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The direct synthesis of wholly aromatic poly(*p*-phenylene)s bearing sulfobenzoyl side groups as proton exchange membranes

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Abstract

Sulfonated poly(*p*-phenylene)s (**SPPs**) containing sulfonic acid groups in their side chains had been directly synthesized by Ni(0) catalytic coupling of sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate and 2,5-dichlorobenzophenone. The synthesized copolymers possessed high molecular weights revealed by their high viscosity, and the formation of tough and flexible membranes by casting from DMAc solution. The copolymers exhibited excellent oxidative stability and mechanical properties due to their fully aromatic structure extending through the backbone and pendent groups. Transmission electron microscopic (TEM) analysis revealed that these side-chain type **SPP** membranes have a microphase-separated structure composed of hydrophilic side-chain domains and hydrophobic polyphenylene main chain domains. The proton conductivities of copolymer membranes increased with the increase of IEC and temperature, reaching values above 3.4×10^{-1} S/cm at 120 °C, which are almost 2–3 times higher than that of Nafion 117 at the same measurement conditions. Consequently, these materials proved to be promising as proton exchange membranes.

Keywords: Sulfonated poly(*p*-phenylene)s; Copolymerization; Proton exchange membrane

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have attracted considerable attention for transport, stationary, and portable applications due to their low emissions and high conversion efficiency [1]. Polymer exchange membrane (PEM) is one of the key materials of the PEMFCs, whose properties are strongly related to the performances of PEMFCs [2]. High proton conductivity, excellent chemical and mechanical stabilities are the essentially required properties for successful PEMFCs. In addition, low cost and low fuel permeability are also needed for practical applications. Perfluorosulfonic acid systems, such as Dupont's Nafion membrane, are typically used as the polymer electrolytes in PEMFCs. They are chemically robust in oxidizing environments and have good proton conductivity when hydrated but are characterized by very high cost, high gas permeability, and loss of the preferable properties at high temperature [3]. In the past decades, many polymers have been designed and studied in an effort to address these drawbacks of perfluorosulfonic acid membranes [4]. Sulfonated aromatic polymers, such as sulfonated poly(ether ether ketone)s [5], sulfonated poly(ether sulfone)s [6], sulfonated poly(arylene ether)s [7], sulfonated polyimides [8], and sulfonated poly(*p*-phenylene)s [9] have been widely investigated as candidates for PEM materials. Although each of such sulfonated aromatic polymers has its own advantages,

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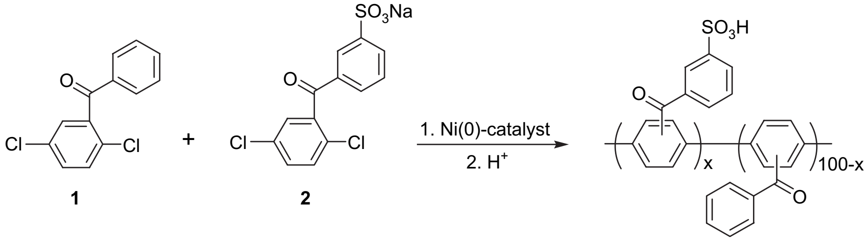

Scheme 1. Synthesis of sulfonated poly(2,5-benzophenone)s (**SPPs**).

fuel cells assembled with these materials can run only for a relatively short time because of membrane damage. This is attributed to their relatively lower oxidative and hydrolytic stabilities when compared with Nafion. Poly(*p*-phenylene)s and especially its derivatives, such as poly(2,5-benzophenone)s, are known to have excellent thermal and oxidative stabilities due to their fully aromatic structure extending through the backbone and pendent groups [10]. These polymers were generally synthesized by nickel(0) catalytic coupling of bis(aryl halide)s or bis(aryl mesylate)s. The active sulfonic acid groups were introduced into poly(*p*-phenylene) derivatives by sulfonation with sulfuric acid or by substitution of activated fluoro groups in the polymers [9b,11]. Sulfonation is an electrophilic substitution reaction. In this reaction, sulfonic acid groups tend to attach onto the electron-rich phenyl rings, which decrease the acidity of sulfonic acid. In a second method, activated fluoro aryl groups were used to generate pendent sulfonated functionalities by their reaction with sodium salt of 4-hydroxybenzenesulfonic acid [9b]. The direct synthesis of the sulfonated polymers from sulfonated monomer has been proven to be more advantageous than that of post-sulfonation, in terms of improved control of the position, number, and distribution of the sulfonic acid groups along the polymer backbone. Sulfonated monomers, such as disodium 3,3′-disulfonated-4,4′-dichloro-diphenylsulfone [6c,12], sodium 5,5′-carbonylbis(2-fluorobenzenesulfonate) [5c] have been prepared and used for direct synthesis of sulfonated polymers. However, to our knowledge, none of the sulfonated monomers has been synthesized and used for the direct synthesis of poly(*p*-phenylene) derivatives. In the present paper, we describe the synthesis of novel sulfonated poly(2,5-benzophenone)s by direct copolymerization of a primarily sulfonated monomer with 2,5-dichlorobenzophenone (Scheme 1). It is expected that these wholly aromatic copolymers with the sulfonic acid groups on the electron-withdrawing phenyl ring should display good proton conductivity, resistance to hydrolysis and oxidation, along with excellent mechanical properties.

