

A Facile Method for Preparation of Cardo Poly(aryl ether sulfone) Bearing Pendent Sulfoalkyl Groups as Proton Exchange Membranes^{*}

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Abstract A series of cardo poly(aryl ether sulfone) copolymers bearing pendent sulfonic acid groups (SPES-*X*) have been prepared by a facile chemical graft method. The structure was confirmed by ¹H-NMR spectra. The side-chain-type SPES-*X* membranes show significantly reduced swelling behavior and excellent mechanical properties as well as appropriate proton conductivity compared to the main-chain-type sulfonated polymers with similar ion exchange capacity (IEC) value. Moreover, they show methanol permeability in the range of 0.6×10^{-7} – 5.7×10^{-7} cm²/s which is lower than that of Nafion 117. All the results indicate that the SPES-*X* membranes are promising candidates for the direct methanol fuel cells.

Keywords: Side-chain type; Cardo poly(aryl ether sulfone); Proton exchange membrane.

INTRODUCTION

The direct methanol fuel cells (DMFCs) are the focus of most attention because of their versatile applications in the automobile and portable fields^[1]. As one of the key components of DMFCs, proton exchange membranes (PEMs) function as an electrolyte for transferring protons as well as providing a barrier to the fuel cross-leaks between the electrodes^[2]. Perfluorosulfonic acid polymers, such as Nafion (DuPont), are commercially available because of their outstanding properties. However, some drawbacks such as high methanol crossover and high cost hinder widespread commercial use in PEM^[3].

Aromatic hydrocarbon-based ionomers including sulfonated poly(arylene ether ketone)^[4, 5], sulfonated polyimides^[6, 7], sulfonated polystyrene-based systems^[8] and sulfonated poly(benzimidazole)^[9] have been suggested as alternative membranes in recent years due to their low methanol permeability and low cost compared to Nafion as well as good thermal stability. Unfortunately, these sulfonated membranes in which the sulfonic acid moieties are incorporated directly onto the backbones generally suffer from high water swelling and poor hydrolytic stability on increasing the degree of sulfonation^[10].

Recently, the sulfonate aromatic polymers with sulfonic acid groups located in side chains have attracted much attention^[11, 12]. The side-chain-type sulfonated polymers generally got better balance between proton conductivity and water dimensional swelling than the corresponding main-chain-type polymers with sulfonic groups directly on main chain aryls^[13, 14]. These side-chain-type PEMs have been prepared by the direct copolymerization method or by chemical grafting the pendants onto polymers. Compared to the direct

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copolymerization method, the chemical graft method avoids preparing sulfonated monomers and offers an easier route to introduce locally and densely populated sulfonated structures into the aromatic polymer backbone.

In previous papers, we prepared a series of cardo poly(aryl ether sulfone) copolymers bearing pendent sulfonated alkoxy groups (SPES-C-X)^[15]. The cardo-based polymers exhibit excellent mechanical toughness, high proton conductivity and low dimensional change. However, the SPES-C-X bears thermally unstable ether bond in the side chains. Herein, we employ a facile chemical graft approach to fabricate a series of cardo poly(arylene ether sulfone) with sulfonic acid groups on flexible aliphatic side chains. The chemical structure, thermal stability, water swelling behaviour, ion exchange capacity (IEC) and proton conductivity of the synthesized copolymers have been investigated for the future application in DMFCs.

