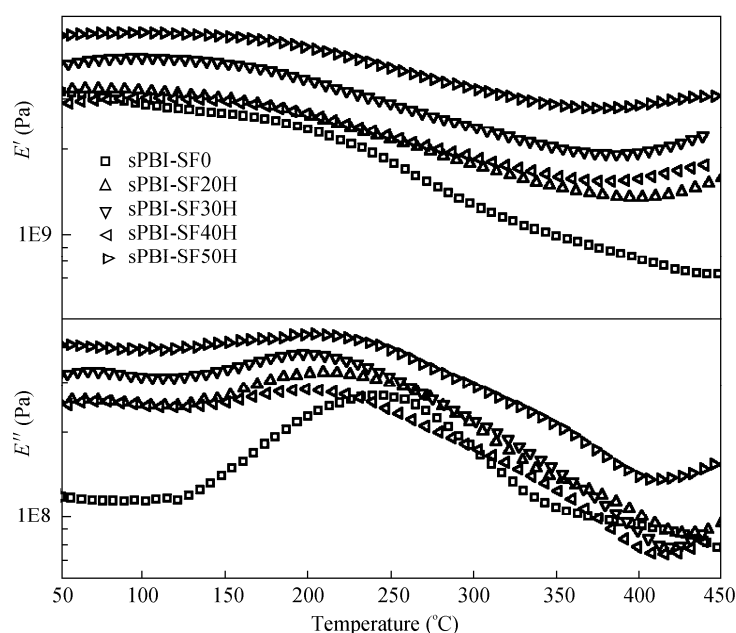


Fig. 6 Temperature curves of E' and E'' for sPBI-SF0 and the acidic form sPBI-SF

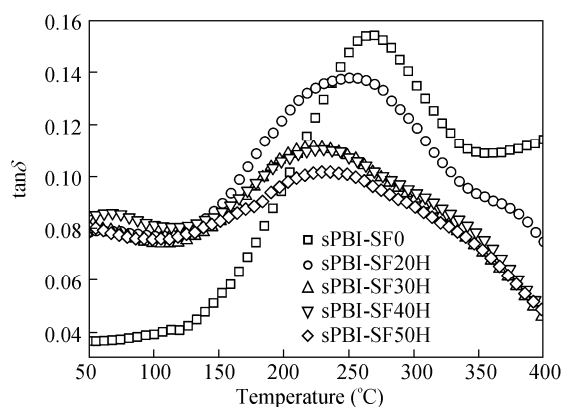


Fig. 7 Temperature curves of $\tan\delta$ for sPBI-SF0 and the acidic form sPBI-SF

The temperature dependence of the $\tan\delta$ for all membranes was illustrated in Fig. 7. The glass-transition temperatures (T_g) determined from the peak temperature of the loss tangent ranged from 269°C to 222°C, as listed in Table 1. The T_g 's of sPBI-SF were lower than that of sPBI-SF0, and the difference was in the range of

11–47°C. It is possibly ascribed that the bulky side sulfonic groups increased the free volume of sPBI-SF, which benefited to the free rotation along the polymer chain at relatively low temperatures. In general, the T_g values of the resulting samples were higher than the potential operating temperature (*ca.* 150°C) of PEMFC.

Typical mechanical properties of the membranes were also measured and summarized in Table 1. The break strength and tensile modulus of all membranes were in the range of 9.8–77.5 MPa and 6.2–4.9 GPa, respectively. The elongation at break observably decreased from 94.5% to 17.0% with increasing SD. However, the sPBI-SF50H membrane still presented excellent flexibility in dry status, in comparison with the brittle sPBI-SS50H one^[32].