2. Experimental

2.1. Materials and instruments

Reagent grade anhydrous $NiBr_2$ was dried at 220 °C under vacuum. Triphenylphosphine (PPh_3) and powdered zinc were used as received. *N*,*N*-Dimethylacetamide (DMAc) and *N*-methylpyrrolidinone (NMP) were dried over CaH_2, distilled under reduced pressure and stored over 4 Å molecular sieves before use.

^{1}H NMR and ^{13}C NMR spectra were measured at 400 MHz on an AV400 spectrometer. FT-IR spectra were obtained with a Bio-Rad Digilab Division FTS-80 FT-IR spectrometer. The inherent viscosities were determined at a 0.5% concentration of the polymer in NMP with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. The thermogravimetric analyses (TGA) were performed under nitrogen with a Perkin–Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min.

2.2. Monomer synthesis

2.2.1. 2,5-Dichlorobenzophenone (*1*)

The compound was prepared by an $AlCl_3$ catalytic Friedel–Crafts acylation of 1,4-dichlorobenzene with benzoyl chloride [13]. The yield was 62%, mp 90–91 °C.

2.2.2. Sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate (*2*)

The compound was prepared by the sulfonation of 2,5-dichlorobenzophenone with sulfuric acid and fuming sulfuric acid with the yield of 97% [14]. ^{1}H NMR (D_2O): δ 8.09 (t, 1H), 8.01–7.99 (m, 1H), 7.88–7.86 (m, 1H), 7.59–7.57 (t, 1H), 7.50–7.48 (m, 1H), 7.46–7.45 (m, 2H). ^{13}C NMR (D_2O): δ 194.4, 143.3, 137.4, 135.2, 132.4, 132.1, 131.5, 131.0, 130.8, 129.1, 128.7, 128.5, 125.9. FT-IR: 1677 cm^{-1} (C=O stretching), 1182 cm^{-1} and 1044 cm^{-1} (asymmetric and symmetric stretching bands of sulfonate groups, respectively), and 625 cm^{-1} (C=S stretching). ESI-mass: *m*/*z* 329 $(M - Na)^-$. Anal. Calcd for $C_{13}H_7Cl_2O_4SNa$: C, 44.21; H, 2.00; Cl, 20.08; S, 7.27. Found: C, 44.02; H, 2.34; Cl, 19.93; S, 7.33.

2.3. Polymer synthesis

SPP-50: to a 100 mL three-necked round-bottomed flask equipped with a serum cap, nitrogen inlet and outlet were added anhydrous $NiBr_2$ (0.087 g, 0.4 mmol), PPh_3 (0.786 g, 3 mmol) and zinc dust (1.56 g, 24 mmol). The flask was evacuated and filled with nitrogen three times. Then dried DMAc was added via syringe through the serum cap. The mixture was stirred at 80 °C. When the mixture changed to red-brown, a nitrogen purged solution of **1** (0.753 g, 3 mmol) and **2** (1.059 g, 3 mmol) in 15 mL dry DMAc was added via syringe. The mixture was stirred at 80 °C for another 2–4 h. The resulting viscous mixture was poured into 300 mL 10% HCl/acetone.

The solid was collected and washed with acetone containing water, then dried in vacuum oven at 150 °C for 12 h to give product with 97% yield. ^{13}C NMR (DMSO-d_6): broad signal at 200–194 (peaks at 197.3, 196.7), 148.2, broad signal at 144–122 (peaks at 138.5, 136.6, 133.7, 130.6, 128.8). FT-IR: 1660 cm^{-1} (C=O stretching), 1098 cm^{-1} and 1028 cm^{-1} (asymmetric and symmetric stretching bands of sulfonic acid groups, respectively).

Copolymers **SPP-30**, **SPP-60** and **SPP-70** were prepared by following the same procedure as above, except that the feed ratio of monomer **1** to **2** was 7:3, 4:6 and 3:7, respectively.

