

Research Article

Synthesis of Highly Sulfonated Poly(arylene ether) Containing Multiphenyl for Proton Exchange Membrane Materials

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A series of sterically hindered, sulfonated, poly(arylene ether) polymers were synthesized by nucleophilic polycondensation reaction using 4,4''''-difluoro-3,3''''-bistrifluoromethyl-2'',3'',5'',6''-tetraphenyl-[1,1',4',1'';4'',1''',4''',1'''']-pentaphenyl and 4,4'-biphenol and were prepared through postpolymerization sulfonation. The chemical structures were confirmed by ¹H NMR. Subsequent to sulfonation, solvent-casting membranes were provided ion exchange capacity (IEC) values ranging from 0.39 to 2.90 mmol/g. Proton conductivities of membranes ranged from 143 to 228 mS/cm at 80°C under fully humidified conditions which were higher than that of Nafion 117. The membrane also exhibited considerably dimension stability, oxidative stability, and hydrolytic stability. The microphase structure was investigated by transmission electron microscopy (TEM) and the ionic aggregation of sulfonic acid groups exhibited spherical ionic clusters with well-developed phase separated morphology. The results indicated that the membranes are promising candidates for application as proton exchange membranes. This investigation demonstrates introducing multiphenylated moieties to create a high free volume polymer that provides dimensionally stable and high proton conductivity membranes.

1. Introduction

In the past few decades, proton exchange membrane fuel cells (PEMFC) as an alternative energy have been widely investigated. The critical component of PEMFC is the proton exchange membrane (PEM). The PEM required high proton conductivity, chemical and thermal stability, and high dimensional stability when operating at high humidity environments, and low permeability to separate the reactant gases [1]. The most widely used PEM, Nafion, was kind of perfluorinated sulfonic acid (PFSA) ionomer membrane and that was first developed by Dupont Inc. Nafion has served as a benchmark of PEM because of its good chemical and electrochemical stability as well as excellent proton conductivity. However, Nafion still has some drawbacks such as high methanol crossover, poor mechanical, chemical stability, and low conductivity at elevated temperatures (>80°C). Moreover, the worst of all disadvantages of Nafion is high cost [2]. Therefore, seeking for alternatives to Nafion is a major topic.

In recent years, sulfonated aromatic hydrocarbon polymer electrolytes are widely studied, such as poly(arylene ether ketone)s, poly(arylene ether ketone)s, poly(arylene ether)s, and polyimides [3–5], which are promising candidates to Nafion because of their relatively low cost, easy tuning of polymer structure, processability, and good mechanical, thermal, and chemical stability [6–9].

In general, sulfonated aromatic hydrocarbon polymers reach comparable proton conductivity with PFSA usually under high ion exchange capacity (IEC) and water uptake because of their lower acidity and degree of phase separation with smaller isolated hydrophilic domains [10]. However, higher IEC values of hydrocarbon PEMs consequently lead to excessive swelling and deteriorate mechanical properties. The strategy for designing PEMs able to maintain water stability without excessive swelling is to induce phase separation of the hydrophilic and hydrophobic regions so as to increase hydrophobic interactions of the polymer chains by locally and densely sulfonated segments on the main chain and to

introduce free volume into the polymer for water to occupy [11, 12].

To overcome the problems of sulfonated aromatic hydrocarbon polymers, many studies have been reported. For example, Chen et al. developed a multiphenylated hydrophilic domain and linear hydrophobic chain copolymer. These designed ionomers gave distinct phase separation and facilitate forming proton conductive channels and also exhibited highly thermal and oxidative stability [13]. Wang et al. reported new poly(ether sulfone) based on fluorene with two pendant phenyl substituents that provided clustered pendant sulfonic acid groups. The sulfonated polymers demonstrated high oxidative stability, good mechanical properties, and a clear phase separation of ionic domains size of 3 to 7 nm [14]. Nakabayashi et al. synthesized highly sulfonated multiblock poly(ether sulfone)s followed by postsulfonation with concentrated sulfuric acid. The membranes with higher IEC values of 2.75–2.79 mmol/g exhibited similar proton conductivity with Nafion 117 in a range of 50–95% RH; AFM image also supported the formation of well-connected proton conductive channels to implement high proton conductivity [15]. Pang et al. reported novel poly(arylene ether)s attached high density sulfonated hexaphenyl pendent group in order to control positions and the degree of sulfonation. These resulting polymers exhibited lower water uptake and good dimensional stability. The membranes showed high proton conductivities and low methanol permeability. Pang et al. also presented novel fluorinated poly(arylene ether ketone)s containing hexa sulfophenyl as a hydrophilic pendent group, which enhanced the difference in polarity of hydrophilic and hydrophobic segments. The membranes demonstrated lower dimensional change value and high proton conductivity attributed to well-defined phase separation [16, 17]. Recently, Jo et al. synthesized poly(p-phenylene) block copolymers introducing trifluoromethyl and multiphenylated pendant groups to improve the hydrophobicity and enhance densely and locally sulfonated domains. The membranes exhibited comparable or superior performance to Nafion 212 in fuel cell testing [18].

