Macromolecules **2008**, *41*, 4165−4172

Synthesis and Properties of Sulfonated Poly[bis(benzimidazobenzisoquinolinones)] as Hydrolytically and Thermooxidatively Stable Proton Conducting Ionomers

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Received January 17, 2008; Revised Manuscript Received April 27, 2008

ABSTRACT: Novel sulfonated poly[bis(benzimidazobenzisoquinolinones)] as hydrolytically and thermooxidatively stable electrolyte for high-temperature fuel cell applications are reported. A series of sulfonated polymers (SPBIBI-*x*, *x* refers to molar percentage of sulfonated dianhydride monomer) were synthesized from 6,6′-disulfonic-4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (SBTDA), 4,4-binaphthyl-1,1,8,8-tetracarboxylic dianhydride (BTDA), and 3,3′-diaminobenzidine. The chemical structures of those polymers as well as model compounds synthesized from SBTDA and *o*-phenylenediamine were confirmed by nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR). The resulting polymers generally showed good solubility in *m*-cresol and DMSO. Flexible and tough membranes with high mechanical strength were prepared. They show very high thermal, thermooxidative, and hydrolytic stabilities and reduced swelling in water at enhanced temperature compared to other sulfonated aromatic polymers such as sulfonated polyimides. The proton conductivity of SPBIBI was slightly lower than that of the perfluorinated ionomer (Nafion 117) below 100 °C but comparable at higher temperature and 100% RH. The highest conductivity of 1.9×10^{-1} S cm^{-1} was obtained for SPBIBI-100 at 140 °C.

Introduction

Proton exchange membrane fuel cells (PEMFC) have aroused increasing interest due to their promising application as a clean, silent, and efficient powder source.[1–3] One of the challenges in the current PEMFC research is to develop novel proton conductive ionomer membranes useable at higher temperature than 120 °C for improving the total performance of PEMFCs.[4–10] Perfluorinated sulfonic acid ionomers (such as Nafion) are the current state-of-the-art PEMs but not suitable for high-temperature use since the conductive and mechanical properties are deteriorated above the glass transition temperature (110 °C).[11] High methanol permeability (in direct methanol fuel cells), high cost, and environmental inadaptability have also impeded their commercial development. This has stimulated many efforts in the development of new PEM materials with low cost and high performance. Sulfonated aromatic polymers are widely investigated as candidate PEM materials.[12–20] These polymer membranes require a high sulfonation level to achieve sufficient proton conductivity due to the lower acidity of Ar−SO_3H than that of −CF_2−SO_3H in Nafion. Unfortunately, addition of more acid conductors may lead to undesirable large swelling and thus result in a dramatic loss of mechanical properties. Degradation due to the existence of weak chemical linkages or backbone is also serious drawbacks of the sulfonated aromatic polymers.

To make aromatic ionomers less susceptible to water swelling and hydrolysis, the selection of a suitable chemically and mechanically stable aromatic polymer as a base skeleton is very important. Polycondensations of aromatic dianhydrides and amines have given rise to several thermally stable polyheterocycles including the conventional polyimides as well as naphthaleneimide polymers[21] and the polyimidazopyrrolones as well as poly[bis(benzimidazobenzisoquinolinones)].[22] Sulfonated naphthaleneimide polymers (SPIs) were extensively developed by several groups[18] due to their superior chemical resistance, excellent thermal and mechanical stability, and good film-forming ability,[23] which are required properties for PEMs. Some SPIs have been claimed to display high proton conductivity at high temperature. Watanabe et al. have found that the incorporation of bulky hydrophobic (fluorenylbiphenylene) groups could effectively introduce water-holding capacity of polyimide membranes. Membranes containing 30 mol % of fluorenyl groups show very high proton conductivities of 1.67 S cm^{-1} at 120 °C and 100% relative humidity (RH).[18d] There was, however, a major obstacle that prevented the aromatic polyimide ionomers from being utilized for PEMFC membranes. Sulfonated polyimides are subjected to hydrolytic degradation via a depolymerization mechanism under high-temperature and high-humidity conditions.[24] Poly[bis(benzimidazobenzisoquinolinones)] (PBIBI) belong to a group of ladder heterocyclic polymers synthesized by further thermal cyclization of the polyimide backbone with amine groups in the α-position to the imide groups [$-N(C{=}O)_2$]. The first polymers of this type were obtained by Van Deusen[25] from the polycondensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride with aromatic tetraamines. These polymers showed high softening temperatures and were soluble only in strong acids (polyphosphoric acid, concentrated H_2SO_4, and methanesulfonic acid), which severely restricted their applications. Since then, several poly[bis(benzimidazobenzisoquinolinones)] have been synthesized from more flexible bis(naphthalic anhydride)s or tetraamines and showed improved solubility in organic solvents (*m*-cresol and phenol-chlorinated hydrocarbon mixtures).[22] They exhibited high thermal stability, high hydrolytic stability, and excellent chemical resistance.[22,26] The need for water and oxidative stable membranes has suggested the possibility of using PBIBI with appropriate ion-conducting sites. Herein, we first report a novel sulfonated poly[bis(benzimidazobenzisoquinolinones)] (SPBIBI) for proton exchange membranes. The obtained membrane shows high thermal stability, good mechanical properties, excellent resistance to hydrolysis and

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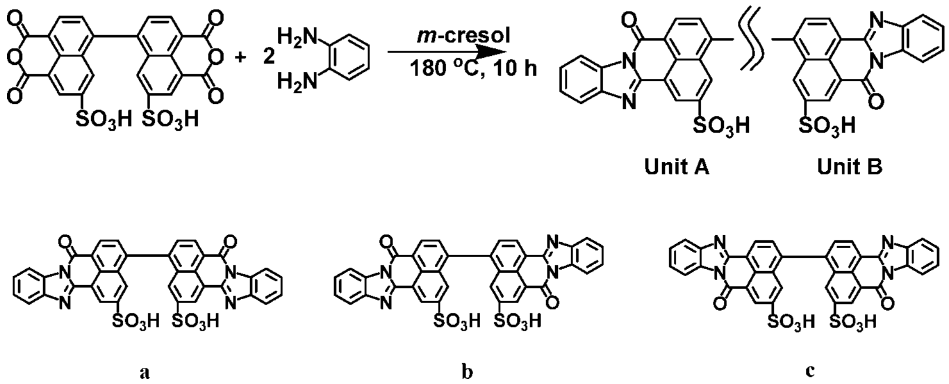
10.1021/ma800119y CCC: $40.75

Scheme 1. Synthesis and Chemical Structure of Benzimidazobenzisoquinolinones Model Compounds (a−c)



oxidation, and high proton conductivity, especially at high temperature (140 °C).

