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Synthesis and characterization of sulfonated fluorene-containing poly(arylene ether ketone) for high temperature proton exchange membrane

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Abstract

A novel fluorene-containing poly(arylene ether ketone) were synthesized followed by sulfonating into a series of sulfonated fluorene-containing poly(arylene ether ketone)s using chlorosulfonic acid. The sulfonated polymers were thereafter cast into membranes from their solutions. The properties of the ionic exchange capacity, sulfonation degree, water-uptake, mechanical properties, thermal and oxidative stabilities as well as proton conductivities of the membranes were fully investigated. It was found that their proton conductivities increased continuously with increasing testing temperature up to 130 °C at 100% relative humidity. The membrane exhibited a higher proton conductivity and other comprehensive properties for proton exchange membrane than Nafion-117 at 130 °C under same testing conditions.

Keywords: Polyaromatics; Sulfonation; Proton conductivity

1. Introduction

Proton exchange membrane fuel cells (PEMFC)s are attracting more and more research interesting due to their potential as high efficient and clean power source for vehicular transportation and other equipments. Proton exchange membrane (PEM) is one of the key components of PEMFC. The functions of PEM are to conduct protons from anode to cathode, to separate anode and cathode, to block fuel and oxidative gas cross-over and to support the catalyst. To fulfill these functions, the PEM should possess the properties such as proper water uptake to conduct the protons, high proton conductivity at low humidity and/or elevated temperature, superior hydrolytic and oxidative stability.

Perfluorosulfonic acid PEMs, such as Dupont's Nafion membrane, are currently the main choice owing to their high proton conductivity and excellent chemical stability. However, some of the drawbacks, such as high cost, loss of conductivity at high temperature due to dehydration, and higher methanol permeability, limit their use in PEMFC [1]. The extremely high cost is a particular hurdle for the large-scale commercialization of Nafion membrane. To overcome these drawbacks, many efforts have been devoted to develop cheap alternative membrane materials for the application in PEMFC. Non-fluorinated membrane materials such as sulfonated aromatic polymers are the important varieties, which include sulfonated polyethersulfone (SPES) [2–5], sulfonated polyetheretherketone (SPEEK) [6–11], sulfonated polyetheretherketonekrtone (SPEEKK) [12] sulfonated polybenzimidazoles (SPBI) [6,13–15], sulfonated polyimide, [16,17] and so on. Most of these membranes were reported to possess high proton conductivity but poor chemical stability.

It was suggested that the short pendant chains between the main chain and the sulfonic acid group can improve the water affinity of the PEM, and can therefore increase the conductivity of the membrane [9]. The polymers with acidic groups on the

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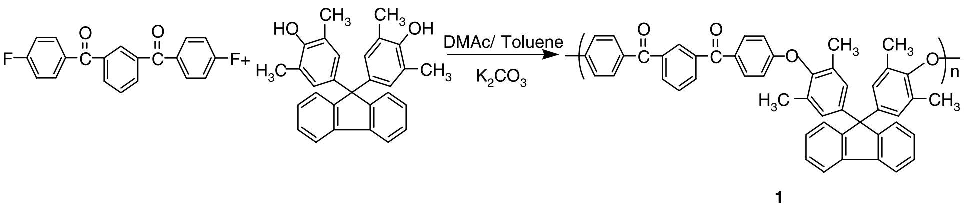


Scheme 1.

pendant chains were reported to be more stable against hydrolysis than those with acidic groups directly on the backbone of the polymers [5]. In this regard, several fluorene-containing polymers have been disclosed in literature [5,16–18].

In previous work [18,29], we have synthesized the fluorene-containing sulfonated poly(arylene ether ketone) with sulfonic acid groups on the fluorene rings by carefully reaction of poly(arylene ether ketone) with chlorosulfonic acid. However, it is difficult to avoid the sulfonation of the phenyl ring on backbone at sulfonation degree (SD, sulfonic acid groups/repeated units) higher than 0.883. In this work, we report the synthesis of a kind of novel sulfonated fluorene-containing poly(arylene ether ketone) (SFPAEK). Considering the easier sulfonation at the positions adjacent to ether bonds, we synthesized the SFPAEK using a biphenol with the positions adjacent to ether bond occupied by methyl groups.