In our previous work, we introduced multiphenylated structure into the polymer main chain which provides good mechanically and dimensionally stable PEMs. The multiphenylated structure on the backbone can increase the free volume. As a result, multiphenylated structure allowed for significant water sorption while maintaining good mechanical strength [19]. Herein, we synthesized a novel alternating poly(arylene ether) comprising commercialized 4,4'-biphenol monomer and sterically hindered multiphenylated monomer. The sulfonated poly(arylene ether)s were easily prepared by treatment with chlorosulfonic acid. Thermal stability, water uptake, mechanical strength, dimensional stability, proton conductivity, and morphology were investigated.

2. Experimental

2.1. Materials. All reactions were performed under prepurified nitrogen. All reagents and solvents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Lancaster,

Fluoko, or Fisher. Toluene was dried over Na with benzophenone as an indicator and freshly distilled under nitrogen atmosphere and deoxygenated by purging with nitrogen for 20 min prior to use. 4,4'-Biphenol and Pd(PPh₃)₄ were purchased from Aldrich Chemical Co. and used without further purification. The polymerization was conducted using standard vacuum-line techniques.

2.2. 4,4''''-Difluoro-3,3''''-bistrifluoromethyl-2'',3'',5'',6''-tetraphenyl-[1,1';4',1'';4'',1''' ;4''',1'''']-pentaphenyl (M1). 4,4''''-Dibromo-2',3'-5'-6'-tetraphenyl-[1,1';4',1'']-terphenyl (5 g, 7.22 mmol), 4-fluoro-3-trifluoromethyl phenylboronic acid (4.5 g, 21 mmol), Pd(PPh₃)₄ (0.05 g, 0.432 mmol), K₂CO₃ (4 g, 28.9 mmol), H₂O (13 mL), and toluene (100 mL) were placed in a flame-dried two-neck flask and refluxed for 48 h under N₂ atmosphere. After cooling, the mixture was poured into water and extracted twice with toluene and NaCl (aq). The organic layer was washed, dried over MgSO₄, and concentrated to give a yellow solid. The crude monomer was purified by recrystallization to obtain pure M1 in 92% yield (¹H NMR (500 MHz, CDCl₃, δ = ppm): 6.79–7.70 (m, 34H, ArH)).

2.3. General Procedure for Polycondensation. The condensation reaction was carried out in a 50 mL, three-neck round-bottom flask equipped with a stir bar and a Dean-Stark apparatus fitted with a condenser and under nitrogen atmosphere. The flask was charged with M1 (2 g, 2.33 mmol), 4,4'-biphenol monomer (0.433 g, 2.33 mmol), potassium carbonate (0.8 g, 5.78 mmol), DMAc (20 mL), and toluene (15 mL). The solution mixture was stirred at 130–150°C for several hours and during the course of the reaction, a slow flow of nitrogen was passed through the reaction vessel to remove water steam produced by the reaction. The reaction solution was stirred under reflux for 24 h after complete removal of the water. The crude mixture was poured into stirred methanol (250 mL) with stirring to precipitate a fibrous polymer, P1, which was collected by filtration, washed, and vacuum-dried for 24 h at 120°C.

2.4. Sulfonation. To a solution of P1 (0.4 g) in dichloromethane (30 mL) at room temperature, 0.125 M chlorosulfonic acid solution in dichloromethane was added dropwise. The reaction mixture was stirred for 24 h and then poured into water. The sulfonated polymer precipitate was filtered, washed thoroughly with deionized water several times until pH neutral, and dried in vacuum at room temperature overnight to provide the sulfonated polymer, SP1. P1 was sulfonated to different extents according to the above procedure by adding 0.3 mL, 0.5 mL, and 0.7 mL of chlorosulfonic acid, respectively. SP1 polymers were readily soluble in polar aprotic solvents such as DMF, DMAc, DMSO, and NMP.

2.5. Membrane Preparation. The salt form of membranes was dissolved in DMSO (5–7 wt%). Then, the solution was filtered and cast onto a glass plate and then the membranes were obtained after the solvent evaporation process. The dry membranes were soaked in 1.0 M HCl solution for 24 h to

protonate the sulfonic acid groups and washed with deionized water to a neutral pH. The membranes were dried at 80°C for 12 h and then under reduced pressure at 80°C for an additional 12 h.

