

Synthesis and characterization of sulfonated poly(arylene ether ketone ketone sulfone) membranes for application in proton exchange membrane fuel cells

Zhe Wang^{a,b}, Xianfeng Li^a, Chengji Zhao^a, Hongzhe Ni^{a,b}, Hui Na^{a,*}

^a Alan G MacDiarmid Institute, College of Chemistry, Jilin University, Jilin 130021, PR China

^b Changchun University of Technology, Jilin 130012, PR China

Received 21 December 2005; accepted 8 March 2006

Available online 25 April 2006

Abstract

A series of sulfonated poly(arylene ether ketone ketone sulfone) (SPAEEKS) copolymers were synthesized by nucleophilic polycondensation. The copolymers exhibit good thermal and oxidative stabilities, all the SPAEEKS copolymers can be cast into tough membranes. Ionic exchange capacities (IEC), water uptake properties, thermal stabilities, methanol diffusion coefficients and proton conductivities were thoroughly studied. Also the microstructures of the membranes were investigated by TEM. The proton conductivity of the SPAEEKS-4 membrane is close to that of Nafion-117 at 80 °C. The methanol diffusion coefficient of the membrane is much lower than that of Nafion-117 under the same testing conditions. The SPAEEKS membranes are promising in proton exchange membranes fuel cell (PEMFC) application.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Sulfonated; Poly(arylene ether ketone ketone sulfone); PEMFC; Proton conductivity

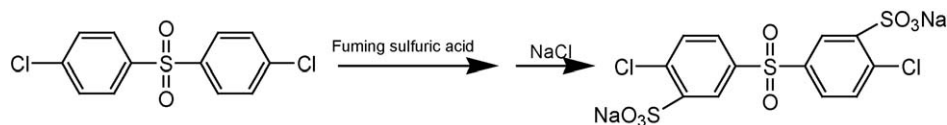
1. Introduction

Proton exchange membrane (PEM) is one of the most important components of the proton exchange membrane fuel cell (PEMFC) which is an attractive energy conversion device for portable power application. In PEMFC, PEM plays parts in two roles: acting as an electrolyte to transferring protons from the anode to the cathode and a separator to prevent the mixing of the fuel and the oxidant. PEM must have both high proton conductivity and good mechanical strength as well as superior thermochemical stability under fuel cell operation conditions. Currently, the membranes broadly used in PEMFC are perfluorinated ionomers, such as Dupont Nafion[®]. However, the high cost, loss of conductivity above 80 °C and higher methanol permeability limit its application in PEMFC. Therefore, many researchers hope to develop hydrocarbon PEM materials that are of high-performance, low-cost and high proton conductivity [1–3].

Recently-developed novel polymer electrolyte membranes include sulfonated poly(arylene ether sulfone) (SPAES) [4–7], sulfonated poly(arylene ether ketone) (SPAEK) [8–10], sulfonated polybenzimidazoles (SPBI) [11,12], and sulfonated polyimide [13,14]. As one type of thermal plastic material, poly(arylene ether ketone ketone sulfone) (PAEKKS) is well known for its excellent thermal and mechanical properties as well as its resistances to oxidation and stability under acidic conditions. It is thought sulfonated PAEKKS copolymers could be used as PEM materials.

In this work, SPAEEKS copolymers with different degrees of sulfonation (D_s) were synthesized by copolymerization of sulfonated monomers with other unsulfonated aromatic monomers, this has advantages over the post-sulfonation method. The position and the content of sulfonated groups can be easily controlled, consequently, ion-exchange capacity (IEC) and proton conductivity could be controlled very well. Also this method avoids cross-linking and other side reactions. A comprehensive study of the synthesis of sulfonated poly(arylene ether ketone ketone sulfone) copolymers by nucleophilic polycondensation, physical and chemical properties of SPAEEKS membranes as a proton exchange membrane was carried out.

* Corresponding author. Tel.: +86 431 5168870; fax: +86 431 5168868.
E-mail address: huina@jlu.edu.cn (H. Na).



Scheme 1. Synthesis of 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS).

2. Experimental

2.1. Synthesis of sodium 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS)

The synthesis of SDCDPS is shown in Scheme 1. The detailed procedure has been described in our previous work [15].

