NRC Publications Archive
Archives des publications du CNRC

Synthesis and characterization of sulfonated poly(phthalazinone ether ketone) for proton exchange membrane materials

Gao, Yan; Robertson, Gilles; Guiver, Michael; Jian, Xigao

Synthesis and Characterization of Sulfonated Poly(phthalazinone ether ketone) for Proton Exchange Membrane Materials*

YAN GAO,[1,2] GILLES P. ROBERTSON,[1] MICHAEL D. GUIVER,[1] XIGAO JIAN[2]

[1]Institute for Chemical Process and Environmental Technology, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada

[2]Department of Polymer Science and Materials, Dalian University of Technology, Zhongshan Road 158-42, Dalian, 116012, People's Republic of China

ABSTRACT: As a novel class of proton exchange membrane materials for use in fuel cells, sulfonated poly(phthalazinone ether ketone)s (SPPEKs) were prepared by the modification of poly(phthalazinone ether ketone). Sulfonation reactions were conducted at room temperature with mixtures of 95–98% concentrated sulfuric acid and 27–33% fuming sulfuric acid with different acid ratios, and SPPEK was obtained with a degree of sulfonation (DS) in the desired range of 0.6–1.2. The presence of sulfonic acid groups in SPPEK was confirmed by Fourier transform infrared analysis, and the DS and structures were characterized by NMR. The introduction of sulfonic groups into the polymer chains increased the glass-transition temperature above the decomposition temperature and also led to an overall decrease in the decomposition temperature. Membrane films were cast from SPPEK solutions in *N,N*-dimethylacetamide. Water uptakes and swelling ratios of SPPEK membrane films increased with DS, and SPPEKs with DS > 1.23 were water-soluble at 80 °C. Proton conductivity increased with DS and temperature up to 95 °C, reaching 10^{-2} S/cm. © 2003 Wiley Periodicals, Inc.* J Polym Sci Part A: Polym Chem 41: 497–507, 2003

Keywords: poly(phthalazinone ether ketone); sulfonation; proton exchange membranes; fuel cell; poly(ether ketones); ionomers; membranes

INTRODUCTION

In recent years, polymer electrolyte fuel cells have been identified as promising power sources for vehicular transportation and other applications requiring clean, quiet, and efficient portable power. As a vital part of fuel cells, proton exchange membranes (PEMs) have become a rapidly growing area of research. Until now, PEMs have been limited mainly to perfluorinated ionomer membranes such as Nafion, developed by DuPont, and similar membranes commercialized by Dow and Asahi. Despite their outstanding properties, such as excellent proton conductivity and oxidative resistance, which are essential for fuel cell applications, perfluorinated ionomer membranes are very expensive (U.S. \$800–2000/m²) and suffer from other serious drawbacks of high methanol permeation and dehydration. To develop alternatives to Nafion, which would be less expensive and free from other disadvantages of perfluorinated ionomer membranes, several

new approaches have been attempted recently, including the synthesis of new polymer electrolytes,[1–5] the chemical modification of available high-performance polymers,[6–10] and blend membranes.[11–14] In these studies, introducing sulfonic acid groups into the main chains of high-performance polymers by a sulfonation reaction is an important and widely used method for imparting polymers with proton exchange capability. Poly(aryl ether ketone)s, poly(phenylene oxide), poly(phenylene sulfide), poly(aryl ether sulfone), and polybenzimidazole are among those that have been studied. The sulfonating agents include concentrated sulfuric acid, chlorosulfonic acid, pure or complex sulfur trioxide, and acetyl sulfate. As an example, the sulfonation reaction of Victrex poly(ether ether ketone) (PEEK) and the conductivity of sulfonated poly(ether ether ketone) (SPEEK) have been studied extensively.[7,11,15–17] The degree of sulfonation (DS) can be controlled by the reaction time and temperature in concentrated sulfuric acid or oleum. For SPEEK with a relatively low DS of 0.65, the conductivity reaches 0.04 S cm^{-1} at 100 °C and 100% relative humidity, which is higher than that of Nafion-117 measured under the same conditions.

Poly(phthalazinone ether ketone) (PPEK) is a new poly(aryl ether ketone) currently under consideration for commercialization, as are others in the class of poly(phthalazinone)s, such as poly(phthalazinone ether sulfone) (PPES) and the copolymer poly(phthalazinone ether sulfone ketone) (PPESK). As a class of thermoplastics, poly(phthalazinone)s have excellent chemical and oxidative resistance, mechanical properties, and thermal stability. PPEK has a very high glass-transition temperature (T_g) of 263 °C, excellent high-temperature stability, and many other good properties. The sulfonation reactions of its copolymer, PPESK, and the nanofiltration and ultrafiltration membrane properties have also been studied.[18–23]

In this work, we investigated the sulfonation reaction of PPEK and acquired suitable PEMs from the sulfonated products. A series of sulfonated poly(phthalazinone ether ketone)s (SPPEKs) with different DSs were prepared via the modification of PPEK with a mixture of concentrated sulfuric acid and fuming sulfuric acid as the sulfonating agent. The structures and some properties of SPPEKs and resulting membrane films were characterized with respect to the sulfonation position, proton conductivity, equilibrium water uptake, swelling ratio, and thermostability as a function of DS.

EXPERIMENTAL

Materials

PPEK was synthesized according to a procedure reported previously.[18,19] All other chemicals obtained commercially were reagent-grade and were used as received.

Sulfonation Reaction

In a typical small-scale experiment, 0.5 g of PPEK powder was added to a 10-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 (RT; 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 and washed with deionized water until the pH value was approximately 6–7.

