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Sulfonated Poly(arylene-*co*-naphthalimide)s Synthesized by Copolymerization of Primarily Sulfonated Monomer and Fluorinated Naphthalimide Dichlorides as Novel Polymers for Proton Exchange Membranes

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ABSTRACT: A novel sulfonated aromatic dichloride monomer was successfully prepared by the reaction of 2, 5-dichlorobenzophenone with fuming sulfuric acid. Copolymerization of this monomer in the form of sodium salt (**1**) with *N*-(4-chloro-2-trifluoromethylphenyl)-5-chloro-1,8-naphthalimide (**2**) or bis(*N*-(4-chloro-2-trifluoromethylphenyl)-1,4,5,8-naphthalimide (**3**) generated two series of novel poly(arylene-*co*-naphthalimide)s **I-*x*** and **II-*x*** where ***x*** represents the content of the sulfonated monomer. The synthesized copolymers with the $-SO_3H$ group in the side chains possessed high molecular weights revealed by their high viscosity and the formation of tough and flexible membranes. The copolymers exhibited excellent stability toward water and oxidation due to the introduction of the hydrophobic CF_3 groups. The sulfonated copolyimides that incorporated with 1,8-naphthalimide (**I-*x***) exhibited better hydrolytic and oxidative stabilities than those with 1,4,5,8-naphthalimide. Copolymer I-50 membrane endured for more than 83 h in Fenton's reagent at room temperature. The mechanical properties of I-50 membrane kept almost unchanged after immersing membrane in boiling water for 196 h. The proton conductivities of copolymer films increased with increasing IEC and temperature, reaching values above 6.8×10^{-1} S/cm at 80 °C. Consequently, these materials proved to be promising as proton exchange membranes.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been identified as promising power sources for transport, stationary, and portable applications due to their low emissions and high conversion efficiency.[1−3] Improvement in performance of the polymer electrolyte membrane (PEM) has been the focus in the development of PEMFCs because the PEM is one of the key components for successful PEMFC fabrications.[4] Nafion (Dupont), a perfluorosulfonic acid polymer, is a currently used PEM in commercial systems. Nafion is chemically robust in oxidizing environments and has good proton conductivity when hydrated. However, some specific limitations exist for Nafion membranes including very high cost, high gas permeability, and loss of the preferable properties at high temperature.[5] These limitations have stimulated many efforts in the development of new PEM materials, aiming to reduce costs and to overcome technical drawbacks of Nafion.[6] Sulfonated aromatic polymers, such as poly(ether ether ketone),[7] poly(ether sulfone)s,[8] poly(arylene ether)s,[9] polyimide,[10] and poly(*p*-phenylene)s[11] are widely investigated as candidate PEM materials. Although each of such sulfonated aromatic polymers has its own advantages, most of them have failed to meet the requirement of high conductivity and durability under fuel cell operating conditions. Their lower conductivity can be attributed to chain rigidity, lack of ion channels, and lower acidity of $Ar-SO_3H$ than that of $-CF_2-SO_3H$ in Nafion. Addition of more sulfonic acid conductors may increase conductivity, but it may lead to undesirable large swelling and thus result in a dramatic loss of mechanical properties. Aromatic polyimides are known to have superior solvent-resistance, excellent mechanical strength and good film forming ability because of the strong charge-transfer interaction between the polymer chains.[12] Okamoto and co-workers have reported that sulfonated copolyimides from naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTDA) and more flexible sulfonated and nonsulfonated diamines show much better water stability than other sulfonated aromatic polymers.[13] Watanabe et al. had shown that NTDA-based sulfonated polyimides with bulky fluorenyl groups having unique water uptake behavior and produced higher conductivities than Nafion.[14] They also reported that polyimides bearing aliphatic sulfonic acid groups had enhanced water stability. The improvement in water stability of polyimides was attributed to the higher basicity of the sulfonated diamine.[15,16]

For PEMFC applications, the long-term durability of the polymer exchange membrane is an important issue. Therefore, the materials with chemical stability are highly required. Among such sulfonated aromatic polymers, poly(*p*-phenylene)s (PPP) have shown excellent thermal-oxidative stability and mechanical property. However, they are characterized by poor film forming ability.[11,17]

The objective of our work is to design and synthesize sulfonated polymers having both high proton conductivity and good thermal oxidation stability. In this paper, we report the synthesis of poly(arylene-*co*-naphthalimide)s by copolymerization of such aromatic dichloride monomers (Scheme 1). The resulting copolymers possessed the CF_3 protected naphthalimide structural

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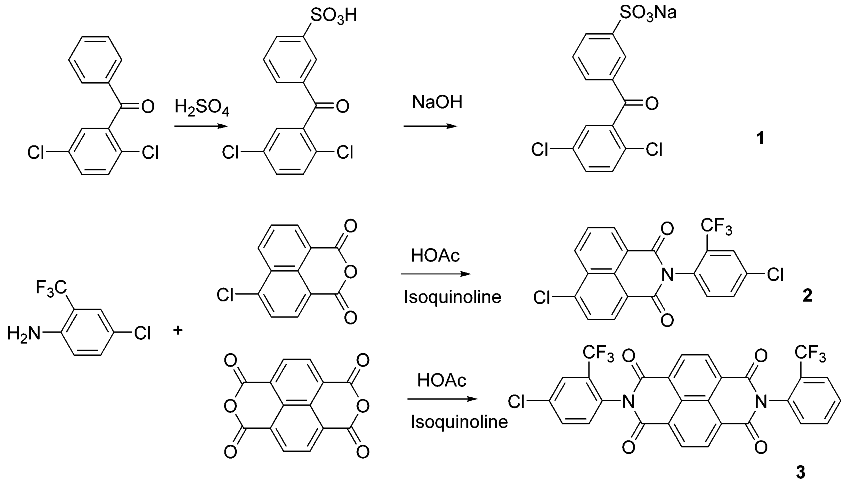
Scheme 1. Syntheses of Monomers



