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Synthesis of Poly(arylene ether ether ketone ketone) Copolymers Containing Pendant Sulfonic Acid Groups Bonded to Naphthalene as Proton Exchange Membrane Materials[†]

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ABSTRACT: A new series of wholly aromatic poly(ether ether ketone ketone) containing pendant sulfonic acid groups (SPAEEKK) were conveniently prepared by potassium carbonate mediated nucleophilic polycondensation reactions of inexpensive commercially available monomers 1,3-bis(4-fluorobenzoyl)-benzene (BFBB), sodium 6,7-dihydroxy-2-naphthalenesulfonate (DHNS), and 4,4′-biphenol or hydroquinone in *N*-methyl-*2*-pyrrolidone (NMP) at 170 °C. FT-IR and NMR were used to characterize the structures and the sulfonate or sulfonic acid contents (SC) of the polymers. Flexible membrane films were obtained by casting *N*,*N*-dimethylacetamide (DMAc) solutions of copolymers. Membrane films in acid form were then obtained by treating the sodium form membrane films in 2 N sulfuric acid at room temperature. Glass-transition temperatures (T_g's) and decomposition temperatures (T_d's) of SPAEEKKs in both sodium and acid forms were determined. Water uptake and swelling ratio values increased with SCs and temperatures. The proton conductivities of acid form membrane films increased with SC value and temperature and reached 5.6×10^{-2} S/cm at 100 °C for SPAEEKK-100.

1. Introduction

Proton exchange membrane fuel cells (PEMFC)s are promising clean power sources for vehicular transportation, residential and institutional, and also for computers and mobile communication equipment.[1] As one of the key components of the membrane electrode assembly (MEA), proton exchange membranes (PEM) support catalyst, provide ionic pathways for protons, and prevent crossover of gases or fuel. Perfluorosulfonic acid PEMs, such as Dupont's Nafion membrane, are typically used as the polymer electrolytes in PEMFCs because of their excellent chemical and mechanical stabilities as well as high proton conductivity. However, their disadvantages of high cost, low operation temperatures, and high fuel permeability are stimulating an intensive search for alternative materials.

Among recently developed polymer electrolyte membranes, sulfonated poly(arylene ether ketone) (SPAEK) and sulfonated poly(arylene ether sulfone) (SPAES) are promising.[2−21] For example, the conductivity of sulfonated Victrex PEEK with an SC of 0.65 reaches 0.04 S/cm^{-1} at 100 °C/100% RH. In 2002, Wang and McGrath[9] reported the synthesis of biphenyl-based sulfonated poly(arylene ether sulfone) by direct polymerization reactions of disodium 3,3′-disulfonate-4,4′-dichlorodiphenyl sulfone (SDCDPS), 4,4′-dichlorodiphenyl sulfone, and 4,4′-biphenol. The conductivity values at 30 °C for the 40% SDCDPS copolymer and the 60% SDCDPS copolymer were 0.11 S/cm and 0.17 S/cm, respectively. In addition, compared with post-sulfonation reactions, this method allows close control of the sulfonate content of polymers and avoids possible cross-linking or other side reactions that could occur under modification conditions. Our group and Xiao et al. also reported the preparation and conductivity results of sulfonated poly(phthalazinone ether ketone) and sulfonated poly(phthalazinone ether sulfone) by both sulfonation reactions and direct polymerization reactions.[12−16] Both methods gave sulfonated polymers with conductivities higher than 10^{-2} S/cm at around SC 1.0.

In sulfonated polymer membrane films, the hydrophobic backbone and the hydrophilic sulfonic acid groups nanophase separate into two domains in the presence of water. The hydrophobic domain provides the polymers with morphological stability and the hydrophilic domain is responsible for transporting protons and water.[19,20] Compared with perfluorinated sulfonic acid membranes, sulfonated poly(aryl ether ketone) is reported[20] to have a smaller characteristic separation length and wider distribution with more dead-end channels and a larger internal interface between the hydrophobic and hydrophilic domains as measured by small-angle X-ray scattering (SAXS).[20] However, if short pendant side chains between the polymer main chain and the sulfonic acid groups exist in the polymer structure, the nanophase separation of hydrophilic and hydrophobic domains may be improved and the amount of dead-end pockets may be decreased.[7,22] Rikukawa and co-workers[7] prepared sulfonated PEEK (SPEEK) and sulfonated poly(4-phenoxybenzoyl-1,4-phenylene, Poly-X 2000) (SPPBP) by post-sulfonation reactions of corresponding parent polymers. They found that SPPBP, which has pendant side chains between polymer main chain and sulfonic acid groups, showed higher and more stable proton conductivity than SPEEK. Jannasch and co-workers devised a new route[22] to increase the dis-

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tance of sulfonic acid groups from the polysulfone main chain via lithiation of polysulfone[23] followed by anionic reaction with sulfobenzoic acid cyclic anhydride. Miyatake and Hay[24] synthesized copolymers containing sulfonated tetraphenylene and fluorinated alkane moieties with sulfonic acid groups attached onto pendant phenyl groups by the post-sulfonation reaction of corresponding polymers.

