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Aromatic Poly(ether ketone)s with Pendant Sulfonic Acid Phenyl Groups Prepared by a Mild Sulfonation Method for Proton Exchange Membranes[†]

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ABSTRACT: The sulfonation selectivity of seven poly(ether ether ketone)s (PEEKs) was investigated, and several possessed targeted single- or double-substituted sites per repeated unit on pendant phenyl groups via the postsulfonation approach. The presence of the various pendant groups enabled postsulfonation to occur under mild reaction conditions, in much shorter times than required for the sulfonation of commercial PEEK. A series of poly(ether ketone)s (PEKs) with ion exchange capacity of 2.23−0.84 mequiv/g could be realized by controlling the length of unsulfonated segments of both homopolymers and copolymers. These side-group sulfonation polymers had excellent mechanical properties, good thermal and oxidative stability, and good dimensional stability in hot water. The methanol permeability values of Me-SPEEKK, Me-SPEEKDK, Ph-SPEEKK, and Ph-SPEEKDK at room temperature were in the range 3.31×10^{-7}−9.55×10^{-8} cm^2/s, which is several times lower than that of Nafion 117. Me-SPEEKK and Ph-SPEEKK also exhibited high proton conductivity of 0.15 S/cm at 100 °C, which is higher than that of Nafion 117. Transmission electron microscopy analysis was used to observe their microstructure for evidence of microphase separation of ionic and hydrophobic domains. The results showed these side-group-acid materials are possible inexpensive candidate materials for proton exchange membranes in fuel cell applications.

Introduction

Fuel cells, devices transforming chemical energy directly into electricity, are regarded as one of the promising clean future power sources. Proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) using polymeric proton conductive membranes as one of key components are drawing more and more attention for their utility in automotive and portable electronic applications.[1,2] A continuous effort is being made to develop new high-performance proton conductive membranes as an alternative to Nafion, which is the principal material used as the polymeric electrolyte in PEMFC systems because of its excellent chemical and mechanical stabilities and high proton conductivity. However, high cost, low operation temperature (≤80 °C), high methanol crossover, and environmental recycling uncertainties of Nafion and other similar perfluorinated membranes are limiting their widespread commercial application in PEMFC and DMFC.[3−6]

Aromatic polymers with sulfonic acid groups are promising materials for PEMs and polymer−inorganic hybrid membranes because of their outstanding thermal and chemical stability. Sulfonated derivatives of poly(ether sulfone) (SPES),[7−9] polyimide (SPI),[10−12] polyimidazole,[13] poly(aryl ether),[14,15] polyphenylene,[16,17] and polybenzimidazole[18] are among those being investigated as potential PEMs. However, to further simplify the preparation process and enhance performance of these materials, there are still some challenges, such as stereo-controllable chemical structures including easily controllable degree of sulfonation (DS) and sulfonation sites and well-refined microstructure by grafting, alternating, and blocking polymerization.[19]

Aromatic poly(ether ketone)s (PEKs) are well-known as high-performance thermoplastics for their overall combination of chemical, physical, and mechanical properties.[20,21] As a class of promising PEM materials, several series of PEKs have been prepared so far. Most of the sulfonated PEK membranes were developed on the basis of postsulfonated commercial polymers or on copolymers produced from sulfonated monomers. Two general synthetic approaches have been used to realize the introduction of sulfonic acid groups into this family of polymers.[3] One approach is postsulfonation of existing polymers, and the other is direct copolymerization of sulfonated monomers. In the case of the postsulfonation approach, this method is attractive because of the available resource of commercial polymers, such as Victrex poly(ether ether ketone) (PEEK) as well as a simple reaction procedure, enabling the process to be readily scaled up. However, difficulties may be encountered in the precise control of the sulfonation sites and the DS, resulting in a random and less defined distribution of sulfonic acid groups along the polymer chain. In addition, rigorous reaction conditions, such as high temperature and strongly acidic sulfonating agent, are usually used to sulfonate polymers such as PEEK, which in some cases may lead to the occurrence of side reactions and degradation of the polymer backbone.[3,19−25] In the case of the sulfonated monomer approach, despite the limited number of available sulfonated monomers and the preparation difficulties of the some sulfonated monomers, the direct copolymerization of sulfonated monomer with other nonsulfonated monomers has the potential for synthesizing random copolymers with a better control of sulfonation content (SC) and more defined chain

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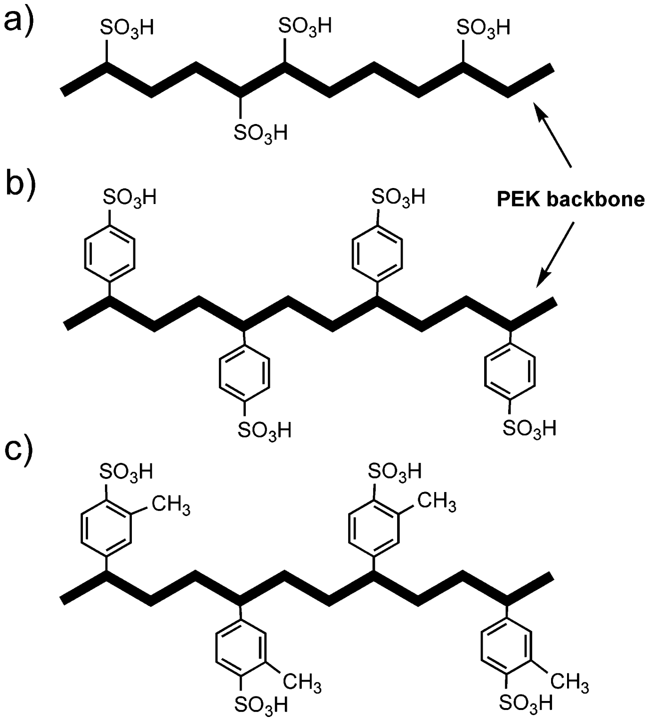
Scheme 1. Representations of (a) Main-Chain-Acid PEKs by Postsulfonation, (b) Side-Group-Acid Ph-PEKs by Postsulfonation, and (c) Side-Group-Acid Me-PEKs by Postsulfonation



structures in comparison with the copolymers by the postsulfonation method.[26−28] Thus, it is of interest to prepare sulfonated polymers via the postsulfonation method whereby the design of the polymeric structures demonstrate controllable specific sulfonation sites and DS in a manner to achieve well-defined sulfonated polymer structures that would normally be accessed by a direct copolymerization method.

Recently, several stereocontrolled sulfonated polymers were reported by Miyatake and Hay et al., and they also suggested that polymers with the sulfonated groups attached to pendant side groups are very stable under heat, hydrolysis, and oxidation.[29,30] Jannasch et al. reported several side-group-acid poly(ether sulfone)s with some attractive properties based on lithiation reaction.[24,31] Polyimides with side-group-acid substituents were also developed by Okamoto et al. and Watanabe et al.[32−34] To our knowledge, there are still no detailed reports related to the control of substitution sites through adjusting their various molecular structures. In addition, there are few reports of side-group-acid PEKs and their properties.

In the present study, the sulfonation reaction of PEEKs with the various side substituents, such as phenyl, methylphenyl, trifluoromethylphenyl, and phenoxylphenyl groups, were investigated. Two series of sulfonated PEKs based on methylphenylated and phenylated PEKs (Me-SPEKs and Ph-SPEKs) with stereocontrolled sites and high sulfonation have been prepared via a postsulfonation method under mild reaction conditions, as shown in Scheme 1. The DS of the copolymers would be controlled by polymer chain composition that contains two types of segments: those that are readily sulfonated and those that are not. The polymer properties related to PEM materials for FC applications have also been thoroughly evaluated.

