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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.memsci.2003.08.020>

Journal of Membrane Science, 227, 2003

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Sulfonation of poly(phthalazinones) with fuming sulfuric acid mixtures for proton exchange membrane materials[☆]

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Received 24 April 2003; accepted 7 August 2003

Abstract

As a novel class of proton exchange membrane (PEM) materials for use in fuel cells, sulfonated poly(phthalazinones) (SPPs), including sulfonated poly(phthalazinone ether sulfones) (SPPEs), sulfonated poly(phthalazinone ether ketones) (SPPEKs) and sulfonated poly(phthalazinone ether sulfone ketones) (SPPESKs), were prepared by modification of corresponding poly(phthalazinones) (PPs). Sulfonation reactions were conducted at room temperature using mixtures of 95–98% concentrated sulfuric acid and 27–33% fuming sulfuric acid with different acid ratios in order to get SPPs with degree of sulfonation (DS) in the desired range of 1.00–1.37. The presence of sulfonic acid groups in SPPs was confirmed by FT-IR analysis, and the DS and structures were characterized by NMR. The introduction of sulfonic groups into the polymer chains led to a decrease in the decomposition temperature. Membrane films were cast from SPPs solution in *N,N*-dimethylacetamide (DMAc). Water uptakes and swelling ratios of SPPs membrane films increased with DS and temperature. Proton conductivities of all SPPs increased with DS and temperature, reaching higher than 10^{-2} S cm⁻¹ at around DS 1.0.

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Keywords: Poly(phthalazinone); Sulfonation; Proton exchange membrane; Ionomer; Fuel cell

1. Introduction

In recent years, stimulated by the legislative pollution control in most industrialized countries, the development of fuel cells has become the focus of intense worldwide R&D activities. Among several

kinds of fuel cells, proton exchange membrane fuel cells (PEMFCs) is one of most efficient portable power sources convenient for vehicles and mobile electronic devices. As the central component of fuel cells, the proton exchange membranes (PEMs) are simultaneously an electrolyte for transportation of protons produced at the anode to the cathode as well as a separator between the fuel and oxygen, an insulator between the electrodes and a binder for the catalyst. In order to qualify for these applications, polymer electrolytes must combine a number of properties

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such as excellent chemical stability especially against attack of oxygen and strong acids and, high proton conductivity, suitable water uptake, resistance to fuel crossover and adequate mechanical properties. In order to favor the reaction kinetics and reduce platinum catalyst poisoning by residual CO in the fuel, the next generation of these types of fuel cells are expected to run at temperatures higher than the present operating temperatures (<80 °C). Correspondingly, the PEMs for use in fuel cells should also have sufficient long-term thermal stability. Although the present commercially used perfluorinated ionomer Nafion™ or Nafion™-like membranes assure high proton conductivity ($\sigma \geq 10^{-2} \text{ S cm}^{-1}$) and excellent durability under the fuel cell operating conditions, large-scale application is limited by the high cost of the membranes. Perfluorinated ionomer membranes also suffer from other serious drawbacks of high methanol permeation and dehydration at higher temperatures.

In order to develop cheaper alternatives to perfluorinated ionomer membranes, which may also be free from other disadvantages of these membranes, a number of routes have been described in literature [1–17]. The principal route is the introduction of sulfonic acid groups into high performance polymers such as poly(aryl ether ketones), poly(phenylene oxide), poly(phenylene sulfide), poly(aryl ether sulfone), and polybenzimidazole.

Poly(phthalazinones) (PPs) including poly(phthalazinone ether sulfone) (PPES), poly(phthalazinone ether ketone) (PPEK) and poly(phthalazinone ether sulfone ketone) (PPESK) are new high performance polymers currently under consideration for commercialization. Among other advantages this class of polymers is distinguished for excellent chemical and oxidative resistance, mechanical strength, high thermal stability and very high glass transition temperatures (295, 263 and 278 °C, respectively). The sulfonation reactions of PPESK, and the nanofiltration and ultrafiltration membrane properties have been studied [18–23] before. Recently we reported both the post-synthesis sulfonation of PPEK and the polymerization reaction of sulfonated monomers as well as the conductivity properties of polymer membrane films [24,25]. In the present investigation, we extend this work to include the preparation and comparative characterization of different sulfonated PPs (SPPs) and the preparation of PEMs from the sulfonated products.

2. Experimental

2.1. Materials

PPs were synthesized according to the procedure reported previously [18–21]. All other chemicals were obtained commercially from Aldrich as reagent grade and used as received.

2.2. Sulfonation reaction

In a typical small-scale experiment, 2 g PPES powder was added to a 40 ml mixture of 95–98% concentrated sulfuric acid and 27–33% fuming sulfuric acid under an argon atmosphere and the mixture was magnetically stirred at room temperature (23 °C) for a certain reaction time. The reported reaction time is the total time for polymer dissolution and reaction. After a determined reaction time, the reaction medium was poured onto crushed ice and the resulting precipitate was recovered by filtration, then washed with deionized water until the pH \sim 6–7.

