Preparation and Characterization of Sulfonated Poly(arylene-*co*-naphthalimide)s for Use as Proton Exchange Membranes

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ABSTRACT: A series of novel sulfonated poly(arylene-*co*-naphthalimide)s (SPPIs) were synthesized by Ni(0) catalytic coupling of sodium-(2,5-dichlorobenzoyl)benzenesulfonate and a naphthalimide dichloride comprising benzophenone groups at the meta-position of the imido groups. These materials were to be used as proton exchange membranes. Viscosity measurements revealed that the as-synthesized SPPI copolymers possessed high-molecular weights. Flexible and tough membranes of considerable mechanical strength were obtained by solution casting after which the electrolyte properties of the polymers were intensively investigated. In boiling water, a low water swelling ratio of less than 10% was found, as characterized by dimensional stability testing; a result superior to that for Nafion 117 (i.e., 21.5 %). Hydrolytic testing indicated that the SPPIs displayed an excellent hydrolytic stability, and in addition, their corresponding membranes demonstrated higher proton conductivities than those of Nafion 117, especially at elevated temperatures. The SPPI-80 membrane presented the highest conductivity of 0.302 S cm^{-1} for an IEC of 2.35 mequiv g^{-1} at 100°C, which was much higher than the corresponding value of Nafion 117 (0.178 S cm^{-1}, at 100°C). A combination of a low methanol crossover with excellent thermo-oxidative properties indicated that the SPPI membranes were good candidate materials for proton exchange membranes in fuel cell applications. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3187–3196, 2010

Key words: sulfonated poly(arylene-*co*-naphthalimide)s; proton exchange membrane; proton conductivity; water stability

INTRODUCTION

Studies on proton exchange membranes (PEMs) for the applications of fuel cells (FCs) have been encouraged by the necessity to reduce pollution.[1–3] Due to the harsh conditions when operating fuel cells (i.e., high temperature, high water activities, and the appearance of highly reactive oxidizing radicals), hydrolytic, thermo-oxidative, and chemical stabilities are key issues in the choice of ionomer. Due to Nafion (Dupont trade name) being a well-known polymer electrolyte, numerous studies have been dedicated to it, and it has received much attention because of its excellent chemical and electrochemical stability, in addition to high proton conductivity with a relatively low ion exchange capacity (IEC). However, its significant hydrogen and methanol "crossover", very high cost and its loss of preferential properties at elevated temperatures ($T > 80°C$) constitute severe disadvantages for these state-of-the-art membrane materials.[4,5] Therefore, nonfluorinated alternative materials have been under development during recent years.[6–10] Aromatic ionomers represent promising candidates since they are thermally stable, easy to modify chemically, and inexpensive.[11–31] However, in order for them to achieve conductivities comparable to that of Nafion, elevated IECs are required, resulting in high water uptake values and a loss of mechanical properties. Furthermore, many of these PEMs are more susceptible to oxidative or acid-catalyzed degradation than Nafion.[32] The stability and proton conductivity of aromatic ionomers thus constitute issues in need of improvement.[33]

The utilization of a fully aromatic polymer, such as poly(*p*-phenylene)s, provides a route to potentially improve the stability of PEMs due to their inherent hydrolytic and thermo-oxidative stability. Some sulfonated poly(*p*-phenylene)s (SPPs) have been claimed to display a high proton conductivity and an excellent thermo-oxidative stability. McGrath and coworkers have found that the substituted poly(*p*-phenylene), i.e., poly(4-phenoxybenzoyl-1,4-phenylene) demonstrated relatively high proton conductivities (10^{-2} S cm^{-1}) and good PEM characteristics.[34]

Moreover, we have recently reported that the sulfonated poly(2,5-benzophenone)s possessing a decent microphase separation structure and high proton conductivity are hydrolytically and thermooxidatively stable.[35] However, this category of polymers–especially polymers with a high sulfonic acid content - has a tendency to swell at high humidity and elevated temperature due to the lack of intermolecular interactions in the polymer chains. As a result, the membranes lose their mechanical strength. Consequently, their ability to function under fuel cell conditions becomes questionable.

Aromatic polyimides are known to have a superior solvent-resistance, an excellent mechanical strength and a decent film-forming ability because of the strong charge-transfer interaction between the polymer chains. In a previous article, we reported on the successful synthesis of sulfonated poly(arylene-co-naphthalimide)s (SPPIs) bearing a CF_3 group at the ortho-position of the imido group. The synthesized material exhibited a high proton conductivity and an improved water stability by Ni(0) catalytic copolymerization, thus showing potential as a polymer for PEM.[28] Consequently, as a continuation of this study, a naphthalimide dichloride monomer containing benzophenone groups at the ortho/meta-position of the imido group and the corresponding sulfonated poly(arylene-co-binaphthalimide)s(SPPIs) were introduced as new polyelectrolytes for PEMFC applications.

The objective of this study was to improve the dimensional and hydrolytic stabilities of SPPIs without sacrificing other properties, such as high proton conductivity and excellent oxidative stability. This article reports on the synthesis of such a novel naphthalimide dichloride monomer containing benzophenone groups at the ortho/meta-position of the imido group and its corresponding sulfonated copolymers. The properties of these materials, such as their thermal and chemical stability, mechanical strength, water uptake behavior and proton conductivity, have been investigated in detail. Furthermore, the properties of the novel SPPI copolymer membranes were compared to those of SPPIs membranes with [SBond]CF_3 groups (F-SPPI) and sulfonated poly(p-phenylene)s (SPP) to increase the knowledge of the "structure-property" relationships of SPPIs.

