

Synthesis and Characterization of Sulfonated Poly(ether sulfone ether ketone ketone) for Proton Exchange Membranes

Weihua Zhou,¹ Jichun Xiao,¹ Yiwang Chen,^{1,2} Rong Zeng,¹ Shuqin Xiao,¹ Xiaohui He,¹ Fan Li,¹ Caisheng Song³

¹Institute of Polymers/Institute for Advanced Study, Nanchang University, Xuefu Road 999, Nanchang 330031, People's Republic of China

²Department of Chemistry, Nanchang University, Xuefu Road 999, Nanchang 330031, People's Republic of China

³Department of Chemistry, Jiangxi Normal University, Ziyang Road 99, Nanchang 330027, People's Republic of China

Received 8 September 2009; accepted 13 December 2009

DOI 10.1002/app.32000

Published online 29 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of sulfonated poly(ether sulfone ether ketone ketone) (SPESEKK) with different degree of sulfonation (DS) are prepared by the postsulfonation of PESEKK using chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent. The chemical structures of the polymers are analyzed by the proton nuclear magnetic resonance. The thermal properties of the SPESEKK show that they are greatly influenced by the DS value and sulfonation time. The water uptake, proton conductivity, and Ion exchange capacity values increase as the sulfona-

tion time increasing. The methanol permeability of the SPESEKK in the range of 7.02×10^{-8} to $4.477 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, is one or two orders of magnitude lower than that of Nafion 115. The morphology of the SPESEKK membranes is investigated by scanning electron microscope. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1436–1445, 2010

Key words: compatibilization; blend; montmorillonite; poly(ethylene terephthalate); poly(methyl methacrylate); nonisothermal crystallization temperature

INTRODUCTION

Proton exchange membrane fuel cells and direct methanol fuel cells (DMFCs) are promising alternative energy devices capable of producing high current densities with high energy conversion efficiency, which make these systems viable for a wide range of portable and mobile applications such as portable, stationary, and automotive applications.^{1–3} The proton exchange membrane (PEM) is a key component in the system, which acts as an electrolyte for protons transferring as well as provides a barrier to the passage of electrons between the electrodes. Commercial perfluorosulfonic acid membranes such as Nafion® are the most commonly used PEMs, due to their superior chemical and electrochemical stability,

as well as high proton conductivity.⁴ However, their critical drawbacks of high cost, high methanol crossover, relatively low operation temperature (<90°C) limit their further wide applications.⁵

In view of this, there has been considerable effort focusing on the development of alternative, low-cost, high-temperature, and polymer-based electrolytical membranes. Due to their low cost, low methanol permeability, high chemical and thermal stability, and easier processing, sulfonated aromatic hydrocarbon polymers have been investigated extensively as promising alternative PEM materials. Some main examples include sulfonated polyimide,^{6–12} sulfonated polybenzimidazole,^{13–16} sulfonated poly(arylene ether sulfone),^{17–22} sulfonated poly(aryl ether ketone)s (SPAEEKs),^{23–27} and so on.

Among them, sulfonated SPAEEKs is one of the most promising for its low cost, the large commercial availability and its easy processability. Preparation of SPAEEKs can be accomplished by either postsulfonation of poly(aryl ether ketone)s or direct polymerization of sulfonated monomers.^{23–27} The sulfonation of poly(arylene ether ketone)s (PAEEKs) can be performed by reacting them with acids such as chlorosulfonic acid, trimethylsilyl chlorosulfonate, sulfur trioxide, and the sulfur trioxide-triethyl phosphate complex.^{28–35} The choice of sulfonating agent is

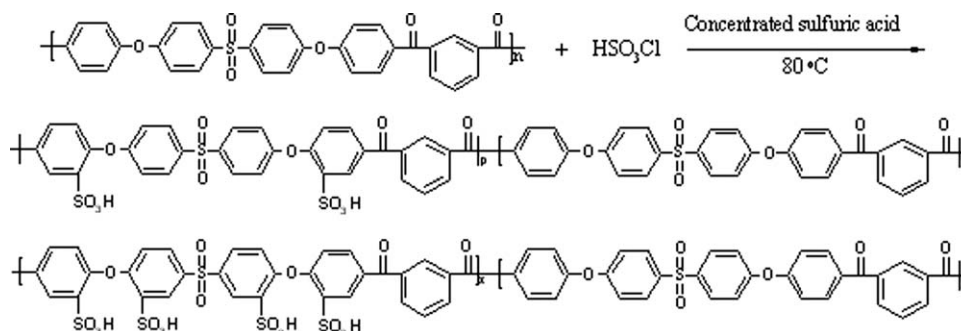
Correspondence to: W. Zhou (dramzwh@126.com) or Y. Chen (ywchen@ncu.edu.cn).

Contract grant sponsor: The Program for Innovative Research Team of Nanchang University.

Contract grant sponsor: The Program for Innovative Research Team in University of Jiangxi Province.

Contract grant sponsor: The Program for Changjiang Scholars and Innovative Research Team in University; contract grant number: IRT0730.

Journal of Applied Polymer Science, Vol. 117, 1436–1445 (2010)
© 2010 Wiley Periodicals, Inc.



Scheme 1 Synthetic procedures of sulfonated PESEKK.

dependent on the level of reactivity required and the need for exact control of the degree of sulfonation (DS). Sulfonation is an electrophilic substitution reaction, and its application will depend on the substituents present on the aromatic ring.³⁶ Furthermore, an evident trend in the design of novel PEM materials and thus the tailoring of properties is the control of polymer architecture, including the number and position of sulfonic acid groups as well as the morphology.