Experimental Section

Materials. 3,3′-Diaminobenzidine (DAB) and *o*-phenylenediamine was purchased from Aldrich. 4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA)[27] and 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride disulfonic acid (SBTDA)[29] were prepared according to the method previously reported. All other reagents were obtained from commercial sources and used as received.

Model Compound Synthesis. *Benzimidazobenzisoquinolinones (BIBI) (Scheme 1)*. 0.5545 g of (SBTDA) (1 mmol), 0.2162 g of *o*-phenylenediamine (2 mmol), 0.2442 g (2 mmol) of benzoic acid, 10 mL of *m*-cresol, and 0.68 mL (about 2 mmol) of Et_3N were successively placed into a 100 mL three-neck round-bottom flask equipped with a reflux condenser, a nitrogen inlet/outlet, and a mechanical stirrer. The mixture was stirred at room temperature for a few minutes and then heated at 80 °C for 4 h. The vigorously stirred mixture was heated gradually to 180 °C for 4 h and then maintained at that temperature for 10 h. After being cooled to room temperature, the solution was poured into 100 mL of diethyl ether. The precipitate was collected by filtration and washed with diethyl ether thoroughly and afforded 0.70 g (yield: 91.0%) of a fine yellow product. IR (KBr): 1698 cm^{-1} ($\upsilon_{sym}C{=}O$), 1617 and 1548 cm^{-1} ($\upsilon_{asym}{=}C{=}N$) and 1347 cm^{-1} (υ_{C-N}). ^1H and ^{13}C NMR spectra are shown in Figure 1a.

Polymer Synthesis. *Sulfonated Poly[bis(benzimidazobenzisoquinolinones)](Scheme 2)*. The typical procedure for the synthesis of SPBIBI-100 is as follows: To a 100 mL completely dried three-necked flask were charged with 0.5545 g (1 mmol) of SBTDA, 10 mL of *m*-cresol, 0.68 mL (about 2 mmol) of Et_3N, and 0.2143 g (1 mmol) of 3,3′-diaminobenzidine (DAB) successively under nitrogen flow. After the homogeneous solution was obtained, 0.2442 g (2 mmol) of benzoic acid was added. The mixture was stirred at room temperature for 2 h and then heated at 80 °C for 4 h and 180 °C for 20 h. After cooling to 80 °C, an additional 5 mL of *m*-cresol was added to dilute the highly viscous solution, and then the solution was poured into 200 mL of acetone. The fiberlike precipitate was filtered off, washed with acetone thoroughly, and dried in vacuum oven for 12 h at 150 °C (yield: >96%).

The above procedures were followed for the synthesis of SPBIBI-*x*, where *x* was the mole fraction of the monomer SBTDA in the feed, except that the molar ratios of non-sulfonated dianhydride (BTDA) were different.

Membrane Preparation and Proton Exchange. Tough, ductile ionomer membrane was prepared with a controlled thickness of 30−50 μm. The triethylamine salt form of the polymer was redissolved in *m*-cresol to form a 5−8% solution at 80 °C. The solution was filtered and cast onto glass plates at 120 °C for 12 h. Then the ionomer membrane was dried in a vacuum oven (150 °C for 24 h, 200 °C for 4 h, 250 °C for 4 h). The as-cast membrane was treated with 1.0 N sulfuric acid at room temperature for 4 days for proton exchange, and the completion of proton exchange was confirmed by ^1H NMR measurement judging from the disappearance of the peaks corresponding to triethylamine. The proton-exchanged membrane was thoroughly washed with deionized water and then dried in vacuum at 100 °C for 10 h.

Measurements. NMR spectra were measured at 300 MHz on an AV 300 spectrometer using DMSO-d_6 as solvent. FT-IR spectra were obtained with a Bio-Rad digilab Division FTS-80 FT-IR spectrometer. The inherent viscosities were determined on 0.5 g dL^{-1} concentration of polymer in *m*-cresol with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min^{-1}. Tensile measurements were performed with a mechanical tester Instron-1211 instrument at a speed of 1 mm min^{-1}. The membranes in the wet state were obtained by immersing the samples in water for 24 h, and the samples in dry state were obtained by putting samples in vacuum oven at 100 °C for 10 h in vacuum and then equilibrated at 30% RH (ambient condition) for 24 h before the measurement.

Ion Exchange Capacity (IEC). The membranes in the H^+ form were immersed in a 1 N NaCl solution for 24 h to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Na^+ ions). The H^+ ions in solution were then titrated with 0.01 N NaOH using phenolphthalein as an indicator.

Water Uptake. The membrane (30−40 mg per sheet) was dried at 100 °C under vacuum for 10 h until constant weight as dry material was obtained. It was immersed into deionized water at the desired temperature for at least 4 h. Then the membranes were taken out, wiped with tissue paper, and quickly weighted on a microbalance. Water uptake of the membranes was calculated from

$$\text{water uptake } (\%) = [(W_w - W_d)/W_d] \times 100\% \qquad (1)$$

where W_w and W_d are the weight of dry and corresponding water-swollen membranes, respectively.