2. Experimental

2.1. Materials

1,3-Bis(4-fluorobenzoyl)-benzene (purity = 99%) was purchased from Aldrich Chemical Corp. *N*, *N*′-Dimethylacetamide (DMAc), toluene, chloroform, dichloromethane, methanol, chlorosulfonic acid, hydrochloric acid, potassium hydroxide and anhydrous potassium carbonate were obtained from commercial sources. DMAc was dried with 4 Å molecule sieves and toluene was dried with sodium wire prior to use. Methylene chloride was dried with anhydrous $CaCl_2$ and anhydrous potassium carbonate was dried at 180 °C for 10 h prior to use. Other chemicals were used as received. 9, 9-Bis(3,5-dimethyl-4-hydroxyphenyl)fluorene was synthesized according to the procedure described in literature [19].

2.2. Instrumentation

Gel permeation chromatography (GPC) analysis was performed at 35 °C on a Waters breeze system equipped with a Waters 2414 refractive index detector, Waters styragel column and Waters 515 HPLC pump, chloroform as an elution solvent at a flow rate of 1 mL/min and polystyrene standards for calibration. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz in a Bruker NMR instrument (model DRX) and were listed in parts per million (ppm) downfield from tetramethylsilane (TMS). FTIR spectra were recorded on a Nicolet 520 Fourier transform infrared spectrometer with film samples. Thermal stability was analyzed using a Seiko TG analyzer (model SSC-5200). The measurement of mechanical properties was carried out by SANS (Shenzhen, China) electromechanical universal test machine (model CMT-4014). The conductivities of the membranes were determined by AC impedance spectroscopy using a Solatron 1260 gain phase analyzer. Inherent viscosity of polymer was determined using an Ubbelohde viscometer in chloroform at 25 °C.

2.3. Synthesis of FPAEK **1**

The synthesis of FPAEK **1** is depicted in Scheme 1. To a 25 mL three necked round bottom flask, equipped with a Dean–Stark trap, a thermometer and a nitrogen inlet. 1.218 g (3 mmol) of 9,9-bis(3,5-dimethyl-4-hydroxyphenyl)fluorene, 0.966 g (3 mmol) of 1,3-bis(4-fluorobenzoyl)-benzene, 0.621 g (4.5 mmol) of anhydrous potassium carbonate, 5 mL of DMAc and 6 mL of toluene were carefully introduced. Toluene was used as an azeotropic solvent to remove the produced water. The reaction mixture was first heated at 140–150 °C for 2 h to remove the resulting water. The temperature was then raised to 150–160 °C and kept for another 1.5 h. Upon cooling down, the resulting viscous mixture was poured slowly into 100 mL of methanol containing 1 mL of concentrated hydrochloric acid with stirring to precipitate the formed polymer. The crude polymer was filtered off and washed with water and methanol continuously, followed by dissolving in 50 mL of chloroform. The solution was filtered to remove inorganic salts. The filtrate was concentrated to about 8 mL and dropped slowly into 100 mL of methanol with stirring to precipitate the final polymer. Pure white polymer (1.936 g, 93.8% yield) in white color was obtained after dried under vacuum at 80 °C for 5 h.

The ^{1}H NMR and FTIR spectra of the synthesized FPAEK **1** are shown in Figs. 1 and 2, respectively. Inherent viscosity was determined to be 0.43 dL/g (0.5% solution in $CHCl_3$ at 25 °C). GPC measurement showed the FPAEK **1** having the molecular weights of $M_w = 74{,}100$, $M_n = 40{,}200$ relative to polystyrene standard.