Sodium 6,7-dihydroxy-2-naphthalenesulfonate (DHNS) is a commercially available and inexpensive naphthalenic diol containing a sulfonic acid side group, which is widely used in dye chemistry. In the present work, DHNS was used to prepare a series of poly(arylene ether ether ketone ketone) copolymers containing sulfonic acid groups (SPAEEKK) via nucleophilic polycondensation with commercially available monomer BFBB. 4,4′-Biphenol or hydroquinone was used in the copolymer composition to adjust the SCs. The properties of new SPAEEKKs were analyzed.

2. Experimental Part

2.1. Materials. DHNS was purchased from Rintech, Inc. and recrystallized from a mixture of ethanol/water (50/50) before use. NMP was purchased from Aldrich Co. Inc. and vacuum distilled before use. All other chemicals were reagent grade and were purchased from Aldrich Co. Inc. and used as received.

2.2. Copolymerization. As an example of a typical reaction, 5 mmol BFBB, 3 mmol DHNS, 2 mmol 4,4′-biphenol, and 7.5 mmol K_2CO_3 were added into a three-neck flask equipped with a magnetic stirrer, a Dean−Stark trap, and an argon gas inlet, then 10 mL NMP and 10 mL toluene were charged into the reaction flask under an argon atmosphere. The reaction mixture was heated to 130−140 °C. After dehydration and removal of toluene, the reaction temperature was increased to about 160−170 °C. When the solution viscosity had increased obviously, the mixture was cooled to 100 °C and coagulated into a large excess of ethanol with vigorous stirring. SPAEEKK-*B*60 resulted, where *B* refers to the comonomer being 4,4′-biphenol; instead, *H* refers to the comonomer being hydroquinone; *n* (60) refers to the DHNS percentage content of aromatic phenol monomers. After washing with ethanol twice, SPAEEKKs were purified by dialysis for a week to remove salt, using MEMBRA-CEL dialysis tubing (MWCO 3500) obtained from Serva Electrophoresis (Germany).

2.3. Copolymer Analysis and Measurement. 1D and 2D NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at a proton frequency of 399.95 MHz and a carbon frequency of 100.575 MHz using a 5-mm indirect detection probe. Deuterated dimethyl sulfoxide (DMSO-d_6) was the NMR solvent and the DMSO signal at 2.50 ppm was used as the chemical shift reference. IR spectra were measured on a Nicolet 520 Fourier transform spectrometer with membrane film samples in a diamond cell.

A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for measuring decomposition temperatures(T_d). Polymer samples for TGA analysis were preheated to 150 °C at 10 °C/min under nitrogen atmosphere and held isothermally for 60 min for moisture removal. Samples were then heated from 90 °C to 750 °C at 10 °C/min for T_d measurement. A TA Instruments differential scanning calorimeter (DSC) model 2920 calibrated with tin at 231.93 °C was used for measuring T_g.

Intrinsic viscosities were determined using an Ubbelohde viscometer for *N*,*N*-dimethylacetamide (DMAc) solutions of copolymer at 30 °C.

2.4. Preparation of Membrane Films. An amount of 0.6 g copolymer in the sodium salt form was dissolved in 20 mL of DMAc and filtered. The filtered solution was poured onto a glass plate and dried at about 40 °C for about 1 day. The acid form (SPAEEKKH-*B* or SPAEEKKH-*H*) membrane films were obtained by immersing corresponding sodium form SPAEEKK-*B* or SPAEEKK-*H* membrane films in 2 N H_2SO_4 for 24 h at room temperature, followed by deionized water for 24 h during which time the water was changed several times.

2.5. Water Uptake Content Measurement and Swelling Ratio. The sample films were soaked in deionized water for 24 h at determined temperatures. The membrane films were then dried at 80 °C for 24 h. 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 5∼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. Proton Conductivity. The proton conductivity measurements were performed on SPAEEKKH-*B* or SPAEEKKH-*H* membrane films by AC impedance spectroscopy over a frequency range of $1-10^7$ Hz with oscillating voltage 50−500 mV, using a system based on a Solatron 1260 gain phase analyzer. A 20 × 10 mm membrane sample was placed in an open, temperature-controlled cell at ambient atmospheric pressure, where it was clamped between two blocking stainless steel electrodes with a permanent pressure of ∼3 kg/cm^2. Specimens were soaked in deionized water for 24−48 h prior to the test. The cell was open to air, and humidity from boiling water was constantly supplied to the area around the cell. The conductivity (σ) of the samples in the transverse direction (across the membranes) was calculated from the impedance data, using 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 intersect of the high-frequency semicircle on a complex impedance plane with the Re (Z) axis.