Water Swelling Ratio. The water swelling ratio of the polymer membranes was investigated by immersing the round shape samples into water at room temperature for a given time; the changes of in-plane and thickness direction were calculated from

$$\Delta Tc = (T - Ts)/Ts \quad \Delta Lc = (L - Ls)/Ls \qquad (2)$$

where Ts and Ls are the thickness and diameter of the membrane at dry state, respectively; T and L refer to those of the membrane immersed in liquid water for 5 h.

Oxidative and Hydrolytic Stability. A small piece of membrane sample with a thickness of about 40 μm was soaked in Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at room temperature. The stability was evaluated by recording the time when the membrane broke into pieces after being shaken drastically and dissolved completely. Furthermore, the oxidative stability was evaluated by changes in weight and η_{inh} of the test samples when the membranes broke into pieces. Hydrolytic stability was evaluated by treating the membrane samples in water at 140 °C as an accelerated testing. Mechanical properties were measured after the treatment.

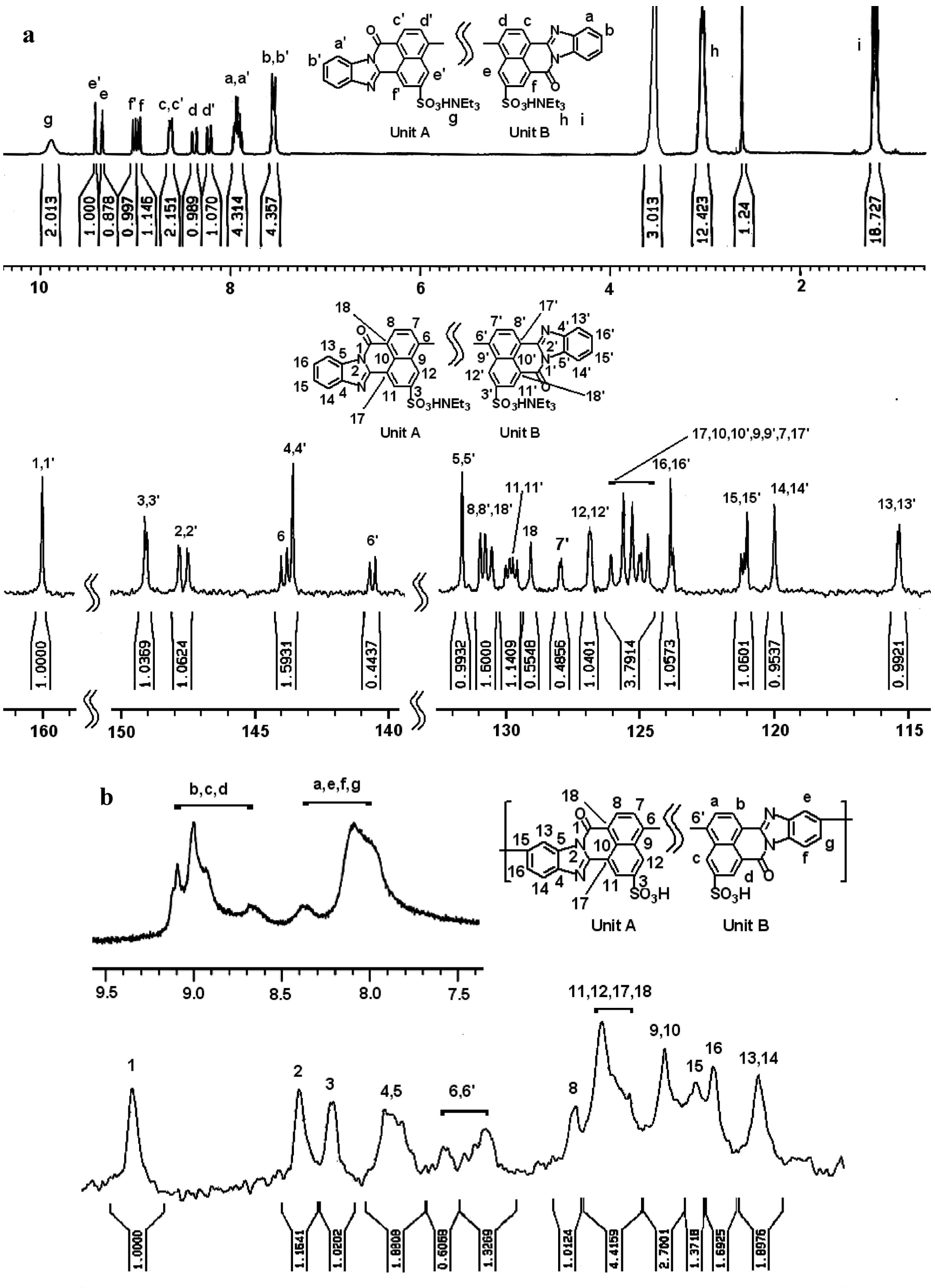
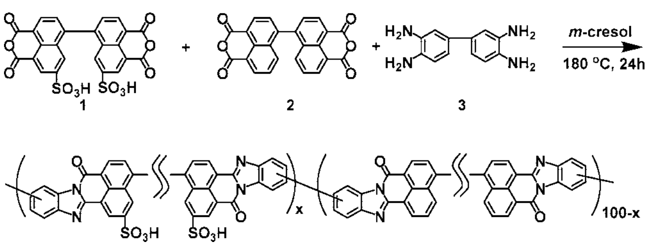


Figure 1. ^{1}H NMR and ^{13}C NMR spectra of the model compounds (a) and SPBIBI-100 (b) in DMSO-d_6.