EXPERIMENTAL SECTION

Materials

Reagent-grade anhydrous $NiBr_2$ was dried at 220°C under vacuum, triphenylphosphine (PPh_3) was recrystallized from hexane. Zinc dust was stirred with acetic acid, filtrated, washed thoroughly with ethyl ether, and dried under vacuum. Isoquinoline

(99 %) and 5-chloro-1, 8-naphthalic anhydride were used as received from Shanghai Kuilin Chemical, and Beijing Multi Technology, respectively. Aluminum chloride and 2-chloro-5-nitrobenzoic acid were purchased from Aldrich and used without further treatment. Sodium 3-(2,5-dicholorobenzoyl)benzenesulfonate was prepared according to a previously described procedure.[28]N,N-Dimethylacetamide (DMAc) was dried over CaH_2, distilled under reduced pressure and stored over 4 Å molecular sieves. All other commercial available chemicals were used without further purification.

Monomer synthesis

2-Chloro-5-nitrobenzophenone (I)

A dried 500 mL three-necked flask were charged with 20.2 g (0.10 mol) of 2-chloro-5-nitrobenzoic acid and 300 mL of $SOCl_2$. The mixture was heated to reflux at 80°C for 8 h. After the excess $SOCl_2$ was distilled at 50°C, the residue was dissolved in 300 mL of benzene. Then, 40.0 g (0.30 mol) of $AlCl_3$ was added part by part. The reaction mixture was kept at room temperature with stirring for 24 h, and then poured into a large amount of ice water containing HCl solution. The resulting solid was filtrated and recrystallized from ethyl acetate to afford 22.8 g of I. (yield: 87%). ^{1}H NMR (300 MHz, DMSO-d6): δ : 7.57–7.61 (t, 2H, Ar[SBond]H), 7.73–7.75 (t, 1H, Ar[SBond]H), 7.78–7.81 (d, 2H, Ar[SBond]H), 7.92–7.95 (d, 1H, Ar[SBond]H), 8.40–8.44 (t, 2H, Ar[SBond]H).

2-Chloro-5-aminobenzophenone (II)

A slurry of I (20.9 g, 80 mmol), $SnCl_2$ (106.2 g, 560 mmol), and 100 mL EtOH was stirred while 100 mL concentrated HCl was added slowly. After all the HCl was added, the mixture was refluxed at 100°C for 12 h. Excess EtOH was evaporated and the solution was poured into 400 mL distilled water, basitified with 500 mL 10% NaOH solution. The precipitate was filtrated off and washed with hot water, recrystallized from DMF/H_2O (v/v=1 : 3) to give wine product (14.7 g), yield 79.2%. ^{1}H NMR(300 MHz, DMSO-d6): δ : 6.60–6.61 (d, 1H, Ar[SBond]H), 6.73–6.77 (t, 1H, Ar[SBond]H), 7.17–7.20 (d, 1H, Ar[SBond]H), 7.53–7.58 (t, 2H, Ar[SBond]H), 7.67–7.71 (t, 1H, Ar[SBond]H), 7.72–7.76 (d, 2H, Ar[SBond]H).

N-(4-chloro-3-benzophenone)-5-chloro-1,8-naphthalimide(III)

In a 500 mL round-bottomed flask, 11.6 g (50 mmol) of 5-chloro-1, 8-naphthalic anhydride, 11.5 g (50 mmol) of 2-chloro-5-aminobensophenone, 0.50 g (3.6 mmol) of isoquinoline, and 200 mL of acetic acid were added. The solution was refluxed for 24 h. The

reaction mixture was then poured into 500 mL of ethanol. The precipitated was filtered, washed with ethanol, and dried in a vacuum. The product was obtained by sublimation under vacuum at 150°C in the yield of 75.2% (16.8 g). ^{1}H NMR (300 MHz, DMSO-$d6$): δ : 7.59–7.72 (m, 4H, Ar[SBond]H),7.74–7.83 (m, 4H, Ar[SBond]H), 8.05–8.10 (m, 2H, Ar[SBond]H), 8.45–8.48 (d, 1H, Ar[SBond]H), 8.60–8.63 (2, 1H, Ar[SBond]H), 8.66–8.69 (d, 1H, Ar[SBond]H).

N-(4-chloro-2-benzophenone)-5-chloro-1,8-naphthalimide(IV)

In a 500 mL round-bottomed flask, 11.6 g (50 mmol) of 5-chloro-1, 8-naphthalic anhydride, 11.5 g (50 mmol) of 2-amino-5-chlorobenzophenone, 0.50 g (3.6 mmol) of isoquinoline, and 200 mL of acetic acid were added. The solution was refluxed at 140°C for 24 h. The reaction mixture was then poured into 500 mL of ethanol. The precipitated was filtered, washed with ethanol, and dried in a vacuum. The product was obtained by sublimation under vacuum at 150°C in the yield of 72.8% (16.2 g). ^{1}H NMR (300 MHz, DMSO-$d6$): δ : 7.34–7.39 (t, 2H, Ar[SBond]H), 7.46–7.51 (t, 1H, Ar[SBond]H), 7.56–7.59 (t, 2H, Ar[SBond]H), 7.68–7.71 (d, 2H, Ar[SBond]H), 7.88–7.92 (d, 1H, Ar[SBond]H), 7.96–8.04 (m, 2H, Ar[SBond]H), 8.36–8.38 (d, 1H, Ar[SBond]H), 8.51–8.53 (d, 1H, Ar[SBond]H), 8.62–8.64 (d, 1H, Ar[SBond]H).