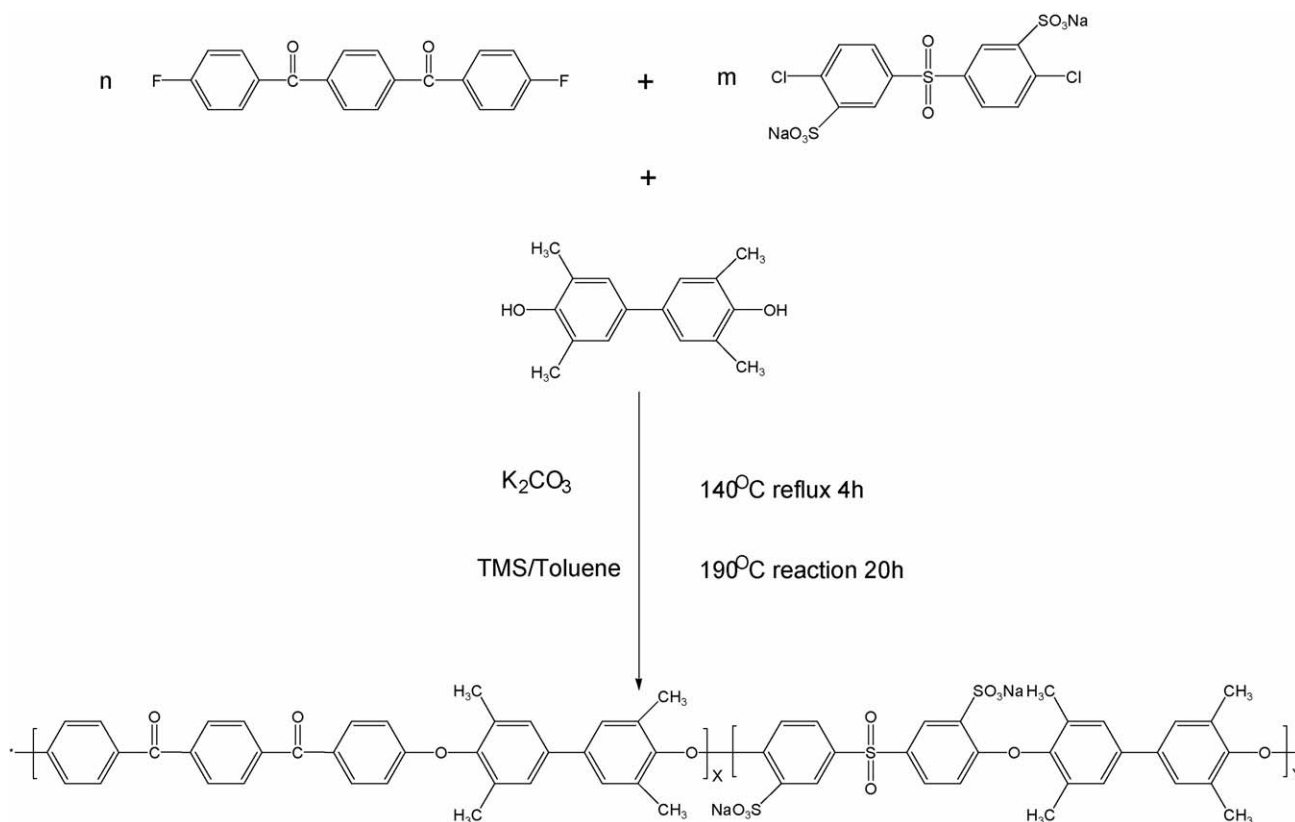
2.2. Synthesis of sulfonated poly(arylene ether ketone ketone sulfone) copolymers

SPAEEKS copolymers with different degrees of sulfonation were prepared by the aromatic nucleophilic substitution polycondensation of 3,3'-5,5'-tetramethyl diphenyl-4,4'-diol (monomer k) with different ratios of 1,4-bis(4-fluorobenzoyl) benzene (monomer n) to disodium 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) (monomer m) in a TMS/toluene solvent system as shown in Scheme 2. The polymerization was carried out in an inert atmosphere of nitrogen in a 500 ml three-neck round-bottom flask fitted with a mechanical stirrer and a Dean–Stark trap with a reflux condenser. The mixture was

refluxed for 4 h at 140 °C until water was removed from the reaction mixture by azeotropic distillation, then the toluene was distilled out, the temperature of the reaction mixture was slowly raised to 190 °C and maintained at that temperature for 20 h. After that the reaction mixture became highly viscous, TMS was added to dilute the solution and was cooled to room temperature. The mixture was poured into deionized water. The inorganic salts were removed by washing with boiling water. The recovered solids were dried at room temperature for 48 h and then dried in a vacuum oven at 80 °C for 24 h. The polymer products were preserved at a desiccator.

2.3. Membrane preparation

About 2 g of the dried copolymers in the sodium salt form were dissolved in 20 ml of NMP and the solution was cast directly onto a glass plate. The glass plate was heated at 60 °C for 48 h until most of the solvent was removed. The SPAEEKS membranes in sodium form were obtained by removing from the glass plate. The membranes in acidic form were obtained by immersing the above membranes in a 2 M HCl solution for 24 h,



Scheme 2. Synthesis of SPAEEKS copolymers.

followed the membranes were washed with deionized water until the pH reached 6–7. The thickness of all membranes was in the range of 50–150 μm .

2.4. Characterization of SPAEKKS copolymers

FT-IR spectra was recorded on a Bruker Vector 22 FT-IR spectrometer, using either powder sample inside a diamond cell or KBr pellets composed of 50 mg of IR spectroscopic-grade KBr and 1 mg of polymer sample. Approximately 25 mg of SPAEKKS copolymers were dissolved in 50 ml DMF and filtered. Intrinsic viscosities of the samples were measured in DMF at 25 °C using an Ubbelohde viscometer. A Pyris TGA (Perkin-Elmer) was used to study the thermal stability behaviors of SPAEKKS copolymers. About 5–10 mg samples of copolymers were heated to 150 °C and kept at this temperature for 20 min to remove any residual water or solvent remaining in the copolymer films in N_2 . The samples were cooled to 80 °C and then reheated to 700 °C at a rate of 10 °C min^{-1} , the temperatures at which 5% weight loss and extrapolated onset for first weight loss occurred were recorded for each material. A METTLER 821^c model DSC was employed to determine the glass transition temperature (T_g) of SPAEKKS samples. The samples were preheated under 200 cc min^{-1} nitrogen from room temperature to 150 °C at a rate of 20 °C min^{-1} to remove moisture and avoid the effects of the thermal history, cooled to 50 °C and then reheated from 50 to 350 °C at a rate of 10 °C min^{-1} .