Scheme 2. Synthesis of Sulfonated Poly[bis(benzimidazobenzisoquinolinones)]s



Proton Conductivity and Methanol Permeability. The proton conductivity (σ, S cm^{-1}) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $\sigma = d/LsWsR$ (d = distance between reference electrodes, and Ls and Ws are the thickness and width of the membrane, respectively). The resistance value (R) was measured over the frequency range from 100 mHz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with 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 gold-plated electrodes. The membranes and the electrodes were set in a Teflon cell, and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water

Table 1. Properties of SPBIBI Membranes

		IEC (mequiv g^{-1})			tensile strength (MPa)		Young's modulus (GPa)		elongation at break (%)	
ionomer	η_{inh} (dL/g)[a]	calculated	titration	EW (g/mol SO_3)	dry	wet	dry	wet	dry	wet
SPBIBI-60	1.21	1.89	1.78	529	104.1	55.2	1.24	0.52	37.6	45.3
SPBIBI-70	1.47	2.16	2.08	463	112.9	59.3	1.17	0.55	51.4	41.9
SPBIBI-90	1.57	2.64	2.57	379	105.6	44.5	1.02	0.44	45.2	51.9
SPBIBI-100	1.68	2.87	2.79	348	98.4	43.4	1.07	0.37	35.8	34.5

[a] 0.5 g dL^{-1} in *m*-cresol at 30 °C.

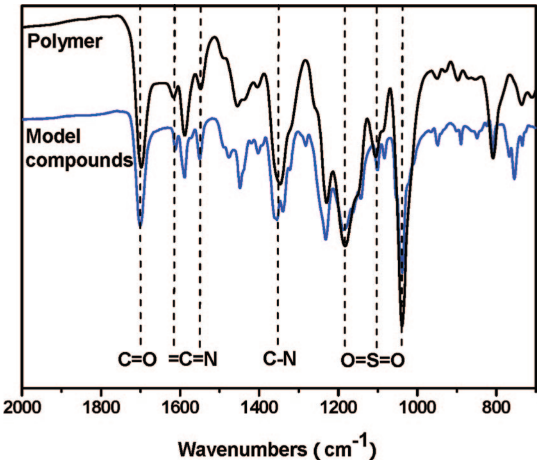


Figure 2. Comparison of the FT-IR spectra of model compounds with SPBIBI-100.

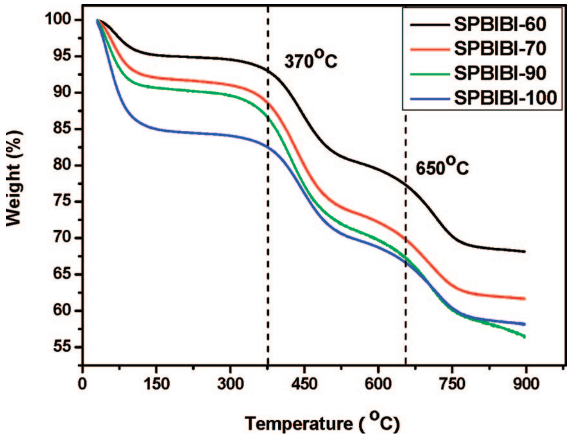


Figure 3. TGA curves of SPBIBI membranes.

for at least 24 h before the conductivity measurements. Repeated measurements were then taken at that given temperature with 10 min interval until no more change in conductivity was observed. For the measurement above 100 °C at 100% RH, a pressure-resistant closed chamber was used. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. The proton conductivities at 70 °C, 50% RH were also studied. Typically, the membranes were placed in a humidity chamber (the relative humidity was controlled at 50% by saturated NaBr aqueous at 70 °C) for at least 24 h before measurements.

The methanol permeability was determined by using a cell basically consisting of two half-cells separated by the membrane, which was fixed between two rubber rings. Methanol (2 mol L^{-1}) was placed on one side of the diffusion cell, and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol was measured by using a Shimadzu GC-1020A series gas chromatograph. Peak areas were converted into methanol concentration with a calibration curve. The methanol permeability was calculated by the following equation:

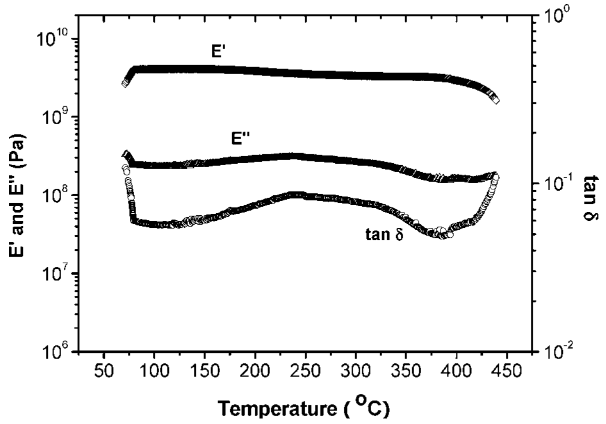


Figure 4. Dynamic modulus as a function of temperature for SPBIBI-100.

$$C_B(t) = \frac{A}{V_B}\frac{DK}{L}C_A(t - t_0) \qquad (3)$$

where C_A and C_B are the methanol concentration of feed side and permeated through the membrane, respectively. A, L, and V_B are the effective area, the thickness of membrane, and the volume of permeated compartment, respectively. DK is defined as the methanol permeability, and t_0 is the time lag.

Results and Discussion

Synthesis of Homo/Copolymers and Model Compounds a–c. The monomers used for the preparation of sulfonated poly[bis(benzimidazobenzisoquinolinones)] were 6,6′-disulfonic-4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (SBTDA) (**1**), 4,4-binaphthyl-1,1,8,8-tetracarboxylic dianhydride (BTDA) (**2**), and 3,3′-diaminobenzidine (DAB) (**3**). SBTDA was synthesized by direct sulfonation of the parent dianhydride, BTDA, with fuming sulfuric acid (SO_3 60%) at 100 °C. Polymerization of SBTDA, BTDA, and DAB was carried out by the one-step method in *m*-cresol in the presence of triethylamine (Et_3N) using benzoic acid as catalyst (Scheme 2). Et_3N was used to neutralize sulfonic groups and improve the solubility of polymers. The molar ratio of sulfonated to non-sulfonated dianhydride was varied to prepare copolymers with degree of sulfonation ranging from 60 to 100%. This yielded polymers with ion exchange capacities ranging from 1.89 to 2.87 mequiv g^{-1} (Table 1), corresponding to equivalent weights from 529 to 348 g mol^{-1} SO_3, respectively. The polymerizations were initially run at ambient temperature for 2 h and at 80 °C for 4 h. Then the temperature was raised slowly to 180 °C and maintained at that temperature for 20 h. In all of the reactions, a homogeneous, deep red, clear viscous solution was formed. The SPBIBI-*x* were obtained almost in quantitative yields (yields were above 96%) and had reduced viscosity values ranging from 1.21 to 1.68 dL g^{-1} (Table 1). The obtained copolymers in triethylamine salt form were found to be soluble with a 10% solid content both in *m*-cresol and in DMSO. SPBIBI-100 and SPBIBI-90 were