Polymer synthesis and membrane preparation

Synthesis of SPPI copolymers

The copolymers were denoted as SPPI-x, where x was the mole fraction of the sodium 3-(2,5-dicholoro-benzoyl)benzenesulfonate in the feed. The synthesis of SPPI-70 is here given as an example: NiBr$_2$ (0.16 g, 0.71 mmol), PPh$_3$ (1.30 g, 4.96 mmol), and zinc (2.60 g, 40.00 mmol) were charged to a 100 mL three-necked round-bottomed flask. The flask was vacuated and filled with nitrogen for three times. Dry DMAc (20 mL) was added via a syringe and the mixture became red in 20 min. The monomer III (1.34 g, 3 mmol) and sodium 3-(2,5-dicholorobenzoyl)benzene-sulfonate (2.46 g, 7 mmol) were added, and the reaction mixture stirred at 90°C for 4 h. The resulting viscous mixture was diluted with 10 mL of DMAc, filtered and then poured into 200 mL of 25% HCl/water. The copolymer was collected by filtration, washed with water, and then dried in vacuum at 200°C for 24 h. The copolymer yield was 97%.

Membrane preparation

The copolymers were dissolved in DMAc to form a 5–8 wt % solution at 80°C, after which the solution was filtered and cast on a glass sheet. The solvent was then evaporated by heating at 120°C for 12 h. The as-cast membranes were soaked in methanol for 24 h to remove the residual solvent, and then treated with 1.0 mol L^{-1} sulfuric acid at room temperature for 72 h for proton exchange. The proton exchange membranes were thoroughly washed with water and subsequently dried in vacuum at 100°C for 12 h.

Polymer characterization

Measurements

Nuclear magnetic resonance (NMR) spectra were measured at 300 MHz on a Bruker AV300 spectrometer (Germany). FTIR spectra of the copolymers were obtained with a Bio-Rad digilab Division FTS-80 FTIR spectrometer (Cambridge, MA). The reduced viscosities were determined on solutions of polymer (at a concentration of 0.5 g dL^{-1}) DMAc with an Ubbelohde capillary viscometer at 30 ± 0.1°C. Thermogravimetric analyses (TGA) were carried out in nitrogen on a Perkin-Elemer TGA-2 thermogravimetric analyzer (Inspiratech 2000, UK) at a heating rate of 10°C min^{-1}. Tensile measurement was performed on a mechanical tester Instron-1211 instrument (Instron) at a speed of 2 mm min^{-1} at ambient humidity (∼50 % relative humidity).

Water uptake and dimensional change

The membrane sample (30–40 mg per sheet) was dried at 80°C under vacuum for 10 h until it reached a constant weight. It was immersed in deionized water at given temperature for 4 h, after which it was quickly taken out, wiped with tissue paper, and quickly weighted on a microbalance. The water uptake (WU) was calculated according to eq. (1):

$$WU = (W_s - W_d)/W_d \qquad (1)$$

Where W_d and W_s are the weight of the dry and corresponding water-swollen membranes, respectively.

The dimension changes of the membranes with respect to their thickness and diameter were characterized by eq. (2a and 2b):

$$\Delta T_c = (T - T_s)/T_s, \qquad (2a)$$
$$\Delta L_c = (L - L_s)/L_s. \qquad (2b)$$

Here T_s and L_s represent, respectively, the thickness and length of the membrane equilibrated at 70% relative humidity (RH), and T and L refer to the corresponding values in a membrane equilibrated in liquid water for 5 h.

The number of water molecules per ionic group (λ) can be determined from water uptake and the IEC of the membrane according to eq. (3):

$$\lambda = n\ (H_2O)/n\ (SO_3^-) = (\text{water uptake})/(18\ IEC), \tag{3}$$

where $n(H_2O)$ is the H_2O mole number, $n\ (SO_3^-)$ the SO_3^- group mole number, and 18 corresponds to the molecular weight of water ($18\ g\ mol^{-1}$).

Oxidative stability and water stability

A small membrane sample (30–40 mg) with a thickness of ~40 μm was soaked in Fenton's reagent (30% H_2O_2 containing 30 ppm $FeSO_4$) at room temperature. The stability was evaluated by recording the time at which the membranes began to break into pieces and completely dissolve.

The water stability test was carried out by immersing a sample into deionized water at 140°C (to represent accelerated conditions) and evaluating the weight and reduced viscosity loss of the membranes after the treatment for 24 h.

Ion exchange capacity

The ion exchange capacity (IEC) was calculated from the molar ratio of sulfonated monomer to dichloride monomer III in the feed and was also determined by titration. The membranes in the H^+ form were immersed in a 1 mol L^{-1} NaCl solution for 24 h to liberate the H^+ ions (which were replaced by Na^+), and the H^+ ions in solution were then titrated with 0.01 mol L^{-1} NaOH.

Proton conductivity

The proton conductivities of the copolymer membranes were evaluated through electrochemical impedance spectroscopy in the temperature range of 20 to 100°C by a four-point probe method. The impedance measurements were carried out on a Solartron 1255B Frequency Response Analyzer and a Solartron 1470 Battery Test Unit (Solartron, UK) coupled with a computer. Membrane samples, with 1 cm^2 surface areas were sandwiched between two Au blocking electrodes. The samples were allowed to equilibrate at the desired temperature for 0.5 h. The impedance spectra were then recorded with the help of a ZPlot/ZView software (Scribner Associates) under an ac perturbation signal of 10 mV in the frequency range of 100 mHz to 100 KHz.

Methanol permeability

Methanol diffusion coefficients were determined using an H's test cell with a solution containing 1 N methanol in water on one side and pure water on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. Methanol con-

centration within the water cell was monitored by SHIMADZU GC-1020A series gas chromatograph. The methanol diffusion coefficients were calculated by the following equation:

$$C_B(t) = \frac{A}{V_B} \cdot \frac{DK}{L} \cdot C_A \cdot (t - t_0), \tag{4}$$

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. t_0 is the time lag.