2.4. Membrane preparation and characterization

The copolymers were dissolved in DMAc and the solutions were cast onto glass plates at 70 °C for 24 h and at 150 °C in vacuo for 12 h. The as-cast films were soaked in 1 M H_2SO_4 at room temperature for 12 h. The proton-exchanged membranes were thoroughly washed with de-ionized water and then dried in vacuo at 120 °C for 12 h. The thickness of the membranes was in the range of 30–50 μm. TEM analysis was performed with slices of Pb^{2+}-stained **SPP** membranes on JEM-1011. The sample in proton form was converted into Pb^{2+} form by immersing the sample on copper grid in 1% $Pb(Ac)_2$ solution overnight, then thoroughly rinsed with water and dried at room temperature for 12 h. Ion exchange capacity (IEC) was determined after soaking the samples in saturated aqueous NaCl solution for 24 h, then titrated with 0.02 M NaOH, using phenolphthalein as indicator at room temperature. Completely dried samples were immersed into de-ionized water at room temperature for 5 h and then quickly taken out to measure water uptake (WU), which was calculated in weight percent as follows:

$$\mathrm{WU} = \left[\left(W_{\mathrm{wet}} - W_{\mathrm{dry}}\right)/W_{\mathrm{dry}}\right] \times 100 \qquad (1)$$

Oxidative stability was determined by soaking a small piece of the membrane sample with a thickness of about 40 μm in Fenton's reagent (30% H_2O_2 containing 30 ppm $FeSO_4$) at room temperature. The stability was evaluated by recording the time when the membranes began to dissolve and dissolved completely. Tensile measurement was performed with Instron-1211 instrument at a crosshead speed of 2 mm/min. The proton conductivity of the membrane was evaluated using electrochemical impedance spectra in the temperature range of 30–120 °C (100% RH). The test cell was similar to that showed in Ref. [8g]. The test cell was placed in a temperature and humidity controlled oven. When the temperature changed, the samples were allowed to equilibrate at the desired temperature for 10 min. The impedance measurements were carried out on a Solartron 1255B Frequency Response Analyzer and a Solartron 1470 Battery Test Unit (Solartron Inc., UK) coupled with a computer. The impedance spectra were recorded with the help of ZPlot/ZView software (Scribner Associates Inc.) under an ac perturbation signal of 10 mV over the frequency range of 1 MHz to 10 Hz. Proton conductivity was calculated from the following equation:

$$\sigma = D/(LBR) \qquad (2)$$

where D is the distance between the two electrodes, L and B are the thickness and width of the membrane, respectively, and R is the resistance value measured.

Methanol diffusion coefficients were determined using an H's test cell with a solution containing 2 M methanol in water in one side and pure water in the other side. Magnetic stirrers were used in each compartment to ensure uniformity. Methanol concentration within the water cell was monitored by Shimadzu GC-1020A series gas chromatograph. The methanol diffusion coefficients were calculated by the following equation:

$$C_{\mathrm{B}}(t) = \frac{A}{V_{\mathrm{B}}}\frac{\mathrm{DK}}{L}C_{\mathrm{A}}(t - t_0) \qquad (3)$$

where C_{A} and C_{B} are the methanol concentrations of feed side and that 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.

Gas permeability for the dry polymer membrane with about 30 μm thickness was measured with a conventional permeability apparatus, which consists of upstream and downstream parts separated by a membrane. The design of permeation apparatus and detailed experimental procedure were carried out following the literature methods [15].

3. Results and discussion

3.1. Synthesis of monomer and copolymers

Monomer **2**, sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate, was synthesized by direct sulfonation of 2,5-dichlorobenzophenone using fuming sulfuric acid as the sulfonating agent and subsequently neutralized with aqueous NaOH solution. The product was purified by recrystallization from ethanol, dried under vacuum at 150 °C for 5 h. ^{1}H NMR, ^{13}C NMR, FT-IR and mass spectrometry confirmed the molecular structure and composition of the sodium sulfonate salt compound. Fig. 1 shows the FT-IR spectrum of monomer **2**. The spectrum displayed typical asymmetric and symmetric stretching vibrations of sulfonate groups at 1182 cm^{-1} and 1044 cm^{-1}, respectively. Peaks that appeared at 1677 cm^{-1} and 625 cm^{-1} are stretching vibrations of –C=O and –C=S, respectively. No strong and broad absorption band at about 3500 cm^{-1} was found, which indicated that monomer **2** was water-free.