2.4. Sulfonation of FPAEK **1**

The sulfonation of FPAEK **1** was carried out by the reaction of FPAEK **1** with chlorosulfonic acid as shown in Scheme 2. The SD of the SFPAEK **2** can be readily controlled by adjusting the molar ratio of the repeated units of FPAEK **1** to chlorosulfonic acid (Table 1). A typical procedure is as follows. To a 150 mL round bottom flask, 75 mL of methylene chloride and 0.344 g (0.5 mmol repeated units) of FPAEK **1**

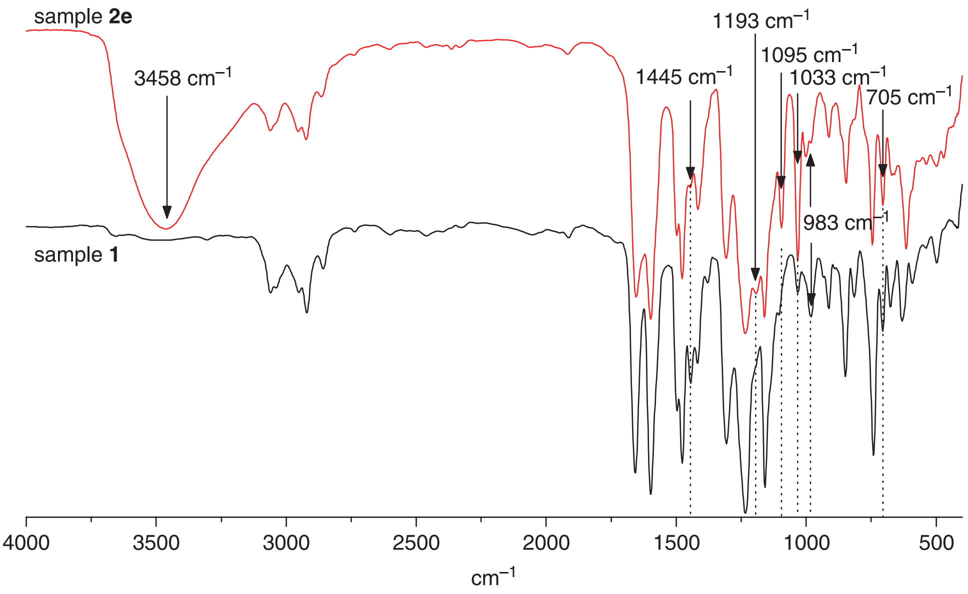
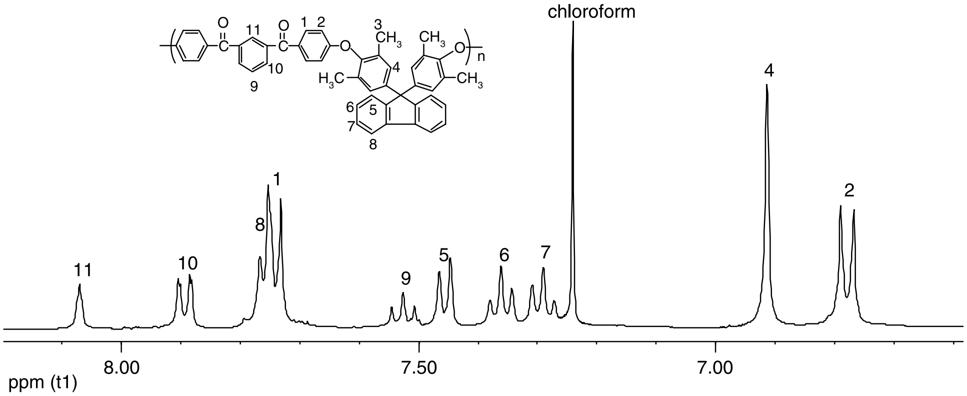
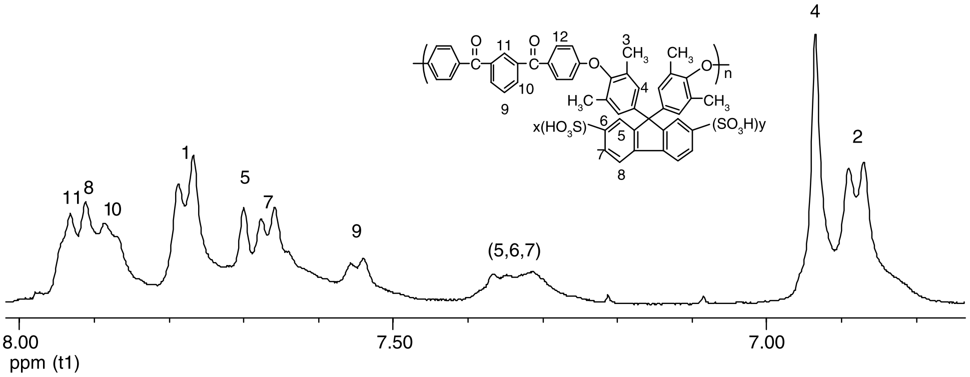