2.6. Measurements. ^1H NMR spectroscopic measurements were carried out on a 500 MHz Varian UNITY INOVA-500 spectrometer using CDCl_3 or $\text{DMSO}-d_6$ as the solvent. The gel permeation chromatographic (GPC) analysis was carried out with Viscotek 270 max with a refractive index detector (Viscotek model 270, THF used as the eluent, flow rate of 1 mL/min). For calibration, polystyrene standard (molecular weight between 6770 and 281000 Da) was used. Thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA) carried out on a Perkin Elmer Pyris 1 instrument with a heating rate of 10°C/min from 100°C to 600°C under N_2 atmosphere. Before the analysis, membranes were dried in the TGA furnace at 150°C under N_2 for 20 min to remove water.

The ion exchange capacity (IEC) of the membranes was determined using titration method. The membranes were weighed and soaked in 1.0 M NaCl for 24 h and the solutions titrated using 0.01 M NaOH to a phenolphthalein end point. IEC (mmol/g) was calculated as in the following equation: $\text{IEC (mmol/g)} = (V_{\text{NaOH}} \times M_{\text{NaOH}}) / W_{\text{dry}}$, where V_{NaOH} and M_{NaOH} are the volume and concentration of the NaOH solution, respectively, and W_{dry} is the weight of the dry membrane.

The water uptake, the hydration number, λ , and the swelling ratios, ΔL and ΔT , were calculated as in the following equations, respectively:

$$\text{water uptake (\%)}: [(W_{\text{dry}} - W_{\text{wet}}) / W_{\text{dry}}] \times 100\%,$$

$$\text{hydration number: } \lambda = [1000 \times (W_{\text{dry}} - W_{\text{wet}})] / (\text{IEC} \times W_{\text{dry}} \times 18),$$

$$\text{in-plane swelling ratio (\%)}: \Delta L = (L_{\text{wet}} - L_{\text{dry}}) / L_{\text{dry}} \times 100\%,$$

$$\text{through-plane swelling ratio (\%)}: \Delta T = (T_{\text{wet}} - T_{\text{dry}}) / T_{\text{dry}} \times 100\%,$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes. L_{wet} and L_{dry} are the lengths of the wet and dry membranes, and T_{wet} and T_{dry} are the thickness of the wet and dry membranes, respectively.

Hydrolytic stability of the membranes was evaluated by immersing the membranes in water at 140°C for 24 h. Oxidative stability was evaluated by immersion into Fenton's reagent (3% H_2O_2 aq. containing 2 ppm FeSO_4) at 80°C for 1 h.

In-plane proton conductivity was performed by AC impedance spectroscopy with an Agilent 4294A Precision Impedance Analyzer according to a procedure described in a previously published paper [17]. Proton conductivity (σ) was calculated as the following equation: $\sigma = L / (RA)$, where L (cm) is the distance between electrodes, R (Ω) is the membrane resistance which was measured over the frequency from 1 Hz to 1 MHz, and A (cm^2) is the cross-sectional area of the membrane. The membranes (10 mm \times 5 mm)

were placed between two of platinum electrodes which were set in a Teflon cell. Conductivity measurements under fully hydrated conditions were carried out in a FIRSTEK BTH80/20 environmental chamber with the cell immersed in water.

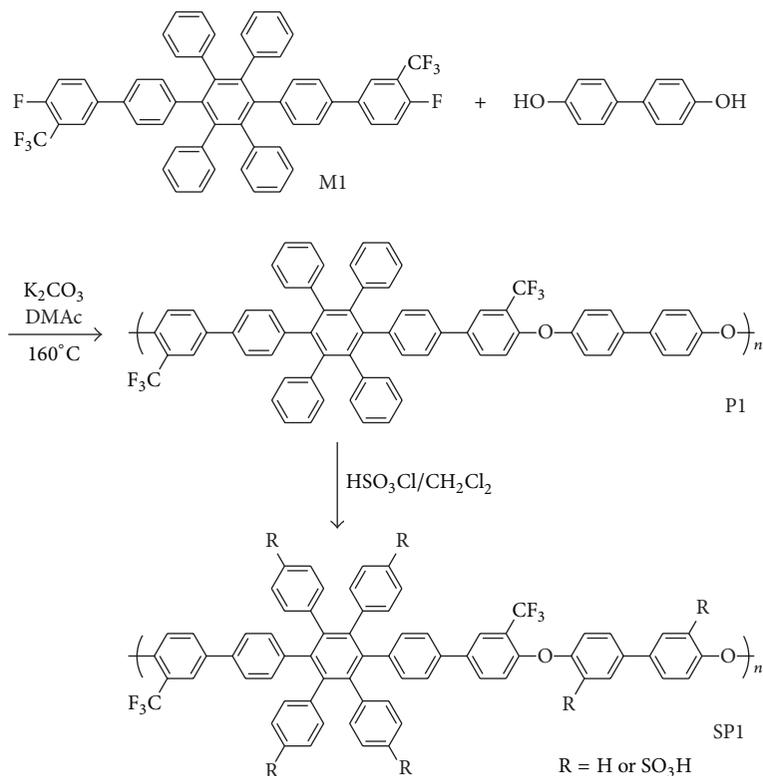
TEM images were performed with a JEOL, JEM-2100 (HR) TEM using an accelerating voltage of 200 kV. For study, the membranes were stained with Ag^{3+} ion by immersion overnight in 1M AgNO_3 . After that the membranes were washed thoroughly with deionized water and dried at room temperature for 24 h. The stained membranes were enclosure of epoxy resin and ultramicrotomed under cryogenic condition with a thickness of 70 nm.