characteristics. The activated sulfonic acid groups are separated from naphthalimide moiety and localized on the meta- position of electron withdrawing carbonyl groups in the side chain of copolymers. The copolymers display good proton conductivity, resistance to hydrolysis and oxidation, along with excellent mechanical properties. A sulfonated monomer, sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate (**1**) and hydrophobic fluorinated naphthalimide dichloride comonomers (**2**) and (**3**) were also synthesized for this study.

Experimental Section

Materials. *N*,*N*-Dimethylacetamide (DMAc) was dried over CaH_2, distilled under reduced pressure, and stored over 4 Å molecular sieves. Isoquinoline (99%) was used as received from Shanghai Kuilin Chemical Co., Ltd. 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. 5-chloro-1,8-naphthalic anhydride and 1,4,5,8-naphthalenetetracarboxylic dianhydride were used as received from Beijing Multi. Technology Co., Ltd. 4-Chloro-2-(trifluoromethy)aniline received from JS (Tianjin) Chemical & Metallurgical Co., Ltd was used after distillation. 2,5-Dichlorobenzophenone was prepared by an $AlCl_3$ catalytic Friedel−Crafts acylation of 1, 4-dichlorobenzene with benzoyl chloride according to a previously described procedure.[18]

Measurements. ^1H and ^{13}C NMR spectra were measured at 300 MHz on an AV600 spectrometer. 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 concentration of polymer in NMP with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elemer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. Tensile measurement were performed with a mechanical tester Instron-1211 instrument at a speed of 1 mm/min. The relative humidity was 50% RH.

Water Uptake. The membrane (30−40 mg per sheet) was dried at 80 °C under vacuum for 6 h until constant weight as dry material was obtained. It was immersed into deionized water at room temperature for 4 h. Then the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake of the membranes was calculated from

$$\mathrm{WU} = (W_s - W_d)/W_d \tag{1}$$

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

Dimensional Change. Dimensions change of the copolymer membranes was investigated by immersing the round shape samples into water at room temperature for a given time, the changes of thickness and diameter were calculated from

$$\Delta T_c = (T - T_s)/T_s$$
$$\Delta L_c = (L - L_s)/L_s \tag{2}$$

where T_s and L_s are the thickness and diameter of the membrane equilibrated at 70% RH, respectively; T and L refer to those of the membrane immersed in liquid water for 5 h.

Oxidative 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 membranes began to dissolve and dissolved completely.

Ion Exchange Capacity. Ion exchange capacity (IEC) was determined through titration. 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.

Proton Conductivity. The proton conductivities of the copolymer membranes were evaluated using electrochemical impedance spectra in the temperature range of 20−80 °C. The impedance measurements were carried out on a Solartron 1255B Frequency Response analyzer and a Solartron 1470 Battery Test Unit (Solartron Inc., U.K.) coupled with a computer. The membranes with 1 cm^2 in area were sandwiched between two stainless steel blocking electrodes. The samples were allowed to equilibrate at the desired temperature for 0.5 h. 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 1 Hz.

Monomer Synthesis. Synthesis of Sodium 3-(2,5-Dichlorobenzoyl)benzenesulfonate (1). To a 50 mL three-neck flask equipped with a magnetic stirred bar was charged 10 mmol of 2,5-dichlorobenzophenone. The flask was cooled in an ice bath. Concentrated sulfuric acid (95%, 1.5 mL) was then added with stirring. After 2,5-dichlorobenzophenone was dissolved, 3 mL of fuming sulfuric acid (SO_3 60%) was slowly added to the flask. The reaction mixture was stirred at room temperature for 2 h and then at 80 °C for additional 2 h. After cooling to room temperature, the slurry was carefully poured into 100 mL of cooled 30% NaOH aqueous solution. The resulting white precipitate was filtered and then redissolved in 30 mL of water. After the solution was adjusted to pH = 7 with 0.5 M HCl, NaCl solid (8 g) was added to the solution, resulting in a white precipitate. The precipitate was filtered, washed with saturated NaCl aqueous solution, and dried at 80 °C in a vacuum. Yield was 97%. ^1H NMR (ppm, D_2O): 8.09 (s, 1H), 7.9−8.0 (d, 1H), 7.7−7.8 (d, 1H), 7.57−7.59 (t, 1H), 7.45−7.50 (m, 3H). ^{13}C NMR (ppm, DMSO-d_6): 194.5 (s), 143.3 (s), 137.4 (s), 135.2 (s), 132.4 (s), 132.1 (s), 131.5 (s), 131.0 (s), 130.8 (s),