Fig. 1. ^{1}H NMR spectra of **1** and **2e**.

were introduced. The reaction mixture was stirred vigorously until the polymer was dissolved completely. Twenty milliliters of 0.1 M solution of chlorosulfonic acid (2 mmol) in methylene chloride was then added dropwise under the vigorously stirring at room temperature over about 3 h. The resulting brown product gradually precipitated out of the solution during the course. The reaction mixture was stirred vigorously for another 5 h. Finally, the solvent of the reaction was removed using a rotary evaporator at about 40 °C. The precipitates were washed with hexane for three times (3×5 mL) and dissolved in 10 mL DMAc. To the solution 10 mL of 3 wt% potassium hydroxide aqueous solution was added. After 5 h reaction, the reaction

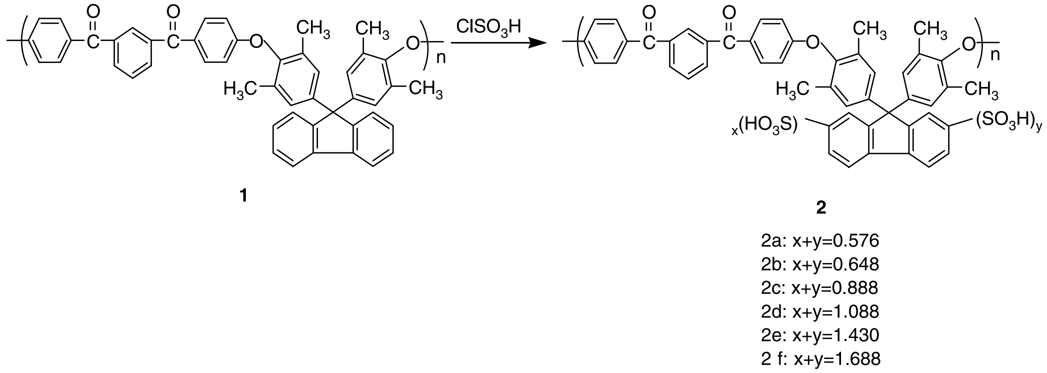


^{1}HNMR spectrum of **1** (in CDCl$_3$) (aromatic section)



^{1}HNMR spectrum of **2e** (in DMSO-d_6) (aromatic section)

Fig. 2. FTIR spectra of **1** and **2e**.



Scheme 2.

mixture was acidified with 100 mL of 5 vol% hydrochloric acid for another 5 h. The resulting solution was dialyzed for 3 days to remove all small molecules. The used dialyzing water was changed once a day, and the used dialyzing bag can only keep the molecules with a molecular weight greater than 8000 Da. **2b** was recovered by removing the water with rotary evaporator at about 60 °C. The ^{1}H NMR and FTIR spectra are shown in Figs. 1 and 2, respectively.