3. Results and Discussion

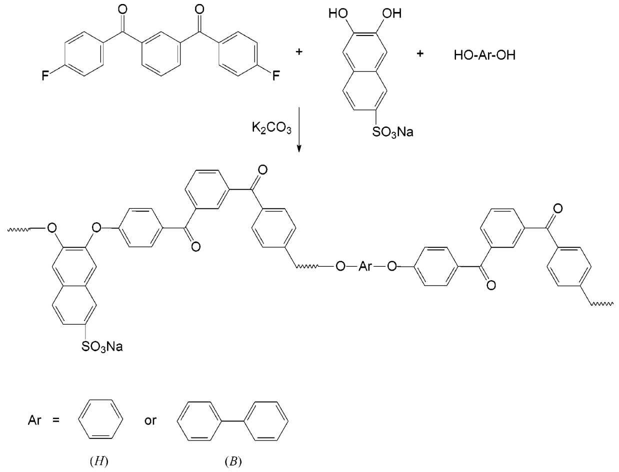
3.1. Synthesis and Characterization of SPAEEKKs. All monomers selected in this study for the preparation of SPAEEKKs are commercially available and inexpensive. The functional monomer DHNS is a diphenol with pendant sodium sulfonate groups. BFBB is industrially used in the preparation of poly(ether ether ketone ketone) (PEEKK). Since DHNS is expected to have a tendency for oligomer cyclization, monomers with a more linear structure, 4,4′-biphenol and hydroquinone, were selected for copolymerizations. The SPAEEKK copolymers were obtained by K_2CO_3 mediated nucleophilic polycondensation.[2−4] As shown in Scheme 1, DHNS, BFBB, and the third monomer, 4,4′-biphenol or hydroquinone, diols were polymerized in NMP and toluene was used to remove the water from starting materials and formed during the reactions. Since the copolymers were prepared by reacting one mole of diols (DHNS) and either 4,4′-biphenol (*B*) or hydroquinone (*H*)) with one mole of BFBB, the SC is expressed as the ratio of DHNS units (bearing the $-SO_3Na$ group) to 1.0 BFBB unit. Hence, the SC is defined as the number of sulfonic acid salt groups per average repeat unit of copolymer. For example, the average repeat unit of SPAEEKK-*H* SC 0.7 is composed of 0.7 units of DHNS, 0.3 unit of hydroquinone (*H*), and 1.0 unit of BFBB. Expressed in this way, both the number of $-SO_3Na$ groups per polymer repeat unit and

Table 1. Syntheses of SPAEEKKs

polymer	DHNS mmol	second diphenol mmol	BFBB mmol	$[\eta]^a$ dL/ g	Meq g/ mol SO_3	SC expected	SC from ^1H NMR data
SPAEEKK-100	4		4	2.77	575	1.0	1.00
SPAEEKK-*B*90	4.5	0.5	5	2.64	628	0.9	
SPAEEKK-*B*80	4	1	5	2.62	699	0.8	0.77
SPAEEKK-*B*70	3.5	1.5	5	1.78	788	0.7	
SPAEEKK-*B*60	3	2	5	1.01	907	0.6	0.56
SPAEEKK-*B*50	2.5	2.5	5	2.74	1058	0.5	
SPAEEKK-*H*90	4.5	0.5	5	1.42	620	0.9	0.87
SPAEEKK-*H*80	4	1	5	1.63	680	0.8	
SPAEEKK-*H*70	3.5	1.5	5	1.34	756	0.7	0.66
SPAEEKK-*H*60	3	2	5	1.19	856	0.6	
SPAEEKK-*H*50	2.5	2.5	5	1.12	997	0.5	0.48

[a] Measured at 30 °C in DMAc.