2.5. Characterization of SPAEKKS membranes

2.5.1. Morphology of membranes

SPAEKKS copolymers in sodium form were immersed in AgNO_3 solution for 24 h in order to make Na^+ form convert into Ag^+ form. Copolymers in Ag^+ form were filtrated and vacuum dried at 80 °C overnight, then were dissolved in DMF and cast onto copper grid for transmission electron microscopy (TEM, JEM-2000EX) investigation.

2.5.2. Ionic exchange capacity

The measurement of ion-exchange capacity (IEC, $\text{meq of SO}_3\text{H g}^{-1}$) measured is based on the following procedures. Membrane in acidic form was immersed into a 50 ml 1 M NaCl solution for 1 day to allow the H^+ form to exchange with Na^+ form. The released H^+ ions were titrated with 0.1 M NaOH solution, in which phenolphthalein was used as an indicator. The ion-exchange capacities of membrane were calculated from the titration date via the following relationship (1) [16]:

$$\text{IEC} = \frac{\text{consumed NaOH (ml)} \times \text{molarity NaOH}}{\text{weight dried membrane}} \quad (1)$$

The theoretical IEC values that calculated from D_s were obtained from formula (2):

$$\text{IEC} = \frac{D_s \times 1000}{524 + 68D_s} \quad (2)$$

2.5.3. Water uptake, swelling ratio and water diffusion coefficient

After membranes were acidified, they were vacuum dried overnight at 120 °C until constant weight and length were obtained, which are recorded as W_d and L_d , then they were immersed in deionized water at different temperatures for some time. Surface attached water was quickly swabbed with tissue paper before measurement. The weight and length were measured several times until a constant W_w and L_w were obtained. The water uptake of membranes is calculated using the following formula (3):

$$\text{Water uptake} = \frac{W_w - W_d}{W_d} \times 100\% \quad (3)$$

The swelling ratio was defined as Eq. (4):

$$\text{Swelling ratio} = \frac{L_w - L_d}{L_d} \times 100\% \quad (4)$$

The water desorption measurement was tested by Pyris 1TGA (Perkin-Elmer) which determined the weight changes of samples with time. During the process of measurement the temperature was kept at 80 °C for 60 min, the pressure of the test cell was kept constant. Pyris 1TGA was used to determine the weight changes of samples with time. Water diffusion coefficient is calculated as follows (5) [17]:

$$\frac{M_t}{M_\infty} = 4 \left(\frac{D_t}{\pi l^2} \right)^{1/2} \quad (5)$$

where D is water diffusion coefficient, M_t/M_∞ the water desorption, l is the membrane thickness.

2.5.4. Methanol permeability

Methanol permeability coefficient D ($\text{cm}^2 \text{s}^{-1}$) was determined by using a cell that consists of two half cells separated by the membrane. Methanol was placed on one side of the diffusion cell (A cell) and water was placed on the other side (B cell). Magnetic stirrer was used on each compartment to ensure uniformity. The concentration of the methanol in B cell was measured by using SHIMADU GC-8A chromatograph. The methanol permeability coefficient was calculated as formula (6) [18]:

$$C_{B(t)} = \frac{A}{V_B} \frac{DK}{L} C_A (t - t_0) \quad (6)$$

where DK is the methanol diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), $C_{B(t)}$ the concentration of methanol in B cell (mol L^{-1}), C_A the concentration of methanol in A cell (mol L^{-1}), A the membrane area (cm^2) and L is thickness of membrane (cm).

2.5.5. Proton conductivity

The proton conductivity of membrane was performed by dc method. All membranes in acid form were initially hydrated by immersing deionized water for 24 h at room temperature. The resistance of the membrane was calculated from the slope of voltage–current (U – I) liner. Conductivity measurements of fully hydrated membranes were performed with the cell immersed in liquid water [19]. All impedance measurements were performed

Table 1
The data of sulfonated polymers

Polymer	m (mmol) ^a	n (mmol) ^a	m/n	D_s (cal) ^b	D_s (meq) ^c	Yield (%)	η_{sp} (dl g ⁻¹) ^d
SPAEEKKS-1	4	36	1:9	0.2	0.18	94	0.72
SPAEEKKS-2	8	32	2:8	0.4	0.37	95	0.91
SPAEEKKS-3	12	28	3:7	0.6	0.58	93	1.24
SPAEEKKS-4	16	24	4:6	0.8	0.76	92	1.48

^a The content of monomer m and monomer n in the reaction.

^b Sulfonation degree obtained by calculation.

^c Sulfonation degree obtained by titration.

^d The intrinsic viscosity in DMF at 25 °C.

from 25 to 80 °C in deionized water. The proton conductivity (σ) of the acid form membrane was calculated from the resistance according to following formula (7):

$$\sigma = \frac{d}{RS} \quad (7)$$

where d is the distance between the two electrodes, R the membrane resistance and S is the cross-sectional area of membrane.