Experimental Part

Chemicals and Materials. The bisphenol monomers, (3-methyl)phenylhydroquinone, (3-trifluoromethyl)phenylhydroquinone, (3,5-dimethyl)phenylhydroquinone, (3,5-ditrifluoromethyl)phenylhydroquinone, and (4-phenoxyl)phenylhydroquinone, were synthesized according to a reported procedure.[35,36] The difluorinated monomers, 4,4′-difluorobenzophenone (Sigma-Aldrich Ltd.), 1,4-bis(4-fluorobenzoyl)benzene (Jilin University), and 4,4′-bis(4-fluorobenzoyl)biphenyl (Jilin University), were recrystallized from ethanol or chlorobenzene before use. Phenylhydroquinone and (4,4′-hexafluoroisopropylidene)diphenol were obtained from Sigma-Aldrich Ltd. and recrystallized from toluene before use. All other chemicals were obtained from commercial sources and used without further purification.

Synthesis of Starting Materials. The synthesis of the following statistical copolymers was accomplished by nucleophilic aromatic substitution polycondensation.[35−37] As an example, Me-PEEK was prepared as follows: To a 100 mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a Dean−Stark trap with a condenser were added (3-methyl)hydroquinone (2.002 g, 0.01 mol), 4,4′-difluorobenzophenone (2.180 g, 0.01 mol), anhydrous K_2CO_3 (1.794 g, 0.013 mol), DMAc (18 mL), and toluene (15 mL). The system was allowed to reflux for 3 h, and then the toluene was removed. The reaction mixture was heated to 180 °C. After 10 h, another 10 mL of DMAc was added into the viscous reaction mixture. The polymerization was complete after another 2 h. The viscous solution was then poured into 150 mL of ethanol. The polymer was refluxed in deionized water and ethanol several times to remove the salts and solvents and was dried at 120 °C for 24 h.

All the other starting polymers were prepared using the same synthesis and purification routine. Their T_gs and molecular weights are listed in Tables 1 and 2.

Preparation of Sulfonated Polymers and Their Membranes. In view of high substitution reactivity of the pendant phenyl groups on the copolymers, a relatively mild sulfonating reagent and ambient temperature conditions were adopted. A typical reaction was shown as follows:

To a 100 mL of flask, 5 g of Me-PEEKK and 100 mL of concentrated sulfuric acid (95−98%) were added. After stirring at room temperature for several hours, the homogeneous viscous solution was poured into a mixture of water and ice to get a silk-like solid. The solid was washed with water until the water reached neutral. The sulfonated Me-PEEKK was dried in a vacuum oven at 100 °C for 24 h.

A1.0 g sample of polymer was dissolved in 20 mL of DMAc and filtered. The filtered solution was poured onto a glass plate and dried at 50 °C under a constant purge of nitrogen for 4−5 days. The resulting flexible membrane was dried in a vacuum oven at 120 °C for 24 h. The thickness of all membrane films was in the range 100−150 μm.

All the other sulfonated polymers were prepared using the same procedure, and ^{1}H NMR spectroscopy was used to monitor the degree of substitution.

Me-SPEEK: ^{1}H NMR (DMSO-d_6): 7.85−7.65 ppm, m, 5H; 7.38−7.16 ppm, m, 7H; 7.10−6.99 ppm, m, 2H; 2.49 ppm, m (overlapped by DMSO signal).

Ph-SPEEK: ^{1}H NMR (DMSO-d_6): 7.86−7.65 ppm, m, 4H; 7.58 ppm, d (8 Hz), 2H; 7.49 ppm, d (8 Hz), 2H; 7.37−7.33 ppm, d (2 Hz), 1H; 7.34−7.17 ppm, m, 4H; 7.07−7.00 ppm, m, 2H.

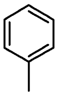
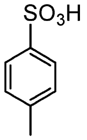
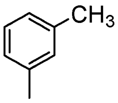
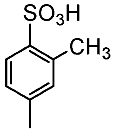
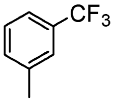
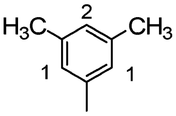
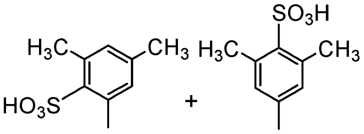
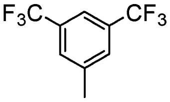
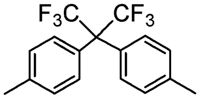
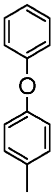
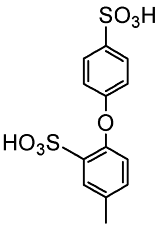
DiMe-SPEEK: ^{1}H NMR (DMSO-d_6): 7.87−7.59 ppm, m, 4H; 7.38−7.15 ppm, m, 4.5H; 7.13 ppm, 1.7H; 7.09−6.96 ppm, m, 2.3H; 6.93 ppm, s, 0.3H; 6.77 ppm, s, 0.3H, 2.56−2.47 ppm, m (overlapped by DMSO signal).

Ph-o-Ph-SPEEK: ^{1}H NMR (DMSO-d_6): 8.00 ppm, s, 1H; 7.87−7.64 ppm, m, 4H; 7.54 ppm, d (8 Hz), 2H; 7.50 ppm, d (8 Hz), 1H; 7.35−7.15 ppm, m, 4.5H; 7.12−6.96 ppm, m, 2.5H; 6.87−6.74 ppm, m, 3H.

Me-SPEEKK: ^{1}H NMR (DMSO-d_6): 7.95−7.64 ppm, m, 9H; 7.40−7.20 ppm, m, 6.70H; 7.10−7.00 ppm, m, 2.3H; 2.49 ppm, m (overlapped by DMSO signal).

Me-SPEEKDK: ^{1}H NMR (DMSO-d_6): 8.02−7.66 ppm, m, 13H; 7.39 ppm, d (2 Hz), 1H; 7.37−7.21 ppm, m, 5.75H; 7.06 ppm, d, 2.5H.

Table 1. Investigation of the Selectivity of Stereocontrolled Sulfonation Reaction

starting PEEKs with the following group	M_n/M_w[a]	Tg (°C)[b]	DT (°C)[c]	$T_{5\%}$ (°C)[d]	PEEKs after sulfonation
 phenyl	40000/ 76000	158	512	524	 Ph-SPEEK
 3-methylphenyl	60000/ 170000	147	453	465	 Me-SPEEK
 3-trifluoromethylphenyl	44000/ 88000	134	525	533	No obvious reaction
 3,5-dimethylphenyl	56000/ 170000	162	438	444	 DiMe-SPEEK
 3,5-ditrifluoromethylphenyl	33000/ 62000	146	520	527	No obvious reaction
 hexafluoroisopropyldiphenyl	68000/ 140000	166	505	521	No obvious reaction
 4-phenoxylphenyl	35000/ 67000	146	516	523	 Ph-o-Ph-SPEEK

[a] Number-average molecular weight (M_n) and weight-average molecular weight (M_w) estimated by GPC using tetrahydrofuran and poly(styrene) as an eluent and standard. [b] From the second heating trace of DSC measurements conducted at a heating rate of 10 °C min^{-1}. [c] Onset temperature of decomposition measured by TGA at a heating rate of 10 °C min^{-1} under N_2. [d] Temperature at 5% weight loss measured by TGA at a heating rate of 10 °C min^{-1} under N_2.

Ph-SPEEKK: ^1H NMR (DMSO-d_6): 7.93−7.72 ppm, m, 8H; 7.58 d (8 Hz), 2H; 7.50 ppm, d (8 Hz), 2H; 7.40−7.21 ppm, m, 5H; 7.06 ppm, d (8 Hz), 2H.

Ph-SPEEKDK: ^1H NMR (DMSO-d_6): 8.02−7.73 ppm, m, 12H; 7.60 ppm, d (8 Hz), 2H; 7.51 ppm, d (8 Hz), 2H; 7.39 ppm, d (2 Hz), 1H; 7.35 ppm, 2 (8 Hz), 1H; 7.31−7.22 ppm, m, 3H; 7.07 ppm, d (8 Hz), 2H.