For scaled-up reactions of 30–35 g polymers, an ice bath was needed initially to eliminate the heat released during dissolution. For example, an amount of 35 g PPES powder was added to a mixture of 200 ml 95–98% concentrated sulfuric acid and 180 ml 27–33% fuming sulfuric acid under an argon atmosphere and the mixture was magnetically stirred in an ice bath. About 0.5 h later, the ice bath was removed and the stirring was continued at room temperature (23 °C). ^1H NMR was used to trace the DSs. After a determined reaction time, the reaction medium was poured onto crushed ice and the resulting precipitate was recovered by filtration, washed with deionized water until the pH \sim 5–6.

2.3. Polymer analysis and viscosity measurement

Proton and carbon NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at a proton frequency of 399.951 MHz and a carbon frequency of 100.578 MHz. Tetramethylsilane was used as the internal standard chemical shift reference. IR spectra were measured on a Nicolet 520 Fourier transform spectrometer with film samples in air.

A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for

measuring the degradation temperatures (T_d). Polymer samples for TGA analysis were preheated to 150 °C at 10 °C min⁻¹ under nitrogen atmosphere, held isothermally for 60 min, equilibrated at 80 °C, then heated to 750 °C at 10 °C min⁻¹ for T_d measurement. Hence, the degradation data reported here were assumed to be in the absence of moisture.

Inherent viscosities were determined using an Ubbelohde viscometer for *N,N*-dimethylformamide (DMF) solutions of polymer with a concentration of 0.5 g dl⁻¹ at 30 °C.

2.4. Preparation of membrane films

An amount of 0.7 g sample was dissolved in 12 ml DMAc and filtered. The filtered solution was poured onto a glass plate and dried at 40 °C for about 2 days. Residual solvent was further evaporated at 120 °C under vacuum for 48 h, resulting in yellow membrane films.

2.5. Water uptake content measurement and swelling ratio

All polymer membranes used were vacuum dried at 120 °C before testing. The sample films were soaked in deionized water for different times at determined temperatures. Weights of dry and wet membranes were measured. The water uptake content was calculated by

$$\text{uptake content (\%)} = \frac{\omega_{\text{wet}} - \omega_{\text{dry}}}{\omega_{\text{dry}}} \times 100$$

where ω_{dry} and ω_{wet} are the masses of dried and wet samples, respectively. The swelling ratio was calculated from films 7–10 cm long by

$$\text{swelling ratio (\%)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100$$

where l_{dry} and l_{wet} are the lengths of dry and wet samples, respectively.

2.6. Conductivity

The proton conductivity was measured by alternating-current (ac) impedance spectroscopy over a frequency range of 1–10⁷ Hz with oscillating voltage 50–500 mV, using a system based on a Solartron 1260

gain phase analyzer. A sample with diameter 13 mm was placed in an open, temperature controlled cell, where it was clamped between two blocking stainless steel electrodes with a permanent pressure of about 3 kg cm⁻². Specimens were soaked in deionized water prior to the test. The conductivity (σ) of the samples in the transverse direction was calculated from the impedance data, using the relationship $\sigma = d/RS$, where d and S are the thickness and face area of the sample, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re (Z) axis.

3. Results and discussion

3.1. Sulfonation reaction

Sulfonation reaction is a frequently used means for polymer modification in order to improve their expected membrane properties such as better hydrophilicity, higher water flux, improved permeability and proton conductivity. In general, sulfonation of polymers can be conducted with several sulfonating agents, including concentrated sulfuric acid, fuming sulfuric acid, sulfur trioxide complexes, chlorosulfonic acid and acetyl sulfate, depending on the reactivity of the polymer. We initially attempted the sulfonation of PPES and PPEK in 95–98% concentrated sulfuric acid. However, the results listed in Table 1 show that only very low DSs were obtained for both SPPEs and SPPEK at 60 °C, even after a long reaction time. This was because of the low nucleophilicity of PPs. It was demonstrated, in an article published recently [24], that sulfonation occurred only at the *ortho*-ether sites of PPEK. Replacing a ketone with a more electron-withdrawing sulfone group will not have an effect on sulfonation sites; therefore it is expected that sulfonation of PPES occurs around the electron-donating ether linkage. In PP repeat units (as shown in Scheme 1), with the exception of ether linkages, all other groups attached to the aromatic rings contain more electron-withdrawing functionality, which decreases the electrophilic reactivity of the polymers. Since sulfonation reactions are also affected by the electrophilicity of the sulfonating agent, fuming sulfuric acid was chosen as a strong sulfonating agent for the preparation of high DS derivatives. As