3. Result and discussion

3.1. Copolymers properties

3.1.1. Synthesis and characterization of copolymers

Copolymers with different D_s were prepared by aromatic nucleophilic substitution polycondensation with different ratios of monomers m, n and k in a TMS/toluene solvent system. In this work, TMS was selected as the reaction solvent and the monomer concentration in TMS was maintained at 25–30 wt% to obtain a rapid reaction. The polymerization results and analytical data were displayed in Table 1. It can be seen from Table 1 that the polymers exhibit high intrinsic viscosity, which indicates the polymers have high molecular weight. And the intrinsic viscosities of polymers increase with the increment of sodium sulfonate groups content. Because: (1) the electron-withdrawing sodium sulfonate groups improve the density of positive charge of the carbon atom that connects with the fluorine atom, and thus enhances the electrophilic reactivity. (2) The steric hindrance of sodium sulfonated groups decreases the reactivity. But the former factor may dominantly influence this reaction [19]. Moreover, D_s measured by titration are in accordance with D_s calculated, which indicated that degree of sulfonation could be readily controlled by varying the feed ratio of sulfonated

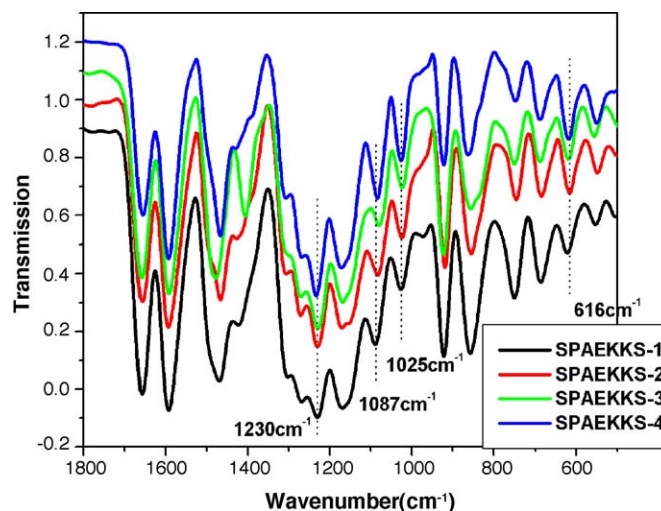


Fig. 1. FT-IR of SPAEEKKS-1 to SPAEEKKS-4.

monomer to unsulfonated monomer. Also it suggests that direct copolymerization has advantage of readily introducing sulfonic acid groups without sulfonation degradation reaction on the polymer chain compared with the post-sulfonated reaction.

The successful introduction of the sodium sulfonate groups was confirmed by Fourier transform infrared (FT-IR) spectroscopy (Fig. 1) of SPAEEKKS-1 to SPAEEKKS-4, where strong characteristic peaks at 1230, 1087 and 1025 cm⁻¹ can be assigned to asymmetric and symmetric O=S=O stretching vibrations of sodium sulfonate groups. The transmission band at 616 cm⁻¹ can be assigned to the S–O stretching vibration of sodium sulfonate groups. The results proved that the sulfonate groups were indeed quantitatively introduced to the copolymers as expected.

Table 2
Thermal properties of SPAEEKKS copolymers

Polymer	T_g (°C)		$T_{d5\%}$ (°C) ^a		T_d (°C) extrapolated onset for first weight loss	
	Sodium form	Acidic form	Sodium form	Acidic form	Sodium form	Acidic form
SPAEEKKS-1	247	241	437	402	421	324
SPAEEKKS-2	257	245	429	333	403	294
SPAEEKKS-3	268	252	406	318	413	282
SPAEEKKS-4	289	261	423	308	420	271

^a Temperature of 5% weight loss.

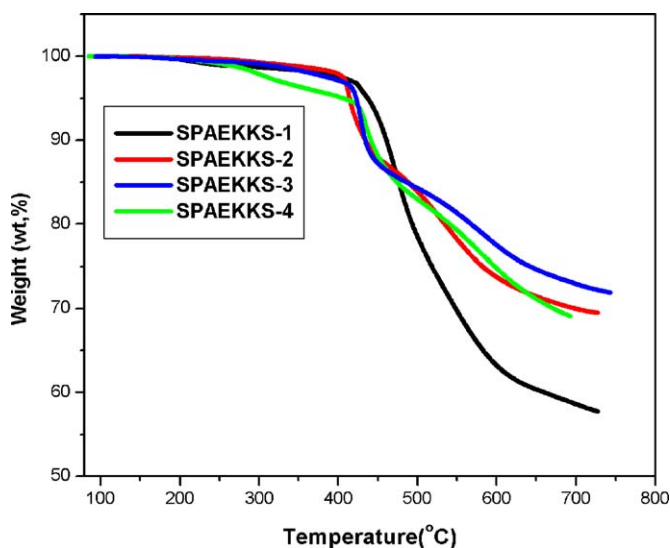


Fig. 2. TGA curves of all SPAEKKS copolymers in sodium form.