Characterization and Measurements. FTIR spectra of the samples were measured on a Nicolet 520 Fourier transform spectrometer, and a diamond cell was used as a holder for the thin films of the polymers. The thin films for the FTIR measurements were cast from DMAc polymer solution. ^1H and ^{13}C NMR spectra of the sulfonated polymers were obtained on a Varian Unity Inova NMR spectrometer operating at frequencies of 399.95 MHz for ^1H and 100.575 MHz for ^{13}C. An indirect detection probe was used for the acquisition of 1D and 2D spectra. Deuterated dimethyl sulfoxide (DMSO-d_6) was selected as the solvent, and the DMSO signals at 2.50 ppm (^1H NMR) and 39.51 ppm (^{13}C NMR) were used as the chemical shift references.

Inherent viscosities (η_{inh}) were measured using an Ubbelohde viscometer at a polymer concentration of 0.5 g/dL in DMAc solutions at 30 °C. Gel permeation chromatography (GPC) was obtained by a Waters 410 instrument with tetrahydrofuran (THF) as the eluant and polystyrene as standards.

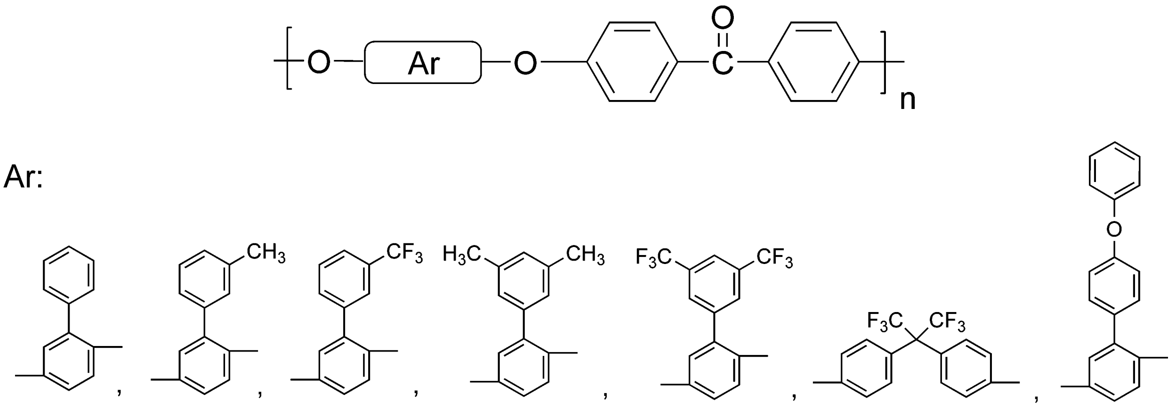
A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for evaluating thermal stability of the polymers. Polymer samples for TGA analysis were preheated at 150 °C for 40 min under a nitrogen atmosphere to remove moisture. Samples were then heated at 10 °C/min from 50 to 800 °C under a nitrogen atmosphere. A TA Instruments differential scanning calorimeter (DSC) model 2920 was used for measuring T_g. Samples for DSC analysis were initially heated at a rate of 10 °C/min under

Table 2. Viscosity, IEC, and Thermal Properties of the Polymers

polymer	η (dL/g) unS[a]	η (dL/g) S[b]	T_g (°C) unS	T_g (°C) S	TD (°C) unS	TD (°C) S	$T_{5\%}$ (°C) unS	$T_{5\%}$ (°C) S	IEC (mequiv/g) calcd	IEC (mequiv/g) expt	EW (g/mol SO_3) calcd
Me-SPEEK	0.96	2.16	147	190	453	207	465	239	2.18	2.19	459
Me-SPEEKK		3.42	159	167	462	206	478	240	1.78	1.80	562
Me-SPEEKDK		1.20	170	182	454	214	472	276	1.57	1.61	637
Ph-SPEEK	0.62	1.50	158	185	512	210	524	241	2.25	2.23	444
Ph-SPEEKK		3.10	166	174	496	204	506	251	1.82	1.76	549
Ph-SPEEKDK		3.35	186		502	212	522	262	1.60	1.60	625
Me-6F-SPEEK-40	0.70	1.46	146	157	451	202	477	278	0.83	0.84	1205
Me-6F-SPEEK-60	0.62	4.85	145	185	448	205	473	254	1.26	1.28	794
Me-6F-SPEEK-80	0.96	2.90	146	185	435	202	455	256	1.71	1.80	585
Ph-6FA-SPEEK-40	0.98	2.98	164	163	510	202	531	253	0.82	0.85	1220
Ph-6FA-SPEEK-60	1.08	3.43	164	167	513	202	536	256	1.27	1.37	787
Ph-6FA-SPEEK-80	1.30	3.19	163	168	518	213	522	264	1.75	1.82	571

[a] The polymers before sulfonation. [b] The polymers after sulfonation.

Scheme 2. Polymers for the Selectivity of Sulfonation Reaction



a nitrogen atmosphere to the temperature below their decomposition temperature, followed by quenching them to room temperature. Following this, the samples were heated at a rate of 10 °C/min under nitrogen atmosphere to evaluate T_g.

The proton conductivities of the membranes were estimated from ac impedance spectroscopy data, obtained over a frequency range of $1-10^7$ Hz with oscillating voltage of 100 mV, using a Solartron 1260 gain phase analyzer. Specimens in the form of 20 × 10 mm strips were soaked in deionized water for at least 24 h prior to the test. Each specimen was placed in a temperature-controlled cell open to the air by a pinhole, where it was equilibrated at 100% RH at ambient pressure. Each end of the membrane strip was clamped in a frame between two stainless steel electrodes. Measurements, in four-point mode, were carried out after sample conditioning in the closed cell overnight or longer. The conductivity (σ) of the samples in the longitudinal direction was calculated, using the relationship $\sigma = L/RdW$, where L is the distance between the electrodes and d and W are the thickness and width of the sample stripe, respectively. R was derived from the low intersect of the high-frequency semicircle on a complex impedance plane with the Re (Z) axis.

Mechanical properties of the thin dry and wet films were evaluated at room temperature on an Instron 5565 instrument at a strain rate of 10 mm/min, and a 500 N load cell was used. The samples were prepared by cut into a dumbbell shape (DIN-53504-S3A). The samples in the wet state were obtained by immersing the samples in water for 48 h, and the samples in the dry state were obtained by putting samples in vacuum oven at 100 °C for 24 h.

TEM samples were stained by immersing films in lead acetate aqueous solution for 24 h, thoroughly washed with water, and dried at room temperature. The polymer samples were embedded in polystyrene. Specimen microtomy was performed using Reichert-Jung UltraCut E. A sample slice was placed onto a 300 mesh carbon-coated holey TEM copper grid and was dried in vacuum. The dried grid was then loaded into a double tilt sample holder. The sample was thus examined with a Philips CM20 STEM equipped with a Gatan UltraScan 1000 CCD camera combined with a Digital Micrograph Software (dm3.4) and an energy dispersive X-ray spectrometer: INCA Energy TEM 200. TEM images were taken at 120 kV.

Water Uptake and Swelling Ratio Measurements. The membranes were dried at 100 °C overnight prior to the measurements. After measuring the lengths and weights of dry membranes, the sample films were soaked in deionized water for 24 h at predetermined temperatures. Before measuring the lengths and weights of hydrated membranes, the water was removed from the membrane surface by blotting with a paper towel.

The water uptake content was calculated by

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

where ω_{dry} and ω_{wet} are the weights of dried and wet samples, respectively.