Table 2. Water Uptake, Swelling Ratio, and Proton Conductivity of SPBIBI Membranes

		20 °C (RT)					100 °C				
				swelling ratio (%)				swelling ratio (%)			
ionomer	IEC	water uptake (%)	λ	t	l	σ^a (S cm^{-1})	water uptake (%)	t	l	σ^a (S cm^{-1})	σ^b (S cm^{-1})
SPBIBI-60	1.89	19.9	6.1	3.5	1.2	1.1×10^{-2}	24.5	4.8	1.9	6.1×10^{-2}	8.2×10^{-4}
SPBIBI-70	2.16	22.9	6.1	4.1	1.8	2.9×10^{-2}	31.3	6.7	3.3	7.8×10^{-2}	1.7×10^{-3}
SPBIBI-90	2.64	29.2	6.3	6.5	2.6	4.5×10^{-2}	39.5	10.6	4.9	1.04×10^{-1}	4.4×10^{-3}
SPBIBI-100	2.87	32.9	6.5	11.2	4.0	5.4×10^{-2}	45.5	16.2	9.0	1.25×10^{-1}	7.8×10^{-3}
Nafion 117	0.90	19.6	12.1		11.4	9.0×10^{-2}	34.5		21.5	1.78×10^{-1}	2.1×10^{-2}
SPI[29]	2.78	89.2	18.4	25.0	15.0	1.61×10^{-1}					
SPBI[20b]	2.57	27.0	5.8			3.6×10^{-4}					

[a] Measured in water. [b] Measured at 70 °C, 50% relative humidity.

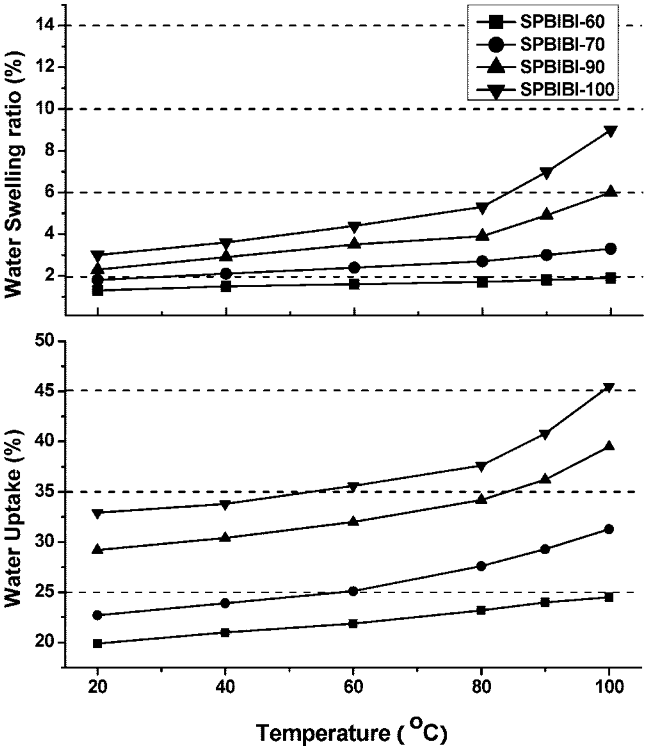


Figure 5. Water swelling ratio in-plane direction and water uptake of SPBIBI membranes as a function of temperature.

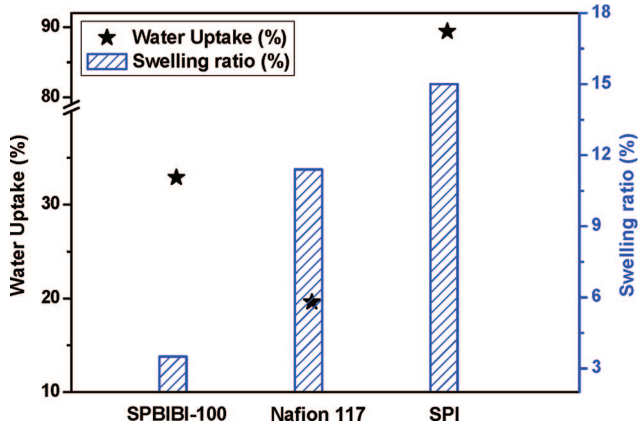


Figure 6. Comparison of the water uptake and swelling ratio in-plane direction of SPBIBI-100, Nafion 117, and SPI (SBTDA/ODA) membranes (measured at room temperature).