For scaled-up reactions of 30–35 g, an ice bath was needed initially to cool the heat released during dissolution. PPEK powder (30 g) was added to a mixture of 240 mL of 95–98% concentrated sulfuric acid and 360 mL of 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 RT (23 °C). ^{1}H 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 and washed with deionized water until the pH value was approximately 6–7.

Polymer Analysis and Measurement

Proton and carbon spectra were obtained on a Varian Unity Inova NMR spectrometer operating at a proton frequency of 399.951 MHz and at a carbon frequency of 100.578 MHz. Tetramethylsilane was used as the internal-standard chemical-shift reference. ^{1}H NMR spectra of PPEK and low-DS SPPEK were acquired at 22 °C in deuterated chloroform (CDCl$_3$). Deuterated methylene

chloride (CD_2Cl_2) was used when accurate integration values were desired for high-field aromatic signals because the signal of residual CH_2Cl_2 (5.31 ppm) did not interfere with the aromatic region. Deuterated dimethyl sulfoxide (DMSO-d_6) was the NMR solvent of choice for higher DS SPPEK. Presaturation of the large water peak always present in SPPEK around 4 ppm improved the spectra by increasing the signal-to-noise ratio and by removing interference signals from the large water absorption. ^{13}C NMR spectra of PPEK were acquired with a 10-mm tunable broadband probe and a concentrated sample in $CDCl_3$ (500 mg in 3 mL). A quantitative spectrum was obtained with a long relaxation delay and hydrogen decoupling only during the acquisition time. IR spectra were measured on a Nicolet 520 Fourier transform spectrometer with powder samples inside a diamond cell.

A TA Instruments model 2950 thermogravimetric analysis (TGA) instrument was used for measuring the degradation temperatures (T_d's), and a TA Instruments model 2920 differential scanning calorimetry (DSC) instrument calibrated with tin at 231.93 °C and with zinc at 419.53 °C was used for measuring T_g. Polymer samples for TGA were preheated to 150 °C at 10 °C/min under a nitrogen atmosphere, held isothermally for 60 min, equilibrated at 80 °C, and then heated to 800 °C at 10 °C/min for T_d measurements. Therefore, the degradation data reported here were assumed to be in the absence of moisture. Samples for DSC analysis were initially heated at a rate of 10 °C/min under a nitrogen atmosphere to well below the polymer T_d point, quenched in liquid nitrogen, and then reheated at the same rate.

The inherent viscosities ($[\eta]$) were determined with an Ubbelohde viscometer for *N,N*-dimethylformamide (DMF) solutions of polymers with a concentration of 0.5 g/dL at 30 °C.

Preparation of the Membrane Films

A sample (0.7 g) was dissolved in 12 mL of *N,N*-dimethylacetamide (DMAc) and filtered. The filtered solution was poured onto a glass plate and dried at 40 °C for about 2 days. The residual solvent was further evaporated at 120 °C *in vacuo* for 48 h, and this resulted in yellow membrane films that were tough and flexible.

Measurements of the Water Uptake Content and Swelling Ratio

All the polymer membranes were vacuum-dried at 120 °C before the testing. The sample films were soaked in deionized water for different times at determined temperatures. The weights of dry and wet membranes were measured. The water uptake content was calculated as follows:

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

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 as follows:

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

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

Conductivity

The proton conductivity was measured by alternating-current impedance spectroscopy over a frequency range of $1–10^7$ Hz with an oscillating voltage of 50–500 mV with a system based on a Solarton 1260 gain phase analyzer. A sample with a diameter of 10 mm was placed in an open, temperature-controlled cell, in which 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 before the test. The conductivity (σ) of the samples in the transverse direction was calculated from the impedance data, with the relation $\sigma = d/RS$, where d and S are the thickness and face area of the sample, respectively, and R was derived from the low intersection of the high-frequency semicircle on a complex impedance plane with the Re (Z) axis.

RESULTS AND DISCUSSION

Sulfonation Reaction

Figure 1 shows the sulfonation reaction. Sulfonation occurred as expected around the electron-donating ether linkage. In general, the sulfonation of polymers can be conducted with several sulfonating agents, including concentrated sulfu-
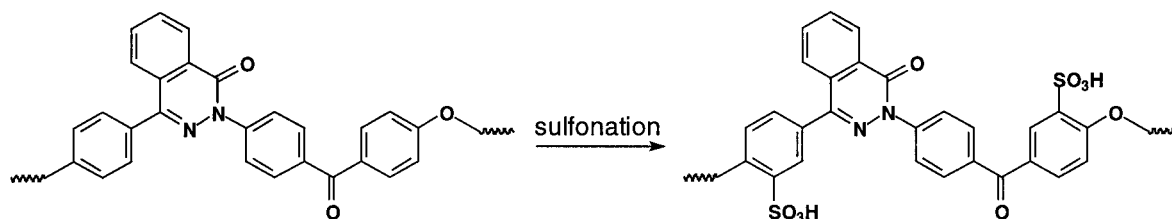
Figure 1. Synthetic pathway for SPPEK.

ric acid, fuming sulfuric acid, chlorosulfonic acid, and acetyl sulfate, depending on the reactivity of the polymer. For Victrex PEEK, a high DS can be achieved with concentrated sulfuric acid because of the high reactivity of the hydroquinone segment in the polymer chain. We initially attempted the sulfonation of PPEK in 95–98% concentrated sulfuric acid at both room and elevated temperatures. However, the results listed in Table 1 show that almost no sulfonation of PPEK took place at RT even for a very long reaction time, and only SPPEK with a very low DS was obtained at 60 °C after 60 h. Sulfonation is an electrophilic reaction affected by both the electrophilicity of the sulfonating agent and the electron-donating characteristics of the polymer. Compared with PEEK, PPEK (as shown in Fig. 1) had more electron-withdrawing functionality per repeat unit, which reduced the reactivity of the electron-donating ether linkage of the polymer.