The polymers **2** with varying SD were synthesized by adjusting the molar ratio of the FPAEK **1** to chlorosulfonic acid. The results were listed in Table 1.

2.5. Preparation of the membranes

The obtained sulfonated polymers were dissolved in 10 mL of DMAc, followed by filtration using a glass funnel with cotton as filter material to remove the un-dissolved materials. The filtrate was transferred to a Petri dish and concentrated to about 3 mL in an oven at about 60 °C. It was then cast onto a piece of glass and dried first in an oven at 60 °C for 8 h and then for another 4 h in vacuum oven. The resulting membranes appeared colorless and transparent with thickness in the range of 110–180 μm.

2.6. Membrane characterization

2.6.1. Ionic exchange capacity (IEC), equivalent weight (EW) and SD

The ionic exchange capacity (IEC), equivalent weight (EW), and SD of the membranes were determined by titration [20]. The dried membrane was weighed and immersed in 1.0 M HCl solution for 5 h to protonize the sulfonic groups and was then washed thoroughly with deionized water until pH was neutral. The membrane was then immersed in a 2.0 M solution of NaCl for 5 h to replace the protons of sulfonic acid groups with sodium ions. The replaced protons were titrated using 0.1 M NaOH solution, with phenolphthalein as indicator. The moles of the proton are equal to the moles of sulfonic group and the IEC, EW and SD were calculated from the titration data using following equations

$$\mathrm{IEC} = \frac{\Delta V_{\mathrm{NaOH}} C_{\mathrm{NaOH}}}{W_{\mathrm{s}}}\ (\mathrm{mol\ g^{-1}}) \tag{1}$$

$$\mathrm{EW} = \frac{1}{\mathrm{IEC}}\ (\mathrm{g^{-1}\ mol}) \tag{2}$$

$$\mathrm{SD} = \frac{\mathrm{FW} \cdot \mathrm{IEC}}{(1 - 80\mathrm{IEC})}\ (\text{sulfonic acid groups/repeated units}) \tag{3}$$

Where ΔV_{NaOH} is the consumed volume of NaOH solution, C_{NaOH} the concentration of NaOH solution, W_{s} the weight of sample, FW the molar weight of the repeat units of FPAEK **1**.

2.6.2. Water uptake and linear expansion ratio

The membrane was dried under vacuum at 80 °C for 24 h. The weighed membrane was immersed in deionized water at room temperature for 24 h. Wet membrane was weighed quickly upon surface wiping up with tissue paper. The water uptake of membrane, *S*, was calculated according to the

Table 1
IEC, EW, SD, water uptake, linear expansion ratio and oxidative stabilities of **2**

Sample	Repeated unit/chlorosulfonic acid (molar ratio)	IEC (10^{-3} mol g^{-1})	EW (g mol^{-1})	(SD) ($x+y$)	Water uptake (wt%)	Linear expansion ratio (%)	Oxidative time[a] (min)
2a	1:3.5	0.772	1295	0.576	18.6	2.3	68
2b	1:4.0	0.875	1143	0.648	20.3	2.6	68
2c	1:5.0	1.169	885	0.888	26.5	2.9	64
2d	1:6.0	1.402	713	1.088	32.3	3.1	60
2e	1:7.0	1.780	562	1.430	37.6	3.4	58
2f	1:8.0	2.049	488	1.688	42.4	17.6	34

[a] Times were recorded from commencement to break of samples in Fenton's reagent (3 wt% H_2O_2 + 2 ppm $FeSO_4$) at 80 °C.

following equation

$$S = \frac{(W_w - W_d)}{W_d} \times 100\% \quad (4)$$

where W_w and W_d are the weights of the wet membrane and dry membrane, respectively.

The linear expansion ratio was calculated from the following equation [21]

$$\text{Linear expansion ratio} = \frac{(L_w - L_d)}{L_w} \times 100\% \quad (5)$$

where L_w and L_d are the lengths of the same side of wet membrane and dry membrane, respectively.