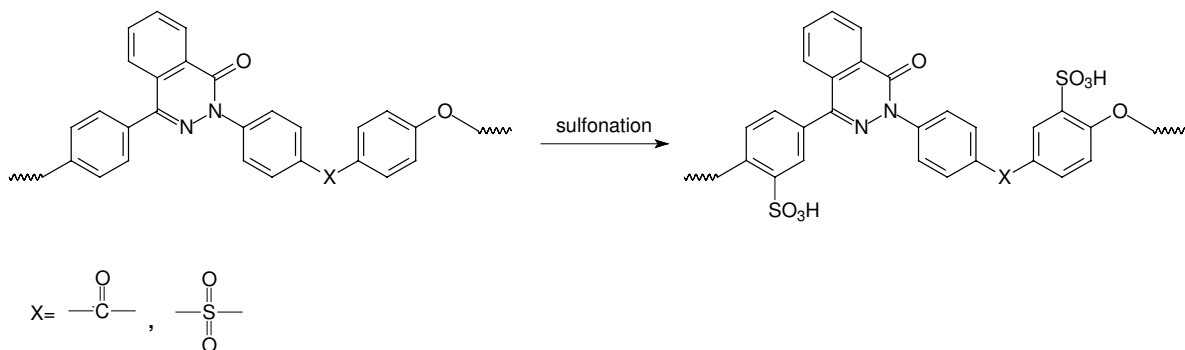
Table 1
Dependence of DS on the reaction conditions

Polymer	Polymer/oleum/concentrated sulfuric acid (g/ml/ml)	Reaction temperature (°C)	Reaction time (h)	DS	$[\eta]^a$ (dl g ⁻¹)
PPEK	0.5/0/10	RT	95	~0	
	0.5/0/10	60	6	<0.10	
	0.5/5/5	RT	7	0.92	
	0.5/6/4	RT	4	1.04	1.83
	0.5/7/3	RT	4	1.23	1.99
	0.5/10/0	RT	1	1.30	
	0.5/10/0	40	1	1.60	1.88
PPES	0.5/0/10	60	63	<0.10	
	2/24/16	RT	1.7	1.02	
	1/5/5.7	RT	8	0.97	2.08
	1/5/5	RT	7	1.21	1.76
	1/7/5	RT	3.5	1.37	1.64
PPESK	2/24/16	RT	2.5	1.07	1.90
	1/5/5	RT	7	1.20	2.00

^aDetermination conditions: SPPEK 0.5 g dl⁻¹ in DMF, 30 °C.

shown in Table 1, the sulfonation of PPEK in 27–33% oleum at 40 °C for 1 h resulted in SPPEK with a DS of 1.60, which is soluble in water and is therefore not suitable for use as a PEM in fuel cells. In order to moderate and maintain control of the sulfonation reaction and prepare SPPs with suitable DSs, the reactions were conducted in fuming sulfuric acid diluted with 95–98% sulfuric acid at room temperature, initially on the PPEK series. As seen in Table 1, by varying the ratio of concentrated sulfuric acid to fuming sulfuric acid and the reaction time, the sulfonation reaction was more readily controlled to obtain DSs such as 1.0 and 1.2. The same reaction conditions were also used to prepare SPPES and SPPEK with DS 1.0.

Comparing the reaction times, one can see that DS 1.0 was achieved in the shortest reaction time for SPPES, followed by SPPEK. These results show that PPEK has higher sulfonation reactivity than PPEK, which is surprising since sulfone groups have more electron-withdrawing ability than ketones. A possible explanation would be greater mobility at the sulfone linkage resulting in accelerated reaction rate. On the basis of higher reactivity of PPEK, more diluted mixtures of fuming sulfuric acid and higher polymer concentrations were tried in preparing SPPES and SPPEK of DS 1.2. The results listed in Table 1 show that both SPPES 1.21 and SPPEK 1.20 were obtained under more moderate reaction conditions than SPPEK



Scheme 1. Synthetic pathway for SPPs.

Table 2
Solubilities of PPs and SPPs

Polymer	DMF	DMAc	DMSO	NMP	CH ₂ Cl ₂	CHCl ₃	THF
PPES	±	+	+Δ	+	+	+	–
SPPEs 0.97	+	+	+	+	–	–	–
SPPEs 1.21	+	+	+	+	–	–	–
SPPEs 1.37	+	+	+	+	–	–	–
PPESK	±	+	+Δ	+	+	+	–
SPPEsK 1.07	+	+	+	+	–	–	–
SPPEsK 1.20	+	+	+	+	–	–	–
PPEK	±	±	–	+	+	+	–
SPPEK 1.03	+	+	+	+	–	–	–
SPPEK 1.23	+	+	+	+	–	–	–

Soluble (+); insoluble (–); soluble at high temperature (+Δ); swelling or partially soluble at high temperature (±).

1.23. Furthermore, sulfonation reactions conducted at much lower reaction temperatures or at much higher concentration resulted in PPs solutions that were too viscous to completely dissolve the polymer, which could result in a heterogeneous sulfonation reaction.