As shown in Scheme 1, sulfonated poly(2,5-benzophenone)s (**SPPs**) were synthesized by Ni(0) catalytic coupling of monomer **1** with **2**. The copolymers were denoted as **SPP-*x***, where ***x*** was the molar fraction of **2** in the feed. The copolymers with different degrees of sulfonation (DS) were obtained by controlling the feed ratio of monomer **1** to **2**. Intrinsic viscosity values of all copolymers were higher than 1.10 dL/g, indicating high molecular weight of the copolymers (Table 1). The ^{13}C NMR spectrum of **SPP-50** is shown in

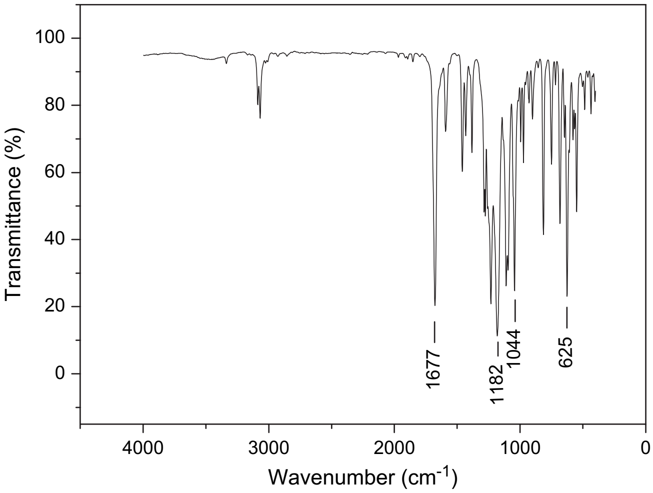

Fig. 1. FT-IR spectrum of sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate.

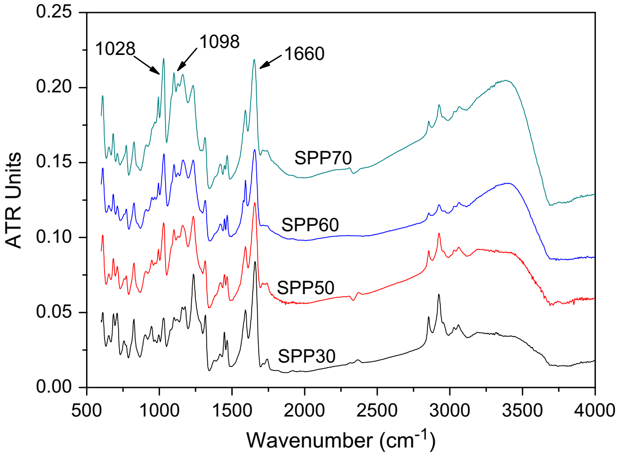

Fig. 3. FT-IR spectra of **SPPs** with different degrees of sulfonation.

Fig. 2. The peak at δ 148.5 ppm could be assigned to the carbon (**C1**) directly linked with $-SO_3H$ group. Peak that appeared at δ 196.8 ppm was assigned to the chemical shifts of carbon atom of carbonyl group in benzophenone units (**C2**). The integration ratio of **C2** to **C1** is very close to 2:1, as expected for the composition of **SPP-50**. The DS value calculated from the ratio of the signal intensity was in very close agreement with the monomer feed ratio, indicating that the sulfonated degree of the polymer could easily be controlled by changing the feed ratio. The comparative FT-IR spectra of **SPPs** with different ratios of monomers are shown in Fig. 3. Peaks at 1660 cm^{-1} are assigned to stretching vibration band of $-C{=}O$ in benzophenone units. The asymmetric and symmetric stretching bands of sulfonic acid groups were at 1098 cm^{-1} and 1028 cm^{-1}, respectively. The intensity of the two peaks was found to increase with increasing amounts of **2**.

Table 1
Physicochemical properties of **SPPs** compared with those of Nafion 117

Samples	η_{inh} (dL/g)	IEC (mmol/g)	WU (wt%)	λ, H_2O/SO_3H	σ^a (S/cm)
SPP-30	1.13	1.40	26.7	10.6	0.034
SPP-50	1.17	2.19	42.1	10.7	0.060
SPP-60	1.18	2.45	47.4	10.7	0.124
SPP-70	1.20	2.78	54.0	10.8	0.174
Nafion 117	–	0.90	33.4	20.6	0.070

[a] Measured at 30 °C, 100% RH.