RESULTS AND DISCUSSIONS

Synthesis and characterization of the monomers

The synthetic route of the dichloride monomers III and IV is outlined in Scheme 1. Compound I was prepared by an $AlCl_3$ catalytic Freidel-Crafts acylation of benzene with an acryl chloride obtained from 2-chloro-5-nitrobenzoic acid and thionyl chloride. The reduction of compound I was conducted with $SnCl_2$/HCl in ethanol at 80°C for 12 h to give the product denoted compound II with a yield of 79.2%. Naphthalimide dichloride monomer III was synthesized via the reaction of 5-chloro-1,8-naphthalic anhydride and 2-chloro-5-aminobensophenone in acetic acid, and purified by recrystallization from acetic acid. For the sake of comparison, naphthalimide dichloride IV, containing a benzophenone group at the *ortho*-position of the imido group, was also synthesized from the commercially available monomer 2-amino-5-chlorobenzophenone and was purified in the same procedure.

The chemical structures of I-IV were characterized by ^{1}H NMR. As an example, the ^{1}H NMR spectrum of monomer III is shown in Figure 1, and it was found that the integration ratio of the peaks corresponded to the expected composition of the dichloride monomer.

Synthesis and characterization of sulfonated poly(arylene-*co*-naphthalimide)s (SPPI-x)

The *meta*- and *ortho*-substituted dichloride monomers III and IV were copolymerized with sulfonated monomer sodium 3-(2,5-dicholorobenzoyl)benzenesulfonate prepared through an Ni(0) catalytic coupling reaction according to a previously described procedure.[28] The synthetic route and chemical structure of the SPPIs are shown in Scheme 2. The hydrophobic segments consisting of benzophenone-substituted naphthalimides were designed to be introduced in the polymer main chain. As expected,
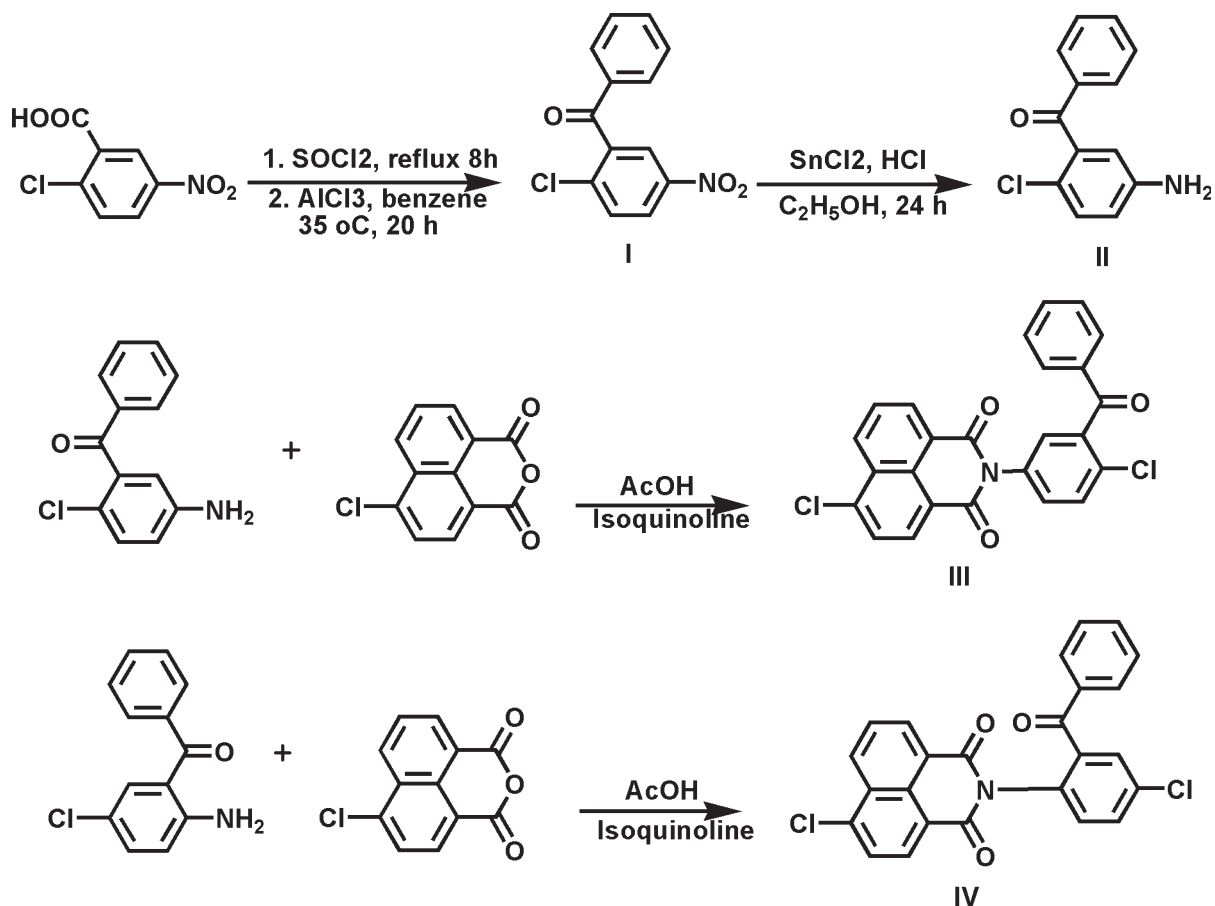
Scheme 1 The synthesis routes for monomers III and IV.

the copolymerization of the *meta*-substituted naphthalimide dichloride with sulfonated monomer was successful, thus giving rise to fiber-like polymers. The degree of sulfonation (DS) of the copolymer could be readily controlled through the monomer feed ratios of III to the sulfonated monomer. The copolymers were denoted SPPI-x, where x represents the mole fraction of the sodium 3-(2,5-dicholorobenzoyl)benzenesulfonate in the feed. However, the copolymerization of the *othro*-substituted dichloride monomer (IV) failed and a high-molecular weight polymer could not be obtained. The underlying reason was unclear.