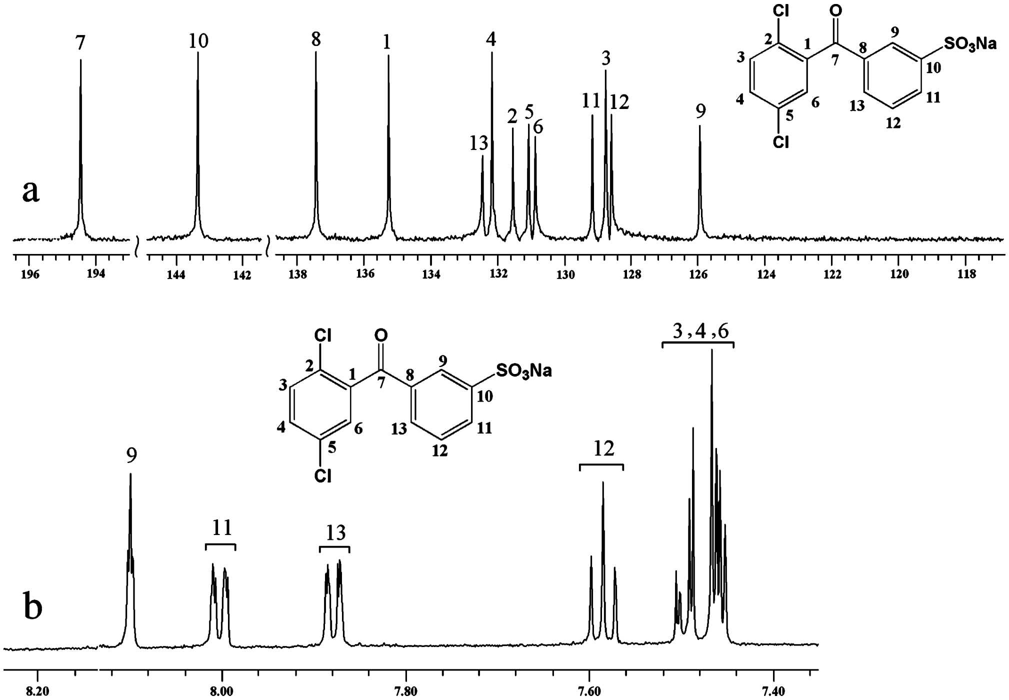


Figure 1. ^{1}H NMR and ^{13}C NMR spectra of monomer **1**.

129.2 (s), 128.8 (s), 128.6 (s), 125.9 (s). FT-IR: 1675 cm^{-1} (C═O stretching), 1233 and 1044 cm^{-1} (asymmetric and symmetric stretching vibration of sodium sulfonate groups).

Synthesis of *N*-(4-Chloro-2-trifluoromethylphenyl)-5-chloro-1,8-naphthalimide (2). In a 500 mL round-bottomed flask, 41.02 g (0.10 mol) of 5-chloro-1, 8-naphthalic anhydride, 19.56 g (0.10 mol) of 4-chloro-2-(trifluoromethyl)aniline, 7.2 mmol of isoquinoline, and 300 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 200 °C in the yield of 76.8% (31.52 g). Mp: 278−279 °C.^{1}H NMR (DMSO-d_6): 8.76−8.73 (1H, d), 8.66−8.64 (1H, d), 8.51−8.49 (1H, d), 8.13−8.00 (4H, m), 7.81−7.78 (1H, d): IR (KBr): 1716 and 1672 cm^{-1} (C═O of imide), 1353 cm^{-1} (C−N stretching), 781 cm^{-1} (C═O bending). Anal. Calcd for $C_{19}H_8Cl_2F_3NO_2$ (410.17): C, 55.64; H, 1.97; N, 3.41. Found: C, 57.12; H, 2.03; N, 3.89.

Synthesis of Bis(*N*-(4-chloro-2-trifluoromethylphenyl)-1,4,5,8-naphthalimide) (3). This compound was prepared from 1,4,5,8-naphathlenetetracarbonxylic dianhydride and 4-chloro-2-(trifluoromethyl)aniline using the same procedure as described above, then sublimed under vacuum at 250 °C. The yield was 87%. Mp > 300 °C. ^{1}H NMR spectrum in DMSO-d_6: 8.79 (4H, s), 8.11−8.08 (4H, m), 7.93−7.90 (2H, d). FT-IR: 1714 and 1684 cm^{-1} (C═O of imide), 1349 cm^{-1} (C−N stretching), 771 cm^{-1} (C═O bending). Anal. Calcd for $C_{28}H_{10}Cl_2F_6N_2O_4$ (623.29): C, 53.96; H, 1.62; N, 4.49. Found: C, 55.05.12; H, 1.73; N, 4.20.

General Procedure for Syntheses of Sulfonate Copolyimides. $NiBr_2$ (0.32 g, 1.42 mmol), PPh_3 (2.60 g, 9.98 mmol), and zinc dust (5.20 g, 80.00 mmol) were placed in a 250 mL three-necked round-bottomed flask. The flask was evacuated and filled with nitrogen three times. Dry DMAc (20 mL) was added via syringe and the mixture became red brown in 20 min. Then, the monomer **1** (10 mmol) and comonomer (**2** or **3**) (10 mmol) were added and stirred at 90 °C for 4 h. The resulting viscous mixture was diluted with 50 mL of DMAc, filtered, and then poured into 200 mL of 10 wt % HCl/acetone. The polymer was collected by filtration, washed with acetone, and dried in a vacuum at 200 °C for 24 h.