3.2. Viscosity and solubility

Solubilities of PPs and SPPs were tested and the results are listed in Table 2. It shows that the solubilities of polymers are different before and after modification. PPs are soluble in some chlorinated solvents such as CHCl₃ and dichloromethane, but insoluble in some polar aprotic solvents such as DMF. However, SPPs with high DSs are soluble in the dipolar aprotic solvents, listed in Table 2, but insoluble in the tested chlorinated solvents. The solubility differences arising from the introduction of sulfonic acid groups can be accounted for by changes in the polarity of the polymers and intermolecular forces relating to hydrogen bond. The introduction of sulfonic acid also has an effect on the viscosities of polymers. DMF was chosen as the solvent for determining the inherent viscosities [η] of SPPs, which are listed in Table 1. The inherent viscosities of starting polymers PPES, PPEK and SPPEsK in CHCl₃ at 25 °C are 0.59, 0.66 and 0.63 dl g⁻¹, respectively. Table 1 shows that the inherent viscosities of SPPs are higher than those of PPs in chloroform and result from increased hydrogen-bonding interactions associated with the sulfonic acid groups. For SPPEsKs and SPPEsKs obtained using diluted mixtures of fuming sulfuric acid, the viscosities increase with increasing DS suggesting that the polymer chain

is not degraded during sulfonation. However, SPPEsKs show decreasing viscosities with increasing DS. This may be caused by degradation of the less stable PPES than other PPs in fuming sulfuric acid.

3.3. NMR

In order to determine the sulfonation sites and the DS values, PPs and SPPs were characterized by ¹H NMR spectroscopy. The ¹H NMR spectra of PPES and SPPEs (Figs. 1 and 2) resemble those of PPEK and SPPEK published recently [24]. The similarity between the sulfone linkage in PPES and the ketone linkage in PPEK is such that there are no significant chemical shift differences in the aromatic ¹H NMR region of the two polymers. The aromatic region of PPES polymer in CD₂Cl₂ is divided into three sections (Fig. 1): H-9 at low field (8.45–8.60 ppm), the *ortho*-ether linkage 4H at high field (7.05–7.30 ppm) and the remaining 11H aromatic hydrogen signals (7.60–8.10 ppm). The resemblance between SPPEK and SPPEs spectra in DMSO-d₆ (Fig. 2) indicates that the substitution similarly occurred at the *ortho*-ether linkage sites of PPES. As reported in details before [24], the DS was determined by presetting the integration value of the low-field hydrogen absorptions to 12H (7.60–8.60 ppm). The DS was then directly obtained by subtracting the intensity value of the *ortho*-ether upfield signals to the 4H of unsubstituted PPES. As just seen in ¹H NMR, the similarities between PPES and PPEK are also reflected in carbon NMR. The ¹³C NMR spectrum of PPES (Fig. 3) resembles that of PPEK reported before [24]. The only

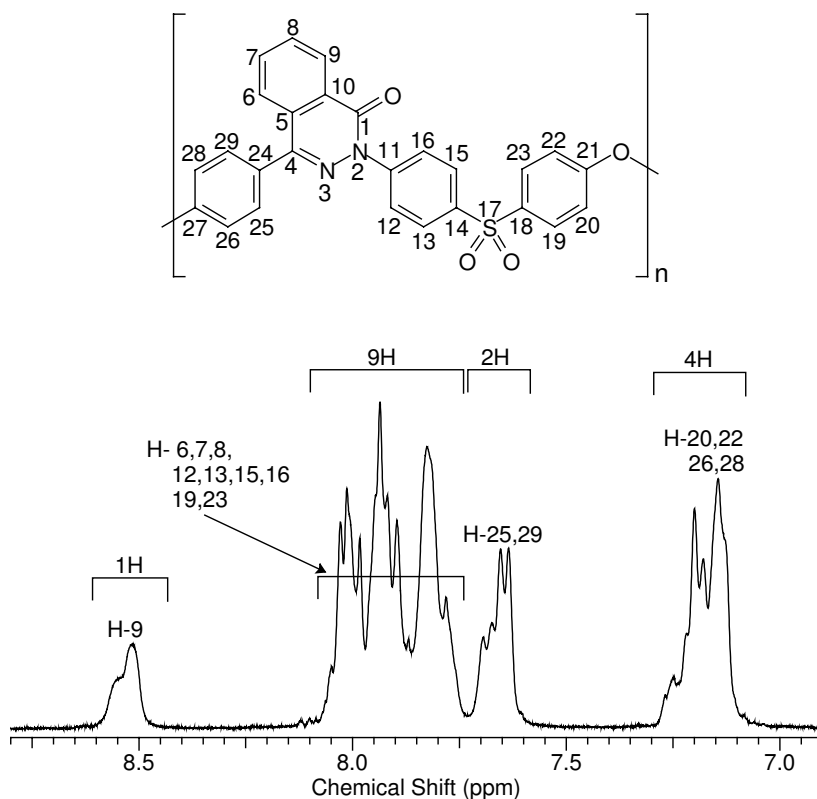


Fig. 1. ^1H NMR spectrum of PPES in CD_2Cl_2 .

apparent differences between the two polymer spectra were observed in the 125–141 ppm region where the majority of aromatic carbon atom signals appeared, including those nearest to the sulfone group. The carbon atoms (C-1, C-4, C-11, C-21, C-27) directly linked to heteroatoms (N and O) appeared at essentially the same low-field chemical shift displacement as seen in PPEK. Similarly, aryl carbon atoms at the *ortho*-ether position (C-20, C-22, C-26, C-28) appeared at high field as also seen in PPEK.