3.1.2. Thermal properties of the SPAEKKS copolymers

Thermal stabilities of the SPAEKKS copolymers in both sodium and acid forms were investigated by TGA and DSC analysis and the results are listed in Table 2. Table 2 shows that the temperatures of 5% weight loss ($T_{d5\%}$) and onset weight loss temperatures (T_d) of SPAEKKS copolymers in sodium form are between 406 and 437 °C and between 403 and 420 °C, respectively. In contrast with sodium forms, $T_{d5\%}$ and T_d of copolymers in acidic form are from 308 to 402 °C and from 271 to 324 °C, respectively, which are lower than corresponding sodium form. But all copolymers possess good thermal stabilities. The TGA data show temperature of $T_{d5\%}$ gradually decreased from SPAEKKS-1 to SPAEKKS-4. The TGA curves of sodium and acidic forms are shown in Figs. 2 and 3. Copolymers in sodium form exhibit only one weight loss step, but copolymers in acidic form exhibit a much earlier decomposition and two distinct transition steps. The first weight losses began

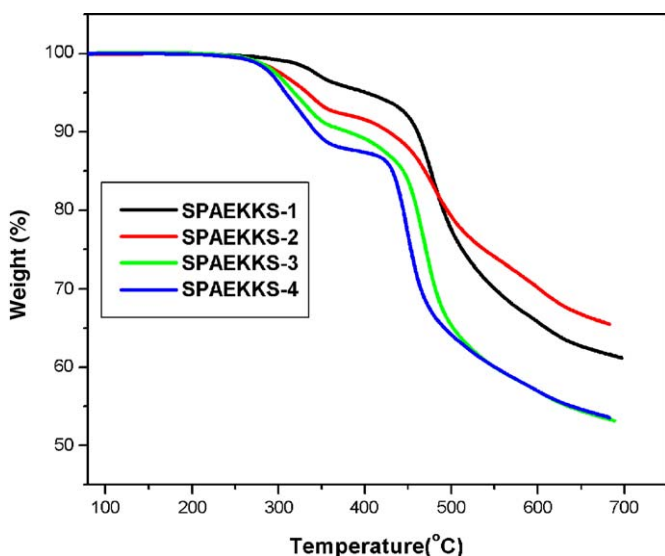


Fig. 3. TGA curves of all SPAEKKS copolymers in acidic form.

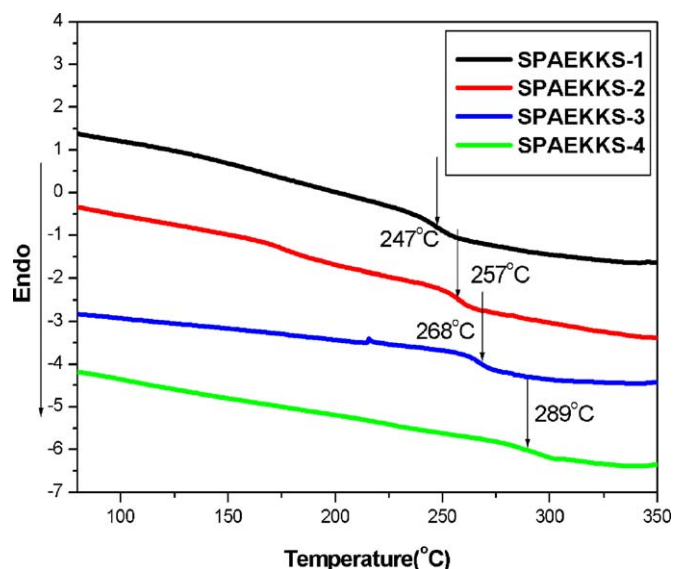


Fig. 4. Glass transition temperature (T_g) of SPAEKKS-1 to SPAEKKS-4.

at around 294 °C for the SPAEKKS-2 in acidic form and 403 °C for the SPAEKKS-2 in sodium form, which were mainly caused by the decomposition of $-\text{SO}_3\text{H}$ groups and $-\text{SO}_3\text{Na}$ groups, respectively. The second step thermal degradation of SPAEKKS-2 attributed to the decomposition of the copolymer main chain. It can be seen from above results that SPAEKKS copolymers in sodium form possess much higher thermal stabilities than the corresponding SPAEKKS in acidic form copolymers.

The glass transition temperatures (T_g) of the SPAEKKS copolymers in sodium and acidic forms were analyzed by DSC through heating the polymers from 50 to 350 °C at a rate of 10 °C min⁻¹. Fig. 4 shows that all samples are amorphous, and only one T_g is discernible on each curve. The obtained T_g s are listed in Table 2. T_g s of all SPAEKKS copolymers in sodium form are between 247 and 289 °C and acid form between 241 and 261 °C, respectively. It also can be seen that the T_g s of copolymers both in sodium form and acidic form showed an increase from SPAEKKS-1 to SPAEKKS-4, respectively. This was because that the introduction of sulfonate groups has two effects on glass transition temperature: firstly, pendant groups increased intermolecular interaction, i.e. ionomer effect; secondly, pendant groups increased molecular bulkiness. Both effects hinder internal rotation, which leads to increase glass transition temperatures of sulfonated copolymers.

3.2. SPAEKKS membranes properties

3.2.1. Morphology of membranes

The physical and electrochemical behaviors of SPAEKKS membranes are related to their internal structure. Eisenberg thought that sulfonated groups may aggregate into hydrophilic clusters, which can provide cation transport pathway or ionic transport channels [20]. In order to investigate the distribution of sulfonated groups in SPAEKKS membranes, in this paper, TEM analysis was performed by using Ag^+ to chelate with ionic groups. Fig. 5 shows the micrographs of SPAEKKS membranes,