Scheme 1. Synthesis of SPAEEKKs



the ratio of diol monomers (SC:1-SC) can be conveniently derived. SPAEEKKs with different SC values were obtained by adjusting the feed ratio of sulfonated monomer diol DHNS to unsulfonated monomer diols 4,4′-biphenol or hydroquinone. To obtain proton conductivities in a useful range, only SPAEEKKSs with relatively high SCs were prepared. The polymerization reactions were conducted at 130−140 °C, initially to effect dehydration; the reaction temperatures were then raised to 160−170 °C to effect the polymerizations, until no obvious further increase in viscosities was observed. All polymerization reactions proceeded smoothly, homogeneously, and quantitatively to give SPAEEKKs. Polymerization conditions and details of the resulting polymers are summarized in Table 1. Intrinsic viscosity values of SPAEEKKs in DMAc at 30 °C were all higher than 1.0 dL/g, which indicated the success of polymerization in producing high polymers. All the polymer series were cast into strong transparent and flexible membrane films, which also indicated the high molecular weight of the polymers. Although the *o*-diphenol DHNS was expected to have a high cyclization tendency, polymerization dominated over the cyclization process in these reactions where BFBB was employed. When 4,4′-difluorobenzophenone and 4-fluorophenyl sulfone were used instead of BFBB, only brittle polymers could be obtained. Compared with post-sulfonation reaction or other modification reactions, the copolymerization method could avoid side reactions of cross-linking or degradation and the sulfonation content was readily controlled through the monomer feed ratio. Unlike Nafion, SPAEEKKs were readily prepared from relatively inexpensive starting materials. All the obtained SPAEEKKs had good solubility in aprotic solvents such as NMP, DMAc, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).

The SPAEEKK copolymers are expected to be more thermohydrolytically stable compared with sulfonated poly(aryl ether ketone) obtained by regular post-sulfonation reactions and direct polymerizations of sulfonated difluorobenzophenone with biphenols. In many other sulfonated polymers, whether the sulfonic acids groups were introduced by post-sulfonation or by direct polymerization, the sulfonic acid groups are normally located on the *ortho* position to the ether linkage. The electron-withdrawing sulfonic acid groups on *ortho* positions are expected to increase the ease of hydrolysis of ether linkage and decrease the stability.[24] In the present SPAEEKKs, sulfonic acid groups are attached on a pendant benzene ring away from the ether linkage, which is expected to decrease the effect on the hydrolysis of ether linkages.

Sulfonic acids or sulfonates are considered to be withdrawing groups able to dissociate from their parent structure during high-temperature reactions, which was observed in the studies of other research groups.[25] FT-IR is a convenient method to analyze the structures of polymers containing sulfonic or sulfonate groups. To verify if part or all of the sulfonate groups were lost during the polymerization reactions, FT-IR was used in this work. FT-IR of SPAEEKKs confirmed the introduction of sodium sulfonate groups into the polymer chains and no decomposition of sodium sulfonate groups was observed during the polymerization reactions. Figure 1 shows the FT-IR spectra of SPAEEKKs. In the spectra of both series of SPAEEKKs, characteristic bands of the aromatic sodium sulfonate symmetric and asymmetric stretching vibrations were observed at 1037 and 1110 cm^{-1} for all resulting polymers. These two characteristic absorption bands increase with increasing DHNS content. In similarity with our previously synthesized SPPEKs,[13] the splitting of characteristic absorption bands of 1,4-aromatic ring substitution at around 1466−1500 cm^{-1} caused by the presence of sodium sulfonate groups were also observed. The absorption band at 1466 cm^{-1} decreases with the decreasing DHNS content and the SC values. In addition, a change in the characteristic absorption bands of aromatic ether link at around 1234−1259 cm^{-1} was also observed.

Stacked spectra of SPAEEKK-100, SPAEEKK-*H*, and SPAEEKK-*B* showing an expansion of the aromatic region are displayed in Figure 2. SPAEEKK-100 (top spectrum) was prepared by polymerization of DHNS and BFBB (1:1) and all of the aromatic hydrogen signals originating from the repeat units (RU) were unambiguously assigned using 1D (^1H, homonuclear decoupling)

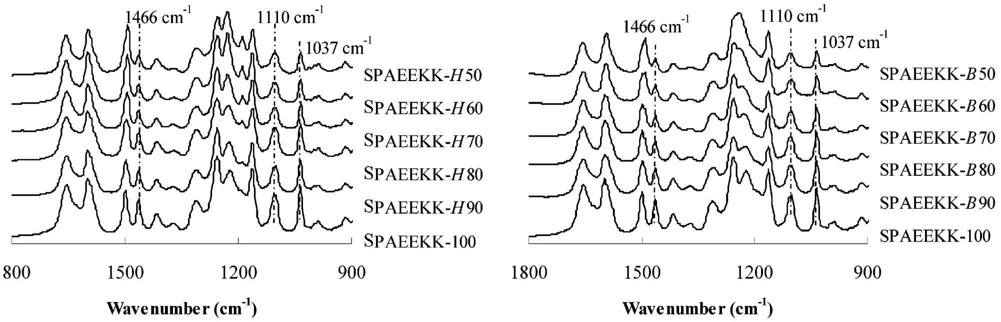


Figure 1. FT-IR spectra of SPAEEKKs.