3. Results and Discussion

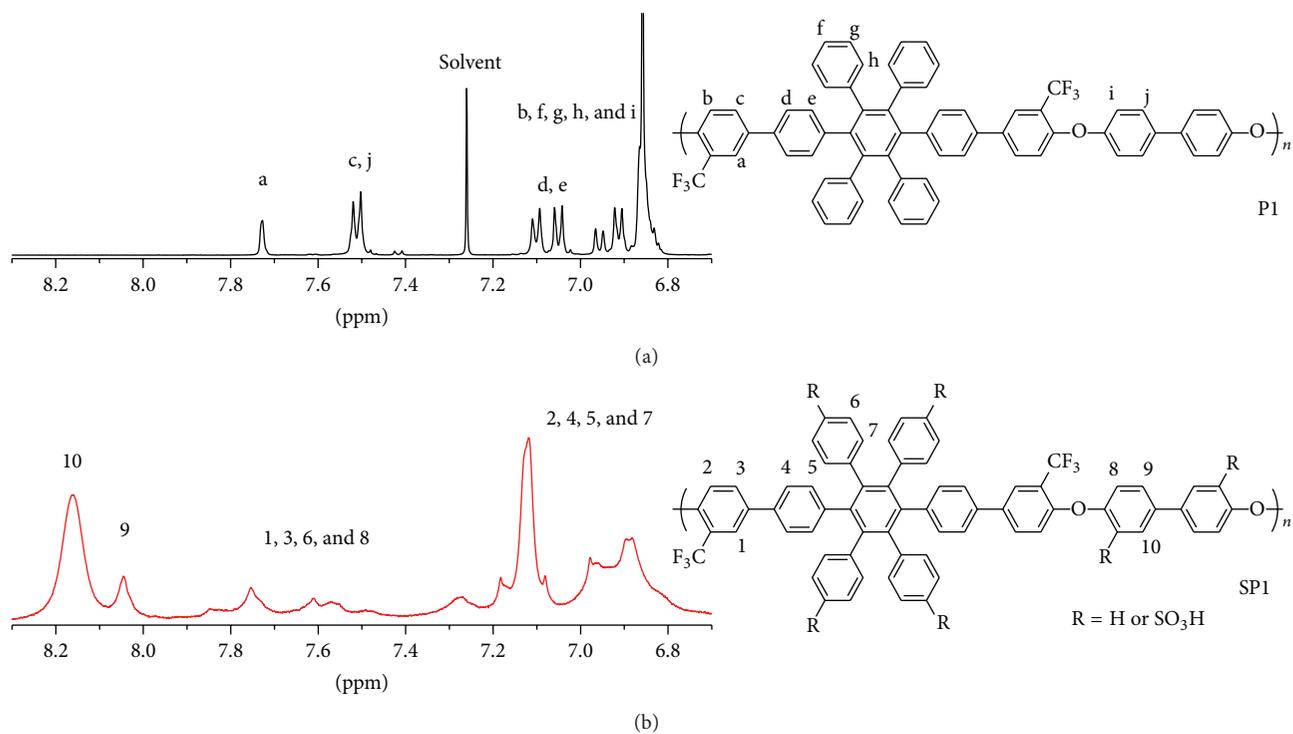
3.1. Synthesis and Characterization of Polymers. Synthetic route of poly(arylene ether) (P1) is shown in Scheme 1. The synthesis of M1 has been reported in previously published. It was synthesized by Suzuki coupling reaction of dibromo monomer with boronic acid and verified structure by ^1H NMR spectroscopy. The polycondensation was synthesized by following previously published procedures [20]. The polymer was prepared by a one-pot nucleophilic polymerization of M1 with 4,4'-biphenol compound which was commercially available and obtained in 92% yield. Obtained polymer was readily soluble in the common solvent such as DMAc, DMSO, NMP, THF, and chloroform. Gel permeation chromatography (GPC) was used to measure the weight-average molecular weights (M_w) of the polymer. M_w of P1 was found to be 193 kDa, with a polydispersity index (PDI) of 3.1. The introduction of trifluoromethyl substitution in phenyl groups enables easier synthesis of high molar mass poly(arylene ether)s by activating the leaving group towards nucleophilic displacement reaction during polymerization [21, 22].