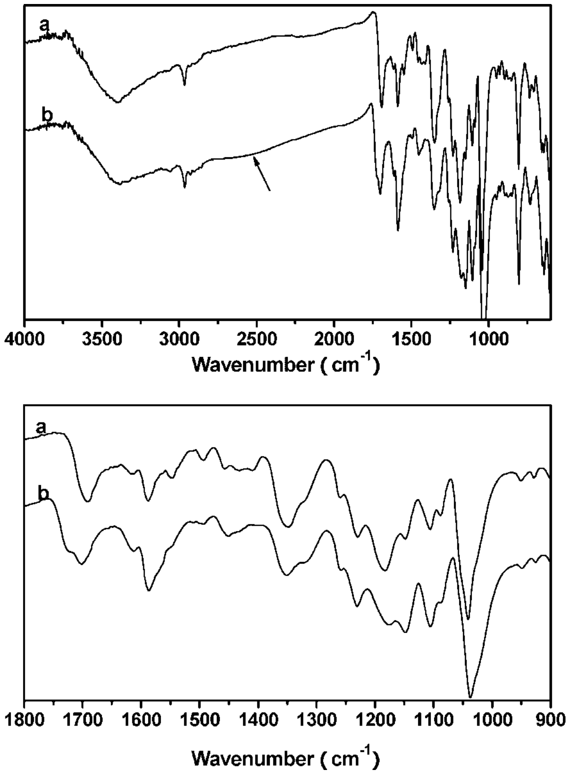
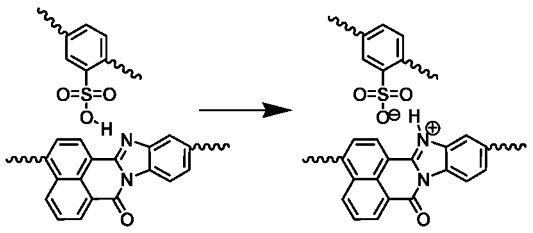


Figure 7. Infrared spectra in the regions 4000−900 and 1800−900 cm^{-1} of SPBIBI-100 after soaking in NaOH aqueous solution (a) and SPBIBI-100 (b).

Scheme 3. Pyridinone Cation Formation in the Polymers



soluble in NMP, DMAc, and DMF, whereas SPBIBI-60 and SPBIBI-70 were partially soluble in these polar aprotic organic solvents. In general, these polymers displayed an enhanced solubility as compared with conventional non-sulfonated PBIBIs, indicating the positive effect of the introduction of sulfonic acid groups in the polymer backbone on the improvement of the solubility.

Polymer Characterization. The structure of the copolymers was confirmed by IR and NMR spectroscopy. In order to get precise data regarding the chemical shifts of ^{1}H and ^{13}C NMR, the model compounds were synthesized by the following reaction shown in Scheme 1. The reaction of **1** with **3** may generate three isomeric reaction products of a, b, and c which contain two pyridinone units (unit A or unit B). As shown in Figure 1a, the peaks at δ 8.21 and 8.36 could be assigned to

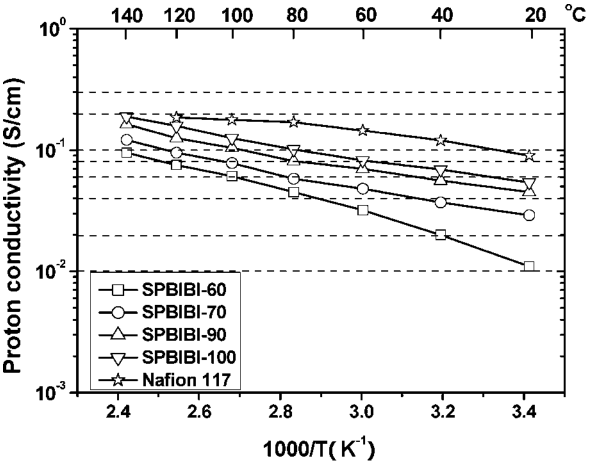


Figure 8. Temperature dependence of the proton conductivity of SPBIBI membranes and Nafion 117 at 100% RH (in water).

the chemical shifts of protons in the α-position of binaphthyl in pyridinone unit A and unit B. The integration ratio of the H_d to $H_{d'}$ is close to 1:1, as expected for the composition of the model compounds. No characteristic chemical shift of $-NH_2$ (around 5 ppm) was found, indicating that a high degree of cyclization has been attained in the products. In the ^{13}C NMR spectrum, the peak around 160.2 ppm was attributed to the chemical shifts of carbon atom of carbonyl groups in the unit A and unit B. The peaks at 149.8 ppm was assigned to carbon atom in the imide groups (N=C−N). The two peaks around 147.5 and 147.9 ppm were assigned to the carbon directly linked with $-SO_3^-H^+NEt_3$ groups. These characteristic chemical shifts of quarternary carbons could all be found in the ^{13}C NMR spectrum of SPBIBI-100 (Figure 1b). FT-IR spectra of SPBIBI-100 and model compounds are shown in Figure 2. The absorption bands at 1698 cm^{-1} were observed along with weak IR absorption bands at 1617 and 1548 cm^{-1}, typical of the =C=N group vibrations.[26c] The former are known to be due to the characteristic stretching vibrations of the ⟩C=O group in the pyridinone ring. The absorption bands at 1706 and 1658 cm^{-1} which correspond to the C=O stretching vibration in a six-membered imide ring were not found. This result also confirmed that the title polymer was completely cyclized into pyridinone rings by the one-stage polycondensation method.

The thermal properties of SPBIBI-*x* in proton form were assessed with thermogravimetric analysis (TGA) and dynamic mechanical thermal analyzer (DMTA-δ). As shown in Figure 3, the polymer thin films exhibit a typical three-step degradation pattern. The first weight loss up to ca. 200 °C is ascribed to the loss of water molecules, absorbed by the highly hygroscopic $-SO_3H$ groups. The second step 5% weight loss temperatures about 370 °C was attributed to the cleavage of sulfonic acid groups. The desulfonation temperature of SPBIBI-*x* was higher than that of sulfonated polyimides based on SBTDA (about 340 °C).[29] The last weight loss starting around 640 °C is assigned to the decomposition of the polymer backbone which is much higher than that of other aromatic polymer.[5,14] Dynamic mechanical properties of SPBIBI-100 are depicted in Figure 4, which showed no obvious glass transition temperature under 500 °C, indicating that stronger interaction among chains of SPBIBI-*x* induced by the $-SO_3H$ groups.