The swelling ratio was calculated by

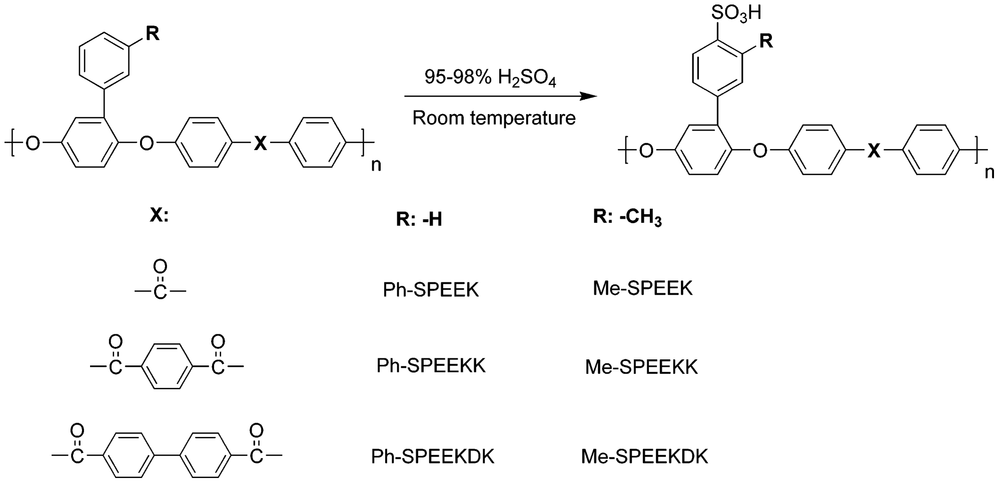
$$\text{swelling ratio (\%)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100\%$$

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

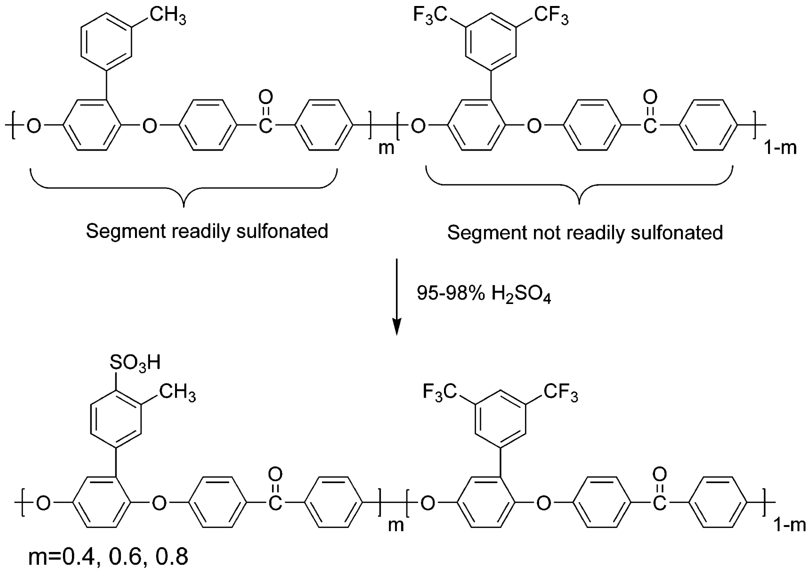
Oxidative Stability, Ion Exchange Capacity (IEC), and Methanol Permeability. Oxidative stability of the membranes was tested by immersing the films into Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. Their retained weights (RW) of membranes after treating in Fenton's reagent for 1 h and the dissolved time (t) of polymer membranes into the reagent were used to evaluate oxidative resistance.

IEC of the sulfonated polymers was measured using a typical titration method. The films in acid form were equilibrated with 100 mL of 1 M NaCl for 24 h. The amount of the H^+ released from the

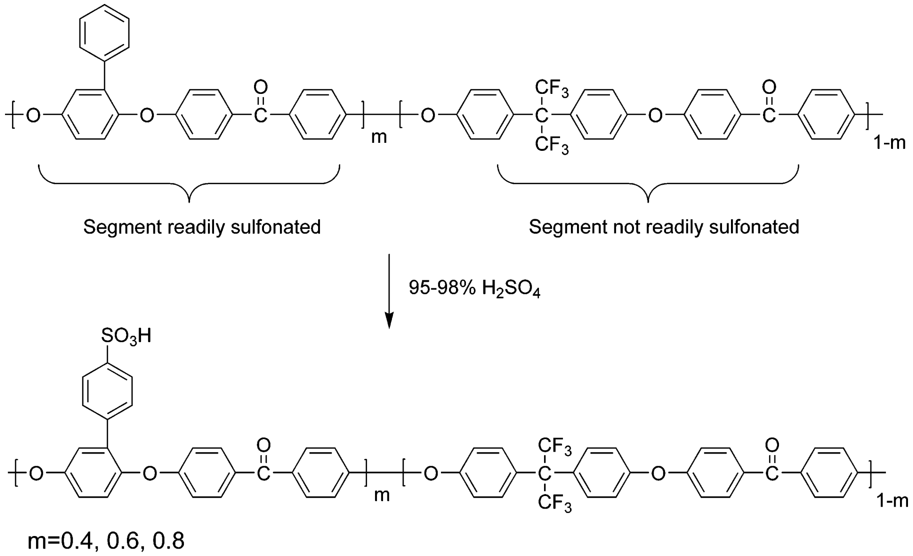
Scheme 3. Structures and Abbreviation of Sulfonated PEKs Based on the Homopolymers



Scheme 4. Preparation of Copolymers with a (4-Sulfonic acid-3-methyl)phenyl Side Group (Me-6F-SPEEK-40,60,80)



Scheme 5. Preparation of Copolymers with a (4-Sulfonic acid)phenyl Side Group (Ph-6FA-SPEEK-40,60,80)



membranes was determined by titration of 0.1 M NaOH aqueous solution and phenolphthalein as an indicator.

Methanol permeability was measured using a simple two-compartment glass diffusion cell. A membrane (2 cm × 2 cm) was placed between two silicone rubber gaskets and with the two compartments clamped together around the gaskets. The active area of the membrane was 1.757 cm^2. Compartment A was filled with 100 mL of 10% or 50 vol % methanol with an internal standard of 0.2 vol % 1-butanol in aqueous solution. Compartment B was filled with 100 mL of 0.2 vol % 1-butanol solution.

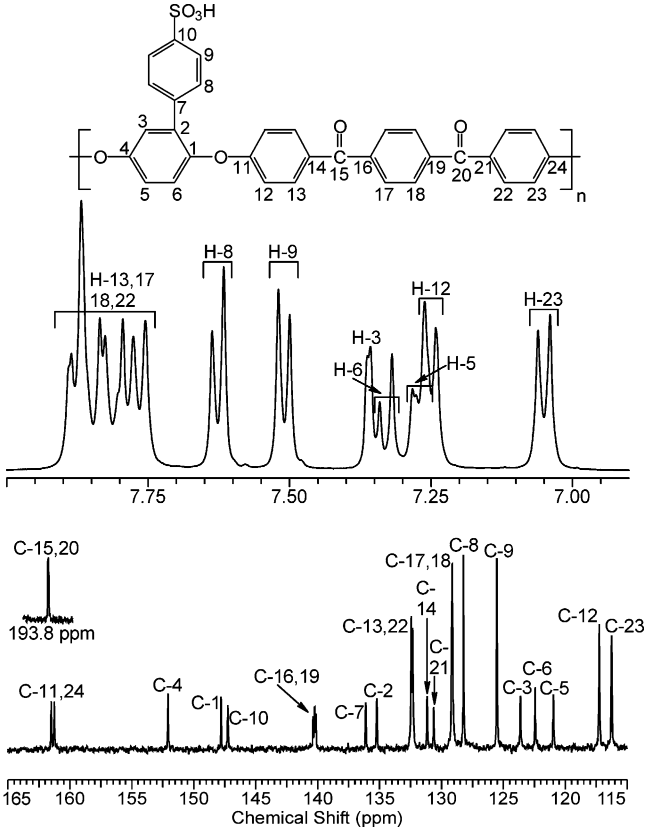


Figure 1. ^1H NMR and ^{13}C spectra for Ph-SPEEKK.