For the preparation of SPPEK with a high DS, 27–33% fuming sulfuric acid and an elevated reaction temperature were employed. As shown in Table 1, the sulfonation of PPEK in oleum at 40 °C for 1 h resulted in SPPEK with a DS of 1.63. The DS did not increase significantly over extended reaction times. This was because the sulfonic acid groups were more than 1.5 per repeating unit, reducing the electron-donating characteristic of the polymer and preventing the further introduction of more sulfonic acid groups. Although a high DS was achieved with fuming sulfuric acid, the reaction proceeded too rapidly for control to be maintained. Abating the reaction to RT reduced the DS to 1.30. However, at a DS of 1.30, SPPEK is water-soluble and cannot be used as a PEM in fuel cells in which high humidity exists. A further reduction in temperature made the PPEK solution in fuming sulfuric acid too viscous to completely dissolve the polymer, and

Table 1. Dependence of DS on the Reaction Conditions[a]

Oleum/ Concentrated Sulfuric Acid	Reaction Temperature (°C)	Reaction Time (h)	DS	$[\eta]$ (dL/g)[b]
0/10	RT	95	≈ 0	
0/10	60	6	<0.10	
4/6	RT	4	0.14	
5/5	RT	1	0.60	1.40
5/5	RT	4	0.80	
5/5	RT	7	0.92	
6/4	RT	1	0.81	1.81
6/4	RT	4	1.04	1.83
6/4	RT	7	1.08	
7/3	RT	1	1.02	
7/3	RT	4	1.23	1.99
10/0	RT	1	1.30	
10/0	40	1	1.60	
10/0	40	2	1.63	1.88
10/0	40	23	1.70	

[a] Reaction conditions: PPEK, 0.5 g; mixture of sulfuric acid, 10 mL; argon atmosphere.
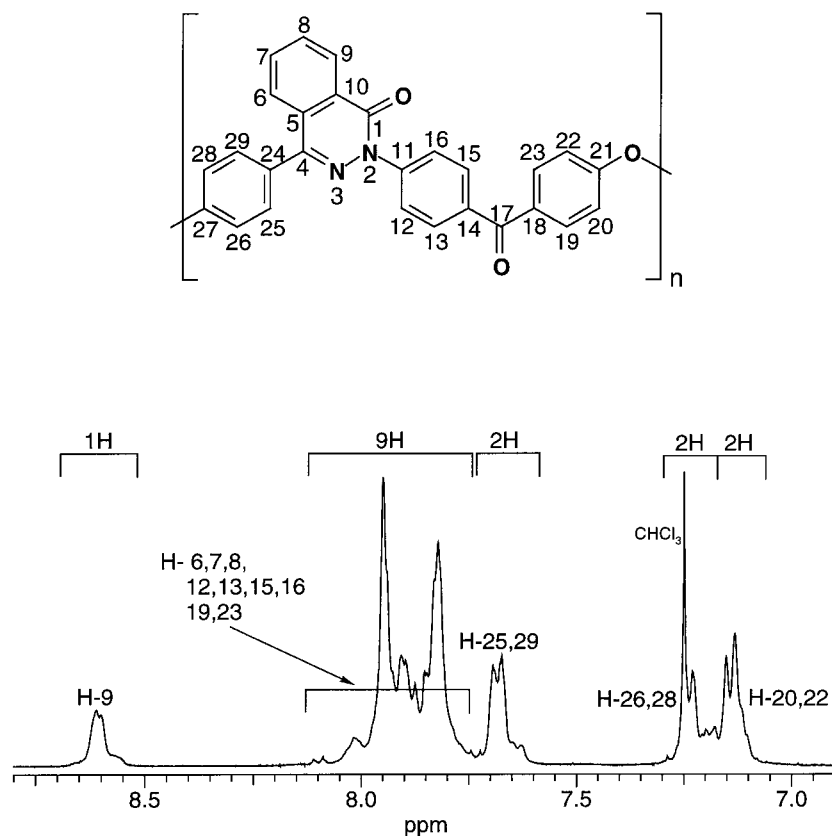[b] Determination conditions: SPPEK, 0.5 g/dL in DMF; 30 °C.