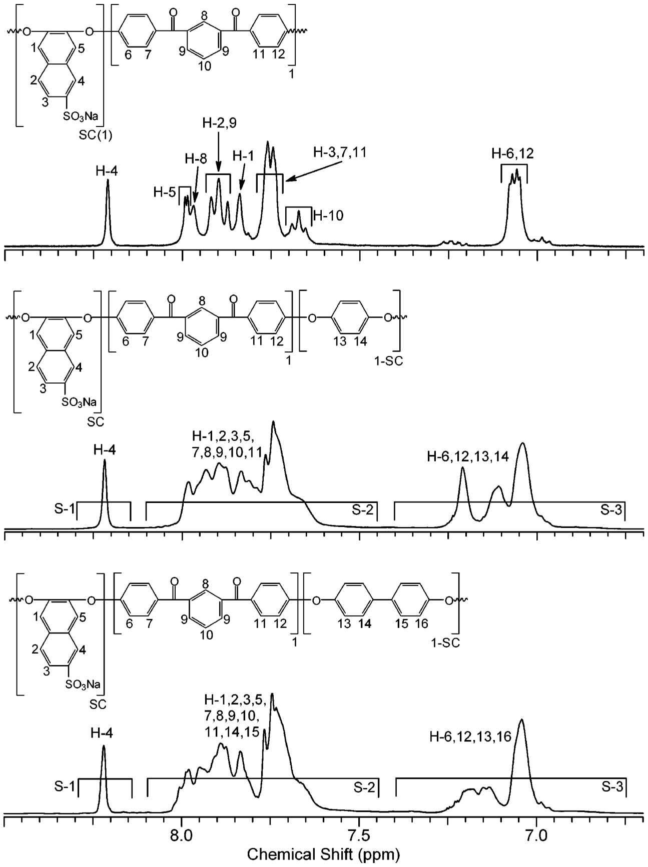


Figure 2. ^{1}H NMR partial spectra of SPAEEKKs in DMSO-d_6 (i = integral value).

and 2D (COSY, HSQC, HMBC) NMR experiments. Although the ^{1}H NMR spectra of SPAEEKK-*H* and SPAEEKK-*B* appear more complex, assignment of the entire spectrum was also unequivocal, on the basis of the comparison with the fully assigned spectrum of SPAEEKK-100. The chemical shifts of the proton signals from hydroquinone or biphenol are well known and predictable. Therefore, aromatic protons located at the electron-rich ortho-ether position of hydroquinone or biphenol will be strongly shielded and will appear at low frequency (6.95−7.30 ppm) while the biphenol proton at the meta-oxygen position will be deshielded by the adjacent phenyl ring and show at higher frequency (7.60−8.05 ppm).

^{1}H NMR was the most convenient method to determine the experimentally obtained SCs from the copolymerization reactions. Having assigned all the NMR signals from the synthetic copolymers, one can use simple mathematical functions and the ratio of spectral line intensities (integral values) to assess the SC. The aromatic region of both polymer derivatives (*H* and *B*) was split in three sections (S1, S2, and S3) and their integral values were used in the calculation of the SCs. using the following equations:

$$\text{SPAEEKK-}H \qquad \frac{\text{S1}}{\text{S3}} = \frac{(n)}{(8 - 4n)} \quad \text{or} \quad \frac{\text{S2}}{\text{S3}} = \frac{(4n + 8)}{(8 - 4n)}$$

$$\text{SPAEEKK-}B \qquad \frac{\text{S1}}{\text{S3}} = \frac{(n)}{(8 - 4n)} \quad \text{or} \quad \frac{\text{S2}}{\text{S3}} = \frac{12}{(8 - 4n)}$$

where

S1 (8.15−8.30 ppm) = $H_4 \times n = 1n = n$

S2 of SPAEEKK-*H* (7.50−8.10 ppm) = $H_{1,2,3,5} \times n + H_{7,8,9,10,11} = 4n + 8$

S2 of SPAEEKK-*B* (7.50−8.10 ppm) = $H_{1,2,3,5} \times n + H_{7,8,9,10,11} + H_{14,15} \times (1 - n) = 12$

S3 of SPAEEKK-*H* = (6.75−7.40 ppm) = $H_{6,12} + H_{13,14} \times (1 - n) = 8 - 4n$

S3 of SPAEEKK-*B* = (6.75−7.40 ppm) = $H_{6,12} + H_{13,16} \times (1 - n) = 8 - 4n$

n = number of DHNS groups = SC (sulfonation content)

For example, the spectrum of SPAEEKK-*H*70 (Figure 2 middle) shows integration values of 1.00 (S1), 15.68 (S2), and 7.91 (S3). Inserting these values in the above equations for SPAEEKK-*H* results into SCs (n) of 0.67 and 0.68. Similarly, SPAEEKK-*B*80 (Figure 2 bottom) has integration values of 1.00 (S1), 15.21 (S2), and 6.31 (S3) leading to SCs of 0.78 and 0.76. The observed SC values listed in Table 1 were averaged after obtaining SC values from each one of the two equations; the difference between the two methods never exceeded 0.02 for any of the polymers. The observed SC values were in agreement with the expected SC derived from the monomer ratios.