2.6.3. Mechanical properties, oxidative and thermal stabilities

The tensile properties were determined at 25 °C and 50% relative humidity. The samples were carefully cut into a size of 5×50 mm^2. The cross-head speed was set at a constant speed of 1 mm min^{-1}. Wet membranes were pretreated in water at 80 °C for 3 h prior to the measurement.

Oxidative stabilities were determined using Fenton's reagent (3 wt% H_2O_2 + 2 ppm $FeSO_4$) at 80 °C [5]. The membranes were immersed in Erlenmeyer flask containing Fenton's reagent, which was put in water-bath of 80 °C beforehand. The flask was shaken constantly until the membrane began to break. The times from commencement to break of samples were recorded. The results are listed in Table 2.

Thermal stabilities of the membranes were determined by thermal gravimetric analysis at a heating rate of 20 °C/min under a protective nitrogen atmosphere (100 mL/min).

2.6.4. Proton conductivity

The proton conductivity of the membrane was determined by AC impedance method. Prior to the measurement, the membrane was immersed in 1 M H_2SO_4 at 80 °C for 5 h and then washed with deionized water to the same PH value as that of deionized water. The membrane was kept in deionized water for further use.

For comparison, Nafion-117 membrane was also subjected to the same measurement. Prior to the measurement, the Nafion-117 membrane was pretreated according to the following steps [22]: boiled in 3% H_2O_2 for 1 h, in deionized water for another 1 h; and in 1 M H_2SO_4 for 1 h followed by immersing in deionized water for future use. The as-treated membrane was tightly clamped between two round gold block electrodes with a diameter of 10 mm and placed in a closed container containing some water to keep the relative humidity of 100%. The total container was placed in a temperature-controlled vessel during the measurement [23].

The proton conductivity (σ) of the specimen in the transverse direction (across the membrane) was calculated from the impedance data according to the following equation

$$\sigma = \frac{d}{RS}$$

where d and S are the thickness and the face area of the specimen, respectively, and R is the impedance of the sample derived from the low intersect of the high-frequency semicircle on a complex impedance plane with the Re (Z') axis [12].

Table 2
Mechanical properties of **2**

Sample	Maximum tensile strength (dry) (MPa)	Tensile strength at break (dry) (MPa)	Maximum tensile strength (wet) (MPa)	Tensile strength at break (wet) (MPa)
2a	33.62	32.44	28.42	18.75
2b	31.37	29.88	26.84	15.68
2c	29.12	26.37	23.55	14.93
2d	26.02	23.18	21.81	10.85
2e	23.79	21.64	20.36	7.23
2f	20.72	16.36	15.75	5.34

3. Results and discussion

3.1. Synthesis and structure characterization

The FPAEK **1** can be readily synthesized in 93.8% yield using standard method. The molecular weight should be controlled in an appropriate range by simply controlling the reaction time because too high molecular weight polymer may form micelles in low-polar solvent during sulfonation. In this case, incomplete sulfonation may occur inside micelles, leading to an insoluble SFPAEK **2** during film casting.

The sulfonation process must be carefully controlled to ensure that the sulfonic acid groups are only introduced on fluorenyl rings. Therefore, chlorosulfonic acid should be added dropwise in enough interval of time at a temperature of lower than 40 °C. High temperature may result in the sulfonation on the phenyl rings on backbone. The sulfonation on the backbone of a polymer can generally lead to a membrane with short lifetime [5,24]. The sulfonation position can be determined using NMR technique. As mentioned above in experimental part, the inherent viscosity of FPAEK **1** was determined to be 0.43 dL/g (0.5% solution in $CHCl_3$ at 25 °C). For sulfonated polymers **2**, no molecular weight data were available because no proper GPC colomn. The inherent viscosity of sulfonated polymer **2e** was determined to be 0.48 dL/g (0.5% solution in DMAc at 25 °C), indicating there was no obvious cleavage occurrence of molecular chain during the sulfonation. Generally, the cleavage occurs during the sulfonation, especially when high concentration of chlorosulfonic acid is used. In this work, trace lower molecular weight products can be removed by dialyzing the solution of sulfonated polymer for 3 days.