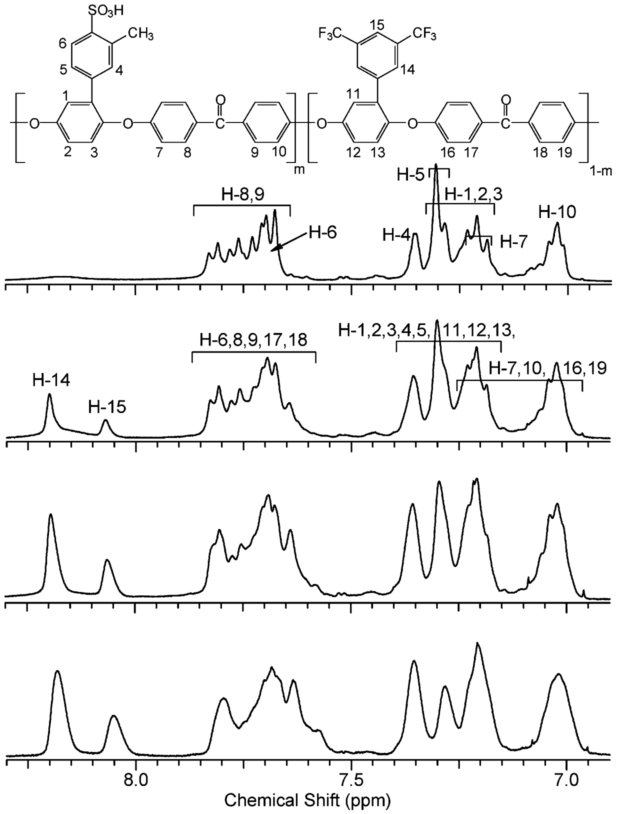


Figure 2. ^1H NMR spectra for Me-SPEEK ($m = 1.0$) and Me-6F-SPEEK-40, -60, and -80 ($m = 0.4$, 0.6, and 0.8).

The diffusion cell was placed in a water bath held at 30 °C, and each compartment was stirred by a separate stir plate to ensure uniform stirring. Samples (4 μL each) were removed from compartment B at intervals of ~15 min each. Methanol concentrations were determined by ^1H NMR spectroscopy.

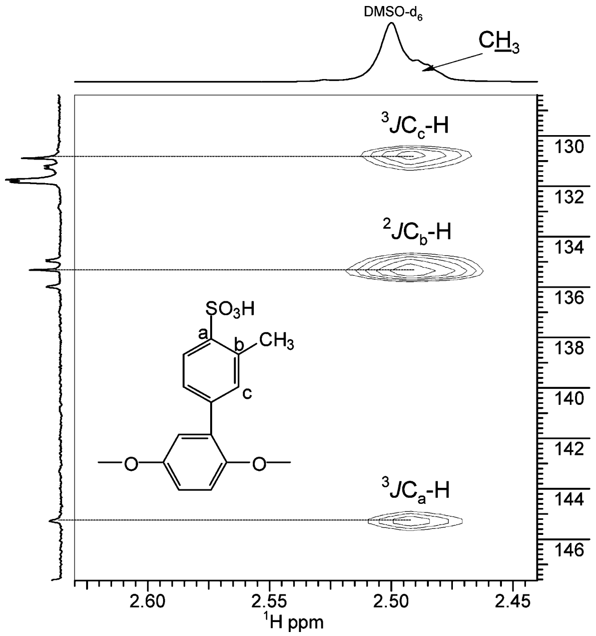


Figure 3. 2D HMBC spectrum of Me-SPEEK.

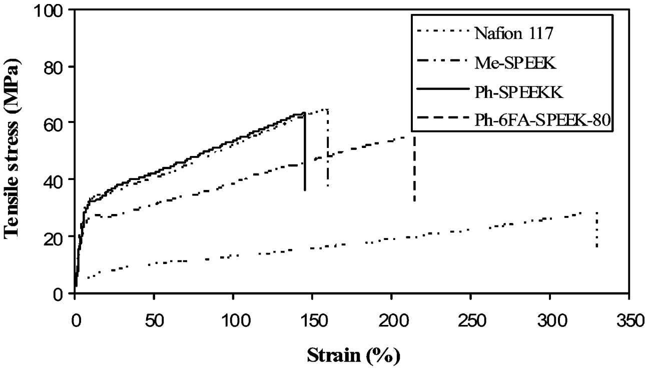


Figure 4. Stress vs strain curves of the PEKs membranes in the wet state.

Results and Discussion

Selectivity of Sulfonation Reaction. Sulfonation is an electrophilic reaction, and the rate and position of substitution of sulfonic acid are determined by the substituents of benzene rings. In order to find an ideal PEEK that could be easily sulfonated via a postsulfonation method, aromatic PEEKs with phenyl, methyl, trifluoromethyl, dimethyl, ditrifluoromethyl, and phenoxylphenyl pendant groups were selected to evaluate the selectivity for sulfonation substitution, as shown in Scheme 2. Their basic properties are listed in Table 1. It is well-known that the two benzene rings connected with strong electron-withdrawing carbonyl group are deactivated, and no electrophilic sulfonation substitution reaction occurred. It was interesting to note that the benzene ring activated by two phenoxy groups on the backbone and bearing a pendant phenyl ring was not obviously substituted by sulfonated groups under the given conditions within 20 h from the ^1H NMR results. This phenomenon could be explained by the effect of steric hindrance and complex interaction of substituents. Because of the good solubility in DMSO, the sulfonation reaction could be readily monitored by NMR spectroscopy. Rigorous sulfonation conditions, such as high reaction temperatures, long reaction periods, and strong sulfonation reagents, may lead to destruction of the polymer chain and the resulting loss of mechanical strength. In the present study, a simple and mild sulfonation reaction condition of room temperature sulfuric acid was applied to affect

Table 3. Mechanical Properties of the Sulfonated Polymers

polymer	tensile strength (MPa) dry	tensile strength (MPa) wet	Young's modulus (GPa) dry	Young's modulus (GPa) wet	elongation at break (%) dry	elongation at break (%) wet
Me-SPEEK	79.6	64.5	1.53	0.72	22.3	159.0
Me-SPEEKK	110.0	42.6	2.03	0.40	20.9	204.5
Me-SPEEKDK	98.0	59.5	1.92	0.85	13.3	114.7
Ph-SPEEK	87.0	45.6	1.76	0.32	9.9	183.8
Ph-SPEEKK	103.2	63.6	2.15	0.60	10.4	145.1
Ph-SPEEKDK	88.6	64.1	2.12	0.70	52.0	128.3
Me-6F-SPEEK-40	107.3	60.1	1.93	1.41	10.3	75.3
Me-6F-SPEEK-60	106.2	52.0	2.03	0.77	15.5	85.4
Me-6F-SPEEK-80	101.2	51.0	2.17	0.67	13.4	80.9
Ph-6FA-SPEEK-40	77.9	61.3	1.80	0.95	52.9	134.9
Ph-6FA-SPEEK-60	103.8	61.2	2.06	0.67	22.5	138.0
Ph-6FA-SPEEK-80	91.6	55.5	1.73	0.52	73.9	214.1
Nafion 117[a]	38.0	28.4	0.18	0.10	301.5	329.2

[a] Data measured in our laboratories.