Membrane Preparation. The sulfonated copolymers were dissolved in *N*-methylpyrrolidinone (NMP) to form a 2−3% solution at 80 °C under argon atmosphere for 8 h. Then the NMP solution was filtered and cast on a glass sheet. The solvent was evaporated by heating from 60 to 70 °C until the membranes were dry and then dried in a vacuum oven at 100 °C for 48 h. The thickness of the resulting membranes was in the range 25−40 μm.

Results and Discussion

Monomer Syntheses. The synthetic route of monomers is outlined in Scheme 1. Monomer (**1**), sodium 3-(2, 5-dichlorobenzoyl)benzenesulfonate, was synthesized with 97% yield by the reaction of 2,5-dichlorobenzophenone with fuming sulfuric acid at 80 °C for 2 h and subsequent neutralization with NaOH. The molecular structure and composition of the sodium sulfonate salt compound (**1**) was confirmed by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. The FT-IR spectrum (KBr substrate) showed a intense absorption band at 1675 cm^{-1} (C═O stretching) and bands at 1100 and 1044 cm^{-1} (asymmetric and symmetric stretch vibration of sodium sulfonate groups). ^{1}H NMR and^{13}C NMR spectra of (**1**) confirmed that the sulfonic group was bonded to the meta-position of carbonyl groups (Figure 1). Naphthalimide dichloride monomer (**2**) was synthesized by the reaction of 5-chloro-1,8-naphthalic anhydride and 4-chloro-2-(trifluoromethyl)aniline in acetic acid, and purified by subliming under vacuum at 200 °C. It was used as a hydrophobic comonomer for copolymerization with the monomer (**1**). Incorporation of hydrophobic trifluoromethyl groups ortho to the imide nitrogen could protect the polymer main chains from being attacked by water molecules containing highly oxidizing radical species. For comparison study, naphthalimide dichloride (**3**) was also synthesized from naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTDA) and 4-chloro-2-trifluoromethylaniline. The chemical structures of **2** and **3** were confirmed by FT-IR and ^{1}H NMR (Figure 2).

Polymer Syntheses. As shown in Scheme 2, two series of sulfonated copolymers were synthesized by Ni(0)-catalyzed coupling polymerization of monomer **1** with **2** or **3**, respectively. The polymerizations were carried out under the reaction conditions reported in the literature.[18] The degree of sulfonation (DS) of the copolymer was readily controlled through the monomer feed ratios of **1** to **2** or **3**. The copolymers were

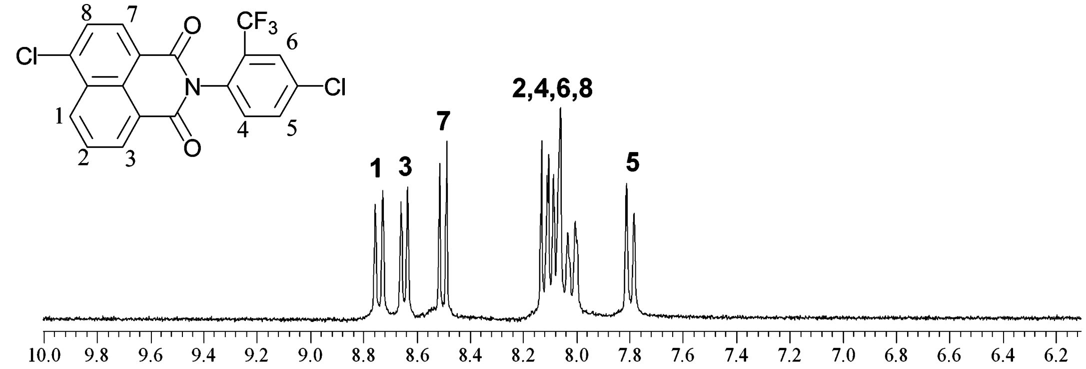
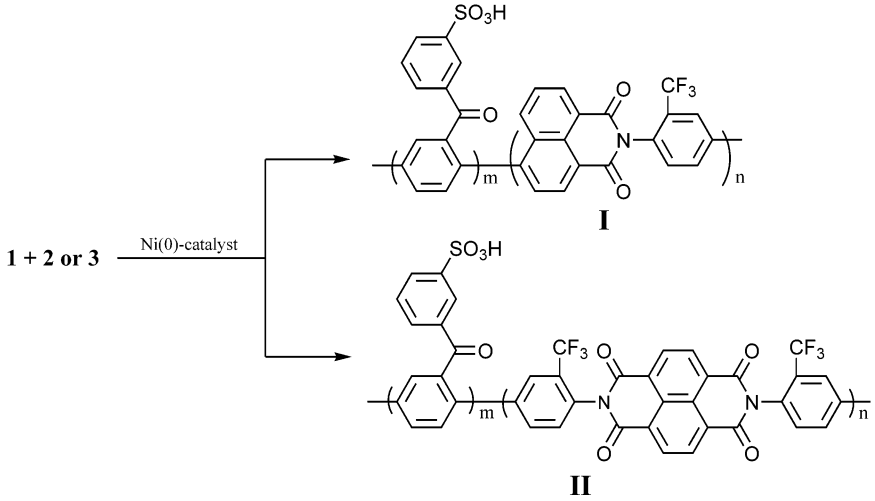


Figure 2. ^{1}H NMR spectrum of **2** in DMSO-d_6.