The ^1H NMR spectrum of P1 is shown in Figure 1(a), which consists of multiplet peaks at 6.8 to 7.7 ppm assigned to aromatic protons. The multiplet peaks between 6.8 to 6.9 ppm are assigned to the proton of pendant benzene ring and labeled f, g, and h. The doublet peaks between 6.9 and 7.5 ppm are assigned to the protons of p-pentaphenyl (labeled b, c, d, e, i, and j). The singlet peak at 7.7 ppm is assigned to the proton next to the trifluoromethyl group and labeled a. P1 was sulfonated using chlorosulfonic acid to various extents to yield SPI-X, where X indicates the value of IEC and the structure was confirmed by ^1H NMR, as shown in Figure 1(b). Generally, the substituent of sulfonic acid groups by chlorosulfonic acid preferentially occurs on electron-rich aromatic rings. The signals at 6.7–7.2 ppm broadened after sulfonation (labeled 2, 4, 5, and 7) showing similar values as has been presented in previous work [23]. According to the literature, new peaks that appear at 8.05 and 8.16 are assigned to sulfonated bisphenol [20].

Thermogravimetric analysis is shown in Figure 2, which demonstrated that P1 exhibited excellent thermal stability, with a 5% weight loss occurring after 538°C. Sulfonated polymers are less thermally stable, exhibiting several distinct degradation steps. An initial weight loss before 200°C consists



SCHEME 1: Synthesis of SP1-X.

FIGURE 1: ^1H NMR spectrum of polymer P1 (a) and after sulfonation SP1-X (b).

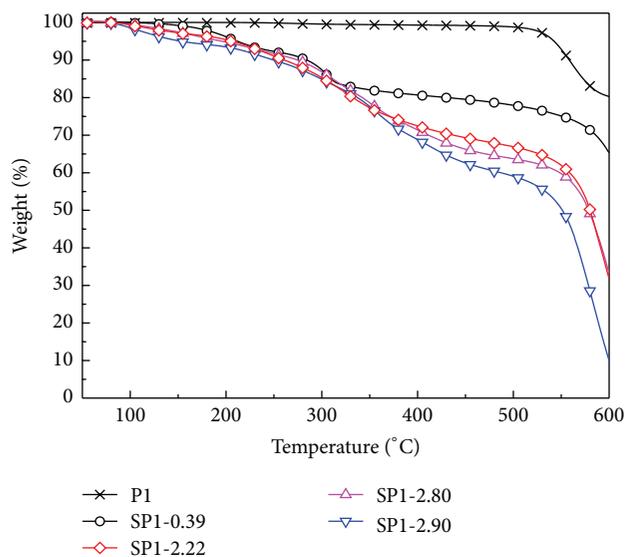


FIGURE 2: Thermogravimetric graph of P1 and SPI-X.

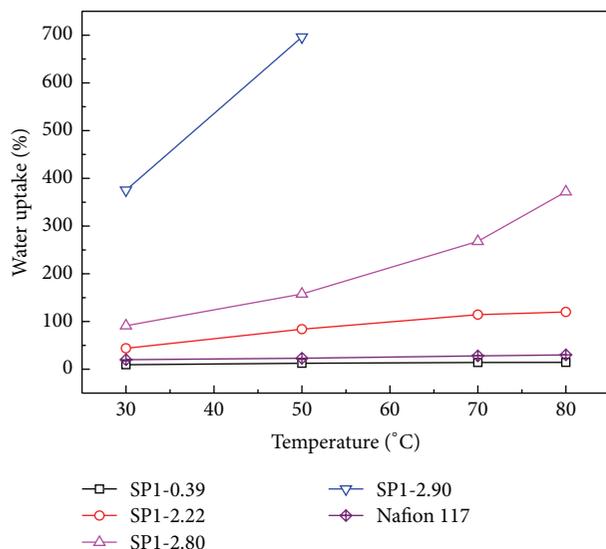


FIGURE 3: Water uptake as a function of temperature for SPI-X membranes.

of loss of hydrated water which relate to sulfonic acid groups number (IEC value); SPI-0.39 with the lowest IEC shows a small amount of weight loss. In contrast, SPI-2.90 shows over 5% weight loss of hydrated water because of the highest IEC. The degradation step observed at around 220–320°C is attributed to the loss of sulfonic acid groups. The final steps starting at about 500°C correspond to the remainder of the polymer main chain.