Table 4. Methanol Permeability, Proton Conductivity, and Oxidative Stability

polymer	methanol permeability (cm^2/s)	σ (S/cm) 30 °C	σ (S/cm) 100 °C	oxidative stability RW (%)[b]	oxidative stability *t* (h)[c]
Me-SPEEK	7.43×10^{-7}	0.049	0.158		
Me-SPEEKK	2.28×10^{-7}	0.033	0.154	97	2.5
Me-SPEEKDK	9.55×10^{-8}	0.021	0.080	98	>6.0
Ph-SPEEK	1.05×10^{-6}	0.060	0.182		
Ph-SPEEKK	3.31×10^{-7}	0.038	0.151	98	2.0
Ph-SPEEKDK	2.30×10^{-7}	0.023	0.088	99	>6.0
Me-6F-SPEEK-40	2.54×10^{-8}	0.006	0.023	98	>6.0
Me-6F-SPEEK-60	5.54×10^{-8}	0.009	0.050	97	4.5
Me-6F-SPEEK-80	1.91×10^{-7}	0.032	0.172	94	2.0
Ph-6FA-SPEEK-40	6.66×10^{-8}	0.009	0.040	98	>6.0
Ph-6FA-SPEEK-60	2.05×10^{-7}	0.012	0.058	97	2.5
Ph-6FA-SPEEK-80	5.28×10^{-7}	0.027	0.109	95	2.0
Nafion 117[a]	1.55×10^{-6}	0.078	0.138	98	>6.0

[a] Data measured in our laboratories. [b] Retained weights of membranes after treating in Fenton's reagent for 1 h. [c] The dissolved time of polymer membranes.

the sulfonation of the evaluated polymers. The results showed that all of monomethylated, phenylated, and phenoxylphenylated PEEKs had outstanding selectivity of sulfonation reaction by sulfuric acid took place, which was achieved within a short reaction period. Because of the existence of the deactivated trifluoromethyl, no substitution reaction was observed for trifluoromethylated and ditrifluoromethylated PEEKs. For dimethylated PEEK (DiMe-SPEEK), it did not have good substitution selectivity. Positions 1 and 2 could be substituted, and the substitution ratios were around 30% and 70%, respectively. Single-acid substitution on the side group every repeat unit for Me-PEEK and Ph-PEEK and double-acid substitution for Ph-*o*-Ph-PEEK could be achieved under these convenient reaction conditions.

Sulfonation Reactivity Comparison of PEEK and Phenylated and Methylphenylated PEEKs. To access low-cost PEM membranes, a straightforward method is to introduce sulfonic acid groups into commercial polymers. Sulfonated PEEK (Victrex) has been widely studied on the basis of its high performance. Bishop et al.[38−41] reported that it took up to around 1 month in 97.4% sulfuric acid at room temperature to obtain the fully sulfonated PEEK. In order to enhance the rate of sulfonation reaction of PEEK, high reaction temperature and strong sulfonation reagent (e.g., fuming sulfuric acid) have to be used. In comparison to the sulfonation of PEEK, the phenylated and 3-methyphenylated PEEKs had considerable advantage over the reaction rate. For both of them, the sulfonation reaction proceeded rapidly in 95−98% sulfuric acid at room temperature, the highly sulfonated polymers being obtained within 3 h. It was also interesting to note that sulfonation was site-specific; only one substitution site on the pendant benzene ring for per repeat unit of Me-SPEEK (DS ≥ 90%) and Ph-SPEEK (DS ∼ 100%) was found by ^{1}H NMR spectroscopy.

Sulfonation Content Adjustment. The sulfonic acid content of PEM materials is an important factor because it is strongly related to proton conductivity, water uptakes, and dimensional stability of the membranes. According to the reported literature, reaction conditions, such as reaction time and temperature, have often been used to control the DS.[3,41] It is obvious that it is usually hard to concisely control the DS via this method. It has also been shown that the sulfonation of PEEK in sulfuric acid cannot be used to produce truly random copolymers at sulfonation levels less than 30% because dissolution and sulfonation occur in a heterogeneous environment. A facile and efficient reaction combined with controllable sulfonation sites would make it possible to control the DS by the length adjustment of the copolymer segments that cannot be sulfonated. The first method utilized in this study for controlling the sulfonic acid content was the polymerization of bisphenol monomer containing pendant group with various difluorodiphenyl ketone monomers of different length to give homopolymers with well-defined molecular structure. The bisphenol segment is readily sulfonated while the phenyl ketone segment is not (Scheme 3).

The second method to control DS we used is based on copolymerization, which is often applied to prepare PEM materials from sulfonated monomers to control DS. In the present work, we prepared copolymers with certain ratios of sulfonable/unsulfonable segments via the copolymerization method and then conducted postsulfonation, as shown in Schemes 4 and 5.

FTIR spectroscopy confirmed the presence of sulfonated groups. In comparison with unsulfonated polymer starting materials, new absorption bands around 1029 and 1085 cm^{-1} arise from symmetric and asymmetric stretching vibrations of sulfonic groups in sulfonated polymers.

Figure 1 shows both ^{1}H and ^{13}C NMR spectra of sulfonated Ph-SPEEKK fully assigned. The simple NMR patterns of both spectra indicate full substitution of the hydrogen at the para position of the pendant group by a sulfonic acid. This is also supported by the accurate peak integration values in ^{1}H NMR which correspond to a fully substituted polymer. Furthermore, we prepared samples of unsulfonated and sulfonated polymers in a common solvent in which they were both soluble in DMF-d_7. The spectra showed obvious changes in signal positions and

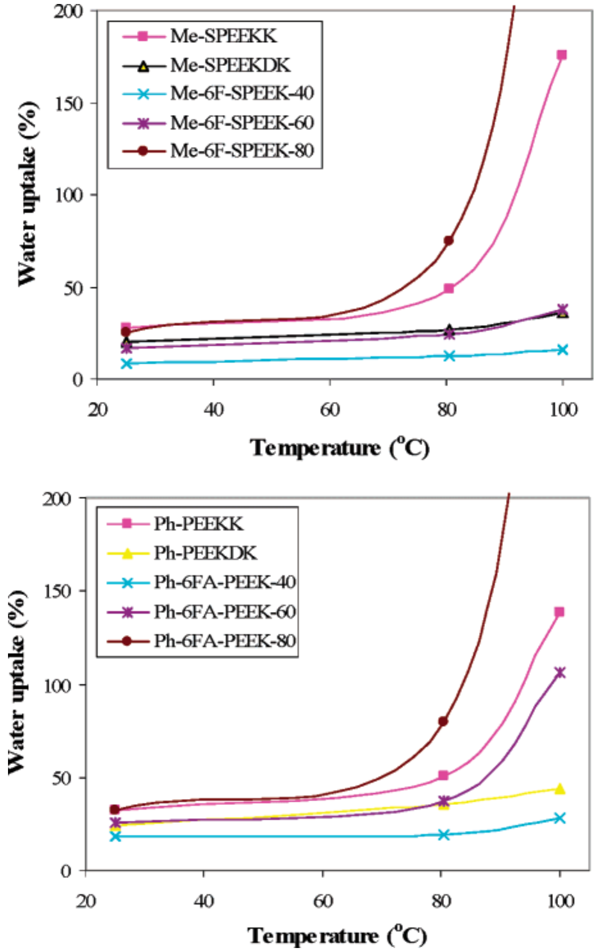


Figure 5. Water uptake of the membranes at different temperature.

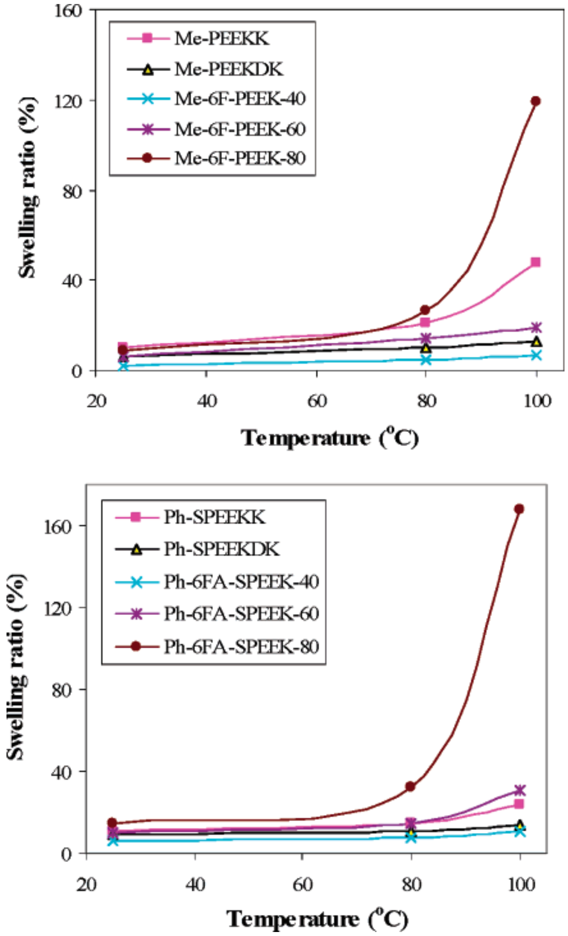


Figure 6. Swelling ratio of the membranes at different temperature.