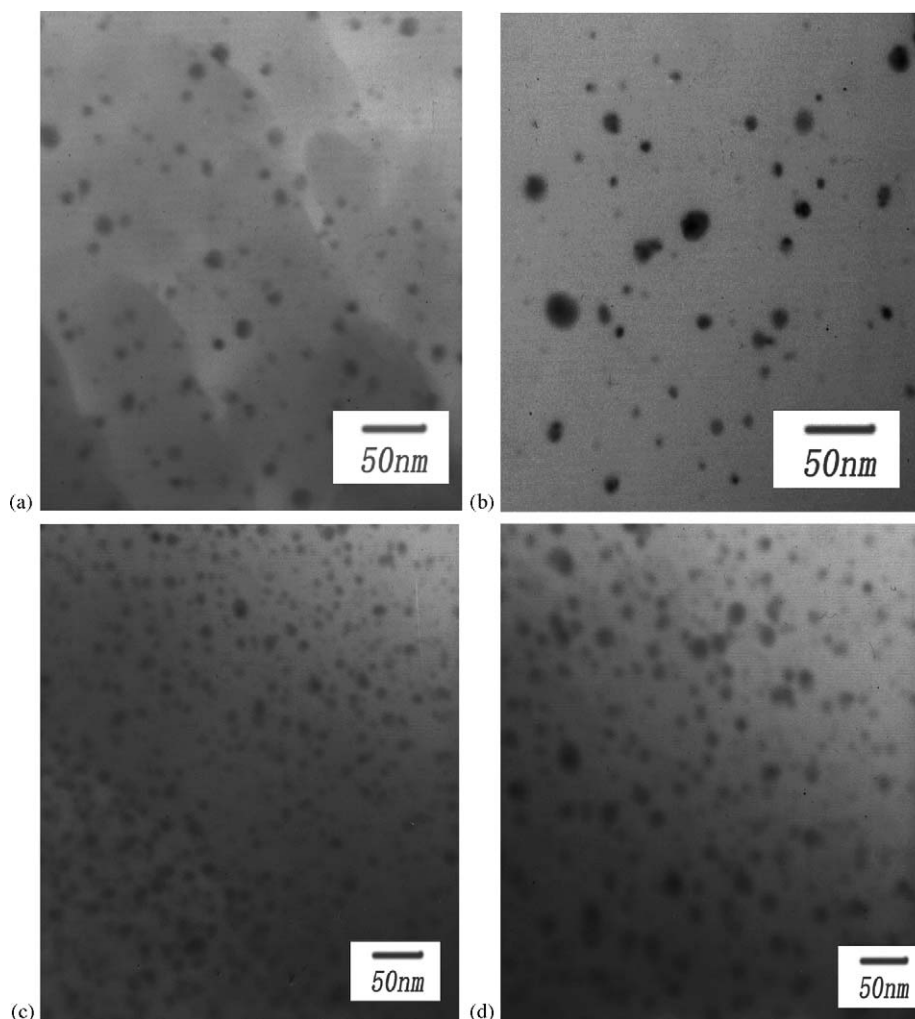


Fig. 5. The micrographs of SPAEKKS membranes.

it can be seen that silver particles in diameter 5–10 nm dispersing in the polymers matrix randomly. This may be explained that the dark regions represent hydrophilic (sulfonate groups) regions and the light regions refer to hydrophobic (polymer backbone) ones. The density and size of sulfonate groups in SPAEKKS membranes increase with an increment of D_s from SPAEKKS-1 to SPAEKKS-4 increasing. Eventually, it resulted in the formation of high density silver particles within the SPAEKKS matrix. So it is concluded that higher degree of sulfonation resulted in relatively large ion domain. This also explained the physical and electrochemical behaviors of SPAEKKS membranes, such

as water uptake, methanol permeability and proton conductivity, etc.

3.2.2. Water uptake, swelling ratio and water desorption

It is well known that water play a critical role in PEM. On the one hand, adequate water uptake is desired to maintain good proton conductivity; on the other hand, water uptake should be minimized to provide the membrane mechanical and dimensional stability. Nafion with low water retention at high temperatures resulting in conductivity falls is one of the drawbacks, which limited their further commercial application. Water uptake and

Table 3
The properties of membranes in acidic form

Polymer	Water uptake (%)		Swelling ratio (%)		Water diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
	25 °C	80 °C	25 °C	80 °C	
SPAEEKS-1	9	14	1.6	2.4	2.49×10^{-10}
SPAEEKS-2	13	19	2.1	3.0	1.12×10^{-9}
SPAEEKS-3	23	38	4.2	6.3	2.56×10^{-9}
SPAEEKS-4	32	46	5.8	8.2	5.75×10^{-9}

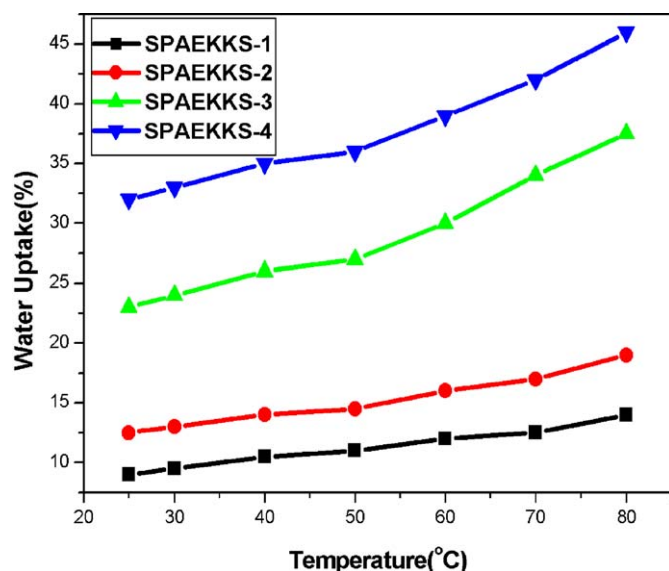


Fig. 6. Water uptakes of the SPAEKKS membranes at different temperatures.