Poly(ether sulfone ether ketone ketone) (PESEKK) is a new member in the family of poly(aryl ether ketone)s, possessing excellent thermal stability and oxidative resistance.³⁷ It was prepared by low temperature solution polycondensation of 4,4'-bis(phenoxy)diphenyl sulfone (DPODPS) and isophthaloyl chloride (IPC), in 1,2-dichloroethane and in the presence of aluminum chloride (AlCl₃) and *N*-methylpyrrolidone (NMP). The electrophilic route is used to synthesize PESEKK because the monomers used are more selective, cheaper, and easily attained in contrast to the nucleophilic route. As far as we know, no literature based on sulfonated poly(ether sulfone ether ketone ketone) (SPESEKK) synthesized by the electrophilic route and used as a PEM material has been reported.

In this article, the SPESEKK samples were successfully prepared with DS between 0.38 and 0.62 using chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent (Scheme 1). The SPESEKK was fabricated into membranes using DMF as casting solvent. The properties of SPESEKK membranes including water uptake, proton conductivity and methanol permeability were investigated to understand the relationship between the membrane structures and properties.

EXPERIMENTAL

Materials

Isophthaloyl chloride (IPC) was purchased from Shuanglin Chemical Co. of China and was purified by distillation under vacuum to give m.p. 43–44°C. Ethylene dichloride was purchased from Tianjin

Damao Chemical Reagent Factory of China and was purified by distillation and dried over 0.5 nm molecular sieve. NMP of C.P. was purchased from Sino-pharm Chemical Reagent Co., and was purified by distillation and dried over a 0.5 nm molecular sieve. Concentrated sulfuric acid (98%) (H₂SO₄), chlorosulfonic acid, and anhydrous aluminum chloride (AlCl₃) were purchased from Tianjin Damao Chemical Reagent Factory of China, and were used as received without further purification. DPODPS was synthesized according to the literature.³⁷

Synthesis of PESEKK

The PESEKK was synthesized as following procedures. The anhydrous aluminum chloride (18 g) was stirred in ethylene dichloride (60 mL) with the addition of the mixtures of NMP (6 mL) and ethylene dichloride (60 mL) at 0°C. The temperature was controlled by the ice/water bath. Then, the DPODPS (8.04 g) and IPC (4.06 g) were added at –15°C, and the reaction mixture was stirred at room temperature for 8 h, followed by the addition of several drops of diphenyl ether. The reaction temperature of –15°C was maintained by the ice/salt bath composing of 100 g ice and 50 g NaNO₃. The mixtures were reacted at low temperatures to avoid the side reactions. Finally, the methanol (100 mL) was added dropwise into the reaction mixture after 2 h to terminate the reaction. The residual solvents such as ethylene dichloride was evaporated using the rotary evaporators, followed by the treatment of HCl acid, ammonia solution and distilled water to remove the AlCl₃ catalysts. After repeating for three times, the residue was extracted by methanol to remove the residual monomers and polymers with low molecular weights. The received polymer was dried at 100°C in vacuum overnight before sulfonation.

Sulfonation of PESEKK

The PESEKK (0.5 g, 0.9 mmol) dissolved in a three-neck flask containing 30 mL of concentrated H₂SO₄ under nitrogen and vigorous stirring for 1 h. After

the formation of a homogeneous solution, the flask was placed in an 80°C oil bath for 10 min. Then, chlorosulfonic acid (4 mL, 56 mmol) was gradually dropped into the solution under vigorous stirring. After reacting for 3–10 h, the mixture was precipitated into a large excess of ice-cold deionized water. The polymer precipitate was filtered and then washed with deionized water until the filtration was neutral. The received SPESEKK was then dried at 80°C under vacuum for 24 h.

Membrane preparation

Membranes were prepared from casting solution containing PESEKK or SPESEKK in DMF at 7 wt %. The solution was cast onto a glass sheet and was then dried in an oven at 100°C for 24 h. Consequently, the transparent membranes with the thickness of 40–60 μm were obtained.

Water uptake

Water uptake was determined by the vacuum dried membrane and fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with an absorbent tissue to remove the excess of water, and the sample was then weighed. The water uptake of the membrane was calculated from:

$$\text{Water uptake (\%)} = (W_s - W_d)/W_d \times 100\% \quad (1)$$

where W_d and W_s are the weights of dried and wet membranes, respectively.

Ion exchange capacity

Ion exchange capacity (IEC) of the membranes was measured by the classical titration method. The SPESEKK membranes were soaked in 1.5M NaCl solution for at least 72 h before measuring IEC. The protons released due to the exchange reaction with Na ions were titrated with 0.005M standardized NaOH solution, using phenolphthalein as an indicator. The IEC of the SPESEKK membranes was calculated from the following equation:

$$\text{IEC} = \frac{V(\text{NaOH}) \times C(\text{NaOH})}{M(\text{membrane})} \quad (2)$$

where $V(\text{NaOH})$ is the volume (mL) of NaOH solution consumed, $C(\text{NaOH})$ is the normality of NaOH solution, and $M(\text{membrane})$ is the weight of the SPESEKK membranes.

Proton conductivity

The proton conductivities (δ) of the SPESEKK membranes at different temperatures were evaluated using

three-electrode electrochemical impedance spectra. The impedance measurements were carried out on a CHI660 electrochemical workstation (CH Instruments) coupled with a computer. An organic glass diffusion cell composed of two symmetrical chambers was divided by a membrane sample. The cell were filled with the electrolyte composed of methanol (1 M) and sulfuric acid (0.5 M). The two platinum wires using as working electrode and counter electrode, as well as a calomel electrode functionalized as the reference electrode were introduced into the electrolyte solution. The impedance spectra were recorded with the help of ZPlot/ZView software under an ac perturbation signal of 5 mV over the frequency range of 0.1 MHz to 1 Hz. The proton resistance of the system (without membrane divided) was measured as R_1 , and the proton resistance of the system (with membrane divided) was measured as R_2 . Proton resistance of membrane under variable temperature (15–50°C) at 100% humidity were obtained as the dispersion of R_2 and R_1 . The proton conductivity δ of the membrane was calculated from the following equation:

$$\delta = I/(RA) \quad (3)$$

where δ , I , R , and A represent the proton conductivity, thickness of membranes, the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