3.2. Thermal Properties of SPAEEKKs. The sodium form membrane films were converted into their corresponding acid forms (SPAEEKKH-*H* or SPAEEKKH-*B*) by immersing the films in 2 N H_2SO_4 for 24 h at room temperature, followed by immersion in deionized water for 24 h to rinse the excess acid, and air-drying at room temperature for 24 h.

Thermal stabilities of SPAEEKKs in both sodium and acid forms were investigated by TGA analysis at a heating rate of 10 °C under nitrogen atmosphere, and the results are listed in Table 2. Table 2 shows that $T_{d5\%}$'s and onset weight loss temperatures (T_d) of SPAEEKKs in sodium form are observed between 456 and 489 °C and 440 to 483 °C, respectively. $T_{d5\%}$'s and T_d's of SPAEEKKs in acid form are observed between

Table 2. Thermal Properties of SPAEEKKs

	T_g (°C)		$T_{d5\%}$ (°C)		T_d (°C) extrapolated onset for first weight loss	
polymer	sodium form	acid form	sodium form	acid form	sodium form	acid form
SPAEEKK-100	321	223	456	328	440	294
SPAEEKK-*B*90	300	223	465	347	446	307
SPAEEKK-*B*80	291	227	468	347	445	300
SPAEEKK-*B*70	275	214	470	339	449	292
SPAEEKK-*B*60	256	212	474	348	454	292
SPAEEKK-*B*50	236	202	470	339	452	294
SPAEEKK-*H*90	299	230	468	346	458	308
SPAEEKK-*H*80	289	218	469	345	448	305
SPAEEKK-*H*70	269	208	472	342	455	297
SPAEEKK-*H*60	253	200	476	341	466	300
SPAEEKK-*H*50	215	180	489	353	483	306

Table 3. Water Uptake and Swelling Ratio of SPAEEKKs

	room temperature				80 °C			
	water uptake (%)		swelling ratio (%)		water uptake (%)		swelling ratio (%)	
polymer	sodium form	acid form	sodium form	acid form	sodium form	acid form	sodium form	acid form
SPAEEKK-100	22.3	41.5	8.93	16.7	958	S[a]	116	S
SPAEEKK-*B*90	16.0	32.8	8.16	11.2	38.6	87	17.9	46.5
SPAEEKK-*B*80	12.7	26.4	7.34	10.1	31.2	43.4	12.2	17.7
SPAEEKK-*B*70	11.5	24.2	6.50	8.89	23.2	28.3	9.26	11.6
SPAEEKK-*B*60	9.23	18.3	4.36	6.48	17.2	21.2	6.03	8.16
SPAEEKK-*B*50	9.00	12.4	3.85	4.42	15.1	14.3	5.10	5.97
SPAEEKK-*H*90	21.3	44.4	8.80	12.5	50.7	62.6	23.3	25.1
SPAEEKK-*H*80	19.5	25.5	7.28	9.68	47.1	57.2	15.2	21.9
SPAEEKK-*H*70	15.0	20.5	6.33	9.60	24.7	33.4	11.0	15.3
SPAEEKK-*H*60	13.6	14.2	4.00	7.87	20.8	30.0	11.0	12.8
SPAEEKK-*H*50	11.3	13.6	2.62	4.97	17.0	21.9	7.91	8.76

[a] S denotes partially soluble.

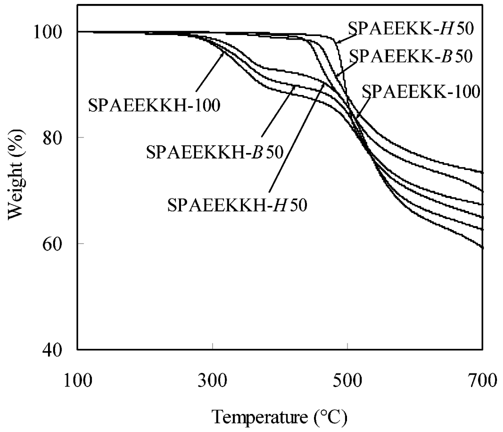


Figure 3. TGA traces of SPAEEKKs.