Scheme 2. Synthesis of Copolymer I and II



denoted as **I-*x*** and **II-*x*,** where ***x*** is the mole fraction of the monomer **1** in the feed**.** The FT-IR spectra of copolymers are shown in Figure 3. The strong absorption bands around 1716 cm^{-1} (υ_{sym}C=O), 1658 cm^{-1} (υ_{asym}C=O) and 1348 cm^{-1} (υ_{CN} imide) are assigned to the naphthalenic imido rings. The band s around 1100 and 1031 cm^{-1} were assigned to the stretch vibration of sulfonic acid groups. The intensity of this peak increased with an increasing sulfonated monomer ratio. The ^{13}C NMR spectrum of **II-50** is shown in Figure 4. The signal at $\delta = 163.0$ and $\delta = 196.8$ ppm was assigned to the carbonyl carbon atom of imide ring (C1) and benzophenone units (C2), respectively. The integration ratio of C1 to that of C2 is close to 4:1, as expected for the composition of **II-50**. The peak at $\delta = 148.5$ could be assigned to the carbon attached $-SO_3H$ group. The sulfonation degree values calculated from the ratio of the signal intensity of C1 to that of C3 in **II-50** was about 50%, which are in very close agreement with the monomer feed ratio during copolymerization. All copolymers are soluble in polar organic solvents (DMAc, NMP) and form a flexible and tough film by casting from the solution. Their solubility behavior is shown in Table 1. Intrinsic viscosity values of all copolymers were higher than 1.52dL/g in NMP at 30 °C, which indicated successful copolymerization in producing high molecular weight copolymers. Figure 5 shows the thermal stability of the copolymer **I-70** and **II-70** investigated by TGA. It can be seen that the polymers thin films exhibited 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 weight loss of around 300 °C is due to the decomposition of sulfonic acid groups by the desulfonation. The third stage weight loss around 500 °C is assigned to the decomposition of polymer main chain.

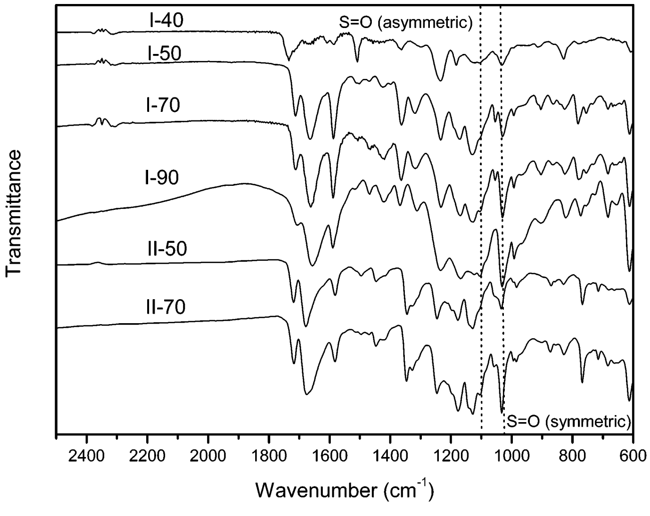


Figure 3. FT-IR spectra of sulfonated polyimides.

Water Uptake, Water Stability, and Mechanical Properties. The water uptake of sulfonated polymers is known to have a profound effect on membrane conductivity and mechanical properties.[19] Water molecules dissociate 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. The water uptake and swelling ratio of copolymer membranes were determined by measuring the changes in the mass and size, respectively, before and after hydration. As shown in Table 2, the room-temperature water uptake of **II-50** and **II-70** films with

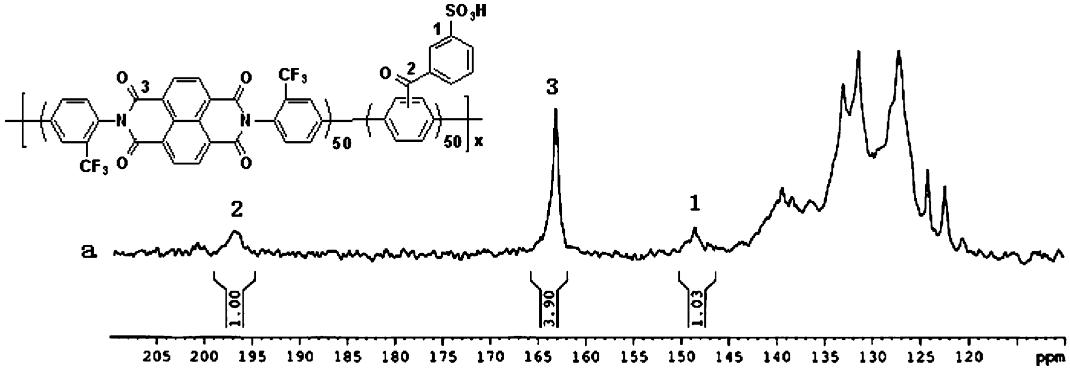


Figure 4. ^{13}C NMR spectrum of **II-50** in DMSO-d_6.

Table 1. Solubilities of Sulfonated Copolyimides in Acidified Forms

		solvents						
polymer	η^a (dL/g)	NMP	DMSO	DMAc	MeOH	DMF	acetone	water
I-40	2.57	++[b]	− −	++	− −	+−	− −	− −
I-50	2.35	++	+−	++	− −	+−	− −	− −
I-70	2.37	++	+−	++	+−	+−	− −	− −
I-90	1.92	++	+−	++	+−	+−	− −	+−
II-50	1.52	++	+−	++	− −	+−	− −	− −
II-70	1.57	++	+−	++	− −	+−	− −	− −

[a] η_{inh} was measured at a concentration of 0.5 g/dL in NMP at 30 °C. [b] Key: (++) soluble at room temperature; (+-) soluble by heating; (- -) insoluble.