The mechanical properties of the SPBIBI membranes are summarized in Table 1. The samples in the dry state had tensile stress at maximum load of 98.4−112.9 MPa, Young's moduli of 1.02−1.24 GPa, and elongation at break of 35.8−51.4%. These SPBIBI membranes showed higher maximum stress, Young's modulus because of their rigid molecular structure. In the wet state, the sample showed excellent mechanical properties with tensile stress of 43.4−59.3 MPa and Young's moduli of 0.37−0.55 GPa, and their elongations at break were 34.5−51.9%. The tension results in both dry and wet states undoubtedly showing they were strong and flexible membrane materials.

Water Uptake and Swelling Ratio. The water uptake of sulfonated polymers is known to have a profound effect on membrane conductivity and mechanical properties.[30] Water molecules dissociate the acid functionality and facilitate proton transport. However, excessively high levels of water uptake can result in membrane fragility and dimensional change, which lead to the loss of mechanical properties. Basically, the amount of water uptake in the sulfonated polymers will be strongly dependent upon the amount of sulfonic acid groups and will also be related to IEC values. The water uptake was measured from the ratio of the weight of water absorbed by the membrane when immersed in water, with respect to the dry membrane weight. It can also be expressed as the number of H_2O molecules per sulfonic acid group (λ). The data are reported in Table 2 along with the swelling ratios. As expected, the water uptake increases with increasing IEC. The water uptake of SPBIBI-*x* membranes with IEC from 1.89 to 2.87 was in the range of 19.9−32.9%. However, the λ remains almost constant for all SPBIBIs. Each sulfonic acid group is solvated by about six water molecules, which is comparable to the reported sulfonated polybenzimidazoles ($\lambda = 5-6$)[20b] but much lower than Nafion 117 ($\lambda = 12.1$) and other proton-conducting sulfonated aromatic polymers.[14] Figure 5 shows the temperature-dependent water uptake and swelling ratio in plane direction of SPBIBI membranes. An increase in water uptake with increase in temperature was observed. For example, at 100 °C, SPBIBI-100 in proton form showed 45.5% water uptake and 9% swelling ratio in plane direction, slightly higher than that at 20 °C (32.9% water uptake and 4% swelling ratio in plane direction). This result indicated that the SPBIBI membranes with high IEC value are dimensionally stable even at high temperature and humidity. Moreover, these membranes show unisotropic dimensional changes between in-plane and thickness directions. For example, the SPBIBI-100 membrane showed about 3 times larger swelling in thickness direction (11.2%) than in plane direction (4%). It was noted that the present SPBIBI polymers show much lower water uptakes and swelling ratios, when compared with Nafion 117 and our previously prepared SBTDA-based sulfonated polyimides (SBTDA/ODA, IEC = 2.78 mequiv g^{-1}) of similar IEC values (Figure 6). We attribute the lower water uptake and swelling ratios (especially at high temperature, above 80 °C) to the combination of rigid polymer backbone and acid−base interaction between the pyridinone ring and the sulfonic acid groups.

The acid−base complex can be prevented when the membrane is soaked in a NaOH aqueous solution.[20b] Figure 7 shows IR spectra of SPBIBI-100 in proton form and in sodium salt form. First evidence of the presence of this interaction on the nontreated membrane is the broadband observed in spectrum (b) near 2500 cm^{-1} which disappears on spectrum (a). Foglizzo et.al[28] attributed this band to the stretching vibration HN^+. In the case of SPBIBI-100, this group comes from the protonation of the imino nitrogen atom by the sulfonic acid group, as shown in Scheme 3. Moreover, the peaks observed at 1617, 1548 cm^{-1} attributable to the =C=N group vibrations and 1452 cm^{-1} (characteristic in-plane ring vibration of the benzimidazole ring) are more intense in spectrum (b). They are characteristics of the modification of the electronic structure and electron delocalization that occurs when the pyridinone rings interact with a sulfonic acid group.[20b,31]

Proton Conductivities and Methanol Permeability. The proton conductivity of the SPBIBI membrane was measured at

Table 3. Oxidative Stability and Methanol Permeability of SPBIBI Membranes

	oxidative stability[a]					
ionomer	τ_1[b] (h)	decrease in weight (%)[c]	decrease in η_{inh} (%)[c]	τ_2[d] (h)	methanol permeability ($cm^2\ s^{-1}$)	selectivity ($\times 10^4$ S cm^{-1} s cm^{-2})
SPBIBI-60	22	5	42	25	1.1×10^{-7}	10.0
SPBIBI-70	22	4	50	25	2.3×10^{-7}	12.6
SPBIBI-90	20	6	48	22	4.0×10^{-7}	11.3
SPBIBI-100	18	8	57	22	5.2×10^{-7}	10.4
Nafion 117	>50				2.4×10^{-6}	3.7

[a] 30 °C in 30% H_2O_2 containing 30 ppm $FeSO_4$. [b] The time when the membrane broke into pieces after being shaken drastically. [c] Changes in weight and η_{inh} of the test samples when the membranes broke into pieces. [d] The time when the membrane dissolved completely.