328 and 353 °C and 292 to 308 °C, respectively. The comparison of SPAEEKKs in sodium and acid forms is also displayed in TGA curves (Figure 3). Referring to our previous studies on SPPEKs,[12−14] SPAEEKK-100 displays a similar thermal stability to that of other sulfonated poly(aryl ether ketone).

T_g's of SPAEEKKs in both sodium and acid forms were also determined. Samples for DSC analysis were initially heated at a rate of 10 °C/min under nitrogen atmosphere to well below the polymer T_d point, ramped to 90 °C, then heated to temperatures below their T_d points at the same rate. The reported T_g's in this article were obtained from the second scan. Results are also listed in Table 2. All SPAEEKKs in sodium form had T_g's between 215 and 321 °C and acid form between 180 and 223 °C, respectively. Generally speaking, T_g's of SPAEEKKs in both sodium and acid forms increase with SC values and the increase in T_g of acid form copolymers is much lower than that of sodium form copolymers. The effect of SC on T_g's of SPAEEKKs with higher SCs is smaller than that on T_g's of SPAEEKKs with lower SCs. Thus, T_g's increase obviously with SC at lower SC values, while the increase becomes less significant at higher SC values. Although T_g's of sodium form SPAEEKKs continue to increase, T_g's of acid form SPAEEKKs attain a certain value at some SC value, and then maintain or even slightly decrease T_g. SPAEEKKs containing hydroquinone show somewhat lower T_g's than SPAEEKKs containing 4,4′-biphenol in both sodium and acid forms. However, the differences are not obvious except for copolymers with SC 0.5.

3.3. Water Uptake and Swelling Ratio. To evaluate the water absorption and dimensional change, the water uptakes and swelling ratios of SPAEEKKs in both the sodium and acid forms were measured at room temperature and at 80 °C. The results are listed in Table 3. The acid form SPAEEKKs membrane films have higher water uptake and swelling ratio values than sodium form ones. At room temperature, the water uptake and swelling ratio increased regularly with SC values for all SPAEEKKs. However, at 80 °C the water uptake and swelling ratio increase regularly with SC values for all copolymers and thereafter increase rapidly at SC 1.0 in both sodium and acid forms. The acid form SPEEK with SC 1.0 is mostly dissolved in water after 24 h heating at 80 °C, indicating that the additional diols hydroquinone or biphenol were necessary for dimensional stability in a fuel cell application. Copolymers containing hydroquinone show a lesser dimensional swelling at 80 °C than those containing biphenol with the same monomer ratios, even though the sulfonic acid content of the former copolymers was greater. The copolymers containing up to 80% DHNS in the diol ratio

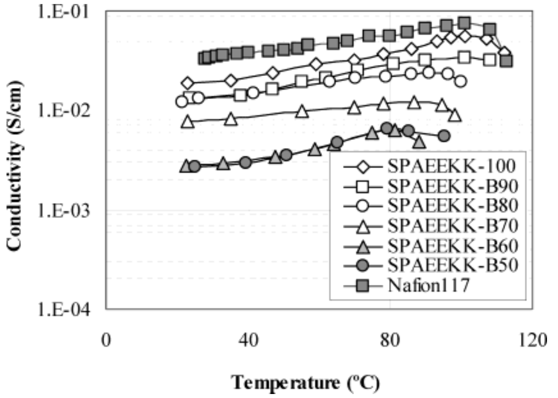


Figure 4. Proton conductivities of SPAEEKK-*B*'s.

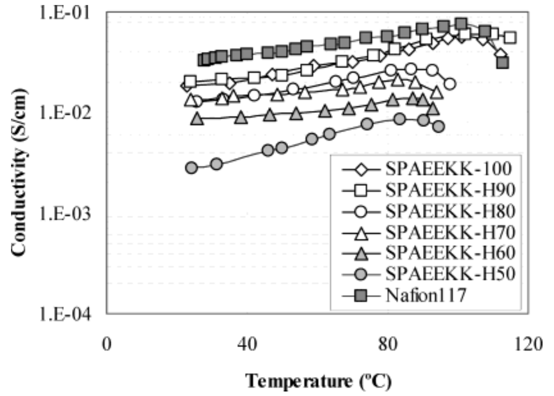


Figure 5. Proton conductivities of SPAEEKK-*H*'s.

did not exhibit excessive dimensional change at 80 °C, although the SPAEEKK-*H*90 exhibited far less swelling than the SPAEEKK-*B*90 copolymer.