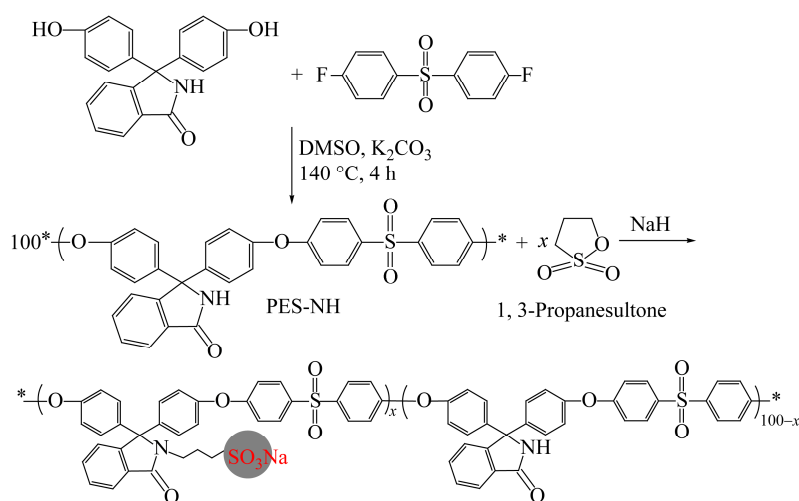
EXPERIMENTAL

Materials

Phenolphthalein was purchased from Beijing Chemical Reagent Company and purified by recrystallization from mixed solvent of ethanol and water. 4,4-Difluorodiphenylsulfone (DFDPS) was obtained from Jiangyan Jiasheng Chemical Co., Ltd., China. 1,3-Propanesultone was obtained from Alfar and used as received. All other chemicals were of reagent grade and used as received.

Synthesis of Cardo Poly(aryl ether sulfone)s with Pendent Sulfonic Acid Groups (SPES-X)

Preparation and characterization of cardo poly(arylene ether sulfone)s containing amide groups (PES-NH) were reported in a previous paper^[16]. Then the cardo-poly(arylene ether sulfone)s with pendent sulfonated aliphatic side chains were synthesized as Scheme 1. The obtained polymers are denoted by SPES-X, where X represents the degree of sulfonation.



Scheme 1 The synthetic route for cardo poly(arylene ether sulfone)s with sulfonated side chains

A typical procedure for SPES-60 is given below: PES-NH (10.632 g, 0.02 mol) and NaH (0.96 g, 0.04 mol) were added to 100 mL of NMP at room temperature and stirred for 30 min. Then 1,3-propanesultone (1.4657 g, 0.012 mol) was added and the reaction was allowed to proceed at room temperature for 12 h. The viscous solution was precipitated into ethanol. The isolated white polymer was washed with deionized water several times before being dried under vacuum at 120 °C overnight. Yield: 97%. Other sulfonated polymers were prepared by the same method described above, except with different amounts of 1,3-propanesultone.

SPES-X: ¹H-NMR (DMSO-d₆, δ): 9.80 1H; 7.93–7.96 4H; 7.57–7.84 4H; 7.32–7.41 4H; 7.17–7.24 8H; 3.43 2H; 2.26 2H; 1.23 2H.

Membrane Preparation

The polymer membranes (sodium form) were cast on glass plate from their DMSO solutions (8 wt%) after filtration. The removal of DMSO was accomplished in an oven at 80 °C for 8 h and then at 120 °C under vacuum for 12 h. The salt form membranes were treated with 1.0 mol/L sulfuric acid at room temperature for 2 days, thoroughly washed with deionized water and then dried under vacuum at 100 °C for 10 h. Tough, ductile ionomer membranes were obtained with a controlled thickness of 40–55 μm.

Characterizations

¹H-NMR spectra were measured at 300 MHz on an AV 300 spectrometer. TEM analysis was performed with slices of Pb²⁺-stained membranes on a JEM-1011 microscope. The sample in proton form was converted into Pb²⁺ form by immersing the sample on copper grid in 1% Pb(Ac)₂ solution for 48 h, then thoroughly rinsed with water and dried at room temperature for 24 h.

The proton conductivity (σ , S/cm) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $\sigma = d/L_s \times W_s \times R$ (d is the distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). Here, ohmic resistance (R) was measured by four-point probe alternating current impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). All samples were equilibrated in water for at least 24 h before the conductivity measurements. At a given temperature, the samples were equilibrated for at least 30 min before any measurements.

Water uptake and linear swelling ratio were measured by soaking the membranes in deionized water for 24 h at the desired temperatures. The water uptake was calculated using the following equation: water uptake (wt%) = $(W_s - W_d)/W_d$, where W_d and W_s are the weight of the dry and wet membranes, respectively. Meanwhile, the length variations of the round-shaped membranes were recorded and the linear swelling ratio was calculated from the following equation: swelling ratio (%) = $(l_{\text{wet}} - l_{\text{dry}})/l_{\text{dry}}$, where l_{dry} and l_{wet} are the length of the dry and wet samples, respectively.