swelling ratio of all membranes in acidic form were measured from 25 to 80 °C (see Table 3). Water uptakes and swelling ratios of all SPAEKKS membranes increased with the increment of D_s and temperature due to the strong hydrophilicity of the sulfonate groups. The water uptake of SPAEKKS membranes increased from 9% for SPAEKKS-1 to 32% for SPAEKKS-4 at 25 °C and 14% for SPAEKKS-1 to 46% for SPAEKKS-4 at 80 °C (Fig. 6).

Water retention of proton exchange membrane has significant effects on their proton conductivity and is also important from view of application in PEMFC. In this paper, water retention was analyzed by water desorptions at 80 °C. The desorption isotherm curves are shown in Fig. 7. The relationships between the water desorption and time may follow Fick diffusion. Plots of M_t/M_∞ versus $t^{1/2}$ initially were linear for Fick diffusion. Diffusion coefficients for desorption were determined from the initial slopes according to formula (5). From Table 3, it can be seen that the water diffusion coefficient of SPAEKKS membranes increases with the increment of D_s . It was related to different microstructures of SPAEKKS membranes. In Fig. 5, hydrophilic domains become larger and their density increased with increasing content of sulfonated groups, which cause the loosen structures of SPAEKKS membranes in high degree of sulfonation. This will make the water in membranes easily

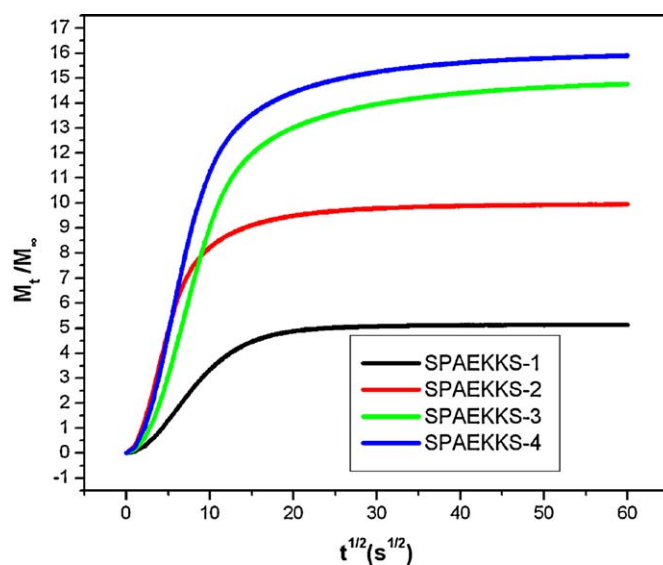


Fig. 7. Water desorption curves of SPAEKKS membranes at 80 °C.

evaporated and the diffusion coefficient of water in membrane increased with the increasing degree of sulfonation.

3.2.3. Ionic exchange capacity and proton conductivity

The IEC values of the SPAEKKS membrane determined by titration and calculation are shown in Table 4. IEC values of membranes were well controlled during synthesis by varying sulfonated monomers feed ratio, but IEC values were limited on the low end by proton conductivity and on the high end by dissolution or gross swelling in liquid water. In this paper, in order to avoid SPAEKKS membranes gross swelling in water, we synthesized SPAEKKS copolymers with relatively lower IEC values (from 0.30 to 1.22 mmol g⁻¹). From Table 4, it can be seen that the experiment IEC values are in good agreement with the calculated IEC values. Also IEC values increased with the D_s increasing. This is because all of the sulfonated monomers were incorporated into the copolymer without any side reactions.

Proton conductivity can be different in different measured approaches and instruments. In this paper, we have selected the Nafion-117 as a reference. Fig. 8 shows the relationship of the conductivity of SPAEKKS membrane with different degrees of sulfonation and temperatures. It can be seen that proton conductivity of membranes increases with D_s (or IEC) and temperature increasing. Although most proton conductivities

Table 4

The properties of membranes in acidic form

Polymer	d^a (μm)	IEC (mmol g ⁻¹)		Methanol diffusion (cm ² s ⁻¹)	Proton (S cm ⁻¹)	
		Calculated ^b	Measured ^c		25 °C	80 °C
SPAEEKS-1	80	0.37	0.30	8.32×10^{-9}	0.004	0.0056
SPAEEKS-2	90	0.78	0.71	6.28×10^{-8}	0.01	0.0158
SPAEEKS-3	80	1.06	0.98	1.72×10^{-7}	0.021	0.036
SPAEEKS-4	90	1.38	1.22	3.65×10^{-7}	0.032	0.044
Nafion-117	175		0.92	2×10^{-6}	0.046	0.050

^a Thickness of membranes.

^b IEC obtained by calculation from D_s .

^c IEC obtained by titration.