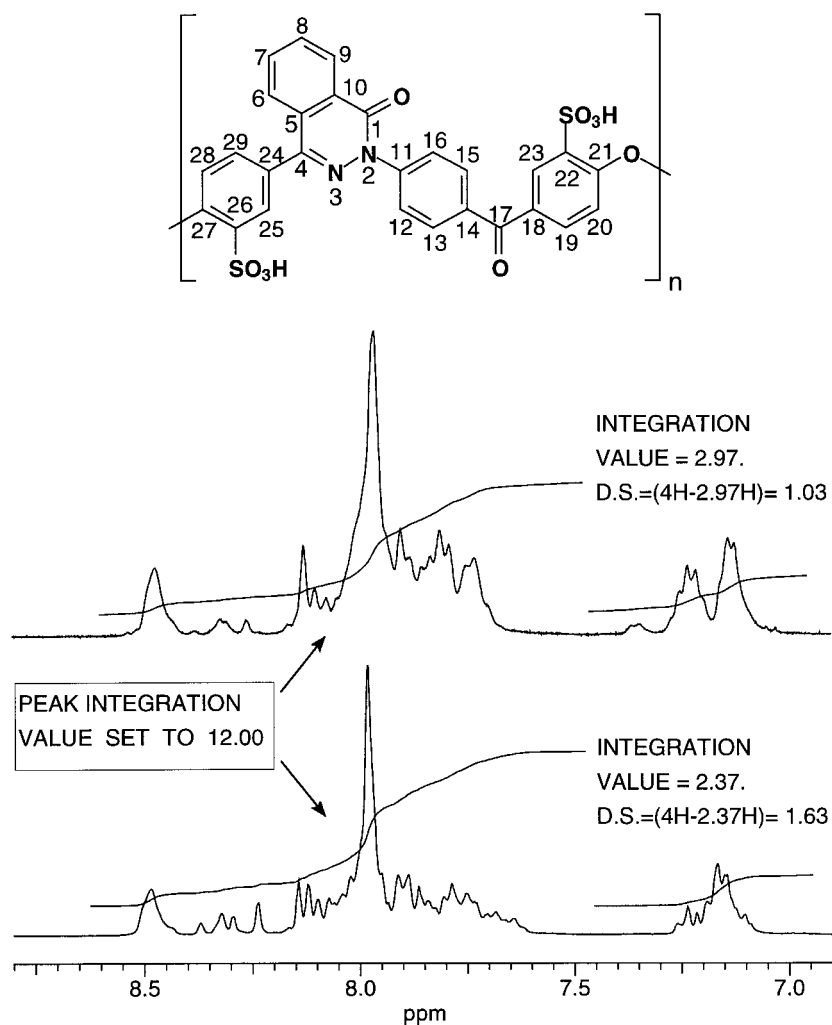**Figure 2.** ^{1}H NMR spectrum of PPEK in CDCl$_3$.

this could result in a heterogeneous sulfonation reaction. For the reactivity of the sulfonating agent to be reduced, a mixture of 95–98% concentrated sulfuric acid and 27–33% fuming sulfuric acid was used for PPEK. As seen in Table 1, through variations in the ratio of concentrated sulfuric acid to fuming sulfuric acid and in the reaction time, the sulfonation reaction was more readily controlled to different DSs in the range of 0.60–1.23.

NMR

For the quantitative determination of the sulfonation site and DS, the ^{1}H NMR spectra of PPEK in CDCl$_3$ (Fig. 2) and SPPEK in DMSO-d_6 (Fig. 3) were characterized. The number system adopted for the protons in the polymer and the derivatives are shown in Figures 2–4. The careful and accurate assignments of NMR spectral signals were essential for determining both the DS and the site of sulfonation.

The starting point for the peak assignment of ^{1}H and ^{13}C NMR of PPEK was the absorptions resulting from atoms surrounding the electron-rich ether moiety. In a PPEK repeat unit, the hydrogen atoms at the ortho position to the ether linkage were more shielded than any other hydrogen atoms because of a resonance effect of the oxygen's lone pair of electrons. The other functional groups present in PPEK had a deshielding effect on nearby nuclei. As a result, the furthest upfield signals (7.08–7.30 ppm) arose from the 4H ortho to the ether linkage. Two-dimensional correlation spectroscopy NMR as well as simple homonuclear decoupling experiments showed the presence of two separate spin coupling systems originating from these high-field signals (Fig. 2). These interactions were a result of spin–spin coupling between the hydrogen atoms at the ortho and meta positions of these phenol rings. One spin system consisted of the high-field ortho ether 2H absorption at 7.16–7.30 ppm coupled with the distinct signal at 7.60–7.72 ppm. The other spin system consisted of the high-field ortho ether 2H absorption at 7.08–7.16 ppm coupled with the multiple absorptions at 7.76–8.06 ppm.

Figure 3. ^{1}H NMR spectrum of SPPEK in DMSO-d_6.

The results of a simple ^{13}C NMR experiment allowed the formal assignment of the preceding hydrogen signals, which were key components for the accurate measurement of the DS of SPPEKs. The H-decoupled ^{13}C NMR spectrum of PPEK is displayed in Figure 4. The carbon peaks of particular interest are those arising from carbon atoms directly linked to an electron-withdrawing heteroatom (N or O) causing absorptions to appear at a lower field (144–195 ppm). The furthest downfield signal (193.6–194.8 ppm) is unequivocally from the ketone carbon. Further upfield, three carbon signals (155–162 ppm) arise from carbon atoms linked to electronegative oxygen atoms in the phthalazinone and ether functionalities. Finally, the less electronegative nitrogen atoms give the carbon absorptions at higher field (144–148 ppm). In one ^{13}C NMR experiment, a spectrum was acquired with decoupling of one of the hydro-