The methanol permeability was determined by using an H's test cell with a solution containing (2 mol·L⁻¹) 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 chromatography. The methanol permeability was calculated by the following Eq. (1):

$$c_B(t) = \frac{A}{V_A} \frac{DK}{L} c_A(t - t_0) \quad (1)$$

where c_A and c_B are the methanol concentration of feed side and permeated through the membrane, respectively. A , L and V_A are the effective area, the thickness of membrane and the volume of permeated compartment, respectively. DK defined as the methanol permeability, and $t - t_0$ is the time lag.

Small angle X-ray scattering was measured for SPES-*X* membranes at 50% RH and room temperature. The range of scattering vectors explored ($q = 4\pi \sin 2\theta/\lambda_i$) was from 0.08 nm⁻¹ to 3.0 nm⁻¹, where λ_i and 2θ are the incident wavelength and total scattering angle, respectively.

Tensile measurements were performed with a mechanical tester Instron-1211 instrument (Instron Co., USA) at a speed of 2 mm/min at ambient humidity (~30% relative humidity). The thermogravimetric analyses (TGA) were obtained with a PerkinElmer TGA-2 thermogravimetric analyzer (Inspiritech 2000 Ltd., UK) at a heating rate of 10 K/min.

The oxidative stability of SPES-*X* membranes was evaluated from the membrane weight retention after immersion in Fenton's reagent (3% H₂O₂ containing 2 mg/L FeSO₄) at 80 °C for 1 h.

RESULTS AND DISCUSSION

Synthesis and Characterization of Sulfonated Copolymers

Initially, the cardo poly(arylene ether sulfone)s containing amide groups (PES-NH) were synthesized *via* a

standard K_2CO_3 -catalyzed aromatic nucleophilic substitution polycondensation^[16]. Synthetic procedure of cardo poly(arylene ether sulfone)s containing sulfonated aliphatic side chains is shown in Scheme 1. The PES-NH contained an amide group in each repeating unit, which provided reactive sites to introduce various functional groups, such as sulfonated aliphatic side chains. The sulfoalkylation reaction of PES-NH and 1,3-propanesultone was carried out at room temperature for 12 h with NaH as the base.

Useful information can be extracted simply from studying the ^1H -NMR spectra of the SPES-*X* polymers. Figure 1 shows ^1H -NMR spectra of SPES-60, SPES-70 and SPES-80. The peak at $\delta = 9.80$ (proton in amide) is still part of the present, and new peaks appear at $\delta = 3.40$, 2.26 and 1.23 which correspond to the protons in the sulfoalkyl group, which confirms that part of the amide groups reacted with 1,3-propanesultone to produce *N*-alkylated product. The integration ratio of H(c) to that of H(1–8) was close to 2*X*:20, suggesting a quantitative conversion of proton in amide (NH) to sulfopropyl groups. The content of the sulfonic acid groups in the copolymers was readily controlled through the feed ratios.