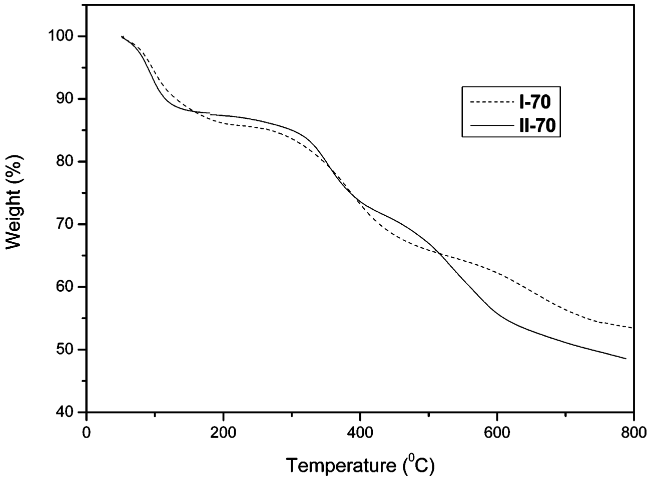


Figure 5. Thermogravimetric analysis thermograms of **I-70** and **II-70**.

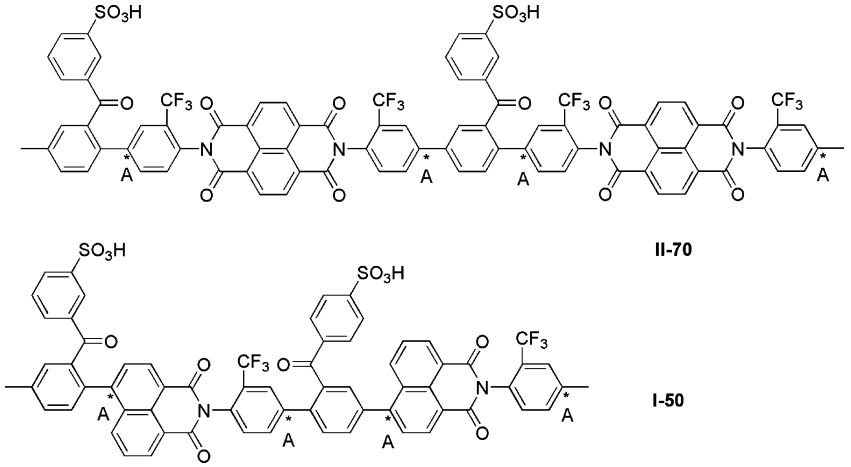
IEC of 1.11 and 1.89 is 20 and 30% corresponded to absorption of, respectively, 9 and 10 water molecules per $-SO_3H$ group. This is in the same range as Nafion, which absorbs 11 water molecules per sulfonic acid group at room temperature.[3] The water uptakes observed for copolymer **I-*x*** varied from 48 to 259% for IEC values varying from 1.28 to 3.36 mequiv g^{-1}, which are much higher than that of **II-*x*** with a comparable IEC values. For example, copolymer **I-50** (IEC = 1.65 mequiv/g) shows almost 2 times water uptake (61%) than that of II-70 (31%) (IEC = 1.89 mequiv/g). The content of hydrophobic CF_3 groups in copolymer **I-50** (11.5 wt %) is almost same as that in copolymer **II-70** (11.9 wt %). Therefore, the difference of water uptake between copolymer **I-50** and **II-70** can be attributed to their difference in molecular structure. Comonomer **3** is structurally symmetrical, the copolymer **II-70** synthesized from **3** possessed a linear rigid-rod chain structure (linkage carbon (A) fall in a line) (Figure 6). However, comonomer **2** is not symmetrical, and the resulting copolymer **I-50** has a bent nature of chain structure, which leads to enhanced free volume and decreased interchain interaction. In addition, the copolymer **I-50** synthesized from less symmetrical monomer **2** contains regio-irregular naphthalimide structure, which is produced by three possible link types of monomer **2**, such as head to head, head to tail, and tail to tail. The breaking regular structures loosened the film packing and markedly increased the interchain space in which water molecules could be confined.

The stability of sulfonated polyimide membranes in water has been the subject of much research because it is one of the important factors affecting membrane performance.[10a,c,e,13] In general, polyimides display relatively low hydrolytic stability due to the inherent hydrolytic feasibility of imido ring. Introducing the diamine moieties with high basicity proved to be highly effective for improving the water stability of polyimides because the high basicity of the sulfonated diamine moieties depresses the hydrolysis of imido ring.[15,16] In the present study, copolyimides **I-*x*** and **II-*x*** all contain the CF_3 group, which is unfavorable to depress the hydrolysis of imido ring due to the electron withdrawing nature of the CF_3 group. However, incorporation of the hydrophobic trifluoromethyl group on the *o*-anilide position could have a positive effect on the stability since it could protect the polymer main chains from being attacted by water molecules containing highly oxidative radical species. The another common structural feature between **I-*x*** and **II-*x*** is that the sulfonic acid groups are attached to deactivated phenyl ring in the side chain of copolymers. It has been reported that the attachment of the sulfonic acid group on the pendent chain is favorable to enhance the proton conductivity and improve water stability of polymer membranes.[20] Although having such similarities in the features of their structures, copolymers **I-50** and **II-70** still showed large differences in water stability as shown in Table 3. The films **I-50** and **II-70** displayed similar initial mechanical properties with a tensile strength, elongation at break, and Young's modulus in the ranges 60−65 MPa, 7−9%, and 1.28−1.80 GPa, respectively. After soaking in the boiling water for 23 h, the **II-70** film became somewhat brittle and was broken after being lightly bent at 25 °C in water. The results indicated the poor stability of **II-70** toward water. However, polyimide **I-50** displayed excellent water stability as the initial tensile strength only decreased to 56 MPa after soaking in water for 196 h. The enhanced stability of **I-50** toward water could be resulted from its unique naphthalimide structure. Copolymer **I-*x*** had two carbonyl groups in the naphthalimide moieties whereas copolymer **II-*x*** had four carbonyl groups. Therefore, copolymer **I-*x*** should possess decreased positive charge density in carbonyl groups compared with that of copolymer **II-*x*** because of the electron withdrawing characteristics of carbonyl groups. In addition, the 1,8-naphthalimide moiety is smaller and less rigid than the 1,4,5,8-naphthalimide moiety, which may also contribute to the excellent