3.4. FT-IR

The sulfonation reactions of PPs were followed by FT-IR spectroscopy. Fig. 4 shows the comparative spectra of PPES and SPPEs with different DS. In the spectra of SPPEs, two new absorption peaks appear at 1019 and 1082 cm^{-1} , which are absent in PPES. These are characteristic of the aromatic SO_3H sym-

metric and asymmetric stretching vibrations, respectively, and increase with higher DS. The absorption at 1507 cm^{-1} , which can be observed in the spectrum of PPES, related to the aromatic ring 1,4-substitution is also affected by the further substitution of sulfonic acid groups. In the spectra of SPPEs, this characteristic band decreases with higher DS. Simultaneously, two new absorption bands related to 1,2,4-substitution appear at 1475 and 1478 cm^{-1} , which increase with higher DS, thus confirming the introduction of sulfonic acid groups. In addition, both PPES and SPPEs show characteristic sulfone asymmetric and symmetric absorption bands at 1325 and 1155 cm^{-1} , C=N absorption at 1587 cm^{-1} , amide absorption at 1670 cm^{-1} and aromatic C–O–C absorption at 1242 cm^{-1} . The sulfonation reactions of PPEK and PPEsK were also followed by FT-IR spectroscopy. Similar results obtained from the comparison of characteristic absorption bands between parent polymers and sulfonated

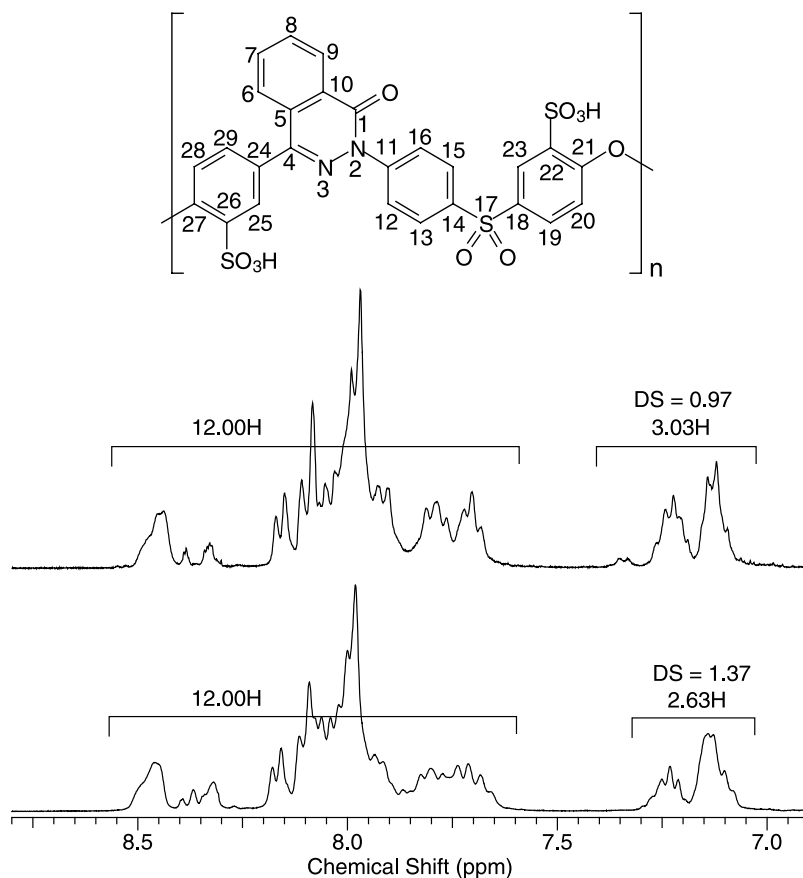


Fig. 2. ^1H NMR spectra of SPPEs in DMSO-d_6 .

polymers confirm the successful introduction of sulfonic acid groups into the polymer chains [24].

3.5. Thermal properties

The thermal stabilities of the PPs and SPPs were determined by TGA. All the samples were preheated to remove moisture, then dynamic TGA experiments were run from 80 to 750 °C at a heating rate of 10 °C min⁻¹ under nitrogen. Examples of TGA of PPES and SPPEs are shown in Fig. 5. The parent PPES is a thermostable polymer of which the 5 wt.% loss temperature is nearly 500 °C and there is only one sharp weight loss that is ascribed to the decomposition of polymer main chain. For the SPPEs, two transitions of loss in weight in two separate temperature ranges can be seen in TGA curves. Sim-

ilar observation was made for other sulfonated high performance polymers [11]. The first one occurs at around 300 °C and could be ascribed to the decomposition of the SO_3H groups, which has been confirmed by comparing the actual weight loss from the initial point to 460 °C with the theoretical value, calculated, assuming the decomposition reaction produces SO_3 . The results listed in Table 4 show that the observed weight loss values are very close to the theoretical ones. For SPPs with high DS, small differences between the determined values and theoretical ones were observed. This suggests that when the polymer main chain begins to degrade, not all sulfonic acid groups have been released. The second thermal degradation of SPPEs at about 490 °C is assigned to the degradation of the main polymer chain. Fig. 5 also shows that SPPEs with higher DS lose weight more quickly