3.2. Water Uptake, Swelling Ratio, Oxidative Stability, and Hydrolytic Stability. Water uptake is an important factor that promotes proton conduction and determines lots of the mechanical durability, especially during dry-wet cycles as a PEM. The resulting water uptake and λ are shown in

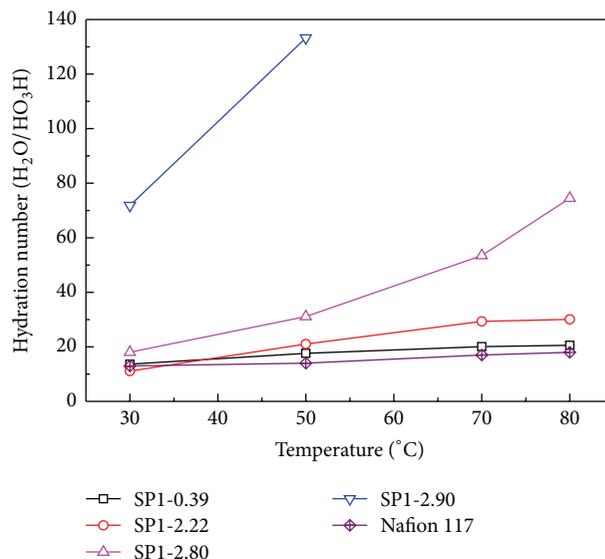


FIGURE 4: Hydration number as a function of temperature for SPI-X membranes.

Figures 3 and 4, respectively. As expected, the water uptake of the membranes increased with an increase in temperature and higher IEC membranes absorbed more water due to the increased hydrophilicity. All membranes in the measured temperature range from 30 to 80°C; SPI-0.39 showed lowest water uptake and without an obvious increase trend even temperatures rising, SPI-2.22 demonstrated gentle rising trends from 43 to 120% and SPI-2.80 displayed a large value of water uptake at 30°C and increased dramatically up to 372% at 80°C. SPI-2.90 showed the highest IEC value but excessive substitution of sulfonic acid groups causes membrane soluble in water when the temperature is higher than 50°C. The above water uptake data were very similar to our previous report; the multiphenylated backbone results in a high polymer free volume, which allowed for water sorption and was able to maintain acceptable mechanical property of the membranes [5, 19].

According to previous literature, λ (hydration number, H_2O/SO_3H) value can estimate the membrane whether applied to the fuel cell. Larger values of hydration number mean that each sulfonate is surrounded by a greater number of water molecules. The different structure would lead to a different molecular chain stacked circumstance. Therefore, the structure conformation would determine how many water molecules distributed into the membrane. The hydration number of SPI exhibited similar tendency to water uptake that increased with elevated temperature, with the exception that SPI-0.39 remained nearly constant. In comparison with Nafion 117, all of SPI membranes showed a higher hydration number at 80°C, as listed in Table 1.

The swelling of SPI membranes was listed in Table 1. Due to a lower degree of sulfonation, the length changing of SPI-0.39 was less than 5% at high temperature. SPI-2.22 exhibited good dimensional stability, increasing in length change by only 27.5% at 80°C, which is similar to that of Nafion 117 [15] or other sulfonated copoly(ether sulfone)s

TABLE 1: IEC, water sorption, and dimensional stability of SPI membranes.

Sample	IEC ^a (mmol/g)	Degree of sulfonation (%) ^b	Water uptake ^c	λ^c	ΔL (%) ^d	ΔT (%) ^d
SPI-0.39	0.39	10	14	20	5	1
SPI-2.22	2.22	56	120	30	27.5	8
SPI-2.80	2.80	70	372	74	105	28
SPI-2.90	2.90	73	— ^e	—	—	—
Nafion 117	0.91	—	29	18	18	20

^aIEC determined by acid-base titration.

^bCalculated assuming six sulfonic acid groups per monomer unit. The theoretical highest IEC value of SPI-X is 4.38 mmol/g (degree of sulfonation: 100%).

^c80°C in water.

^dChange in film length (ΔL) and thickness (ΔT) 80°C in water.