gen frequencies (7.60–7.72 ppm) responsible for the 2H at the meta position of one of the phenol rings. The resulting spectrum was compared with a ^{13}C NMR spectrum acquired with full hydrogen coupling. Of all the downfield carbon signals, the C—O absorption at 156.0–157.1 ppm and the C—N at 147.0–148.0 ppm both lost a 6–7-Hz long-range (3-bond C—C—C—H) carbon–hydrogen coupling when the hydrogen frequency 7.60–7.72 ppm was irradiated. Therefore, the long-range C—H interaction could only originate from C(O)-27 coupled with H-25,29 and C(N)-4 coupled with H-25,29. Decoupling of the other meta ether protons (H-19,23) would not affect any of the 2 C-N carbons. This experiment led to the unequivocal assignment of H-20,22 and H-26,28, which were essential for the DS calculations. The assignments of H-25,29 and H-19,23 were also derived from this experiment. Further one-dimen-
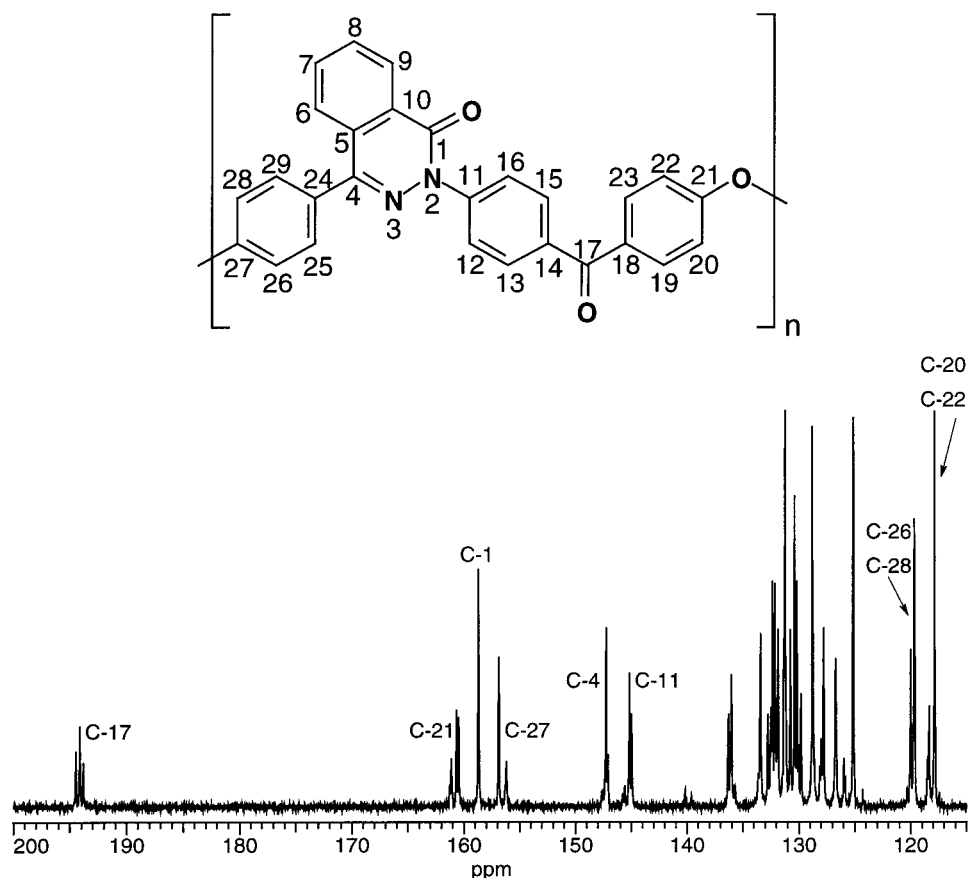
Figure 4. ^{13}C NMR spectrum (hydrogen-decoupled) of PPEK in CDCl$_3$.

sional and two-dimensional heteronuclear (C and H) NMR experiments confirmed the previous assignments. Table 2 lists the chemical shifts of the ^{13}C NMR spectra of PPEK.

The hydrogen absorption at a low field (8.54–8.68 ppm) was believed to arise from H-9 (Fig. 2), although it could not be formally proved. This uncertain assignment was based on the ^{1}H NMR spectra of the phthalazinone monomer in which H-9 absorbed at a low field in both CDCl$_3$ (8.50 ppm) and DMSO-d_6 (8.33 ppm) because of its proximity to the carbonyl group. Note that the assignment of this low-field hydrogen signal was not required for the DS measurements and determination of the sulfonation sites.
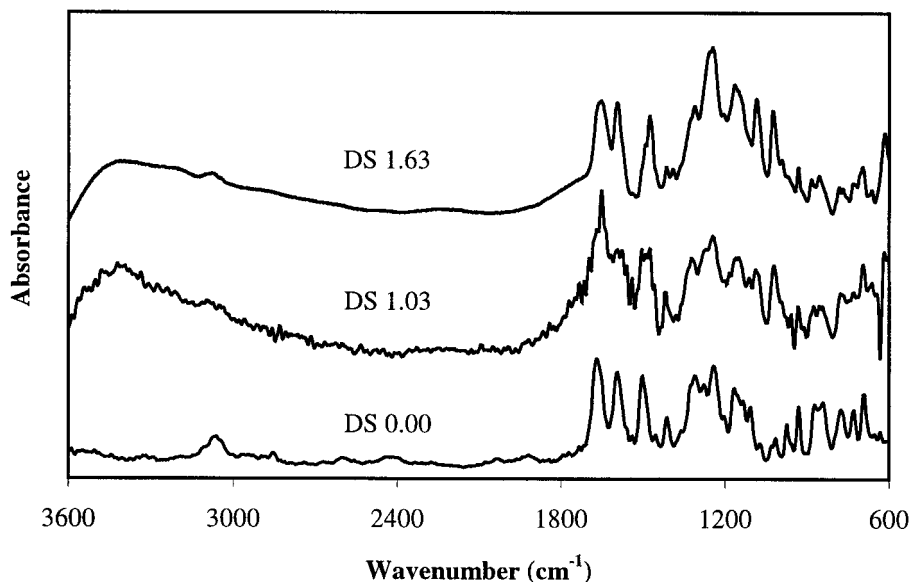
DS Calculations from ^{1}H NMR