peak intensities, indicating full substitution had occurred. It was important to fully characterize the homopolymer and ascertain without doubt that substitution occurred because the copolymer spectra are complex, having broad lines which make complete characterization impractical. As an example, Figure 2 shows ^{1}H NMR stacked spectra of Me-6F-SPEEK copolymers and Me-SPEEK homopolymer with peak assignments. Me-SPEEK was fully characterized to ascertain the presence of a sulfonic acid and also its exact position on the phenyl ring. The sulfonated site was identified as the para position on the pendant phenyl ring. The 2D HMBC spectrum displayed in Figure 3 clearly shows three multiple bond couplings between the hydrogen of the methyl group at 2.49 ppm and three carbon atoms at 145.3, 135.3, and 130.9 ppm. Of the three signals, only the carbon peak at 130.9 ppm is a CH; the other two are quaternary carbon atoms as determined by HSQC. Since one coupling is from $^{2}JC_{b}-H$ (135.3 ppm), it leaves two other couplings for $^{3}JC_{a}-H$ and $^{3}JC_{c}-H$. One of these carbon atoms is a CH carbon (C_c at 130.9 ppm), and the other is quaternary and is also at high frequency which is typical of carbon atoms attached to heteroatoms; hence, C_a at 145.3 ppm is $C-SO_3H$. It was also found from the ^{1}H NMR that sulfonic acid substitution was not 100%. The smaller aromatic signals in Figure 2 and especially the second smaller CH_3 signal at 2.22 ppm (from DMSO-d_6) led us to believe there could be unsubstituted repeat units. That was confirmed, as it was previously done before with sulfonated Ph-SPEEKK, by running samples of unsulfonated and sulfonated polymers in a common solvent in which they were both soluble in DMF-d_7. As expected, the unsubstituted pendant group had a methyl signal at the exact same chemical shift as the smaller signal in the sulfonated polymer. The ratio of substituted to unsubstituted repeat units was found to be 9:1 from the intensities of the two CH_3 signals in the sulfonated polymer ^{1}H spectrum, which meant that DS of Me-SPEEK was ~0.90.

Ion exchange capacity (IEC) is a method to indicate the exchangeable ions of polymer membranes, which offer an indirect method to evaluate the degree of sulfonation reaction. The IEC data from titration test were in the range 2.23−0.84 mequiv/g, which were close to the expected values. Consequently, the DS values of this family of copolymers could be well controlled by their structural makeup. Thus, the DS could be expected from the ratios of feed ratios of monomers, which is a considerable advantage over the method controlled by reaction time and temperature.

Thermal Properties. In order to maintain their good mechanical strength, polymer materials usually operate below the glass transition temperature (T_g). Higher temperature fuel cell operation thus demands PEM materials with high T_g.[42] Only one transition temperature was found in the DSC curve before decomposition temperature for all the samples, which indicated their amorphous nature. For unsulfonated polymers, T_g values were mainly affected by backbone rigidity. They were in the range 145−186 °C mainly decided by their chain rigidity. In general, polymers had higher T_g values after sulfonation because of the introduction of polar sulfonic acid groups. They were in the range 157−190 °C, which determined by both the sulfonation contents and backbone rigidity.

All the unsulfonated polymers showed excellent thermal stability judged by their TGA curves. After sulfonation, the thermal decomposition temperatures decreased to 202−214 °C because of the introduction of sulfuric acid groups. The first

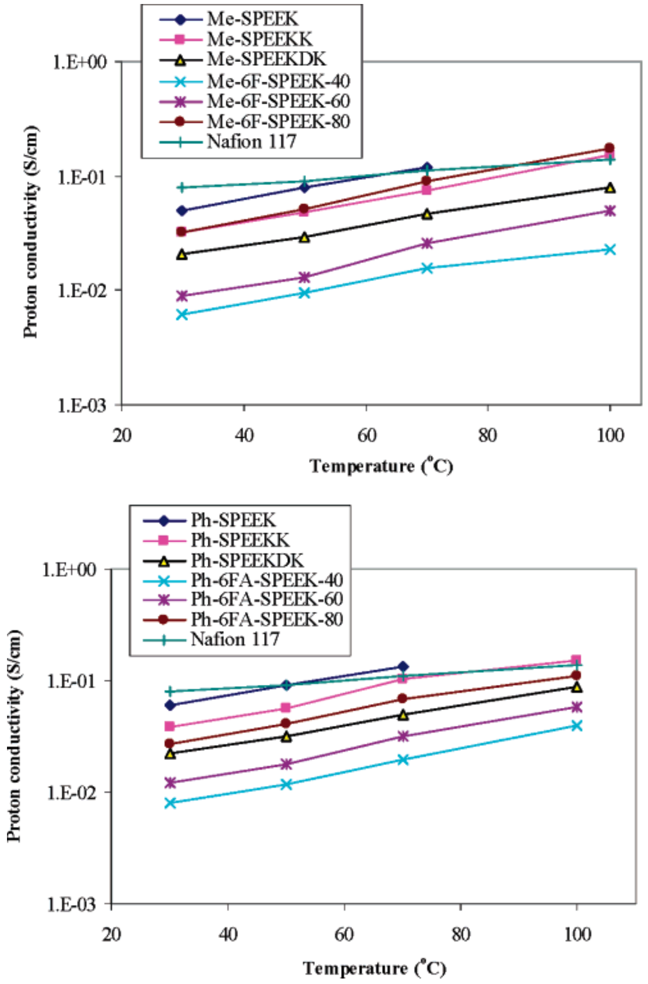


Figure 7. Proton conductivities of the membranes and Nafion 117.

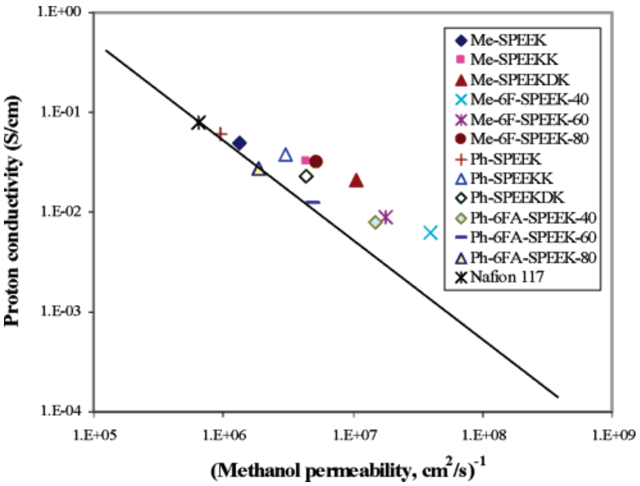


Figure 8. Methanol permeability vs proton conductivities of the membranes and Nafion 117 at 30 °C.

decomposition stage around 210 °C was possibly associated with the loss of water and degradation of the sulfonic acid groups, and the second decomposition stage around 500 °C was related to the degradation of the main chains.

Mechanical Property. Good mechanical properties of the PEMs in either the anhydrous or hydrous states are one of necessary demands for their applications. A comparison of the novel membranes with side-group-acid substituents and Nafion 117 were tested in our study and are listed in Table 3. The samples in the dry state had tensile stress at maximum load of 77.9−110.0 MPa, Young's moduli of 1.53−2.17 GPa, and elongation at break of 9.9−73.9%. In the wet state, the samples showed excellent mechanical properties with tensile stress of 42.6−64.5 MPa and Young's moduli of 0.32−1.41 GPa. Especially, their elongations at break were up to 75.3−214.1%, which showed they were very flexible materials. As shown in Figure 4, these materials showed much higher tensile strength and the lower elongation than Nafion 117. The tension results in both dry and wet states undoubtedly showed they were strong and flexible membrane materials.