3.2. Copolymer properties

The copolymers were soluble in polar organic solvents (DMAc, NMP, and DMSO). The most noticeable feature of the copolymers was their ability to form more flexible ductile films compared with poly(2,5-benzophenone) and sulfonated poly(2,5-benzophenone) obtained by the post-sulfonation method [10c,d]. Dynamic mechanical properties of **SPP-70** and poly(2,5-benzophenone) are depicted in Fig. 4, which showed that poly(2,5-benzophenone) has a glass transition temperature at about 185 °C. However, **SPP-70** showed no obvious glass transition temperature under 500 °C, indicating that stronger interaction among chains of **SPP-70** was induced by the $-SO_3H$ groups on the side chains, which should be responsible for the improvement of the film forming ability compared with poly(2,5-benzophenone).

TGA test showed that the degradation temperature of sulfonic acid groups in the present study (300 °C) is higher than that of sulfonated poly(4-phenoxybenzoyl-1,4-phenylene (**S-PPBP**) (250 °C) in which the sulfonic acid groups are linked directly to the pendent oxyphenyl groups of polymer [9a], suggesting that the sulfonic acid groups attached to electron-deficient phenyl rings have high thermal stability. These

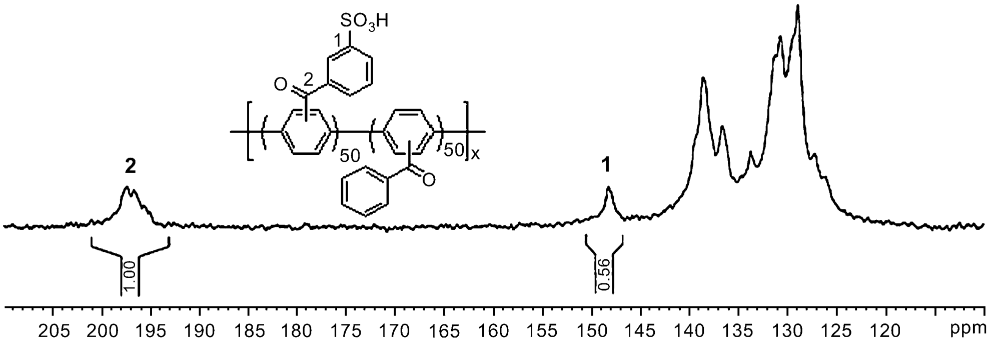

Fig. 2. ^{13}C NMR spectrum of **SPP-50** (DMSO-d_6).

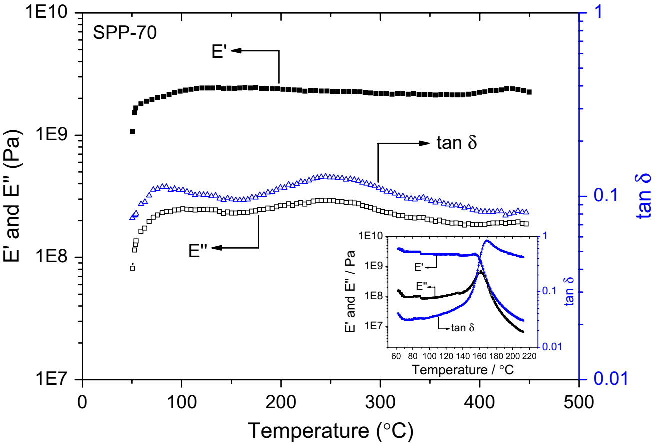

Fig. 4. Dynamic mechanical behaviors of **SPP-70**. Inset shows the dynamic mechanical behaviors of poly(2,5-benzophenone).

thermal properties, high decomposition temperature without glass transition, would be preferable for an electrolyte material for PEMFCs.

3.3. Oxidative stability and mechanical properties

The stability of **SPP** membranes to oxidation was investigated by soaking the film samples in Fenton's reagent (30% H_2O_2 containing 30 ppm $FeSO_4$) at 25 °C (Table 2). The oxidative stability of the samples was characterized by the elapsed time at which the membranes started to dissolve and dissolved completely in the solution. **SPP-70** membrane endured for 37 h before it started to dissolve. It was more than 70 h until the membrane had completely dissolved. These results indicated that the **SPP** membranes showed excellent oxidative stability compared with other sulfonated polymers [16,17] due to their fully aromatic structure extending through the backbone and pendent groups.