The ^{1}H NMR spectra (aromatic section) of **1** and **2e** (SD = 1.430) are shown in Fig. 1 (chemical shift of methyl groups located at 1.984 ppm for **1** and 1.945 ppm for **2e**). The use of different solvents is responsible for changes on the chemical shifts of the same proton in both spectra. It can be seen that the peak 1, 2 and 4 of **2e** have the same integration strength, indicating the same amount of H_1, H_2 and H_4. This demonstrates that the phenyl rings on backbone were not sulfonated because the positions 2 and 4 are easier to be sulfonated than position 1. The peaks around 7.34 ppm in the spectrum of **2e** show the existence of H_5, H_6 and H_7 of the un-sulfonated positions due to the incomplete sulfonation. Hence, we can conclude that the sulfonic acid groups were introduced only on fluorenyl rings.

As shown in Fig. 2 for the comparative FTIR spectra, In the spectrum of sample-**2e**, the new broadband appearing at 3458 cm^{-1} was assigned to O–H vibration from sulfonic acid groups interacting with molecular water; dwindled 1445 cm^{-1} absorption can be attributed to stretching vibrations of the residual unsubstituted fluorenyl ring; the new 1189, 1095 cm^{-1} and intensive 1033 cm^{-1} absorption were assigned to symmetric asymmetric and stretching vibration of O=S=O [11]; the new 997 cm^{-1} absorption and 976 cm^{-1} can be attributed to the split of 983 cm^{-1} absorption in the spectrum of sample-**1** due to new substitution upon sulfonation; the new 705 cm^{-1} absorption was assigned to O–S vibration of sulfonic acid groups [25]. This confirms the existence of sulfonic acid group in SFPAEK **2e**.

3.2. Water affinity and mechanical properties

It is well known that water, in proton exchange membranes, determines the proton conductivity of the membrane. However, excess water uptake can lead to the mechanical property deteriorating of membrane due to the soluble nature of membrane in water. As can be seen from Table 1, the water uptakes as well as the linear expansion ratio of the membrane increase with increasing SD, owing to the increase of the hydrophilicity.

The mechanical properties of the membrane are listed in Table 2. Both maximum tensile strength and tensile strength at break decreased with increasing SD value because of the increase of absorbed water in the membrane. This is due to that the absorbed water acts as a plasticizer or solvent for the membrane, and therefore results in the deterioration in mechanical strength.

It was documented that the water uptake of Nafion-112 was about 20 wt% [26] and the maximum tensile strength of wet Nafion-112 was 19.1 MPa [27]. Apparently, both water uptake and mechanical properties of the membranes **2a**–**2e** are better than those of Nafion-112.

3.3. Oxidative and thermal stabilities

As listed in Table 1 for the oxidative stability, the membranes **2a**–**2e** exhibited much better oxidative stability when compared with the reported fluorene-containing sulfonated poy(arylene ether sulfone) [5]. It is also evident that the oxidative stabilities decreased with increasing SD value, especially in the case of SD greater than 1.430. This is because it is difficult to avoid the sulfonation on the phenyl ring on backbone when SD is greater than 1.430.

The TGA curve of **2e** is shown in Fig. 3. It can be seen that big weight loss start at about 270 °C due to the degradation or the loss of sulfonic acid groups. The high weight-loss temperature indicates the thermal stability of **2e** is better than reported SPES (250 °C) [5] and comparable to that of Nafion membrane (280 °C) [28].