The SPPI polymers were obtained in almost quantitative yields (above 96 %) and displayed reduced viscosity values ranging from 0.96 to 1.21 dL g^{-1} (Table I). All the copolymers with varying degrees of sulfonation displayed good solubilities in common aprotic solvents, such as DMSO, NMP, DMAc, etc. However, they were insoluble in MeOH and THF. A dissolution of the SPPI copolymers in DMAc gave rise to a tough and flexible membrane by way of solution casting. The polymers were characterized by FTIR, and Figure 2 displays a spectrum of SPPI-70. The strong absorption bands around 1704 cm^{-1} ($v_{sym}C=O$), 1658 cm^{-1} ($v_{asym}C=O$) and

1363 cm^{-1} (v_{C-N} imide) were assigned to the naphthalenic imido rings, and those around 1104 and 1035 cm^{-1} were attributed to the stretch vibration of the sulfonic acid groups. The results indicated a successful copolymerization in producing the poly(arylene-*co*-naphthalimide)s.

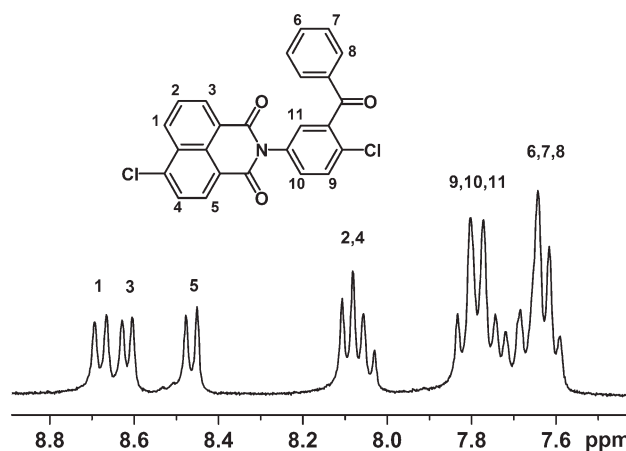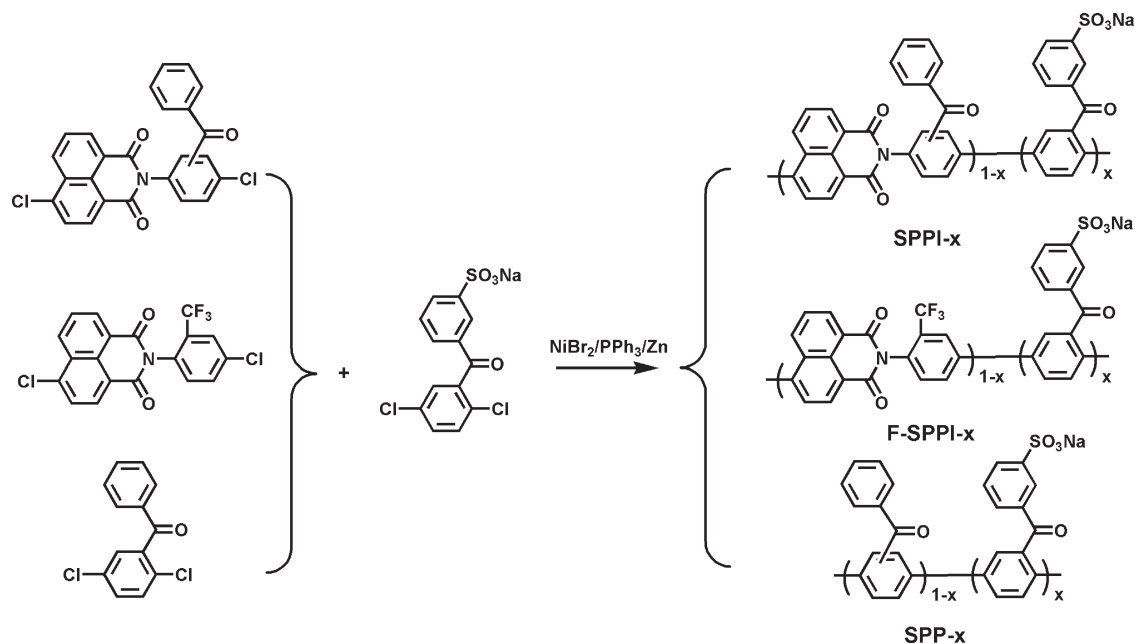The mechanical properties of the SPPI membranes were characterized and are listed in Table I. The

Figure 1 An ^1H NMR spectrum of the dichloride monomer III.

Scheme 2 The synthesis of sulfonated copolymers.

membranes displayed values of tensile strength, Young's modulus, and elongation at break ranging between 61.9–82.1 MPa, 1.09–1.77 GPa, and 6.5–8.3%, respectively. This indicated that the SPPI membranes were strong and tough, which have potential for fuel cell applications, even at high degrees of sulfonation. TGA analysis was used under a dry N_2 atmosphere to evaluate the thermal behavior of the copolymers, and Figure 3 shows the thermal stability of the SPPI-70 copolymer as investigated by TGA. It can be seen that thin films of the polymer exhibited a typical three-step degradation pattern. The first weight loss at about 200°C was ascribed to the loss of water molecules, absorbed by the highly hygroscopic [SBond]SO_3H groups. The second weight loss at around 300°C was due to the decomposition of sulfonic acid groups through desulfonation, and the third weight loss at ~ 500°C was assigned to the decomposition of the polymer main chain.