^eDissolved in water.

TABLE 2: Proton conductivity and stability of SPI membranes.

Sample	Proton conductivity (30°C) (mS/cm)		Proton conductivity (95% RH) (mS/cm)		Oxidative stability ^a residual weight (%)	Hydrolytic stability ^b residual weight (%)
	40% RH	95% RH	50°C	80°C		
SPI-0.39	— ^c	— ^c	— ^c	— ^c	100	99
SPI-2.22	1.91	47.7	84.8	143	91	82
SPI-2.80	6.41	83.2	151	222	85	73
SPI-2.90	7.05	71	135	228	— ^d	— ^d
Nafion 117	5	64	60	106	—	—

^aAfter heating in Fenton reagent at 80°C for 1 h.

^bAfter heating in water at 140°C for 24 h.

^cNo data.

^dDissolved in reagent.

[16]. SPI-2.80 showed much larger dimensional length change (105% at 80°C) caused by its larger water sorption ability. Despite the larger water sorption, the change in thickness of SPI is relatively low (<28%), which is attributed to the high free volume and rigidity of tetraphenylated structure.

The oxidative stability of the SPI membranes was evaluated in Fenton's reagent at 80°C for 1 h. SPI-0.39 showed good oxidative and hydrolytic stability (>99%), because of its very low IEC value which reduced the positions where the free radical can be attacked directly. SPI-2.22 is immersed into reagent after 1 hr; it exhibited acceptable oxidative and hydrolytic stability which still maintain 91% and 82% residual weight, respectively. However, oxidative and hydrolytic residual weight of higher IEC membrane, SPI-2.80, decreased to 85% and 73%, respectively. SPI-2.90 completely dissolved in Fenton's reagent and water. The oxidative stability of the membranes decreased with increasing degree of sulfonation.

3.3. Proton Conductivity. The proton conductivity of Nafion 117 was also measured under the same conditions, as a reference. The degree of sulfonated PI-0.39 was too low to be measurement of proton conductivity. The proton conductivity of SPI-X membranes showed relative humidity dependence at 30°C ranging from 40 to 80 mS/cm, as shown in Figure 5. Compared to Nafion 117, SPI-2.80 exhibited a comparable conductivity from 40% to 80% RH and is able to exceed when relative humidity over 80% (83 mS/cm at 30°C, 95% RH). The proton conductivity of SPI-X membranes increased with increasing temperature from 30°C to 80°C

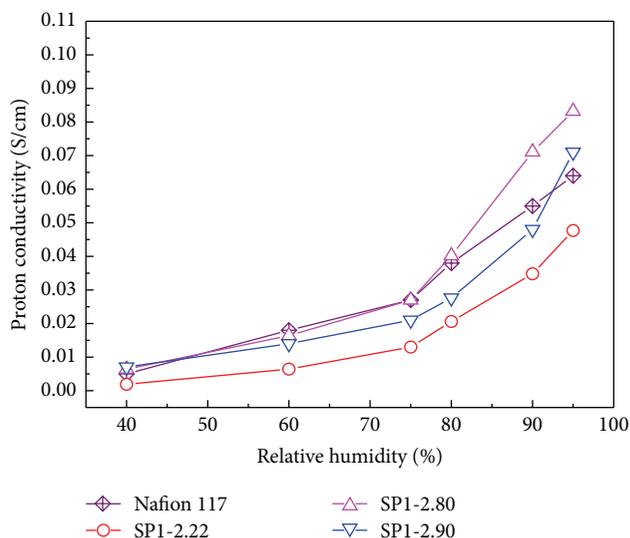


FIGURE 5: Proton conductivity of SPI-X membranes as a function of RH at 30°C.

under fully hydrated states (95% RH) as shown in Figure 6 and listed in Table 2. SPI-2.22, SPI-2.80, and PI-2.90 exhibited the proton conductivities of 143, 222, and 228 mS/cm at 80°C under fully hydrated states, respectively, higher than that of Nafion 117. Compared to other hydrocarbon-based membranes, the proton conductivity of SPI-X demonstrated beneficial results; for example, a poly(aryl ether) comprising