Table 4. Mechanical Properties Soaking in Water at 140 °C for SPBIBI-100 Membrane

iomomer	soaking time (day)	decrease in weight (%)	maximum stress (MPa)	Young's modulus (GPa)	elongation at break (%)
SPBIBI-100	0	0	98.4	1.07	35.8
	1	2	97.5	1.05	30.7
	4	3	97.3	1.03	32.3
	12	6	90.8	1.13	28.2

100% RH (in water) and compared with that of Nafion 117 (Table 2). SPBIBI membranes exhibited lower room temperature conductivity of $(1.1-5.4) \times 10^{-2}$ S cm^{-1} than Nafion 117 of 9.0×10^{-2} S cm^{-1}. However, the conductivity of SPBIBI was about 100 times higher than that of the sulfonated polybenzimidazole (SPBI) (3.6×10^{-4} S cm^{-1}, at 20 °C, IEC = 2.57 mequiv g^{-1}).[20b] Mercier et al. explained the low conductivities of SPBI by the formation of an strong acid−base complex between benzimidazole and the sulfonic acid groups of the polymer. They concluded that when forming a complex with a basic unit, the acid proton of the SO_3H is no longer available for proton conduction. In present study, the improved proton conductivity of SPBIBI compared with SPBI may suggest the weaker acid−base interactions between the basic benzimidazole and sulfonic acid group. This is because the H atom on N atom was substituted by a strong electron-withdrawing group (C═O), and it decreased basicity of the benzimidazole ring dramatically. Similar behavior was observed with *N*-sulfophenylbenzimidazole.[20b] The temperature dependence of the proton conductivity was investigated at 20 to 140 °C (Figure 8). The highest conductivity of 1.9×10^{-1} S cm^{-1} was observed for SPBIBI-100 at 140 °C, while the measurement was not possible for Nafion 117 at such a high temperature due to the loss of mechanical strength. It is worth noting that SPIBIB-100 still retained a low swelling ratio of 9% while achieve a high proton conductivity of 1.25×10^{-1} S cm^{-1} at 100 °C. These values of dimensional swelling and proton conductivity compare very favorably with those of Nafion 117, shown in Table 2. The proton conductivity of membranes showed Arrhenius-type temperature dependence even above the boiling temperature of water. Furthermore, the proton conductivity under low humidity (70 °C, 50% RH) of membranes also was measured, and the results are shown in Table 2. The membranes of non-fluorinated poly[bis(benzimidazobenzisoquinolinones)] showed lower proton conductivity at this condition (for example, 7.8×10^{-3} S cm^{-1} of SPBIBI-100) than Nafion 117 (2.1×10^{-2} S cm^{-1}), which is a common phenomenon observed with many other sulfonated polymer membranes.[17c,18c,g] This is attributed to the lower acidity of the non-fluorinated sulfonic acid groups and the fact that Nafion has unique ion-rich channels (clusters), which are favorable for proton transport,[32] whereas the SPBIBI membranes might have a rather homogeneous structure (no clear ionic domains were separated from the polymer matrix).

The methanol permeability (*P*) of SPBIBI ionomers (Table 3) were in the range of $(0.11-0.52) \times 10^{-6}$ $cm^2\ s^{-1}$ at room temperature, which is much lower than Nafion 117 (2.4×10^{-6} $cm^2\ s^{-1}$) at the same test condition. The low methanol permeability is attributed to the low water uptake. It is known that the methanol transport across the proton exchange membranes is strongly dependent upon the water uptake because the methanol permeates through the membranes as complex forms such as $CH_3OH_2^+$ and H_3O^+. The selectivity between the proton and methanol transport (σ/P) represents the performance tradeoff between permeability and conductivity. The SPBIBI membranes were about 3 times more selective than Nafion 117.

Hydrolytic and Oxidative Stability. It has been known that polyimidazopyrrolones exhibit a better hydrolytic stability than polyimides.[33] The hydrolytic stability of SPBIBI membrane was evaluated by treating the membrane sample at 140 °C in water as an accelerated testing.[34] All the ionomer membranes showed excellent hydrolytic stability without any changes in appearance, flexibility, and toughness after 12 days testing. The IR analyses revealed that the absorption bands at about 1780 cm^{-1} (−COOH) due to the hydrolysis of pyridinone ring were not observed after the testing. Table 4 lists the mechanical properties and weight loss of SPBIBI-100 membrane before and after the aging tests. The gravimetric measurements revealed that SPBIBI-100 membrane retained more than 94% of their original weight. After soaking in water for 12 days at 140 °C, the membranes almost retained the initial mechanical properties as the initial tensile strength of 98.4 MPa only decreased to 90.8 MPa, and the elongation at break decreased from 35.8% to 28.2%. The results revealed that the SPBIBI membranes are water stable at high temperature.

The membranes were also subjected to oxidative stability testing in Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at 25 °C (Table 3). The oxidative stability of the membranes decreased with increasing sulfonated degree because the oxidative attack by radical species ($HO^\bullet$ and $HOO^\bullet$) should mainly occur in or in the proximity of water-containing hydrophilic domains. The time which the SPBIBI membranes started to break into pieces for all was more than 18 h, and it took more than 22 h before it disappeared into solution. Additionally, in this paper, the changes in weight and reduced vi,scosity in pure DMSO of the polymers were recorded before and after the oxidative stability test. All of the polymers displayed a little decrease in weight, while a significant decrease in reduced viscosity (about 50%) after the membranes broke into pieces (Table 3). The oxidative stability is comparable to that of other sulfonated hydrocarbon polymers.[5,14]

Conclusion

In conclusion, novel sulfonated poly[bis(benzimidazobenzisoquinolinones)] can be prepared through direct polycondensation reaction of sulfonated dianhydride and tetraamine in *m*-cresol. The as-made ionomer membrane showed excellent thermal, oxidative, and water stability. The ionomer membrane showed excellent hydrolytic stability without any changes in appearance, flexibility, and toughness after 12 days testing in water at 140 °C. The strong interchain interaction resulted in the low water uptake, the excellent dimensional stability, and low methanol permeability of the SPBIBI membranes despite the high IEC value. The proton conductivity is comparable to or even better than that of Nafion 117 at high temperature and high RH (in water). The highest conductivity of 1.9×10^{-1} S cm^{-1} was obtained for SPBIB-100 at 140 °C. These preliminary results have demonstrated the potential availability as an electrolyte for high-temperature PEMFCs application. These results will aid in designing better membranes, such as the SPBIBI from SBTDA and sulfonated aromatic tetraamines and the acid-doped SPBIBI, for improved membrane performance.

Acknowledgment. We thank the National Basic Research Program of China (No. 2003CB615704) and the National Science Foundation of China (No. 50673087) for financial support.

References and Notes

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MA800119Y