Table 2. Water Uptake, Size Chang, IEC, and Proton Conductivity of Copolymer Membranes

membrane	thickness (μm)	IEC[a] (mequiv/g) calculated	measured	water uptake (% W/W) in water	70% RH	σ (S/cm) at 80 °C	size change Δt	Δl
I-40	30	1.30	1.28	48	28	0.075	0.15	0.02
I-50	34	1.67	1.65	61	35	0.260	0.19	0.03
I-70	41	2.47	2.41	118	53	0.687	0.45	0.07
I-90	35	3.36	3.27	259	108	-	0.80	0.19
II-50	25	1.13	1.11	20	10	0.025	0.12	0.01
II-70	35	1.92	1.89	31	18	0.075	0.15	0.02

[a] Calculated, IEC calculated from DS; measured, IEC measured with titration.



II-70

I-50

Figure 6. Chain structure of copolymers **I-50** and **II-70**.

Table 3. Mechanical Properties Soaking in Water at 100 °C for Copolymer

membrane	IEC (mmol·g^{-1})	soaking time (h)	maximum stress (MPa)	elongation at break (%)	Young's modulus (GPa)
I-50	1.67	0	60	9	1.28
		48	57	7	1.27
		96	57	6	1.29
		196	56	7	1.27
II-50	1.13	0	65	7	1.80
		23	-	-	-

water stability of **I-50** because the flexible chain structure is favorable to improve the stability of polymers toward water.[13]

Oxidative Stability. Membrane stability toward oxidation was examined by observing the dissolving behavior in Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at 25 °C, which is one of the standard tests for oxidative stability. Copolymer **II-70** becomes brittle in the solution after 50 h. The membrane had completely dissolved after 93 h. Copolymer **I-50** showed better oxidation stability and it took 263 h until the membrane complete disappearance in the solution. These results suggested that the new copolyimide membranes displayed excellent stability toward oxidation and much better than that of the polyimide reported in the literature.[21] For example, under identical test conditions, polyimide containing trifluoromethyl groups dissolved in the solution within 9 h.[22] Again, the hydrophobic trifluoromethyl groups that are localized on the ortho-position of the imido bond in copolymers may play an important role in the observed oxidation stability enhancement. Coplymer **I-50** showed much better stability than that of copolymer **II-70**, which is probably due to their difference in structure of naphthalimide moieties and membrane morphology.

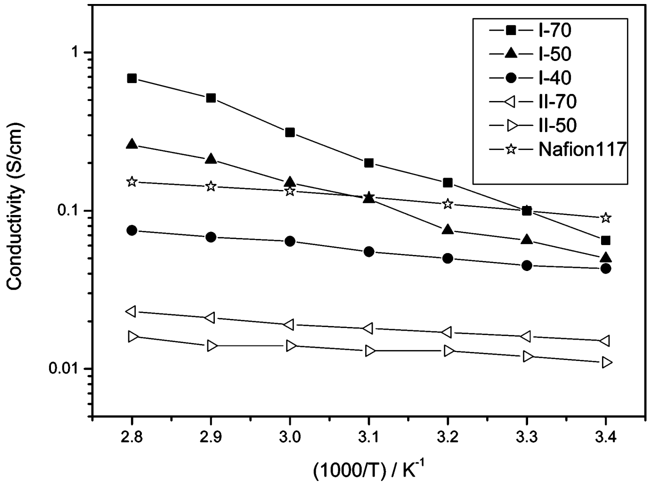


Figure 7. Temperature dependence of the proton conductivities of Nafion 117 and SPI.