Methanol permeability

An organic glass diffusion cell was used to obtain the methanol permeability of the PESEKK and SPESEKK membranes. The diffusion cell was composed of two chambers divided by a membrane sample. One chamber of the cell (V_1) was filled with a 5 M (C_1) methanol solution in distilled water. The other chamber (V_2) was filled with water. A sample (effective area 0.385 cm²) was clamped between the two chambers. Methanol permeates across the membrane by the concentration difference between the two chambers. The methanol concentration in the receiving chamber as a function of time is given by:

$$C_2(t) = [ADK C_1(t - t_0)]/(V_2 l) \quad (4)$$

where A (cm²) is the membrane area, l (cm) is the membrane thickness, D is the methanol diffusivity, and K is the partition coefficient between the membrane and the adjacent solution. The product DK means the membrane permeability (P):

$$P = (C_2(t)V_2 l)/[A C_1(t - t_0)] \quad (5)$$

C_2 is measured several times during the permeation experiment, and the methanol permeability is

obtained from the slope of the straight line. The methanol concentration was measured by using a gas chromatography of Agilent GC 6820 equipped with a FID detector.

Characterization

The proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded on a Bruker ARX 400 NMR spectrometer with dimethyl sulfoxide-*d* as solvent and tetramethylsilane ($\delta = 0$) as internal reference. The thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer instruments TGA 7 at a heating rate of $20^\circ\text{C min}^{-1}$ under a nitrogen atmosphere (50 mL min^{-1}). Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer instruments DSC 7 at a constant heating or cooling rate of $10^\circ\text{C min}^{-1}$ from -50 to 280°C under nitrogen protection. The samples were first heated rapidly to 280°C and were maintained for 3 min to erase the thermal history. The corresponding cooling and second heating curves were recorded. The morphology of the PESEKK and SPESEKK membranes were investigated by scanning electron microscope (SEM), using a JEOL JSM-6700F electron microscope. All the samples were soaked in the liquid nitrogen and fractured, followed by mounting on an aluminum alloy stub and sputtering with a thin layer of platinum. The cross-section was then observed by the SEM performing at an accelerating voltage of 5 kV.

RESULTS AND DISCUSSIONS

Structure analysis

The PESEKK³⁷ was synthesized by the low temperature solution polycondensation of DPODPS and IPC in 1,2-dichloroethane and in the presence of aluminum chloride (AlCl_3) and NMP. It is noted that the PESEKK was synthesized according to the electrophilic route because the monomers are more selective, cheaper, and easily attained as compared with the nucleophilic route. The structure of the received PESEKK was characterized by $^1\text{H-NMR}$.

Sulfonation of PAEKs was an electrophilic substitution reaction in which the sulfonic groups were introduced into the hydroquinone segment of the polymer chain activated for electrophilic substitution by the ether linkage. The other two phenyl rings connected through the ether linkages were therefore deactivated for electrophilic sulfonation by the electron-withdrawing effect of the carbonyl group. In related PAEKs, oxy-phenylene-carbonyl units of poly(ether ketone) (PEK) and poly(ether ketone ether ketone) (PEKEKK) were substituted by sulfonic groups³⁸ when strong sulfonation conditions

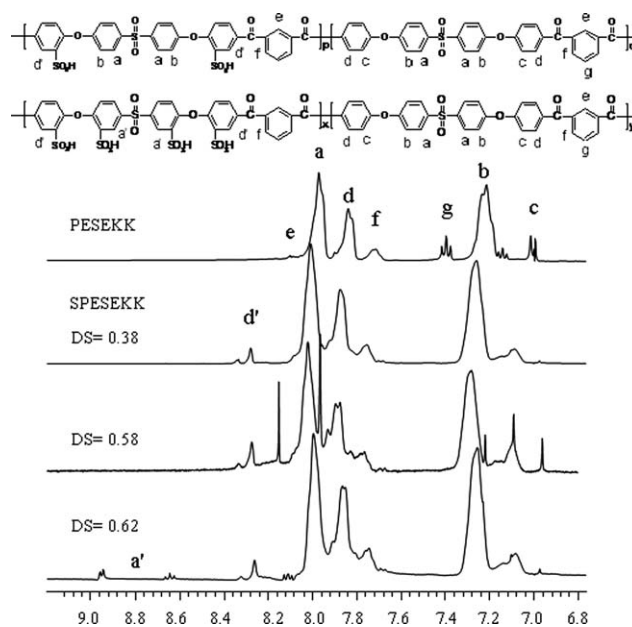


Figure 1 $^1\text{H-NMR}$ spectra of PESEKK and SPESEKKs with different DS.

were employed. Dai et al.¹⁸ prepared SPES samples with DS between 0.15 and 0.50 using chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent by homogeneous sulfonation of poly(ether sulfone). In this article, due to the existence of large amount of electro-withdrawing segment of the carbonyl groups and sulfone groups in the main chain of PESEKK, the phenyl rings were heavily deactivated. The usage of concentrated sulfuric acid as well as the relatively high temperature of 100°C led to the formation of SPESEKK samples with DS values lower than 10%. Therefore, the chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent were applied in this article, and a series of SPESEKK samples with different DS were prepared simply by alternating the sulfonating time. The synthetic procedure of SPESEKK is illustrated in Scheme 1.