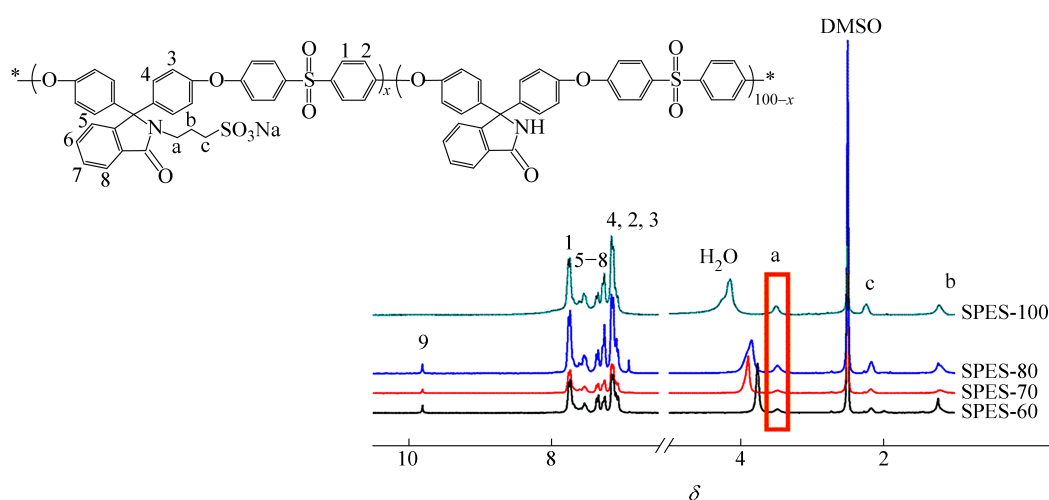


Fig. 1 ^1H -NMR spectra of SPES-*X* in $DMSO-d_6$

Water Uptake and Swelling Ratio

Table 1 shows the properties of the synthesized SPES-*X* membranes. IEC is a constant representing the amount of the exchangeable protons in ionomer membranes. The IEC values were determined by a titration method, which were close to the theoretical values calculated according to the content of $-NH$ groups, indicating a quantitative reaction between $-NH$ groups and 1,3-propanesultone. The IEC values in the range of 0.90–1.51 mequiv./g were readily controlled by adjusting the feed ratios.

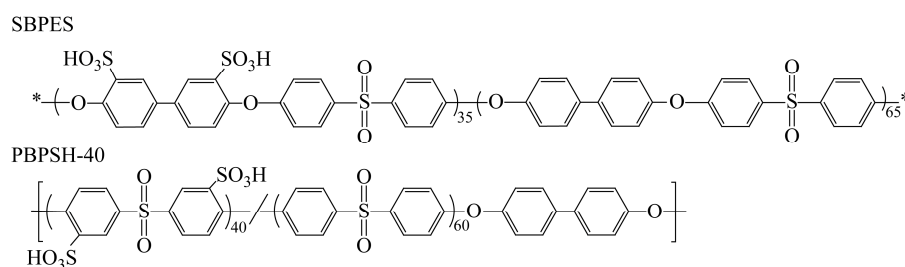
The water within the membrane provides a carrier for the proton and maintains high proton conductivity. However, the excessive high level of water uptake will deteriorate the dimensional stability, which leads to loss of mechanical properties. Therefore, the preparation of sulfonated polymers with better water uptake and dimensional stability is one of the critical requirements for their applications as PEMs. As shown in Table 1, the water uptake increased from 7.3% for SPES-60 to 20.0% for SPES-100. Also, the swelling ratio increased from 4.4% for SPES-60 to 7.5% for SPES-100. On the whole, the side-chain-type SPES-*X* membranes showed moderate water uptake and much lower swelling ratio than main-chain-type SBPES and PBPSH-40 membrane with similar IEC, which was attributed to their different molecular structures (Fig. 2). Compared with main-chain-type SBPES membrane, side-chain-type SPES-*X* contained short flexible side chains which separate hydrophilic sulfonic acid groups from the hydrophobic polymer main chain. Therefore, water molecules can be restricted to hydrophilic domains in the membranes and separated from hydrophobic domains which may suppress the water swelling.

Table 1. Properties of the SPES-*X*, SBPES and PBPSH-40 membranes

Samples	IEC (meq./g)		Water uptake (%)		Swelling ratio (%)		References
	IEC ^a	IEC ^b	20 °C	80 °C	20 °C	80 °C	
SPES-100	1.53	1.51	20.0	30.0	7.5	9.8	This work
SPES-80	1.27	1.18	14.4	22.3	6.2	8.0	This work
SPES-70	1.13	1.08	12.6	20.1	4.8	5.6	This work
SPES-60	0.99	0.90	7.3	12.2	4.4	5.0	This work
SBPES	1.58	1.55	34.3	60.9	8.9	19.7	[15]
PBPSH-40	1.7	1.5	39.0	—	—	—	[17]

^a Calculated IEC values based on complete reaction of —NH groups with 1,3-propanesultone;