3.4 Proton Conductivity. Proton conductivities as a function of temperature are displayed in Figures 4 and 5 for SPAEEKK-*B*'s and SPAEEKK-*H*'s, respectively. For SPAEEKK-*B*'s, it is obvious that the proton conductivities increase with SC values as they do with the water uptake. SPAEEKK-*B*80, SPAEEKK-*B*90, and SPAEEKK-100 show room-temperature proton conductivities higher than 10^{-2} S/cm, which is the lowest value of practical interest for use as PEMs in fuel cells. Conductivities also increase with temperature and attain a certain value, then begin to decrease presumably because of dehydration of membrane films in the open cell at elevated temperatures. SPAEEKK-*B*90 and SPAEEKK-100 showed increased proton conductivities up to 3.4×10^{-2} and 5.6×10^{-2} S/cm at 100 °C, respectively. The temperature points for maximum proton conductivities also increase with SC values. For example, SPAEEKK-*B*50, SPAEEKK-*B*80, and SPAEEKK-100 show maximum proton conductivities at about 79 °C, 90 °C, and 100 °C, respectively. The temperature points for maximum proton conductivities of SPAEEKK-*B*'s with lower SC values are lower than those of SPAEEKK-*B*'s with higher SC values and might be caused by their lower water uptake. Since SPAEEKK-*B*'s with low SC values absorb less water than high SC SPAEEKKs, a slight loss of absorbed water at elevated temperatures will result in a deficiency proton carriers earlier and cause a decrease in proton conductivities sooner.

SPAEEKK-*H*'s also showed proton conductivities increasing with temperature and SC values. Generally speaking, SPAEEKK-*H*'s showed higher proton conductivities than SPAEEKK-*B*'s at the same SC value since they have lower equivalent molecular weights, which are listed in Table 1. All SPAEEKK-*H*'s with SCs higher than 0.7 showed room-temperature proton conductivities higher than 10^{-2} S/cm. SPAEEKK-*H*90 showed almost the same proton conductivity curve with SPAEEKK-100 and its conductivity increased with temperature and reached 6.0×10^{-2} S/cm at 110 °C and then decreased.

Compared with that of Nafion 117, the proton conductivities of SPAEEKKs are all lower. Although the conductivities of the present materials do not exceed that of Nafion 117, the differences are not great and they are of the same order of magnitude. The present materials are adequate for practical application in fuel cells and they have other qualities such as ease of preparation from inexpensive starting materials. In addition, as shown in Figures 4 and 5, the proton conductivity profiles with temperature for SPAEEKK-100, SPAEEKK-*H*90, and SPAEEKK-*B*90 show a similarity to Nafion 117; that is, the proton conductivities show less temperature-dependent behavior compared with other post-sulfonated SPAEKs.[13] The less temperature-dependent characteristics of proton conductivity of SPAEEKKs could be the result of an improved separation between hydrophilic and hydrophobic phases as described in Introduction.

4. Conclusions

Wholly aromatic poly(arylene ether ether ketone ketone) copolymers containing pendant sulfonic acid groups with different SC values were successfully synthesized via K_2CO_3 mediated nucleophilic polycondensation reactions from commercially available monomers 1,3-bis(4-fluorobenzoyl)benzene (BFBB), the sulfonated diol sodium 6,7-dihydroxy-2-naphthalenesulfonate (DHNS), and other diols. The content of sulfonic acid groups in the copolymers was controlled by varying the ratio of the sulfonated diol monomer to either biphenol or hydroquinone diol monomers. When the copolymerization was conducted using either 4,4′-difluorobenzophenone or 4-fluorophenyl sulfone instead of BFBB, only brittle polymers were obtained. In comparison with most sulfonated poly(arylene ether ketone)s in which the sulfonic acid groups are situated *ortho* to ether linkage, thereby rendering the polymers more susceptible to thermohydrolytic instability, the present SPAEEKKs have sulfonic acid groups situated apart from the polymer main chain and ether linkage and are thus anticipated to have superior thermohydrolytic stability. The SPAEEKK series have high intrinsic viscosities and show good solubilities in aprotic solvents, enabling them to be cast into strong flexible films. T_g's of both sodium and acid forms SPAEEKKs increase with DS. SPAEEKKs are thermally stable up to 400 °C in sodium form and up to 300 °C in acid form. Both sodium and acid form sulfonated membrane films show continuous increases in water uptake and swelling ratio with DS and temperature, and the acid form membrane films show higher and more rapid increases than those of sodium forms. The polymer comprised solely of BFBB and DHNS was partially soluble in water at 80 °C, indicating that the additional diols were necessary for dimensional stability in a fuel cell application. Copolymers containing hydroquinone show a lesser dimensional swelling at 80 °C than those containing biphenol for the same monomer ratios. SPAEEKKs showed proton conductivities higher than 10^{-2} S/cm, which is close to that of Nafion, but the cost of the present SPAEEKKs is much lower that that of Nafion. Therefore, SPAEEKK may potentially find application as PEM materials for fuel cells.

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