Oxidative Stability. The oxidative stability of the polymers was evaluated in Fenton's reagent at 80 °C. This method is regarded as one of the standard tests to gauge relative oxidative stability and to simulate accelerated fuel cell operating conditions.[43] It has been known that the oxidative attack by $HO^\bullet$ and $HOO^\bullet$ radicals mainly occurs in the hydrophilic domains to cause the degradation of polymer chains. It is expected that side-group-acid polymers have improved oxidative resistance over main-chain-substituted sulfonic acid polymers. All the polymers except Me-SPEEK and Ph-SPEEK exhibited excellent oxidative stability, as shown in Table 4. Their weight was retained above 94% after treatment in Fenton's reagent at 80 °C for 1 h, and most of them did not dissolve in Fenton's reagent within 2.0 h treatment at 80 °C. As expected, the polymers with the higher EW had the better oxidative stability. Me-SPEEKDK, Ph-SPEEKDK, Me-6F-SPEEK-40, and Ph-6FA-SPEEK-40 maintained dimensional shapes and flexibility even after 6 h treatment, which suggested their outstanding oxidative stability.

Water Uptake and Dimensional Swelling Ratio. Water uptake and dimensional 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 a dimensional mismatch when incorporated into a membrane electrode assembly (MEA).[3] Therefore, the preparation of sulfonated polymers with ideal water uptakes and dimensional stability is one of the critical demands for their application as PEMs. The water uptake and swelling ratios of PEKs membranes were measured at different temperatures, and the results are shown in Figures 5 and 6. Swelling ratios of homopolymers, Me-SPEEKDK and Ph-SPEEKDK, were about 15% even at 100 °C. Compared with previously reported copolymers with comparable IEC values, Me-SPEEK(D)K and Ph-SPEEK(D)K had lower water uptakes and dimensional swelling ratios, especially at evaluated temperature.[3,41,43] It was interesting to note that Me-6F-SPEEK-80 and Ph-6FA-PEEK-80 with similar IEC values to those of Me-SPEEKK and Ph-SPEEKK had extremely high water uptakes and swelling ratios at elevated temperature, although they showed comparable values at room temperature. This may be associated with the distribution of sulfonic acid groups along the mainchains. The dimensional swelling ratios of both homopolymers Me-SPEEKK and Ph-SPEEKK especially showed significantly different profiles with temperature to those of the copolymers.

Proton Conductivities and Methanol Permeability. The proton conductivities of the membranes were estimated using impedance diagrams, acquired in the frequency range $1-10^7$ Hz. The results at different temperatures are presented in Table 4 and Figure 7. The figure shows that the conductivities of all the samples increase with temperature, and if one traces the isotherms of the conductivity, they approximately increase with

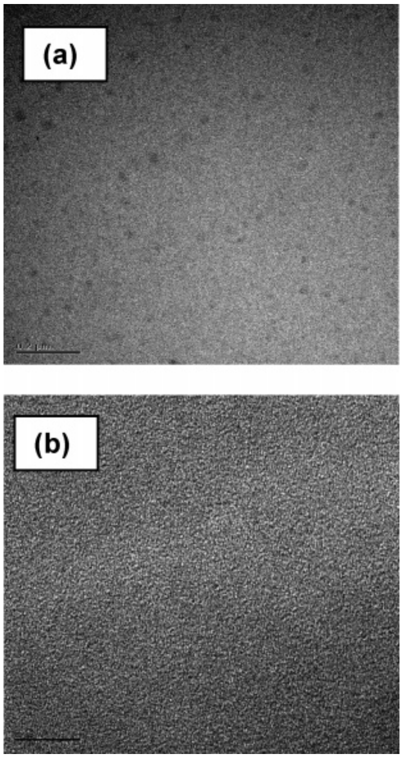


Figure 9. TEM photographs of Me-SPEEK (a) and Me-SPEEKK (b). The scale bars are 0.2 μm.

SC. With the exception of Me-6F-SPEEK-40,60 and Ph-6FA-SPEEK-40, all the other samples exhibited room temperature conductivities higher than 1×10^{-2} S/cm. Me-SPEEKK, Ph-SPEEKK, and Me-6F-SPEEK-80 membranes exhibited proton conductivities comparable to that of Nafion 117 above 80 °C. Undoubtedly, PEMs with high proton conductivity and low swelling ratio will be attractive for fuel cell application. Proton conductivities of Me-SPEEKK and Ph-SPEEKK were as high as 0.154 and 0.151 at 100 °C, respectively, surpassing the value of 0.138 S/cm of Nafion 117. Meanwhile, they still showed relatively low swelling ratios, which meant they were dimensionally stable in hot water. Me-PEEK and Ph-SPEEK exhibited higher proton conductivity, but its applicability in FC is limited by its poor dimensional stability in hot water.

Membranes intended for direct methanol FC (DMFC) must both possess high proton conductivity and to be an effective barrier for methanol crossover from the anode to the cathode compartment.[44] Among the most significant of Nafion's drawbacks is its high methanol crossover in the DMFC application. This limitation is associated with the microstructure of Nafion, where interconnected ionic domains strongly contribute to its high proton conductivity, but at the same time contribute to fast methanol diffusion. The PEK membranes containing the ketone diphenyl ketone moiety (Ph-SPEEKDK and Me-SPEEKDK) exhibited extremely low methanol permeability, presumably arising from a well-refined microstructure caused by regular and rigid backbone molecular structure (Table 4). The methanol permeability values for 10% methanol of Me-SPEEKK, Me-SPEEKDK, Ph-SPEEKK, and Ph-SPEEKDK at room temperature were in the range of 3.31×10^{-7}−9.55×10^{-8} cm^2/s, which is several times lower than the value of Nafion 117 of 1.55×10^{-6} cm^2/s. Pivovar et al. suggested evaluating membranes according to a figure which has the logarithm of the proton conductivity as the ordinate and the logarithm of the reciprocal of methanol permeability as the abscissa.[44] Figure 8 shows the relationship of proton and the inverse of methanol permeability of polymeric films. The methanol permeability at high methanol concentration (50 vol %) for Ph-SPEEKK, Me-SPEEKDK, and Ph-SPEEKDK was also evaluated, and the values were 4.29×10^{-7}, 2.90×10^{-7}, and 2.89×10^{-7} cm^2/s, respectively. Combined with all the other relative properties, Ph-SPEEKDK and Me-SPEEKDK could be promising materials for DMFC applications at high methanol feed concentration.

Microstructure of the Membranes. Two-phase separation morphology has been observed in the microstructure of Nafion and polyimide films.[45,46] Proton conductivity and dimensional stability of the membranes are closely related to their morphology. Wide ion channels formed by hydrophilic domains are helpful to the movement of protons but are possibly detrimental for mechanical properties and dimensional stability in hot water. The microstructure of the present membranes was studied by TEM, as shown in Figure 9. In the image of highly sulfonated Me-SPEEK, small black clusters (~20 nm) corresponding to hydrophilic domains dispersing among continuous area (hydrophobic domains) were observed. However, no obvious phase separation was observed for the samples with lower IEC values, such as Me-SPEEKK, which well supported their behaviors of good hot water stability and low methanol permeability.

Conclusions

PEKs with phenyl and 3-methylphenyl pendant groups were found to have controlled sulfonation sites with single substituted sulfonic acid per repeated unit via a postsulfonation approach under a mild reaction condition, leading to structurally well-defined sulfonated polymers that would normally be achieved only by a copolymerization route. A family of both homo- and copolymers with ion exchange capacities of 2.23−0.84 mequiv/g could readily prepared by controlling the length of unsulfonated segments. These side-group sulfonation polymers had excellent mechanical properties, good thermal and oxidative stability, and good dimensional stability in hot water. The methanol permeability values of Me-SPEEKDK and Ph-SPEEKDK were in the range of 9.55×10^{-8} and 2.30×10^{-7} cm^2/s, which is several times lower than that of Nafion 117. Me-SPEEKK and Ph-SPEEKK also exhibited high proton conductivity of 0.15 S/cm at 100 °C. The results showed that some of them are promising for application as PEM materials for PEMFC and DMFC. The single cell performance for these polymers will be reported in another publication.

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