Proton Conductivity. The proton conductivities of copolymers membrane were measured after the membranes were initially hydrated by immersion in deionized water for 24 h at room temperature. Proton conductivity can be different with the difference of experimental approaches and instruments. For comparison, Nafion 117 was measured under the same conditions and resulted in a value of 0.09 S/cm at 25 °C, which is similar to that reported by Okamoto et al.[13b] Copolymer **I-40**, **-50**, and **-70** with IEC 1.30−2.47 showed proton conductivities in the range 4.3×10^{-2} to 6.2×10^{-2} S/cm at 25 °C. Their proton conductivities increased both with IEC and with temperature. The temperature dependence of the proton conductivities of copolymer membranes **I-*x***, **II-*x***, and Nafion 117 measured in liquid water are summarized in Figure 7. When considering both proton conductivity and water stability, copolymer **I-50** with IEC 1.67 has the best combination of properties for application in PEM for FC. Its proton conductivity reaches 2.6×10^{-1} S/cm, at 80 °C), which is higher than that

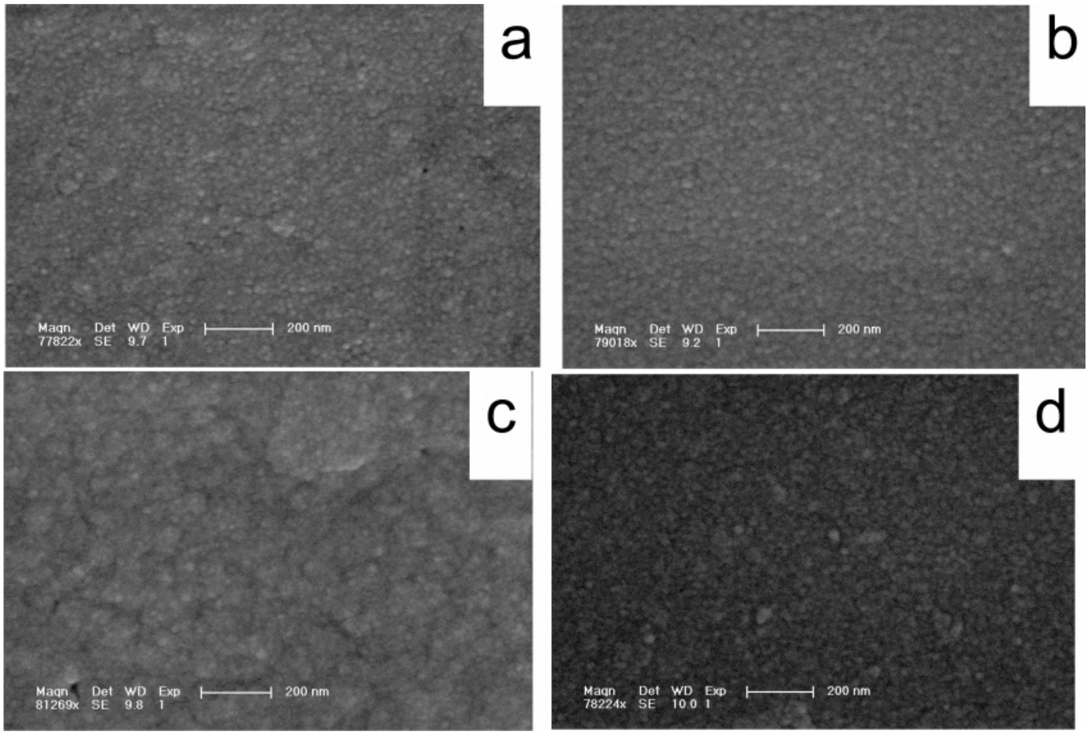


Figure 8. SEM micrographs of polymer membranes: (a) **I-50**; (b) **I-70**; (c) **I-90**; (d) **II-70**.

of Nafion 117 (1.5 × 10^{-1} S/cm, at 80 °C). Copolymer **I-50** and **I-70** membrane also showed sharper increase in the proton conductivity with the temperature than that of Nafion 117. Among the two types of copolymer **I** and **II**, copolymer **I** showed higher conductivities with comparably similar IEC values. For example, the proton conductivity of I-50 with IEC 1.65 is about 3.5 times higher than that of II-70 with IEC 1.89 at 80 °C. These proton conducting properties seem to reflect their water uptake behavior.

SEM. Figure 8 shows the morphology of sulfonated copolymer. The lighter regions represent localized ionic domains; the dark regions represent hydrophobic domains. The enhancement in the size of pores with the degree of sulfonation of the membranes can be observed clearly. The micrographs provide direct evidence of biphasic morphology for the polymers. The ionic aggregates are visibly connected to yield a continuous ionic network. The density of the ionic pathways increases with ionic content as evidenced from Figure 8a−d and explains why the ionic conductivity rises to relatively high values.

Conclusion

The primarily sulfonated aromatic dichloride monomer and hydrophobic dichloride monomers containing trifluoromethyl-substituted 1,8-naphthalimide or 1,4,5,8-naphthalimide moieties were synthesized and used as comonomers to generate oxidative and water stable copolymers for proton exchange membranes. The synthesized copolymers with the $-SO_3H$ group in the side chain of polymers possessed high molecular weights, revealed by their high viscosity and the formation of tough and flexible membranes. The copolymer membranes exhibited excellent water and oxidative stabilities due to the introduction of the hydrophobic CF_3 groups on the ortho-position of imido groups, which could protect the polymer main chains from being attacked by water molecules containing highly oxidizing radical species. The sulfonated copolyimides containing 1,8-naphthalimide moiety (**I-*x***) exhibited better hydrolytic and oxidative stabilies, and higher proton conductivity than those containing 1,4,5,8-naphthalimide moiety with a similar IEC values. When considering both proton conductivity and water stability, copolymer **I-50** with IEC 1.67 has the best combination of properties for application in PEM for FC. Its proton conductivity reaches 2.6 × 10^{-1} S/cm, at 80 °C), which is higher than that of Nafion 117 (1.5 × 10^{-1} S/cm, at 80 °C). Consequently, these materials proved to be promising as proton exchange membranes.

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