Water uptake and dimensional change

It is well-known that water management within the membrane is a critical factor in the performance of PEM materials. Excessively high levels of water in the membrane can result in extreme dimensional changes leading to failures in mechanical properties. The water uptake is typically a function of the degree of sulfonation or the ion exchange capacity (IEC), which is a measure of the exchangeable protons in the material. As shown in Table II, at room temperature, the water uptake of membranes with IEC from 1.94 to 2.79 mequiv g^{-1} was in the range of 40–65 %. With a similar IEC, the water uptake of SPPI membranes was comparable to that of sulfonated poly(p-phenylene)s (SPPs) membranes, but was much lower than that of sulfonated poly(arylene-co-imide) containing ─CF_3 groups (F-SPPI).[28] For instance, the water uptake of the SPPI-70 membrane (IEC = 2.35 mequiv g^{-1}) was 48 %; a

TABLE I
Properties of the SPPI-x Membranes

Samples	η_{red} (dL g^{-1})[a]	IEC (mequiv g^{-1})		Tensile strength[b] (MPa)	Young's modulus[b] (GPa)	Elongation at break[b] (%)
		Calculated	Titration			
SPPI-60	1.21	1.94	1.89	82.1	1.77	8.3
SPPI-70	1.13	2.35	2.31	61.9	1.09	7.8
SPPI-80	0.96	2.79	2.70	65.6	1.16	6.5

[a] 0.5 g dL^{-1} in DMAc at 30 °C.
[b] The samples were dried at ambient conditions for one day and tested at 30°C, 50% RH.
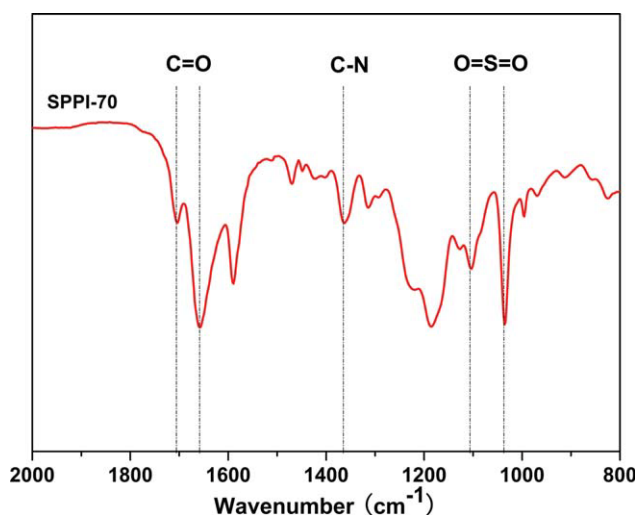
Figure 2 The FTIR spectrum of the SPPI-70 membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3 A TGA curve of the SPPI-70 membrane.

value close to that of the sulfonated poly(p-phenylene)s (i.e., 47%, IEC = 2.45 mequiv.g^{-1}),[35] but much lower than that of F-SPPI-70 (i.e., 118%, IEC = 2.47 mequiv g^{-1}).[28] Furthermore, these F-SPPI membranes exhibited a much more substantial increase in water content with increasing IEC, as shown in Table II.

F-SPPI membranes possessing IEC values >1.67 mequiv g^{-1} swell excessively in water, and further exhibit poor mechanical properties. In contrast, the SPPI membranes have a significantly lower water uptake for similar IECs, which remains moderately low even for IECs as high as 2.79 mequiv g^{-1}. The higher water uptake of F-SPPI membranes with CF$_3$ groups could be interpreted as the CF$_3$ groups weakening intermolecular interactions and producing more free volume in the bulk membrane.

Generally, a high water uptake will lead to a considerable swelling ratio. However, the structure of the polymer chain also has an obvious 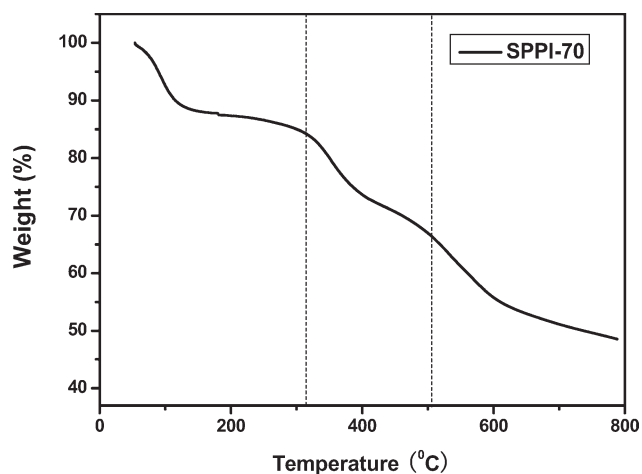effect on the dimensional stability. Although the SPPI demonstrated a higher water uptake than SPP, a lower swelling ratio was observed due to the strong charge-transfer interaction between the imide rings. As an example can be mentioned that the swelling ratio in the length direction of SPPI-70 was 2%, which is much lower than that of SPP-60 (8%),[35] as shown in Table II. This function became very evident at high temperature. Figure 4 shows the temperature dependence of the water uptake and swelling ratio of the SPPI membranes.

When compared to SPP-60, all SPPI membranes displayed a weaker dependence on temperature and the same was found for F-SPPI. For example, at 100°C, SPPI-70 in proton form presented a water uptake of 61.0% and a swelling ratio in the length direction of 3.0%. This was only slightly higher than the corresponding values at 20°C (48.0 % water uptake and 2.0% swelling ratio in length direction). However, the excess water uptake of 128% for SPP-60 was observed at this temperature with an unacceptable 25% swelling ratio of the membrane in the length direction, giving rise to a deterioration in the mechanical properties.[35] In addition, the SPPI membranes showed anisotropic dimensional changes