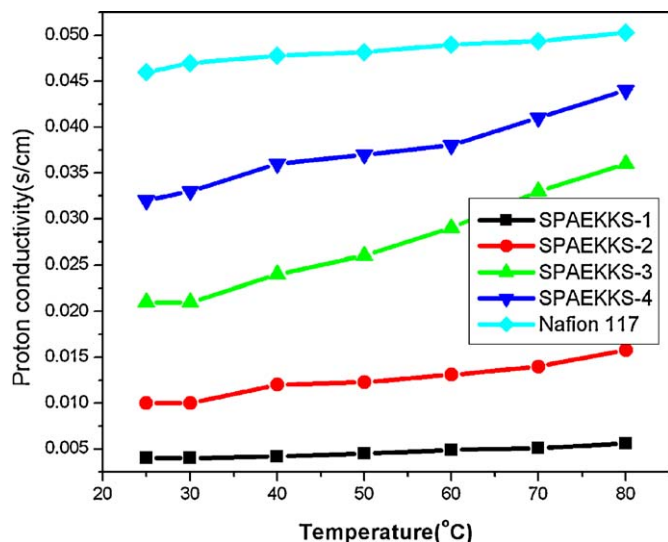


Fig. 8. Proton conductivities of the SPAEKKS membranes at different temperature.

of SPAEKKS membranes are higher than 0.01 S cm^{-1} at room temperature, proton conductivities of SPAEKKS membranes are relatively lower than that of Nafion-117 although IEC values of Nafion is only 0.91. This may be due to the sulfonated groups of SPAEKKS copolymers are dispersed throughout the copolymer matrix and not easily lead to phase separation [21]. While the sulfonate groups of Nafion-117 are on the side chains of polymers, which may easily form phase separation. And sulfonate groups may provide much larger transport channel than SPAEKKS. Therefore, proton conductivity of Nafion is higher than that of SPAEKKS membrane.

4. Conclusions

A series of sulfonated poly(arylene ether ketone ketone sulfone) (SPAEKKS) copolymers were synthesized by nucleophilic polycondensation. The degree of sulfonation of copolymers can be controlled by varying the feed ratios of sulfonated monomer to unsulfonated monomer. The SPAEKKS copolymers show good thermal stability and can be cast into

tough membranes. Water uptake and proton conductivity of SPAEKKS membrane increased with the increment of D_s , IEC and temperature. Microstructures of membranes were investigated by TEM. SPAEKKS-4 membranes reach equilibrium between water uptake and proton conductivity. Methanol diffusion coefficients of all SPAEKKS membranes are lower than that of Nafion-117. The SPAEKKS membranes show very good prospects in proton exchange membranes fuel cell usages.

References

- [1] W.L. Harrison, M.A. Hickner, Y.S. Kim, J.E. McGrath, *Fuel Cells* 5 (2005) 201.
- [2] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, *Chem. Rev.* 104 (2004) 4587.
- [3] M.A. Hickner, B.S. Pivovar, *Fuel Cells* 5 (2005) 213.
- [4] F. Wang, J.K. Li, T.L. Chen, J.P. Xu, *Polymer* 40 (1999) 795.
- [5] F. Wang, M.A. Hickner, Q. Ji, W.L. Harrison, J.F. Mecham, T.A. Zawodzinski, J.E. McGrath, *Macromol. Symp.* 175 (2001) 387.
- [6] J.J. Dumais, A.L. Cholli, L.W. Jelinski, J.E. McGrath, *Macromolecules* 19 (1986) 1884.
- [7] Y.S. Kim, L. Dong, M.A. Hickner, B.S. Pivovar, J.E. McGrath, *Polymer* 44 (2002) 5729.
- [8] X.F. Li, Z. Wang, H. Lu, C.J. Zhao, H. Na, *J. Membr. Sci.* 254 (2005) 147.
- [9] X.F. Li, C.J. Zhao, H. Lu, Z. Wang, H. Na, *Polymer* 46 (2005) 5820.
- [10] X.F. Li, C.P. Liu, H. Lu, C.J. Zhao, Z. Wang, H. Na, *J. Membr. Sci.* 255 (2005) 149.
- [11] X. Glipa, M.E. Haddad, D.J. Jones, J. Roziere, *Solid State Ionics* 97 (1997) 323.
- [12] P. Staiti, A.S. Arico, E. Passalacqua, V. Antonucci, *J. Membr. Sci.* 188 (2001) 71.
- [13] X.X. Guo, J.H. Fang, T. Watari, K. Tanaka, H. Kita, K.I. Okamoto, *Macromolecules* 35 (2002) 6707.
- [14] J.H. Fang, X.X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K.I. Okamoto, *Macromolecules* 35 (2002) 9022.
- [15] Z. Wang, X.F. Li, C.J. Zhao, H. Na, et al., *Ect. Chem. J. Chin. U* 26 (2005) 2149.
- [16] J.A. Kerres, *J. Membr. Sci.* 185 (2001) 3.
- [17] T. Watari, H.Y. Wang, K. Kuwahara, K. Tanaka, H. Kita, K. Okamoto, *J. Membr. Sci.* 219 (2003) 137.
- [18] B. Jung, B.Y. Kim, J.M. Yang, *J. Membr. Sci.* 245 (2004) 61.
- [19] F. Wang, M.A. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, *J. Membr. Sci.* 197 (2002) 231.
- [20] A. Eisenberg, *Macromolecules* 3 (1970) 147.
- [21] H.B. Zhang, J.H. Pang, D. Wang, A.Z. Li, X.F. Li, Z.H. Jiang, *J. Membr. Sci.* 264 (2005) 56.