A ^{1}H NMR spectrum of PPEK in CD$_2$Cl$_2$ was acquired, and the integration value of the upfield H-26,28 and H-20,22 absorptions was set to 4.00. The integration values of the other regions of the spectra corresponded exactly (Fig. 2) to the number of hydrogen atoms expected from the chemical structure of the PPEK repeat unit. Similarly, in a quantitative ^{13}C NMR experiment, the upfield carbon signals C-26,28 and C-20,22 were also set to an intensity of 4.00, and the integration values of the other peaks were again matched precisely. SPPEK at DS $\geq$ 0.6 is only soluble in highly polar

Table 2. ^{13}C NMR Data of PPEK (Hydrogen-Decoupled) in CDCl$_3$

Carbon Number	δ (ppm)
C-1	158.72
C-4	147.0–148.0
C-5–10,12–16,18,19,23–25,29	125.0–137.0
C-11	144.8–146.0
C-17	193.6–194.8
C-20,22	117.6–118.6
C-21	160.2–161.4
C-26,28	119.4–120.4
C-27	156.0–157.1

Figure 5. FTIR spectra of PPEK and SPPEK.

solvents, and DMSO-d_6 was chosen to dissolve SPPEK. Spectra of SPPEK (DS = 1.03 and 1.63) are displayed in Figure 3. In comparison with PPEK, several new signals for the SPPEK derivatives appeared with different chemical shifts due to the different solvents used and perturbation by different DSs of —SO$_3$H groups. The ortho ether hydrogen atoms remained at a high field, but their intensity decreased as they were replaced by —SO$_3$H groups. More importantly, the ratio of low-field H-9 (8.40–8.55 ppm) to multiple peaks (7.60–8.40 ppm; which do not include ortho ether protons) always remained 1.00:11.00 for low and high DSs. This is proof that substitution occurred only at the ortho ether sites of the PPEK repeat unit. Another phenomenon supporting this was the variation in size of the small high-field signal at 7.30–7.40 ppm due to monosubstitution on SPPEK repeat units. When strong electron-withdrawing sulfonic acid groups are attached to benzene rings, they induce deshielding of hydrogen in the ortho and para positions. In monosubstituted SPPEK (DS ∼ 1), H-20 is deshielded by the —SO$_3$H group and, therefore, is shifted downfield. In disubstituted SPEEK repeat units (DS > 1), H-20 is still deshielded by the —SO$_3$H group present on the phenol ring, but it is also shielded by the proximity through space of the electron-rich oxygen atoms of the other —SO$_3$H group nearby on the other phenol ring. The DS was simply measured by the presetting of the integration value of the low-field hydrogen absorptions to

12H (7.50–8.60 ppm) and by the determination of the intensity value of the upfield hydrogen signals. This value represents the number of hydrogen atoms not converted into —SO$_3$H groups, and so subtracting it from 4H (unmodified PPEK) gives a direct DS value for SPPEK.

Fourier Transform Infrared (FTIR)

FTIR spectroscopy was used to confirm the pendant SO$_3$H group on the polymer chain. Figure 5 shows the FTIR spectra of the parent PPEK and its sulfonated derivatives with DSs of 1.03 and 1.63. In comparing these spectra, one can see that in addition to the predicable absorptions at 3400 cm^{-1} due to the stretching of the hydroxyls of SO$_3$H groups, the SPPEK absorption bands at 1020 and 1081 cm^{-1} are characteristic of the aromatic SO$_3$H symmetric and asymmetric stretching vibrations, respectively. These two characteristic peaks increase with higher DS. In addition, the reaction can be readily followed by the signal at 1500 cm^{-1} related to 1,4-aromatic ring substitution. The introduction of SO$_3$H onto the aromatic ring induced the formation of two new absorptions at 1471 and 1475 cm^{-1}, which at higher DSs completely replaced the adsorption at 1500 cm^{-1}. The introduction of sulfonic acid groups in the modified polymer was, therefore, confirmed. In addition, both PPEK and SPPEK showed characteristic carbonyl absorption bands at 1653
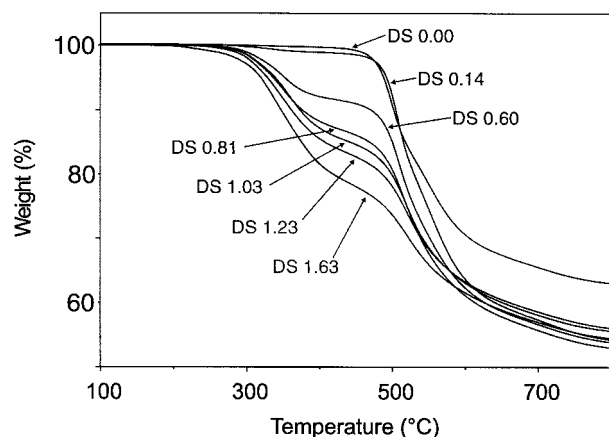
Figure 6.   TGA traces of PPEK and SPPEK.

cm^{-1}, C=N absorption at 1593 cm^{-1}, and aromatic C—O—C absorption at 1249 cm^{-1}.

Thermal Analysis

The thermal stabilities of the SPPEKs were determined by TGA. All the samples were preheated at 150 °C for 60 min in the TGA furnace for the removal of moisture, and then dynamic TGA experiments were run from 80 to 800 °C at a heating rate of 10 °C/min under nitrogen. Figure 6 shows the degradation curves. The parent PPEK was a thermostable polymer, of which the 5% weight-loss temperature was nearly 500 °C. For SPPEK, there were two transitions of weight loss. The first one occurred at about 300 °C and could be ascribed to the decomposition of the SO_3H groups. For the confirmation of our speculation, the weight loss from the initial point to 455 °C of SPPEK with a DS of 1.0 was analyzed. A value of about 15% was obtained, which was close to the theoretical SO_3H weight-loss percentage of 16% in SPPEK with a DS of 1.0. The second thermal degradation at about 490 °C was assigned to the degradation of the main polymer chain, which was in close agreement with the weight-loss step in the TGA curve for the parent PPEK. In addition, SPPEKs with higher DSs lost weight more quickly than those with lower DSs in the temperature range of 300–460 °C. This also indicates that the weight loss during this period was due to the elimination of —SO_3H groups.