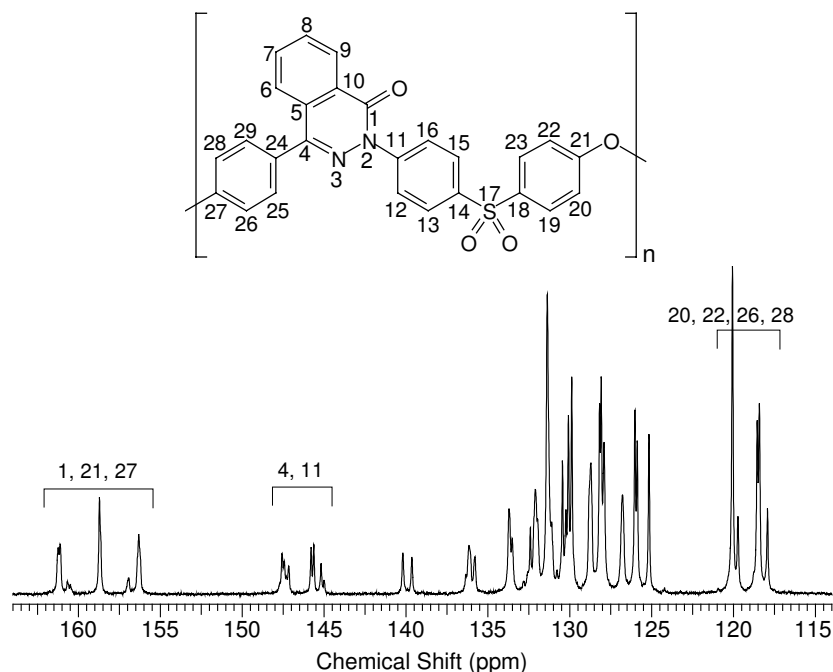


Fig. 3. ^{13}C NMR spectrum (hydrogen decoupled) of PPES in CDCl_3 .

than those with lower DS in the temperature range of 300–460 °C. It also indicates that the weight loss during this period is due to the elimination of residual $-\text{SO}_3\text{H}$ groups. The thermal degradation curves of PPEK and SPPEKs [24], PPEK and SPPEKs are similar to those of PPES and SPPESSs. The decomposition temperatures of both parent PPs and SPPs are listed in Table 3. T_{d1s} (T_{d1} is the extrapolated onset temperature for first weight loss) of all SPPs are close to 300 °C and show that the SPPs appear

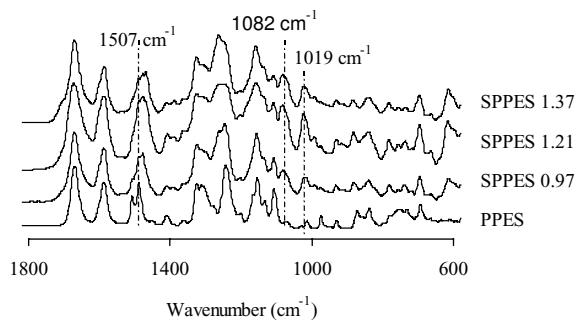


Fig. 4. FT-IR spectra of PPES and SPPESSs.

to have adequate thermostability for their intended fuel cell application. Interestingly, when the TGA curves of SPPs with DS 1.0 are plotted in the form of first derivative of heat flow to temperature, three weight loss changes can be seen (Fig. 6). The first two changes are in the range of 230–460 °C, which

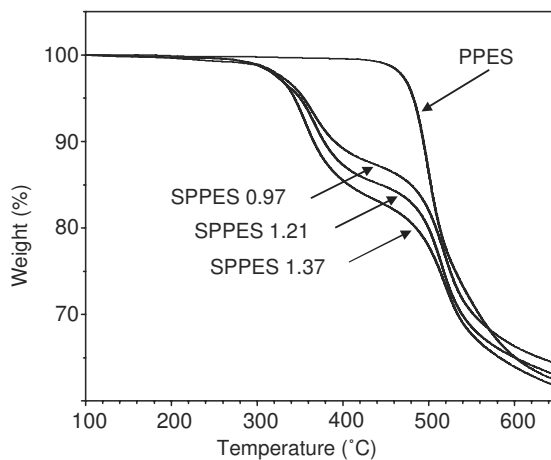


Fig. 5. TGA traces of PPES and SPPESSs.