TABLE II
Water Uptake, Swelling Ratio, and Proton Conductivity of SPPI Membranes

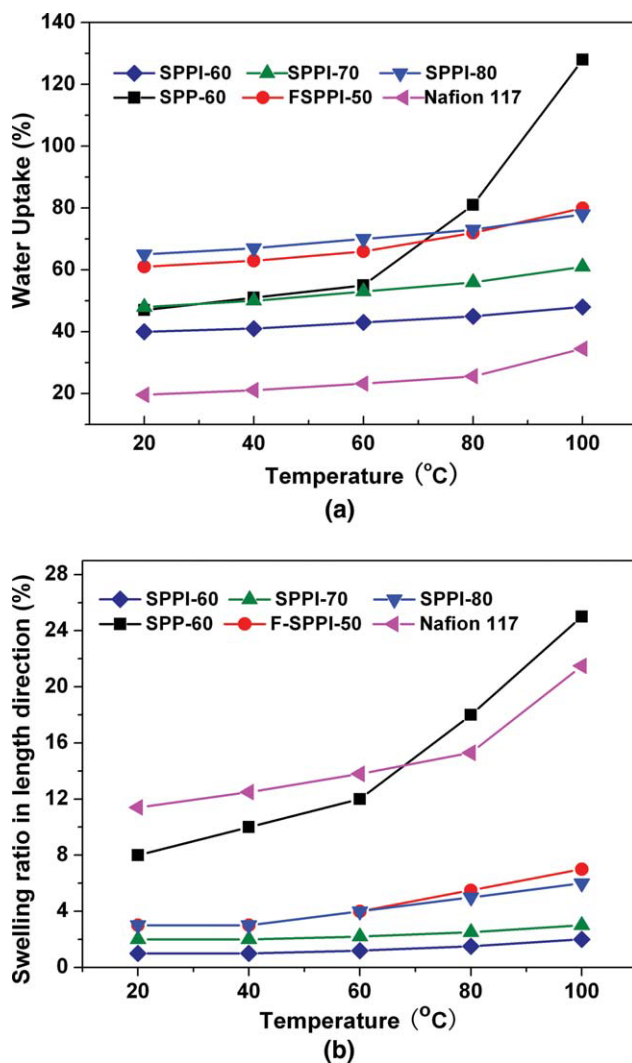| Samples | IEC | Water uptake (%) | | | Swelling ratio (%) | | | | Proton conductivity (S cm^{-1}) | |
| | | | | | 20°C | | 100°C | | | |
		20°C	λ	100°C	Δt	Δl	Δt	Δl	20°C	100°C
SPPI-60	1.94	40	11.4	48	15	1	20	2	0.072	0.249
SPPI-70	2.35	48	11.3	61	15	2	24	3	0.091	0.302
SPPI-80	2.79	65	12.9	78	18	3	30	6	0.121	0.334
SPP-60	2.45	47	10.7	128	28	8	62	25	0.124	0.251
F-SPPI-50	1.67	61	11.9	80	19	3	34	7	0.060	–
F-SPPI-70	2.47	118	26.7	–	45	7	–	–	0.075	–
Nafion 117	0.90	19.6	12.1	34.5	–	11.4	–	21.5	0.090	0.178

Figure 4 (a) The water uptake and (b) the swelling ratio in the length direction of the sulfonated copolymers and Nafion 117 as functions of the temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

between their length and thickness directions. The SPPI membranes demonstrated a more than 3-fold swelling ratio in the thickness direction as opposed to in the length direction (Table II). This result indicated that the SPPI membranes were dimensionally stable even at high temperature and humidity. Such an excellent dimensional stability is required of an electrolyte material for PEMFC applications.

Proton conductivity

In PEM fuel cells, the proton conductivity of the membrane is particularly important since it plays a significant role in the fuel cell performance. To achieve good conductivity, a high acid loading (water uptake) is desirable. As shown in Table II, membranes with a high water uptake typically display a

high proton conductivity. Moreover, the concentration of sulfonated monomers increase; a fact that has been commonly observed for sulfonated aromatic polymers.[9] As the IEC increased from 1.94 to 2.79 mequiv g^{-1}, the proton conductivity of the SPPI membranes experienced a rise from 0.72×10^{-1} to 1.21×10^{-1} S cm^{-1} at 20°C in water. These values were comparable to that of Nafion 117 (0.9×10^{-1} S cm^{-1}). Figure 5 shows the proton conductivity as a function of temperature, and from the graph it can be seen that all SPPI membranes had an Arrhenius-type temperature dependence. The highest proton conductivity of 0.334 S cm^{-1} was obtained for the SPPI-80 membrane with a high IEC of 2.79 mequiv g^{-1}.

Hydrolytic and oxidative stability

The hydrolytic and oxidative stabilities of the SPPI membranes were tested under wet conditions. The obtained changes in weight and reduced viscosity of the copolymer membranes are summarized in Table III. For the sake of comparison, stability data is also given for the SPP-60 and F-SPPI-50 membranes. The SPPI-60 and SPPI-70 membranes presented high stabilities without any changes in appearance or toughness after testing in water for 24 h at 140°C. Contrarily, the SPPI-80, with a high IEC of 2.79 mequiv g^{-1}, and the SPP-60 membrane, became completely dissolved in hot water thus experiencing a weight loss of 100%. Furthermore, the loss in η_{red} of SPPI membranes was dependent on the concentration of sulfonated monomer with a general trend of higher loss for a higher concentration of sulfonated monomer membranes while the SPP-60 maintained its original reduced viscosity. The SPPI membranes became brittle when the decrease in η_{red} exceeded about 40%. Under equivalent conditions, the F-SPPI-50 membrane demonstrated a reduction
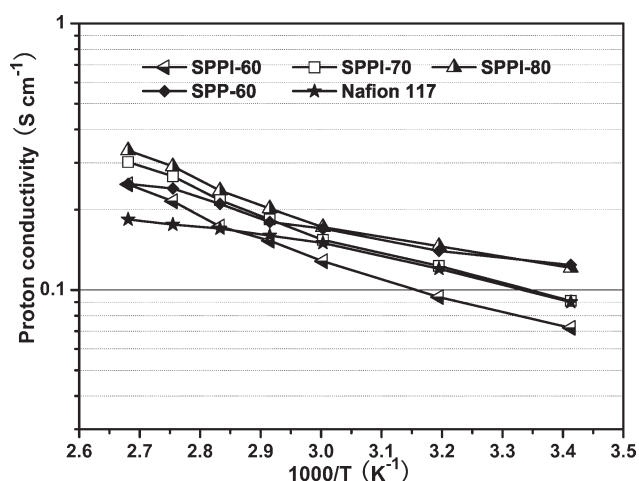

Figure 5 The temperature dependence of the proton conductivity for SPPI-x, SPP-60, and Nafion 117 membranes.