The T_g of the starting material was 263 °C. For the sulfonated product, only the T_g of SPPEKs with DSs of 0.14 was detected at 270 °C. The introduction of sulfonic groups into polymer chains led to increased T_g's because of the increased intermolecular ionic interactions. For SPPEK with a DS higher than 0.60, no T_g's were detected because the decomposition temperatures were lower than the T_g's.

Solubility and Viscosity

PPEK was soluble in $CHCl_3$, dichloromethane, and some other chlorinated solvents but was insoluble in polar aprotic solvents such as DMF, DMAc, and DMSO. SPPEK with a low DS, such as 0.14, had solubility characteristics similar to those of the parent polymer. However, SPPEKs with high DSs were soluble in these dipolar aprotic solvents but insoluble in chlorinated solvents. DMF was chosen as the solvent for determining [η] values of SPPEKs with high DSs, which are listed in Table 1. It shows that the [η] values of SPPEKs were higher than that of PPEK of 0.60 in $CDCl_3$ and generally increased with increasing DS; this suggested that the polymer chain was not degraded during sulfonation. Only SPPEK with a DS of 1.63, which was obtained with 27–33% fuming sulfuric acid, had a slightly reduced viscosity. A significant increase in the viscosity might have arisen from two factors: the introduction of sulfonic acid into the polymer chain caused an overall increase in the polymer molecular weight and hydrogen bonding related to sulfonic acid groups increased the molecular forces. The slight decrease in the viscosity of SPPEK with a DS of 1.63 might have been caused by degradation taking place during the sulfonation reaction in undiluted fuming sulfuric acid.

Water Uptake and Swelling Ratio

The adequate hydration of membranes is critical to fuel cell applications. Water assists in the transportation of protons from the anode to the cathode. If the electrolyte membrane is too dry, its conductivity falls; however, excess water results in cathode flooding and morphological instability of the membrane. The water uptake and swelling ratio of SPPEK membranes were determined by the measurement of the change in the mass and length before and after hydration. The results are listed in Table 3, which shows that the water uptake of SPPEK increased with the DS at both RT and an elevated temperature. At 80 °C, the water uptake and swelling ratio of SPPEKs with lower DSs reached equilibrium values quickly. However, the water uptake and swelling ratio of SPPEK with DS $\geq$ 1 increased with time, and

Table 3. Water Uptake and Swelling Ratio of SPPEK[a]

| | RT | 80 °C | | | | | |
| | 3 days | 2h | | 24 h | | 40 h | |
DS	Water Uptake (%)	Water Uptake (%)	Swelling Ratio (%)	Water Uptake (%)	Swelling Ratio (%)	Water Uptake (%)	Swelling Ratio (%)
0.14	6	14	2.4	14	2.4		
0.60	15	16	3.6	16	3.6	—	—
0.81	19	21	6.4	22	6.4	—	—
1.03	19	44	12	63	20	170	34, PSw
1.23	32	Sw	SOL	—	—	—	—
1.63	100	SOL	—	—	—	—	—

[a] Sw = swelling; PSw = partial swelling; SOL = soluble.

some samples were swollen or dissolved in water. The molecular structure of SPPEK was composed of a hydrophobic backbone and hydrophilic sulfonic acid groups. Absorbed water also acted as plasticizer and promoted the phase separation. When the DS was high enough, it became easy for the SPPEK chains to be separated by water and dissolved.

Proton Conductivity

Before the conductivity measurements, all membrane samples were soaked in water 1 or 2 days for hydration. The effect of the DS on the conductivity of SPPEK is shown in Figure 7, which shows that the conductivity of SPPEK at RT increased with DS and reached 2×10^{-2} S/cm for SPPEK with a DS of 1.23. This value is similar to that of Nafion 117, which shows a conductivity of 3×10^{-2} S/cm. Figure 7 also shows the influence of temperature on the conductivity for SPPEKs with DSs of 1.03 and 1.23. The conductivities of these two SPPEKs increased with increasing temperature up to 95 °C and reached 4×10^{-2} and 6×10^{-2} S/cm,
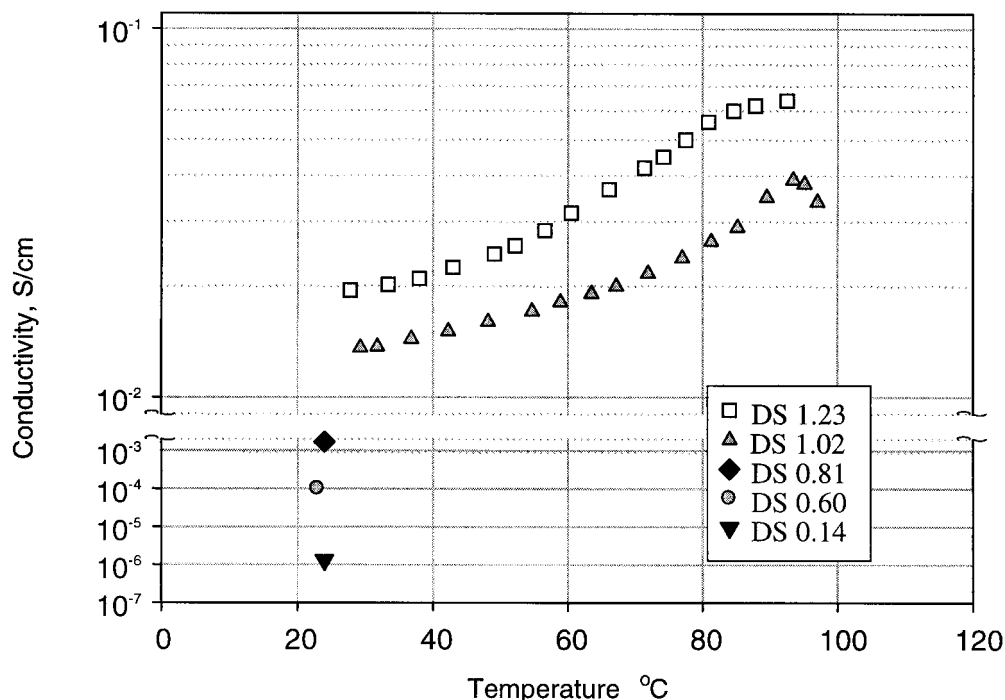
Figure 7. Conductivity of SPPEK.