Swelling Degree and Water Uptake

The effect of SD on swelling degree (S_{water}) and water uptake (W_{water}) of the membranes prepared here were evaluated at 80°C, as shown in Fig. 8. The values of S_{water} and W_{water} presented similar trend with an increment of SD. The membranes with sulfonic groups had higher S_{water} and W_{water} than the non-sulfonated. However, the S_{water} and W_{water} of sPBI-SF with hexafluoropropane were lower than those of sPBI-SS containing sulfone^[32]. The sPBI-SF50H membrane with a theoretical ion exchange content (IEC) of 1.75 mmol/g only presented a maximal S_{water} of 9.18%, comparing with 12.2% of sPBI-SS50H. The supreme W_{water} was 16.3% for sPBI-SF30H. It was lower than 23.4% of sPBI-SS30H, which is possibly due to the hydrophobic effect of hexafluoropropane.

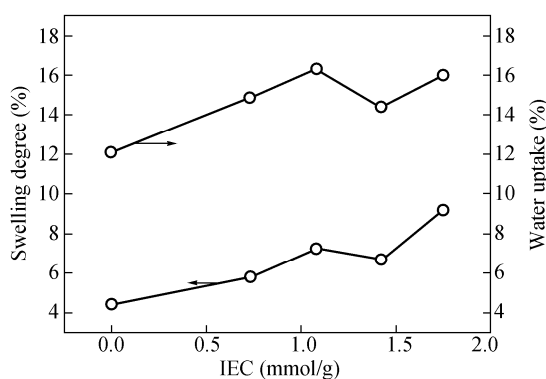


Fig. 8 S_{water} and W_{water} of sPBI-SF0 and the acid form sPBI-SF as a function of IEC at 80°C

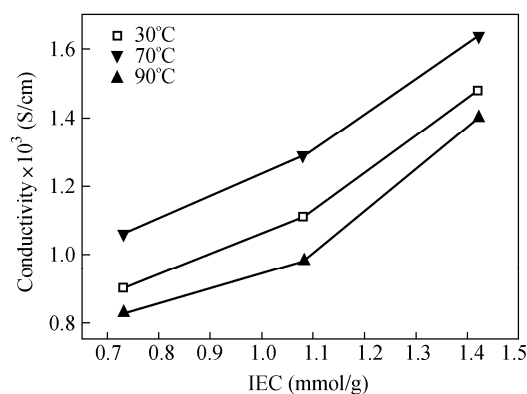


Fig. 9 The proton conductivities of sPBI-SF membranes at different temperatures

Proton Conductivity

The proton conductivities of sPBI-SF membranes with SD value in the range of 40%–80% were investigated at 30, 70 and 90°C, respectively. As shown in Fig. 9, the conductivity increased with increasing SD. There was a strong interaction between the proton of sulfonic group and the nitrogen in imidazole rings. Thus, the proton conduct was limited and the proton conductivity only maintain at the level of 10^{-3} S/cm. The proton conductivity of sPBI-SF enhanced with a temperature increment from 30°C to 70°C. However, it dropped sharply at 90°C. sPBI-SF was also a kind of thermal shrinkage membrane, similar to sPBI-SS membranes reported previously^[32]. The interesting property of sPBI-SF possibly induced to narrow proton conducting channel at higher temperature. Therefore, it was difficult for proton to conduct, and the proton conductivity decrease.

CONCLUSIONS

In this paper, we reported a series of sPBI-SFs synthesized from BIS-B-AF, DSDCDPS and DAB. The resulting polymers were characterized by FTIR, ^1H -NMR, GPC, TGA and DMA, *etc.*. As a result, the sPBI-SFs with high molecular-weights can be highly soluble in polar aprotic solvents and cast easily to form transparent and flexible membranes. The swelling degrees of these membranes were below 12% and water uptake was about 16%. Their

proton conductivities achieved 1.64×10^{-3} S/cm at 70°C. In addition, the E_{dl} values of sPBI-SF40 H calculated by Kissinger and Ozawa method were respectively 280.4 and 270.5 kJ/mol, indicating that the sulfonic groups grafted in the PBI chain had excellent thermal stability.

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