TABLE III
Hydrolytic and Oxidative Stabilities of SPPI and Nafion 117 Membranes

Samples	IEC	Hydrolytic stability: loss in (%) [a]		Oxidative stability [b]	
		Weight	η_{red}	τ_1 (h) [c]	τ_2 (h) [d]
SPPI-60	1.94	4	18	51	128
SPPI-70	2.35	6	27	42	116
SPPI-80	2.79	100	54	34	70
SPP-60	2.45	100	2	49	124
F-SPPI-50	1.67	10	60	52	263
Nafion117	0.90	1	–	>50	>50

[a] measured at 140°C for 24 h in water.
[b] 30°C in 30% H_2O_2 containing 30 ppm $FeSO_4$.
[c] The time at which the membrane broke into pieces after being drastically shaken.
[d] The time at which the membrane dissolved completely.

in the reduced viscosity of ~60%. This led to a complete loss of mechanical strength, indicating a much poorer hydrolytic stability as opposed to for the SPPI membranes.

The stability of SPPIs toward oxidation was examined by observing the dissolution behavior in Featon's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at 25°C. The oxidative stability was characterized by the time at which the membranes began to dissolve (τ_1) and the time at which they had dissolved completely (τ_2). As shown in Table III, the SPPIs with polyimide moieties in the polymer backbone exhibited an excellent oxidative stability as it was comparable to that of sulfonated poly(p-phenylene)s (SPPs). The time at which the SPPI membranes began to dissolve was in all cases superior to 34 h, which indicated that the fully aromatic structure had a positive effect on the oxidative stability. These results suggest that the introduction of benzophenone groups at the meta-position of the imido group of SPPIs had a positive influence on the hydrolytic stability all the while maintaining other excellent properties (such as the dimensional and oxidative stabilities).

Methanol permeability properties

Table IV lists the methanol permeability of the obtained membranes, and as can be seen, the SPPI membranes demonstrated a methanol permeability in the range of 1.1–2.6 $\times$ 10^{-7} cm² s⁻¹ at room temperature.

This value was close to that of F-SPPI and SPP membranes, but almost 10 times lower than that of Nafion 117 (i.e., 2.4 $\times$ 10^{-6} cm² s⁻¹). Moreover, it was clear that the methanol permeability of SPPI membranes increased with the contents of hydro-

philic moieties; a behavior very similar to those of the IEC values, the water uptake and the proton conductivity. For a fully hydrated membrane, the methanol transport across a PEM should be strongly dependent upon the water uptake, due to the methanol permeating through the membranes as complex forms, such as $CH_3OH_2^+$ and H_3O^+. To understand the performance trade-off between the permeability and conductivity, an investigation was carried out using the selectivity as a representation of the transport characteristics of both proton and methanol ($\Phi = \sigma/P$) for the copolymer and Nafion 117 membranes. The copolymer membranes showed Φ values almost 10 times higher than their Nafion 117 counterparts, indicating their high performance level.

CONCLUSIONS

Proton conductive SPPIs with benzophenone groups at the meta-position of the imido groups were synthesized from N-(4-chloro-3-bensophenone)-5-chloro-1,8-naphthalimide and 3-(2,5-dicholorobenzoyl) -benzenesulfonate by Ni(0) catalytic coupling reaction. The obtained copolymers were envisaged as PEM. The substances with an –SO_3H group on the polymer side chains were found to possess high-molecular weights which could be revealed by their high viscosity and the formation of tough membranes. The SPPI membranes demonstrated an excellent dimensional stability, especially at elevated temperatures, which was attributed to the strong charge-transfer interactions between the imide rings. When compared to the SPPIs with CF_3 groups, the as-made SPPI membranes had an excellent hydrolytic stability. Moreover, this was obtained without sacrificing other excellent properties (such as dimensional and oxidative stabilities) indicating that the benzophenone groups at the meta-position of the imido groups had a positive effect on the hydrolytic stability. The materials remained unchanged with regard to appearance and toughness after 24 h of hydrolytic testing in water at 140°C. Under humidified conditions, the SPPI-70 membranes were found to be highly proton conductive, with a conductivity

TABLE IV
Methanol Permeabilities and Φ of Sulfonated Copolymers and Nafion 117

Samples	IEC (mequiv g⁻¹)	Methanol permeability (cm² s⁻¹)	Φ (10^4 S cm⁻¹ sec cm²)
SPPI-60	1.94	1.1 $\times$ 10^{-7}	65.4
SPPI-70	2.35	1.5 $\times$ 10^{-7}	60.1
SPPI-80	2.79	2.6 $\times$ 10^{-7}	46.5
SPP-60	2.45	4.1 $\times$ 10^{-7}	30.2
F-SPPI-50	1.67	3.1 $\times$ 10^{-7}	19.4
Nafion 117	0.90	2.4 $\times$ 10^{-6}	3.8

of 3.02×10^{-1} S cm^{-1} at 100°C. This was ~2 times higher than that of Nafion 117. Consequently, a combination of an excellent oxidative stability and a low methanol permeability suggested that these materials were promising candidates as PEM for PEMFCs.

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