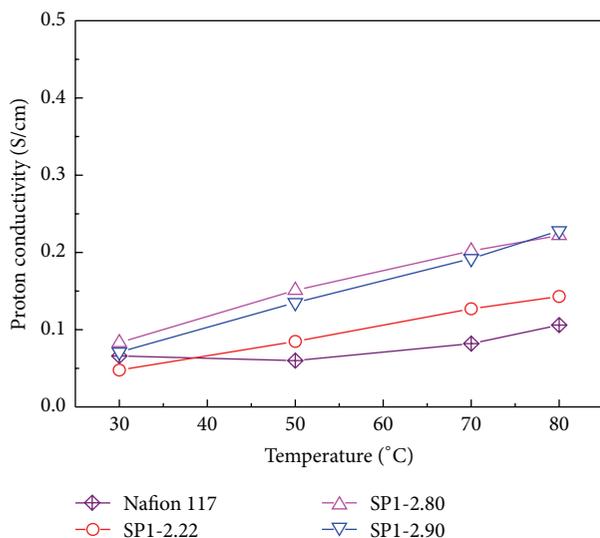


FIGURE 6: Proton conductivity of SPI-X membranes as a function of temperature under 95% RH.

of fluorine and bisphenol A units showed a conductivity of 100 mS/cm at 80 °C [24]. As mentioned above, proton conductivities of SPI-X satisfy the requirement of proton exchange membrane for fuel cell.

3.4. Morphology of the Membranes. The morphology of the sulfonated polymers SPI-2.22, SPI-2.80, and SPI-2.90 was investigated by transmission electron microscopy (TEM); the images are shown in Figure 7. The dark regions represent localized hydrophilic (sulfonate groups) ionic domains and the brighter regions refer to the domains formed by hydrophobic polymer backbones. All of the membranes exhibited spherical ionic clusters with relatively uniform size. But the polymer at lower sulfonation degree, as SPI-2.22, only formed small part of particle aggregation and ionic clusters. In contrast, the polymers with higher sulfonation degree, as SPI-2.80 and SPI-2.90, show well-developed hydrophilic/hydrophobic phase separation. SPI-2.22, SPI-2.80, and SPI-2.90 relative diameter of ionic cluster sizes is 3–7, 6–9, and 10–15 nm, respectively. Compared to poly(p-phenylene) containing multiphenylated pendant (IEC = 2.58 mmol/g) (5–10 nm diameter) [18] and Nafion 117 (4–5 nm diameter) [25], these sulfonated membranes exhibit similar or larger ionic cluster sizes.

4. Conclusions

In summary, we introduced a new series of sulfonated poly(arylene ether)s as proton conducting polymer electrolyte membranes. The polymer (P1) was synthesized by nucleophilic polycondensation and sulfonated polymers (SPI-X) were obtained through postsulfonation by using chlorosulfonic acid. ¹H NMR spectroscopy confirmed the structures of monomer and polymer. SPI-X exhibited good dimensional stability under high water uptake. SPI-2.22 and SPI-2.80 showed acceptable oxidative and hydrolytic stability.

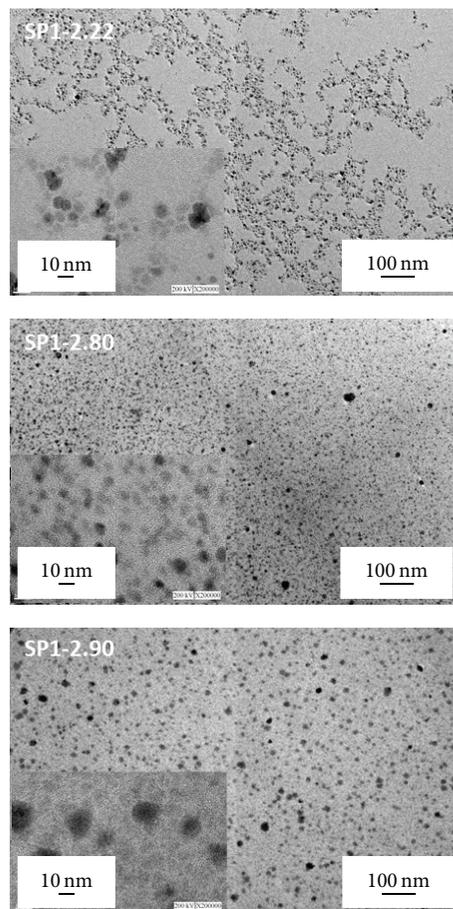


FIGURE 7: TEM image of SPI-2.22, SP-2.80, and SPI-2.90 membranes.

The proton conductivity of membranes (SPI-2.22, SPI-2.80, and SPI-2.90) reached 143, 222 and 228 mS/cm at 80 °C under fully hydrated conditions, which was much higher than that of Nafion 117. TEM images analysis of sulfonated membranes revealed spherical ionic cluster and a well-dispersed phase separation, with slightly interconnected ionic clusters (3–15 nm). The combination of good thermal stability, high proton conductivity, and well-dispersed phase separation makes SPI-X conspicuous as PEMs for fuel cell applications.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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