respectively. The conductivity of SPPEK with a DS of 1.03 dropped sharply after that, and this was probably caused by the dehydration of the membrane. Compared with that of Nafion 117, the drop in conductivity at 80 °C occurred at a higher temperature for SPPEK.

CONCLUSIONS

A series of SPPEKs with different DSs were prepared from PPEK with mixtures of fuming and concentrated sulfuric acid as both the solvent and sulfonating agent. The structure of SPPEK was confirmed by FTIR, and the DS of SPPEK was determined by ^{1}H NMR. As the DS of SPPEK increased, T_d decreased and T_g increased above T_d. Membrane films prepared from SPPEKs showed a continuous increase in the water uptake and swelling ratio with DS. Membranes prepared from SPPEKs with DSs of 1.03 and 1.23 showed an attractively high conductivity of 10^{-2} S/cm at both RT and an elevated temperature.

REFERENCES AND NOTES

1. Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Teramoto, T. J Polym Sci Part A: Polym Chem 1993, 31, 853–858.
2. Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Polymer 2001, 42, 359–373.
3. Miyatake, K.; Hay, A. S. J Polym Sci Part A: Polym Chem 2001, 39, 3211–3217.
4. Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. J Membr Sci 2002, 197, 231–242.
5. Faure, S.; Cornet, N.; Gebel, G.; Mercier, R.; Pineri, M.; Sillion, B. In Proceedings of the Second International Symposium on New Materials for Fuel Cell and Modern Battery Systems, Montreal, Canada, July 6–10, 1997; Savadogo, O.; Roberge, P. R., Eds.; École Polytechnique de Montréal, 1997; p 818.
6. Nolte, R.; Ledjeff, K.; Bauer, M.; Mülhaupt, R. J Membr Sci 1993, 83, 211–220.
7. Kobayashi, T.; Rikukawa, M.; Sanui, K.; Ogata, N. Solid State Ionics 1998, 106, 219–225.
8. Glipa, X.; Haddad, M. E.; Jones, D. J.; Rozière, J. Solid State Ionics 1997, 97, 323–331.
9. Kerres, J.; Cui, W.; Reichle, S. J Polym Sci Part A: Polym Chem 1996, 34, 2421–2438.
10. Soczka-Guth, T.; Baurmeister, J.; Frank, G.; Knauf, R. Int. Patent WO 99/29763, 1999.
11. Zaidi, S. M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. J Membr Sci 2000, 173, 17–34.
12. Jones, D. J.; Rozière, J. J Membr Sci 2001, 185, 41–58.
13. Nunes, S. P.; Ruffmann, B.; Rikowski, E.; Vetter, S.; Richau, K. J Membr Sci 2002, 203, 215–225.
14. Wilhelm, F. G.; Pünt, I. G. M.; Van der Vegt, N. F. A.; Strathmann, H.; Wessling, M. J Membr Sci 2002, 199, 167–176.
15. Huang, R. Y. M.; Shao, P.; Burns, C. M.; Feng, X. J Appl Polym Sci 2001, 82, 2651–2660.
16. Helmer-Metzmann, F.; Osan, F.; Schneller, A.; Ritter, H.; Ledjeff, K.; Nolte, R.; Thorwirth, R. U.S. Patent 5,438,082, 1995.
17. Yen, S.-P. S.; Narayanan, S. R.; Halpert, G.; Graham, E.; Yavrouian, A. U.S. Patent 5,769,496, 1998.
18. Jian, X. G.; Meng, Y. Z.; Zheng, H. B. Chinese Patent 93109180.2, 1993.
19. Jian, X. G.; Meng, Y. Z.; Zheng, H. B. Chinese Patent 93109179.9, 1993.
20. Meng, Y.; Hill, A. R.; Hay, A. S. J Polym Sci Part A: Polym Chem 1999, 37, 1781–1788.
21. Meng, Y. Z.; Hay, A. S.; Jian, X. G.; Tjong, S. C. J Appl Polym Sci 1998, 68, 137–143.
22. Dai, Y.; Jian, X.; Liu, X.; Guiver, M. D. J Appl Polym Sci 2001, 79, 1685–1692.
23. Dai, Y.; Jian, X.; Zhang, S.; Guiver, M. D. J Membr Sci 2002, 207, 189–197.