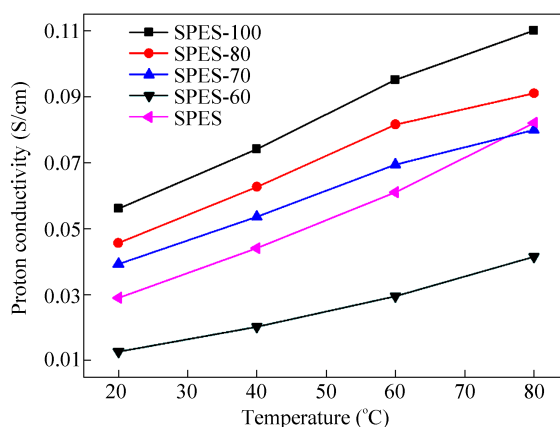
^b Determined from titration

**Fig. 2** The structure of SBPES and PBPSH

In addition, the swelling ratio of SPES-*X* membranes also displayed a weaker dependence on temperature. For example, at 80 °C, SPES-80 membrane showed a swelling ratio of 8.0%, which was only slightly higher than the corresponding value at 20 °C (6.2% swelling ratio).

Proton Conductivity and Methanol Permeability

Proton conduction ability is the most important characteristic for DMFCs applications. The proton conductivity of membranes as a function of temperature at 100% relative humidity is shown in Fig. 3. Conductivities of these membranes were all above 0.01 S/cm and their conductivities increased with IEC values. The conductivities of SPES-*X* membranes steadily increase with temperature because the free volume, in favor of ion transport and the mobility of cations, increases as the temperature rises.

**Fig. 3** Proton conductivity of SPES-*X* membranes as a function of temperature

As compared to the main-chain-type SBPES membrane, the side-chain-type SPES-100 with similar IEC value showed higher proton conductivity at 20 °C (0.056 S/cm for SPES-100 membrane and 0.030 S/cm for SBPES)^[15]. Meanwhile, the conductivities of the SPES-80 and SPES-70 membranes also are sufficient to pass

current for both fuels. According to the results, we could conclude that “side-chain-type” structures facilitate ionic transport. Sulfonic acid groups on the flexible aliphatic side chain of the polymers could decrease the limitation of main-chain rigidity on the mobility of sulfonic acid groups, making ionic network more permeable and thus enhancing proton conductivity^[18]. Moreover, the PBPSH-40 membrane showed proton conductivity of 0.082 S/cm at 30 °C, which was higher than that of SPES-100 membrane (0.065 S/cm). This was probably due to the higher water uptake of PBPSH membrane^[17]. Besides, the SPES-60 material is not sufficient for current flow.

Membranes intended for direct methanol fuel cells (DMFCs) should act as not only a high proton conductor, but also an effective barrier to prevent methanol from crossing over. The methanol permeability of the SPES-*X* membranes varied from 5.70×10^{-7} cm²/s (SPES-100) to 4.98×10^{-7} cm²/s (SPES-70) (Table 2), which were an order of magnitude lower than the methanol permeability of Nafion 117 measured under the same experimental conditions (2.40×10^{-6} cm²/s). Hence the SPES-*X* membranes have good methanol barrier properties. Main-chain-type SBPES membrane exhibited methanol permeability of 8.7×10^{-7} cm²/s, which was higher than those of SPES-*X* membranes due to high water uptake.

Table 2. Methanol permeability P_M and selectivity of membranes

Samples	σ (S/cm) 20 °C	P_M ($\times 10^{-6}$ cm ² /s) 20 °C	Selectivity ($\times 10^4$ S·s/cm ³) 20 °C
SPES-100	0.0560	0.570	9.82
SPES-80	0.0456	0.523	8.72
SPES-70	0.0392	0.498	7.87
SPES-60	0.0126	0.060	21.00
SBPES	0.0300	0.870	3.44
Nafion 117	0.0900	2.400	3.75

The selectivity represented the performance tradeoff between proton conductivity and methanol permeability. As listed in Table 2, the SPES-*X* with pendent sulfonated aliphatic chains exhibited several times higher selectivity than Nafion 117 and SBPES. Thus, the SPES-*X* membrane can act as both a good conductor and a good separator for DMFCs.

TEM

Transmission electron micrographs (TEMs) of membranes are shown in Fig. 4. The dark areas represent hydrophilic domains and the white areas represent hydrophobic domains. The TEM micrograph of SPES-100 membrane showed the spherical ionic clusters in a uniform distribution with the average size of 2 nm (Fig. 4a). The other membranes showed reduced density of the hydrophilic domain with the lower IEC. The all membranes revealed excellent phase-separated morphologies, indicating that the side chain structure played an important effect on the morphology of membrane. It is considered that the pendent sulfonic acid groups are more likely to aggregate and form ionic clusters because of their higher polarity and flexibility.