The sulfonation level is commonly expressed using DS and IEC, where DS is defined as the average number of sulfonated groups per repeat unit and IEC (m eq g^{-1}) indicates the number of milliequivalents of ions in 1 g of dry polymer. The DS was calculated from $^1\text{H-NMR}$ spectroscopy using a variation of the method described in literature for sulfonated poly(ether ether ketone) (SPEEK) polymers.³⁹ Figure 1 shows the $^1\text{H-NMR}$ spectroscopy of PESEKK and the SPESEKK polymers with different degree of sulfonation. All the proton signals were unambiguously assigned from the NMR spectra. As expected, the resonance signals of the ortho sulfonyl and carbonyl protons appear at higher frequencies than those of the electron-rich protons such as the ortho-ether linkage, because of deshielding from the

TABLE I
DS and IEC Values of SPESEKK Membranes

Samples	Sulfonation time (h)	Degree of sulfonation		Ion exchange capacity (m eq g ⁻¹)	
		¹ H-NMR	Titration	¹ H-NMR	Titration
SPESEKK	3	0.38	0.36	0.68	0.61
	6	0.55	0.52	0.95	0.91
	8	0.58	0.55	1.01	0.95
	10	0.62	0.58	1.06	1.01

sulfonyl or carbonyl groups. The disappearance of resonance peaks at 7.40 ppm (g), as well as the appearance of new peaks at 8.26 ppm (d') confirmed that the sulfonic groups were introduced onto the phenyl rings connected by the ether linkage. Furthermore, the new peaks were observed at 8.64 and 8.94 ppm (a'), attributable to the protons in the phenyl rings connected to sulfonyl groups after the introduction of sulfonic acid groups. The relative intensity of the peaks at 7.04 ppm (c) decreased as compared with the pristine PESEKK due to the electrophilic substitution. In our experiment, the content of sulfonation reagent is higher than the SPESEKK content in molar ratio, and a number of sulfonic acid groups in a repeat unit are more reasonable. For the PESEKK, the integral ratio of "b" to "a" is 1 : 1. After sulfonation, the sulfonic acid groups were introduced onto the phenyl rings. However, the integral ratio of "b" to "a" remains constant as the DS value is lower than 0.58. When the DS value is as high as 0.62, part of the b protons is substituted by the sulfonic acid groups, showing a decrease of the integral ratio of "b" to "a". The ratio is calculated to be about 0.88. The results indicate that the protons on the phenyl rings linked to carbonyl groups are more easily substituted than those to sulfonyl groups by the sulfonic acid groups.

The area of peak at $\delta = 8.26$ ppm could be used for estimation of the proton d' content which is equivalent to the $-\text{SO}_3\text{H}$ group concentration or the degree of sulfonation per repeat unit. The DS can be calculated by the following equation:

$$\frac{\text{DS}}{20 - 2\text{DS}} = \frac{A_{d'}}{\sum A_x} \quad (6)$$

where the $A_{d'}$ represents the integrated area of the proton d', and the $\sum A_x$ represents the peak area of the signals corresponding to the other aromatic hydrogens.

In general, the degree of sulfonation was readily controlled by varying the sulfonation time. It is observed that the sulfonation occurred at the ortho-ether sites of ether ketone segment as the sulfonation time was less than 8 h. However, sulfonic acid groups were incorporated into the ortho-ether sites

of ether sulfone segment as the sulfonation time increased to 10 h. The appearance of new signals at 8.64 and 8.94 ppm (a') confirmed the sulfonation at ortho-ether sites of ether sulfone segment, and the DS could be calculated by the following equation:

$$\frac{\text{DS}}{20 - 2\text{DS}} = \frac{A_{d'} + A_{a'}}{\sum A_x} \quad (7)$$

where the $A_{a'}$ represents the integrated area of the proton a', the $A_{d'}$ represents the integrated area of the proton d', and the $\sum A_x$ represents the peak area of the signals corresponding to the other aromatic hydrogen.

The DS can be also calculated from the corresponding IEC value of SPESEKK membranes using the following equation:

$$\text{DS} = \frac{532 \times \text{IEC}}{1000 - 81 \times \text{IEC}} \quad (8)$$

where DS is defined as the average number of sulfonated groups per repeat unit, and IEC indicates the number of milli-equivalents of ions in 1 g of dry polymer. The molecular weight of PESEKK repeat unit is 532, and the molecular weight of the $-\text{SO}_3\text{H}$ group is 81. The DS values are listed in Table I, showing that the values obtained by the ¹H-NMR analysis, and the titration method are consistent with each other. The IEC and DS values slightly increase as the sulfonation time increasing based on the ¹H-NMR results. It is suggested that the above equation could be used to the determination of the relative content of sulfonic groups introduced into the polymer chain. Furthermore, the IEC values obtained by the titration method are similar to those calculated by the ¹H-NMR analysis.

Thermal analysis

Figure 2 shows the TGA curves for PESEKK and SPESEKK samples. It is noted that the pristine PESEKK exhibit two distinct steps. The first weight loss step is mainly associated with the loss of residual solvents in the range of 150–250°C. The second weight loss step is related to the decomposition of