It should be noted that the dry and hydrated **SPP** membranes all exhibited attractive mechanical properties as displayed in Fig. 5. The hydrated membranes showed larger elongation at break and lower stress and Young's modulus than those of the dry state because of the plastic effect of the absorbed water. As can be seen from Fig. 5 and Table 3, **SPP-50** exhibited relatively better mechanical properties than the other samples. It seems to us that there is an optimum equilibrium point in the water uptake and the mechanical properties for **SPP-50** membrane. The tensile strength and Young's modulus of the dry and hydrated **SPP-70** membranes are more than 79 MPa and 20 MPa, and 1.7 GPa and 0.5 GPa, respectively, which indicated that the **SPP** membranes were strong and tough enough for fuel cell application even at high sulfonated degree. Also, the membranes can retain

Table 2
Oxidation stabilities of **SPP** membranes

Samples	τ_1[a] (h)	τ_2[a] (h)
SPP-30	64	>250
SPP-50	57	135
SPP-60	49	124
SPP-70	37	71

[a] τ_1 and τ_2 refer to the elapsed times at which the membranes started to dissolve and dissolved completely in the solution, respectively.

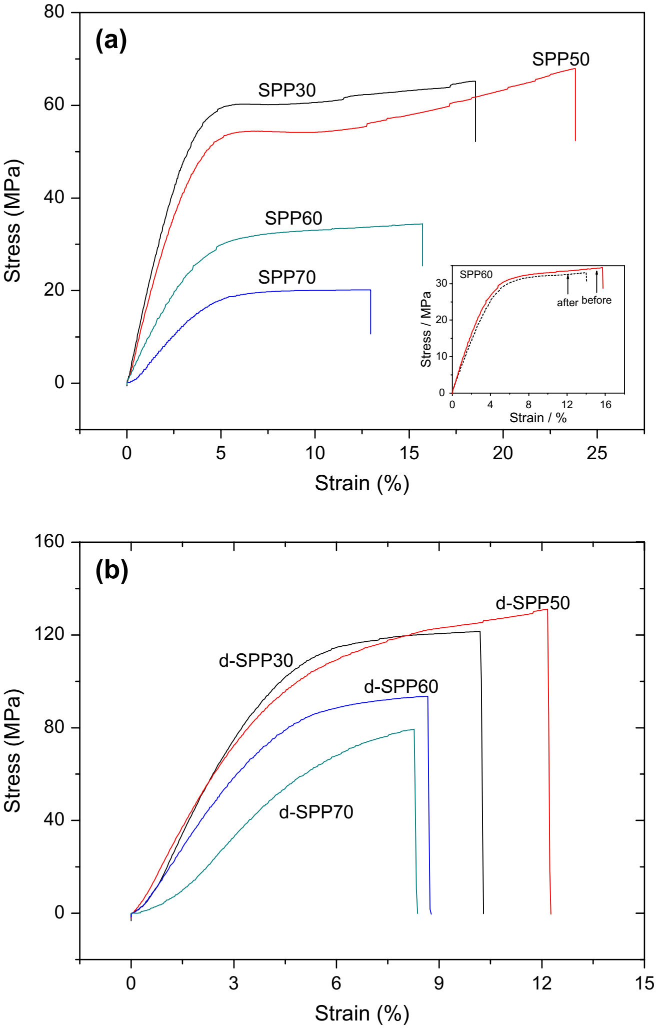

Fig. 5. Stress vs strain curves of **SPP** membranes in hydrated (a) and dry state (b). Inset shows stress–strain curves of **SPP-60** membrane before and after ageing in de-ionized water at room temperature for 1 year. (a) Samples were soaked in de-ionized water for 3 weeks at room temperature and tested in fully hydrated state at 30 °C, (b) samples were dried at ambient conditions for 1 day and tested at 30 °C, 25% RH.

Table 3
Mechanical properties of **SPP** membranes in dry and hydrated states

Samples	Dry state[a]			Hydrated state[b]		
	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
SPP-30	121.5	3.0	9.8	65.2	1.9	18.6
SPP-50	131.1	2.8	12.0	67.8	1.5	23.8
SPP-60	93.6	2.2	8.6	34.2	0.8	16.5
SPP-70	79.5	1.7	8.2	20.2	0.5	12.7

[a] Samples were dried at ambient conditions for 1 day and tested at 30 °C, 25% RH.

[b] Samples were soaked in de-ionized water for 3 weeks at room temperature and tested in fully hydrated state at 30 °C.