Table 3
Decomposition temperatures of PPs and SPPs

	T_{d1} (°C)	Weight change from 200 to 460 °C (%)		T_{d2} (°C)	Weight change from 460 to 700 °C (%)
		Theoretical	Determined		
PPES	–	–	–	466	–
SPPEs 0.97	289	13.5	13.4	490	22.5
SPPEs 1.21	325	16.3	15.4	491	22.9
SPPEs 1.37	327	18.1	17.6	492	22.1
PPESK	–	–	–	465	–
SPPEsK 1.07	288	15.8	14.4	486	25.5
SPPEsK 1.20	330	17.9	14.9	489	21.6
PPEK	–	–	–	464	–
SPPEK 1.03	299	16.5	15.3	489	24.9
SPPEK 1.23	306	19.1	17.1	489	22.5

is believed to be due to sulfonic acid group loss. The sulfonic acid groups were released in two steps. However, two weight changes in the range of 230–460 °C were not always found, particularly for SPPs with high DS. The process of losing sulfonic acid groups is not clear.

3.6. Water uptake and swelling ratio

Absorbed water in membrane films is important for fuel cell applications since this affects their mechanical properties and proton conductivity. Water absorbed by the hydrophilic sulfonic acid groups in the membrane films results in some swelling and assists proton transport from the anode to the cathode. However, too much water absorption results in excessive swelling,

mechanical fragility and morphological instability of the membrane films. The water uptake and swelling ratio of SPPs membrane films were determined by measuring the changes in the mass and length, respectively, before and after hydration. The results are listed in Table 4, which shows that the water uptake of SPPs increases with DS and temperature and all three kinds of SPP films are soluble at $DS > 1.2$ in 80 °C water. At room temperature, the water uptake and swelling ratio of the three types of SPP films at same DS did not show much variability. However, at elevated temperature, SPPEs absorbed much more water and showed marked swelling compared with SPPEsKs and SPPEKs at the same DS.

3.7. Proton conductivity

The proton conductivities of SPPs with DS from 0.97 to 1.37 were measured at different temperatures. Prior to measurements, all membrane samples were soaked in water 1 or 2 days for hydration. The conductivities of SPPEs, SPPEsKs and SPPEKs are plotted in Figs. 7–9, respectively, which show that the conductivities of tested SPPs are all higher than 10^{-2} S cm^{-1} . The values are close to that of NafionTM 117 under similar conditions, 3×10^{-2} S cm^{-1} . These figures also show that the SPPs behave similarly. Their conductivity increases with DS and temperature up to some temperature, then decrease. The decrease is probably caused by the dehydration of membrane films at high temperatures. Generally, SPPs with higher DS start to lose conductivity at higher temperature, obviously due to better water retention. Figs. 7–9 show

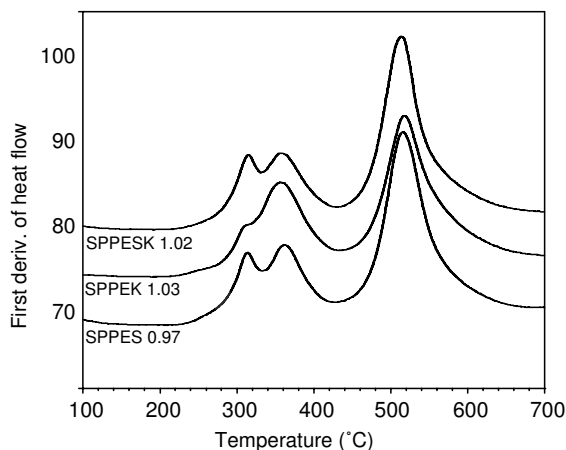


Fig. 6. First derivative TGA trace of SPPs.

Table 4
Water uptake and swelling ratio of SPPs

Polymer	Room temperature, 3 days		80 °C, 1 day	
	Water uptake (%)	Swelling ratio (%)	Water uptake (%)	Swelling ratio (%)
SPPEs 0.97	21	5.1	152	43
SPPEs 1.21	30	7.6	SOL	–
SPPEs 1.37	71	18	SOL	–
SPPEsK 1.07	18	4.4	86	27
SPPEsK 1.20	34	8.3	SOL	–
SPPEK 1.02	19	4.8	63	20
SPPEK 1.23	32	7.9	SOL	–

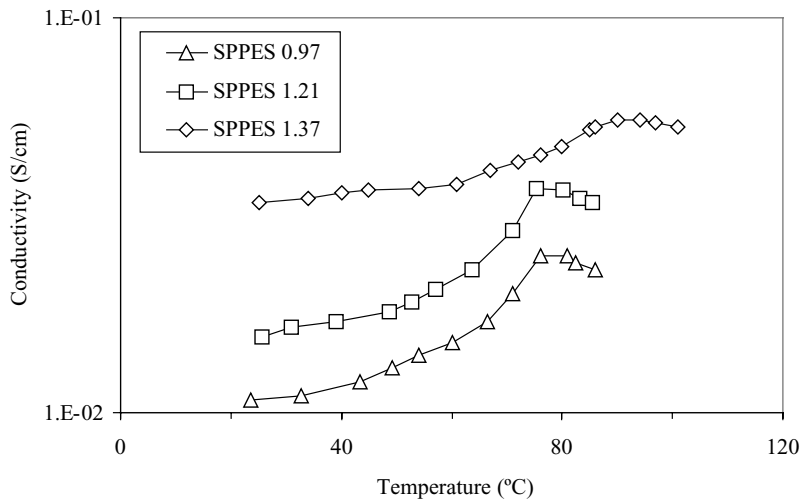


Fig. 7. Conductivities of SPPEs.