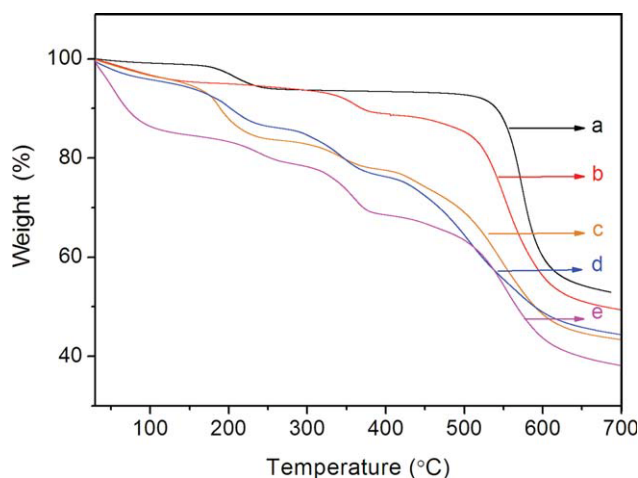


Figure 2 The TGA curves of (a) PESEKK and SPESEKKs with different DS of (b) 0.38, (c) 0.55, (d) 0.58, and (e) 0.62, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the main chain of PESEKK in the range of 500–650°C. In contrast, the sulfonated PESEKK samples present different degradation behaviors, showing an additional weight loss step in the range of 300–400°C, which is ascribed to the loss of the sulfonic groups. Furthermore, the main chain degradation temperature of SPESEKK is lower than that of PESEKK because of the catalytic degradation of polymer chain caused by the $-\text{SO}_3\text{H}$ groups. It is noted that the SPESEKK exhibits weight loss below 100°C due to the evaporation of water adsorbed by the sulfonic acid groups.

Figure 3 shows the DSC cooling and heating curves for PESEKK and SPESEKK, both of them show glass transitions. The PESEKK as well as the SPESEKK exhibits one single glass temperature (T_g), showing that no phase separation behavior occurred after the introduction of sulfonic groups into the main chain. It is further noticed that the T_g increases slightly and then decreases with the increase of DS values. The sulfonic groups tend to aggregate and restrict the mobility of the polymer chains, leading to the increase of T_g . The SPESEKK was obtained by the treatment of chlorosulfuric acid and concentrated sulfuric acid. After long time of sulfonation, the cleavage of polymer chain may happen, resulting in the reduction of the molecular weight. Though more content of sulfonic groups were introduced into the polymer chain, the reduction of the molecular weight eventually led to the decrease of T_g . The reduction of the molecular weight could be reflected by the decrease of the viscosity of the polymer in solution as determined by the Ubbelodde viscometer at 30°C. The inherent viscosity η_{inh} of PESEKK is 1.16, which is much higher than the critical η_{inh} value (about 0.6) of the polymer. The SPESEKK

show lower inherent viscosity η_{inh} in comparison with pristine PESEKK, which is probably due to the degradation of the polymer main chains by the treatment in sulfuric acid and chlorosulfuric acid.

Water uptake, proton conductivity, and methanol permeability

Water uptake and swelling ratio of PEMs are closely related to IEC, proton conductivity, dimensional stability, and mechanical strength. The water within the membrane provides a carrier for the proton and maintains high proton conductivity. However, excessive water uptake in a PEM leads to unacceptable dimensional change or loss of dimensional shape, which could lead to weakness or dimensional mismatch when incorporated into a membrane electrode assembly. The water uptake of SPESEKK membranes were determined by measuring the changes in the mass. As shown in Table II, SPESEKK membranes

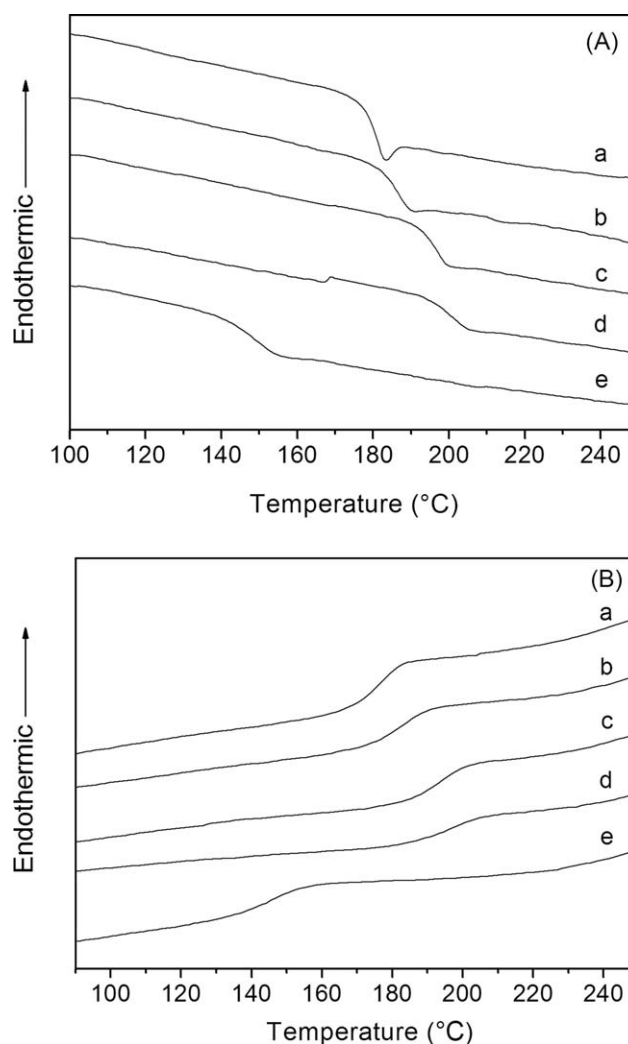


Figure 3 DSC (A) cooling and (B) heating curves for (a) PESEKK and SPESEKKs with different DS of (b) 0.38, (c) 0.55, (d) 0.58 and (e) 0.62, respectively.

TABLE II
Water Uptake, IEC, Proton Conductivity and Methanol Permeability of SPESEKK with Different DS

Membrane	DS	IEC ^a (m eq g ⁻¹)	Water uptake ^b (wt %)	Proton conductivity at 14°C (S cm ⁻¹)	Methanol permeability at 20°C (cm ² s ⁻¹) (×10 ⁻⁸)	Selectivity (Φ) 10 ⁶ S scm ⁻³
PESEKK		0	0	0	2.37	–
SPESEKK	0.38	0.61	8.5	9.57 × 10 ⁻⁵	7.02	1.36
	0.55	0.91	10.9	3.75 × 10 ⁻⁴	9.10	4.12
	0.58	0.95	14.3	2.98 × 10 ⁻³	11.49	25.93
	0.62	1.01	20.5	3.38 × 10 ⁻³	44.77	7.55
Nation115 ^c		0.88	32.6	1.81 × 10 ⁻²	239.90	7.54

^a IEC measured with titration at room temperature.