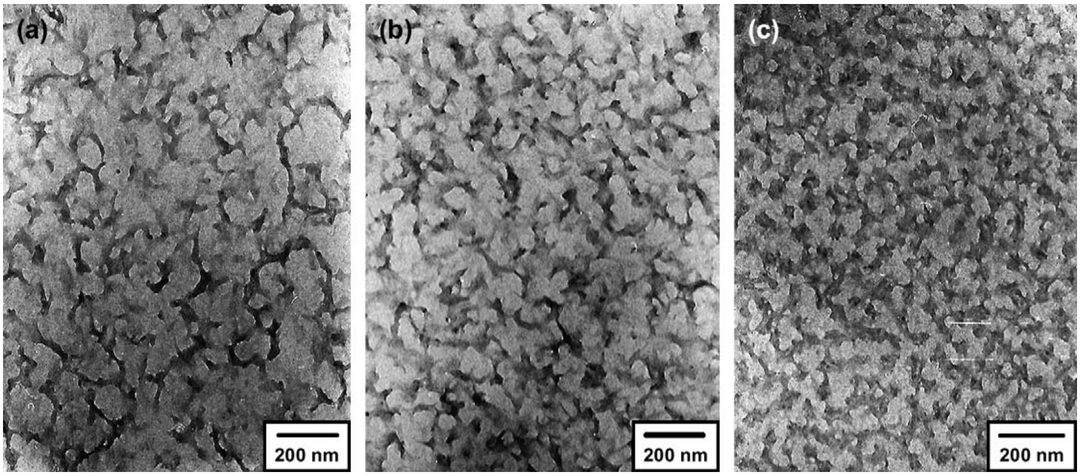

Fig. 6. TEM images of **SPP-30** (a), **SPP-50** (b) and **SPP-70** (c).

good mechanical properties after swelling in water. The inset in Fig. 5(a) is stress–strain curves of **SPP-60** membrane before and after ageing in de-ionized water for about 1 year at room temperature, which revealed a little loss in mechanical properties after ageing.

The morphologies of the copolymer membranes have been studied by transmission electron microscopy performed on Pb^{2+}-stained **SPP** ultra thin films on the copper grid. Three micrographs are shown in Fig. 6, corresponding to the morphologies of **SPP-30**, **SPP-50** and **SPP-70**. The dark regions represent localized ionic domains and the light regions refer to hydrophobic polymer backbone. The images exhibited clear microphase-separated structure composed of hydrophilic domains and hydrophobic moieties. The sulfonic acid groups in the present study are localized on the benzoyl side groups, which facilitate sulfonic acid groups to move together to form ion-rich channels. The ionic domains with the size about 10–30 nm for **SPP** membranes were continuous and became wider and denser with DS increasing. The formation of continuous ionic channel is favorable for water keeping and proton transport while the nonionic hydrophobic domains allow mechanical strength. Similar continuous ionic channel structures were also observed for Nafion 117 ionomer and some side-chain type sulfonated aromatic polymers, such as polyimides [18] and polysulfone [19].

3.4. Water uptake and proton conductivity

Water uptake (WU) was measured by weighing the polymer films under dry and wet conditions. As anticipated, the amount of water uptake was closely related to the amount of sulfonic acid groups in the copolymers (Table 1). Furthermore, the number of water molecules per sulfonic acid group (λ) was calculated and found to be equal to about 11 for all **SPP** membranes. This value was larger than that of sulfonated poly(4-phenoxybenzyol-1,4-phenylene) ($DS = 65\%$, $\lambda = 8.7$) [9a].

The temperature dependence of the proton conductivities (σ) of **SPP** membranes and Nafion 117 was tested at 30–120 °C (100% RH) (Fig. 7). The conductivity of **SPPs** showed a linear dependence on the temperature, and no decrease of proton conductivity was found at high temperature, which indicated that the pendent side chains of **SPPs** might maintain the hydrated state even at elevated temperatures. The proton conductivities of **SPP** membranes increased from 0.03 S/cm of **SPP-30** to 0.17 S/cm of **SPP-70** at 30 °C. **SPP-70** with 54% water uptake, showed a conductivity of 0.17 S/cm at 30 °C and 0.34 S/cm at 120 °C, which was about 2–3 times higher than those of Nafion 117 (0.06 S/cm and 0.12 S/cm, respectively) measured at the same conditions. These values are much higher than that of oxyphenyl sulfonic acid poly(phenylene) derivatives reported previously (10^{-2} S/cm at room temperature) with similar sulfonation level (65%) [9a]. This is most likely due to the higher acidity of benzoyl sulfonic acid group than that of oxyphenyl sulfonic acid group.