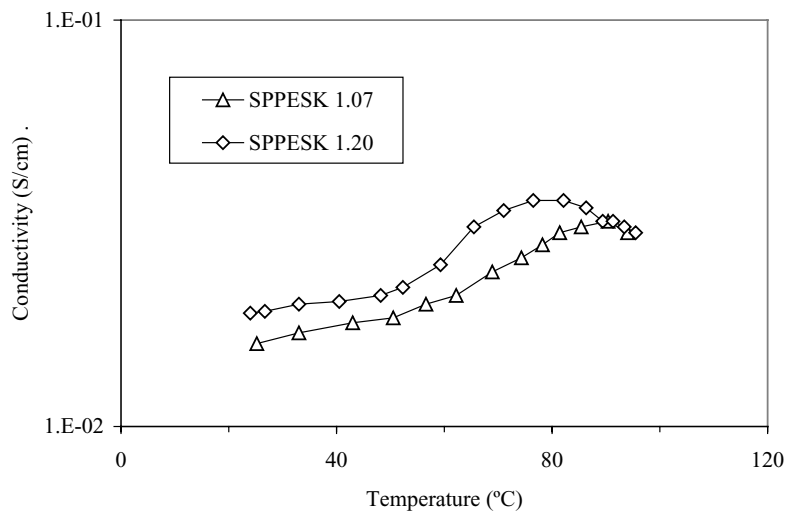


Fig. 8. Conductivities of SPPEsKs.

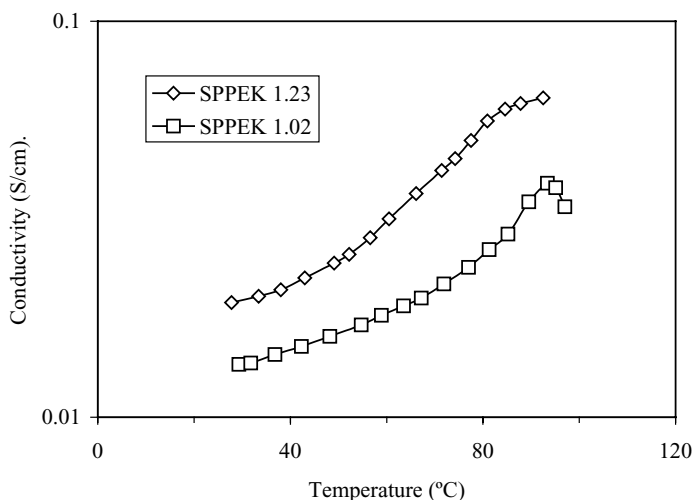


Fig. 9. Conductivities of SPPEKs.

that the conductivities of SPPEKs with DS 0.97, 1.21 and 1.37 increase with increasing temperature reaching $2.5 \times 10^{-2} \text{ S cm}^{-1}$ at 76°C , $3.7 \times 10^{-2} \text{ S cm}^{-1}$ at 75.3°C and $5.5 \times 10^{-2} \text{ S cm}^{-1}$ at 90°C , respectively, then begin to drop. For SPPEKs with DS 1.07 and 1.20, the conductivities increase with increasing temperature reaching $3.2 \times 10^{-2} \text{ S cm}^{-1}$ at 90°C and $3.6 \times 10^{-2} \text{ S cm}^{-1}$ at 82°C , respectively. The conductivities of DS 1.03 and 1.23 SPPEKs increase with increasing temperature up to 95°C and reach 4×10^{-2} and $6 \times 10^{-2} \text{ S cm}^{-1}$, respectively. The conductivity of SPPEK with DS 1.03 drops sharply after this temperature. Among the three types of SPPs, SPPEKs show highest conductivities at comparably similar DS values.

4. Conclusions

SPPs with different DS from 1 to 1.37 were prepared from PPs with dilute fuming sulfuric acid as both the solvent and sulfonating agent. The structures of SPPs were confirmed by FT-IR and the DS of SPPEK was determined by $^1\text{H NMR}$. Three weight loss steps were found from the first derivative of heat to temperature TGA plot and the process was assumed to be losing of sulfonic acid groups in two steps followed by degradation of polymer main chain. Membrane films were prepared from SPP solutions in DMAc. Water uptake

and swelling ratio test showed that the membrane films absorbed water and swollen with DS and temperature and were soluble at around DS 1.2 in 80°C water. Membrane films obtained from highly sulfonated PPs showed proton conductivity above $10^{-2} \text{ S cm}^{-1}$ at both room temperature and elevated temperature, which is in the range needed for high performance fuel cell PEM. A comparison of the three types of SPPs indicated that SPPEKs are the best PEM materials based on the results of this comparative study.

Acknowledgements

This work was supported by the National Research Council of Canada. Partial support was also provided by the National Natural Science Foundation of China (Contract grant number: 20104001).

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