SAXS

The microstructures of these membranes were further characterized by SAXS. As shown in Fig. 5, the corresponding SAXS profiles exhibited a clear peak for SPES-100 membranes. This result indicated that phase separation between the hydrophilic units and the hydrophobic backbones was locally correlated. The values of d for SPES-100 membranes, calculated from $d = 2\pi/q$, were in the range of 8.8–9.8 nm, which were larger than that of Nafion 117 ($d = 3.4$ nm)^[19]. This large d is convenient to form nanochannels for efficient proton-transport. No peak appear in the curve of SPES-60 revealed the lack of proton channel.

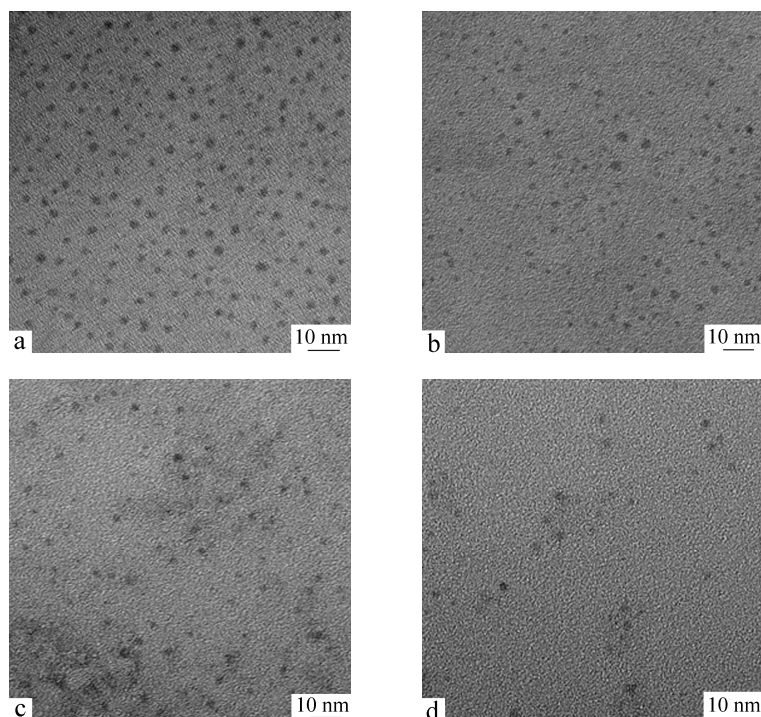


Fig. 4 TEM micrographs of membranes (in Pb^{2+} form): (a) SPES-100, (b) SPES-80, (c) SPES-70 and (d) SPES-60

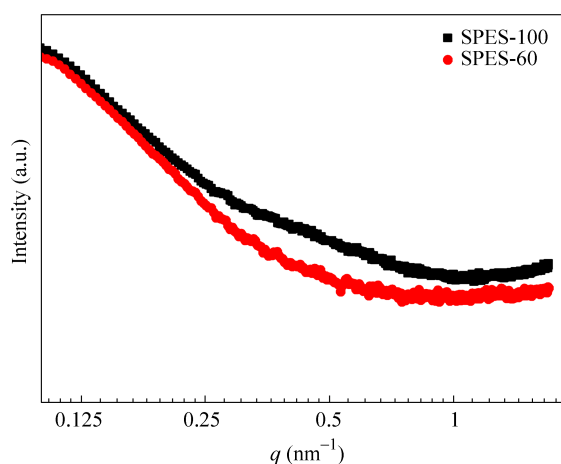


Fig. 5 SAXS data recorded on SPES-*X* membranes ion-exchanged with lead acetate

Thermal and Oxidative Stability

The thermal stability of SPES-*X* in acid form was investigated by TGA measurements, and the results are illustrated in Fig. 6. All polymers exhibited a two-step degradation curve.