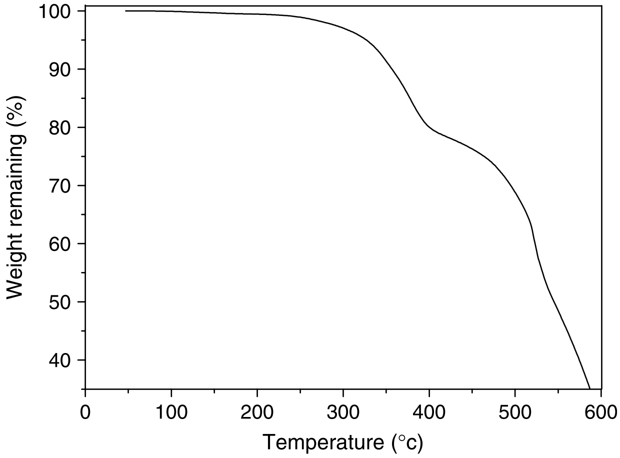


Fig. 3. TGA curves of **2e**.

3.4. Proton conductivity

Different proton conductivity can be obtained using different experimental method and instruments. The conductivity of Nafion-117 was ever reported in different values [16,21,23]. Nafion-117 was used for the comparison with the membrane synthesized in this work.

Considering both mechanical properties and oxidative stabilities, the proton conductivities of **2b**, **2c** and **2e** were determined as shown in Fig. 4. It can be seen that the proton conductivities of increased with increasing testing temperature. The conductivities of **2b** and **2c** were quite low because of their low SD value. Low SD value can lead to the formation of the dead-end of proton transporting channel [21], resulting in a low conductivity. The membrane of **2e** showed a higher proton conductivity than that of Nafion-117 at a higher temperature of 130 °C and the relative humidity of 100% under the same test conditions, demonstrating its

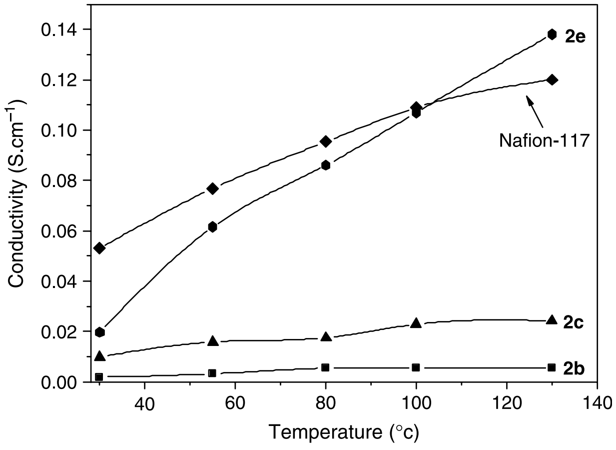


Fig. 4. Proton conductivities of **2b**, **2c**, **2e** and Nafion-117.

potential application in PEM fuel cell, especially in high temperature PEM fuel cell.

4. Conclusions

The FPAEK **1** can be readily synthesized in high yield using conventional method and sulfonated by chlorosulfonic acid. Both sulfonation position and degree can be controlled by adjusting the reaction conditions but it is difficult to avoid the sulfonation on the phenyl ring on backbone when SD of SFPAEK **2** greater than 1.430. The resulting SFPAEK **2** is soluble in aprotic solvent and can be cast into tough and transparent membranes. The water uptake and linear expansion ratio of the membrane increased with increasing SD value. The mechanical properties, however, decreased with this increase. The mechanical property for the membrane with SD of 1.43 was superior to that of Nafion-112. The mechanical properties of wet membranes became poor in case of SD greater than 1.43. Similarly, the oxidative stabilities decreased with increasing SD value. The thermal stability of **2e** is comparable to that of some other reported sulfonated hydrocarbon polymers and Nafion membrane. The proton conductivities increased with increasing SD value and temperature. SFPAEK **2e** exhibited higher proton conductivity than Nafion-117 at 130 °C under same testing conditions. This demonstrates it as excellent candidate of proton exchange membrane for high temperature fuel cell.

Acknowledgements

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