^b Measured at room temperature.

^c Measured under the same conditions as SPESEKK membranes.

exhibited water uptake in the range of 8.5–20.5%, depending on the sulfonation time. Furthermore, the water uptake value of SPESEKK is lower than that of Nafion 115 of 32.6%.

It is generally accepted that the IEC values depend on the content of sulfonic acid groups incorporated into the polymer, and, thus, they are indicative of the actual ion exchange sites available for proton conduction. High value of IEC is desirable to achieve higher proton conductivity in polymer electrolyte membranes. However, the continuous increase in the content of sulfonic acid group may result in the deterioration of mechanical properties of the membranes because of highly hydrophilic property of the polymer. Therefore, it is essential to control the amount of sulfonic acid groups. The IEC values of the pristine PESEKK and SPESEKK are also listed in Table II. The IEC values of SPESEKK increase from 0.61 to 1.01 m eq g⁻¹ as the sulfonation time increasing, in contrast to the value of 0.88 m eq g⁻¹ of Nafion 115. It is believed that the IEC value could be modulated simply by the control of the sulfonation time.

In general, for ionomeric membranes, the proton conductivity depends on the number of available acid groups and their dissociation capability in water, which is accompanied by generation of protons. The proton conductivities of SPESEKK membranes were measured after the membranes were initially hydrated by immersion in electrolyte composed of 1 M methanol and 0.5 M sulfuric acid at room temperature. It is accepted that the values of proton conductivity can be different depending on the experimental approaches, as well as the instruments. For comparison, Nafion 115 was chosen to measure the proton conductivity under the same conditions. Figure 4 shows the proton conductivity of the Nafion 115 and SPESEKK membranes with different DS as a function of temperature. At a given temperature, the proton conductivity of SPESEKK membranes increases with the increase of DS values. In addition, the values of proton conductivity

increase as the temperatures increasing. However, the Nafion 115 membranes exhibit the highest values of proton conductivity since it has long side chains and easily phase-separated to form ion channels. The proton conductivity of the SPESEKK was much lower than that of Nafion 115 due to the lower acidity of sulfonic acid on these aromatic carbon-hydrogen polymers.⁴⁰

Methanol permeability and proton conductivity are the two transport properties, which determine the fuel cell performance. Low methanol permeability and high proton conductivity are required for direct methanol fuel cells. The methanol permeability of the membranes is also presented in Table II. It is noticed that the methanol permeability of the PESEKK and SPESEKK membranes is in the range of 7.02 × 10⁻⁸ to 4.477 × 10⁻⁷ cm² s⁻¹, which is one or two orders of magnitude lower than that of Nafion 115. The methanol permeability increased with the increase of DS value, suggesting that the appropriate content of sulfonic groups determine the properties of the membranes. There is a strong

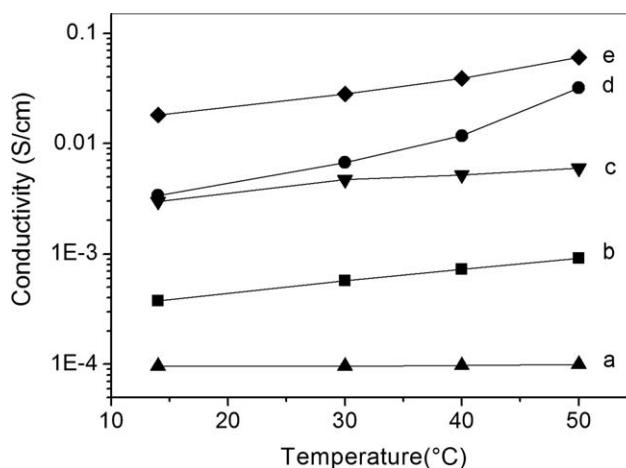


Figure 4 Proton conductivity of the SPESEKK membranes with different DS of (a) 0.38, (b) 0.55, (c) 0.58, (d) 0.62, and (e) Nafion 115 as a function of temperature.