The first weight loss step from 280 °C to 370 °C was attributed to the decomposition of the sulfonic acid and alkyl moieties. Meanwhile, the weight loss in this temperature range increased with the rise of IEC. The second weight loss step began at about 370 °C, associated with the degradation of polymer main chains^[20]. The temperature of the 5% weight loss was above 301 °C, which was sufficiently high for fuel cell applications. It was also observed that the polymer SPES-60 exhibited better thermal stability than the polymer SPES-100 at the range of 280–370 °C. It was probably because the ratio of sulfonated fragments in the polymer decreased as the ratio of PES-NH and 1,3-propanesultone increased.

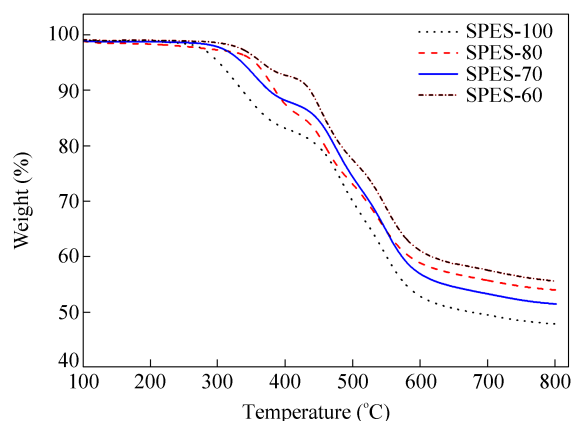


Fig. 6 TGA curves of SPES-*X* in nitrogen

The oxidative stability of SPES-*X* membranes was evaluated in hot Fenton's reagent for 1 h as an accelerated test. As presented in Table 3, the residue of all the membranes is above 94%, which show excellent oxidative stability. Compared to SPES-100 membranes, the SPES-70 membranes are better. Because the oxidative attack mainly occur in the hydrophilic domains, the aliphatic side chains separated the polymer main chain from hydrophilic sulfonic acid groups to keep the main chain in a hydrophobic atmosphere that minimized the decomposition of polymer chains.

Table 3. Oxidative stability of the SPES-*X*

Samples	Residual ^a (%)
SPES-100	94
SPES-80	95
SPES-70	97
SPES-60	95

^a Residual weight of membranes after treatment in Fenton's reagent (3% H₂O₂ containing 2 mg/L FeSO₄) for 1 h at 80 °C

Mechanical Properties

Good mechanical properties of the sulfonated polymers are important properties demanded for proton exchange membrane. The mechanical properties of the SPES-*X* membranes are shown in Fig. 7.

The SPES-*X* membranes had tensile strength in the range of 54.8–74.6 MPa, which were much higher than that of Nafion 117. All the four membranes showed Young's moduli of 1120–2460 MPa and elongation at break of 33%–55%. The results displays that the prepared membranes are appropriate for proton exchange membrane.

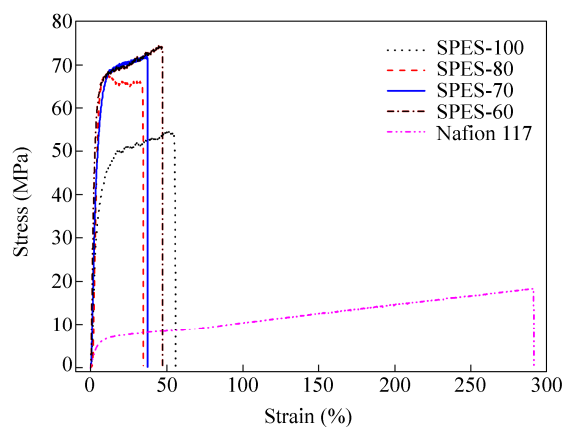


Fig. 7 Stress-strain curves for Nafion 117 and SPES-*X* membranes

CONCLUSIONS

A series of cardo poly(aryl ether sulfone) copolymers containing sulfonic acid groups on aliphatic side chains have been prepared by a facile chemical graft method. This synthetic strategy avoids the use of toxic and corrosive sulfonation reagents such as sulfuric acid and chlorosulfonic acids. The side chain architectures promote proton conduction and depress swelling ratio. Furthermore, the methanol permeability of the SPES-*X* membrane is 10^{-7} cm²/s, which is an order of magnitude lower than that of Nafion 117. Combined with their good thermal stability and high mechanical properties, they can be used as potential PEMs material for fuel cells.

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