3.5. Methanol diffusion coefficient and gas permeation properties

SPP membranes exhibited slightly increased methanol diffusion coefficients at 25 °C with increasing DS (Table 4). The methanol diffusion coefficients of **SPP** membranes are of the

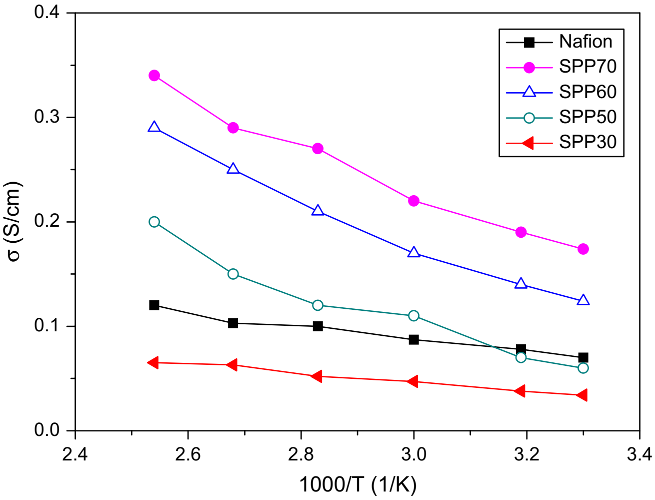

Fig. 7. Temperature dependence of the proton conductivities for **SPP** membranes and Nafion 117 in 100% RH.

Table 4
Methanol permeabilities of **SPP** membranes and Nafion 117

Samples	IEC (mmol/g)	Methanol permeability[a] (cm^2/s)
SPP-30	1.40	1.1×10^{-7}
SPP-50	2.19	1.5×10^{-7}
SPP-70	2.78	7.3×10^{-7}
Nafion 117	0.90	2.4×10^{-6}

[a] Measured at 25 °C.

order of magnitude of 10^{-7} cm^2/s and the methanol diffusion coefficient of **SPP-70** membrane is about 4 times lower than that of Nafion 117 (2.4×10^{-6} cm^2/s) at the same temperature. The lower methanol crossover of **SPP-70** would be ascribed to the lower methanol affinity of hydrocarbon polymers than that of perfluorinated materials [19]. Gas permeation through the proton exchange membrane is an important factor that affects fuel cell performance, because the permeated gas causes direct chemical reaction combustion resulting in lower utilization of fuels. It has been generally recognized that the gas permeates mainly through the hydrophobic domain of the polymer electrolyte membrane. Hydrogen and oxygen permeability coefficients for **SPP-70** membrane under dry condition are summarized in Fig. 8 as a function of temperature. In the range of tested temperature, dry hydrogen and oxygen permeabilities of **SPP-70** membrane are more than 1 order of magnitude lower than those of sulfonated polyimides and more than 2 orders of magnitude lower than those of Nafion [20]. This behavior could be attributed to the rigid main chains of copolymers which resulted in the better molecule packing, hence lower gas permeation.

4. Conclusions

Wholly aromatic poly(*p*-phenylene)s with sulfonic acid groups linked to the pendent chains of polymers were successfully synthesized by Ni(0) catalytic coupling polymerization of 2,5-dichlorobenzophenone with sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate. The sulfonated copolymers displayed excellent film forming abilities and mechanical properties due to the increased interaction between chains induced by the $-SO_3H$ groups. The copolymer membranes also showed stability to oxidation, as evaluated by Fenton's reagent due to the fully aromatic structure of these copolymers. Significant hydrophilic/hydrophobic microphase-separated structures were observed for these membranes, which were favorable for water keeping, proton transport and limitations of swelling. The attachment of the active sulfonic acid groups onto the electron-deficient benzoyl group results in better morphology and higher proton conductivity of the membranes. **SPP-70** membrane showed 2–3 times higher proton conductivity than that of Nafion 117 at the same measurement conditions. These electrolyte properties (oxidative stability, mechanical strength, and proton conductivity) seem promising for the application to high temperature PEMFCs and DMFCs.

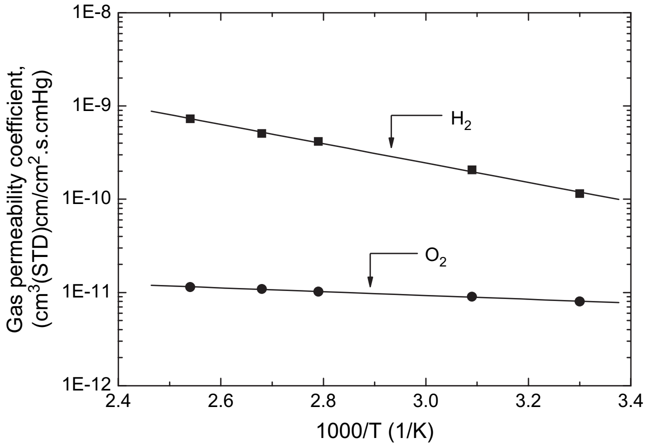

Fig. 8. Temperature dependence of H_2 and O_2 permeabilities for dry **SPP-70** membrane.

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