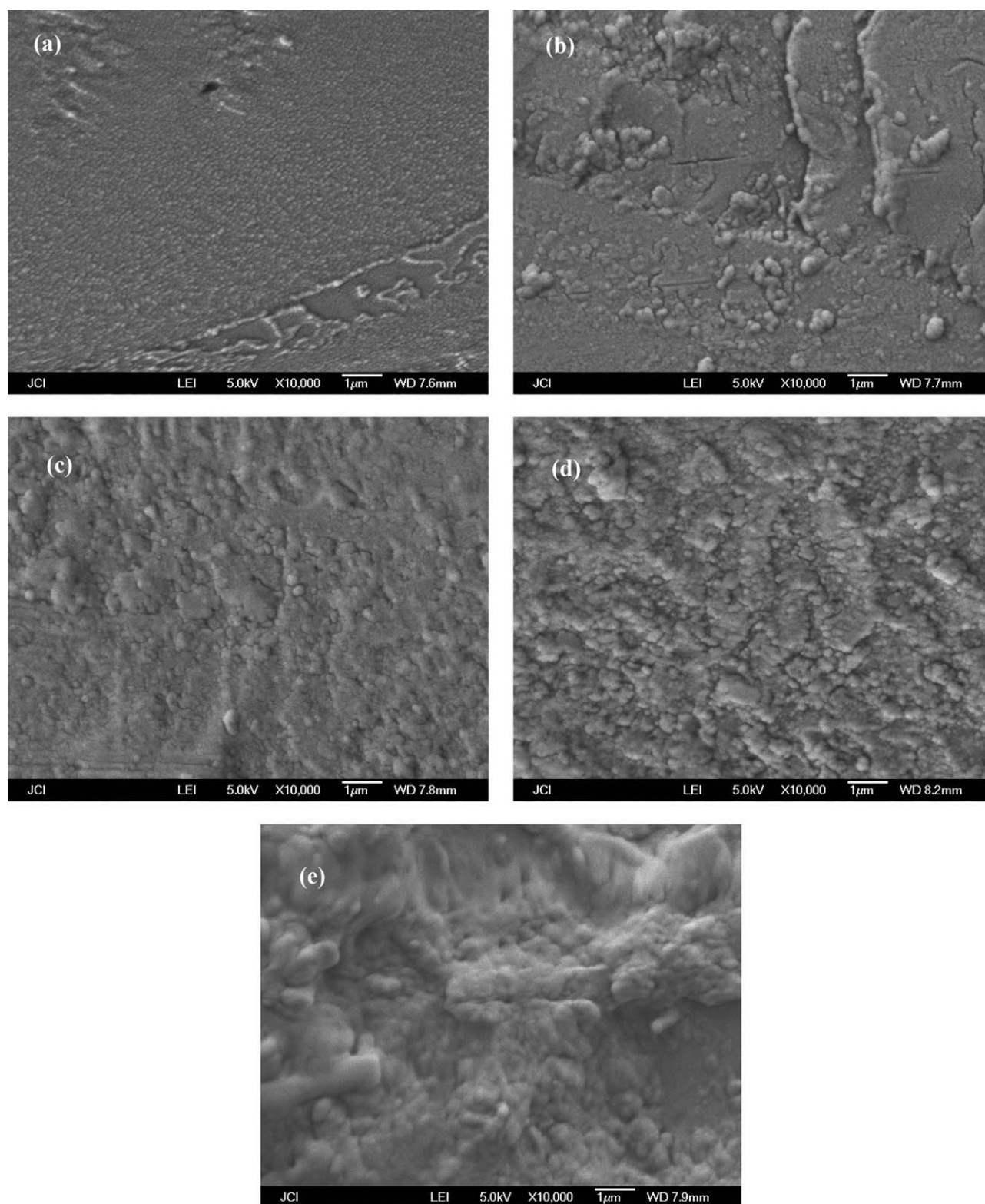


Figure 5 The cross-sectional SEM graphs of the (a) PESEKK membrane and SPESEKK membranes with different DS of (b) 0.38, (c) 0.55, (d) 0.58 and (e) 0.62, respectively.

tradeoff relationship between the proton conductivity and the methanol permeability when designing a new PEM for DMFC applications. The selectivity is defined by the ratio of proton conductivity to metha-

nol permeability measured at room temperature, which is a characteristic factor for evaluating membrane performances. In Table II, the selectivity of the SPESEKK first increases and then decreases as the

DS values increasing, in contrast to the selectivity of Nafion 115 of $7.54 \times 10^{-6} \text{ S scm}^{-3}$.

Morphology of the membranes

It is reported that the microphase separation comprised of hydrophilic regions and hydrophobic regions existed in the membranes of sulfonic containing polymers. The sulfonic acid groups tended to aggregate together to form ionic clusters. Generally, the ionic clusters were observed to be dark spots in the TEM analysis, as well as the dark area in atomic force microscopy (AFM) phase image.^{19,21,41} Figure 5 shows the SEM images of PESEKK and SPESEKK membranes. It is observed that the pristine PESEKK membranes exhibit the relatively smooth surface, and no obvious phase separation is observed. After the incorporation of sulfonic acid groups, bright spots are observed, and the amount of the bright spots increases as the content of sulfonic acid groups increasing. Due to the rigid backbone of SPESEKK polymers and the sulfonic acid groups incorporated into the main chain of the polymers, the sulfonic acid groups are difficult to aggregate into hydrophilic clusters, resulting in the relatively low value of proton conductivity in contrast to Nafion 115.

CONCLUSIONS

A series of SPESEKK with different DS values were prepared by the postsulfonation of PESEKK using chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent. The values of DS and IEC obtained by the titration method were consistent with the results calculated by the ¹H-NMR analysis, showing that both of the techniques are useful. The sulfonation made the SPESEKK membranes less thermally stable due to the degradation caused by the sulfonic acid groups. DSC results indicated that the glass transition temperatures were greatly influenced by the DS values and sulfonation time. The water uptake, proton conductivity, and IEC values increased as the DS values increasing, and they could be modulated by control of the sulfonation time. The proton conductivity of the SPESEKK was much lower than that of Nafion 115 due to the lower acidity of sulfonic acid on these aromatic carbon-hydrogen polymers. The methanol permeability of the SPESEKK in the range of 7.02×10^{-8} to $4.477 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, was one or two orders of magnitude lower than that of Nafion 115. The SPESEKK membranes could be potentially used as the PEMs, however, more research work is needed to improve the properties of the membranes. Anyway, the electrophilic route to synthesize the PESEKK exhibits superior advantages, because the monomers used are more selective, cheaper, and easily attained in contrast to the nucleophilic route.

References

- Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; Mcgrath, J. E. *Chem Rev* 2004, 104, 4587.
- Pereira, F.; Valle, K.; Belleville, P.; Morin, A.; Lambert, S.; Sanchez, C. *Chem Mater* 2008, 20, 1710.
- Xu, K.; Li, K.; Khanchaitit, P.; Wang, Q. *Chem Mater* 2007, 19, 5937.
- Mauritz, K. A.; Moore, R. B. *Chem Rev* 2004, 104, 4535.
- Li, Q. F.; He, R. H.; Jensen, J. O.; Bjerrum, N. J. *Chem Mater* 2003, 15, 4896.
- Li, W. M.; Cui, Z. M.; Zhou, X. C.; Zhang, S. B.; Dai, L.; Xing, W. *J Membr Sci* 2008, 315, 172.
- Lee, C. H.; Park, H. B.; Chung, Y. S.; Lee, Y. M.; Freeman, B. D. *Macromolecules* 2006, 39, 755.
- Yan, J. L.; Liu, C. P.; Wang, Z.; Xing, W.; Ding, M. X. *Polymer* 2007, 48, 6210.
- Hu, Z. X.; Yin, Y.; Kita, H.; Okamoto, K.; Suto, Y.; Wang, H.; Kawasato, H. *Polymer* 2007, 48, 1962.
- Zhang, F.; Li, N. W.; Cui, Z. M.; Zhang, S. B.; Li, S. H. *J Membr Sci* 2008, 314, 24.
- Bai, H.; Ho, W. S. W. *J Membr Sci* 2008, 313, 75.
- Guo, X. X.; Zhai, F. X.; Fang, J. H.; Laguna, M. F.; Lopez-Gonzalez, M.; Riande, E. *J Phys Chem B* 2007, 111, 13694.
- Peron, J.; Ruiz, E.; Jones, D. J.; Roziere, J. *J Membr Sci* 2008, 314, 247.
- Jouanneau, J.; Mercier, R.; Gonon, L.; Gebel, G. *Macromolecules* 2007, 40, 983.
- Li, N. W.; Zhang, S. B.; Liu, J.; Zhang, F. *Macromolecules* 2008, 41, 4165.
- Xu, H. J.; Chen, K. C.; Guo, X. X.; Fang, J. H.; Yin, J. *J Membr Sci* 2007, 288, 255.
- Grunzinger, S. J.; Watanabe, M.; Fukagawa, K.; Kikuchi, R.; Tominaga, Y.; Hayakawa, T.; Kakimoto, M. *J Power Sources* 2008, 175, 120.
- Dai, H.; Guan, R.; Li, C. H.; Liu, J. H. *Solid State Ionics* 2007, 178, 339.
- Lee, H. S.; Roy, A.; Lane, O.; Dunn, S.; Mcgrath, J. E. *Polymer* 2008, 49, 715.
- Bae, B.; Miyatake, K.; Watanabe, M. *J Membr Sci* 2008, 310, 110.
- Kim, D. S.; Robertson, G. P.; Guiver, M. D. *Macromolecules* 2008, 41, 2126.
- Pang, J. H.; Zhang, H. B.; Li, X. F.; Wang, L. F.; Liu, B. J.; Jiang, Z. H. *J Membr Sci* 2008, 318, 271.
- Zhao, C. J.; Li, X. F.; Lin, H. D.; Shao, K.; Na, H. *J Appl Polym Sci* 2008, 108, 671.
- Zhong, S. L.; Fu, T. Z.; Dou, Z. Y.; Zhao, C. J.; Na, H. *J Power Sources* 2006, 162, 51.
- Liu, B. J.; Kim, D. S.; Murphy, J.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S.; Kaliaguine, S.; Sun, Y. M.; Liu, Y. L.; Lai, J. Y. *J Membr Sci* 2006, 280, 54.
- Matsumura, S.; Hlil, A. R.; Du, N.; Lepiller, C.; Gaudet, J.; Guay, D.; Shi, Z. Q.; Holdcroft, S.; Hay, A. S. *J Polym Sci Part A: Polym Chem* 2008, 46, 3860.
- Matsumura, S.; Hlil, A. R.; Lepiller, C.; Gaudet, J.; Guay, D.; Shi, Z. Q.; Holdcroft, S.; Hay, A. S. *Macromolecules* 2008, 41, 281.
- Wang, L.; Meng, Y. Z.; Wang, S. J.; Hay, A. S. *J Polym Sci Part A: Polym Chem* 2004, 42, 1779.
- Jin, X.; Bishop, M. T.; Ellis, T. S.; Karasz, F. E. *Br Polym J* 1985, 17, 4.
- Bishop, M. T.; Karasz, F. E.; Russo, P. S.; Langley, K. H. *Macromolecules* 1985, 18, 86.
- Lee, J.; Marvel, C. S. *J Polym Sci Polym Chem Ed* 1984, 22, 295.
- Ogawa, T.; Marvel, C. S. *J Polym Sci Polym Chem Ed* 1985, 23, 1231.

33. Schauer, J.; Brozova, L. *J Membr Sci* 2005, 250, 151.
34. Bailly, C.; Williams, D. J.; Karasz, F. E.; Macknight, W. J. *Polymer* 1987, 28, 1009.
35. Huang, R. Y. M.; Shao, P.; Burns, C. M.; Feng, X. *J Appl Polym Sci* 2001, 82, 2651.
36. Jeong, M. H.; Lee, K. S.; Hong, Y. T.; Lee, J. S. *J Membr Sci* 2008, 314, 212.
37. Wen, H. L.; Song, C. S.; Tong, Y. F.; Chen, L.; Liu, X. L. *J Appl Polym Sci* 2005, 96, 489.
38. Xing, P. X.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Wang, K. P.; Kaliaguine, S. *J Membr Sci* 2004, 229, 95.
39. Guan, R.; Zou, H.; Lu, D. P.; Gong, C. L.; Liu, Y. F. *Eur Polym J* 2005, 41, 1554.
40. Gu, S.; He, G.; Wu, X.; Guo, Y.; Liu, H.; Peng, L.; Xiao, G. *J Membr Sci* 2008, 312, 48.
41. Einsla, M. L.; Kim, Y. S.; Hawley, M.; Lee, H. S.; Mcgrath, J. E.; Liu, B. J.; Guiver, M. D.; Pivovar, B. S. *Chem Mater* 2008, 20, 5636.