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Comparative Effect of Phthalazinone Units in Sulfonated Poly(arylene ether ether ketone ketone) Copolymers as Proton Exchange Membrane Materials

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ABSTRACT: A new series of aromatic poly(arylene ether ether ketone ketone) copolymers containing pendant sulfonic acid groups (SPAEEKK-D) were synthesized from commercially available monomers 1,3-bis(4-fluorobenzoyl)-benzene, sodium 6,7-dihydroxy-2-naphthalenesulfonate, and 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one (DHPZ). Structure–property relationships of the phthalazinone SPAEEKK-D series poly(arylene ether ether ketone ketone) copolymer were compared with copolymers SPAEEKK-B and SPAEEKK-H containing different diols such as 4,4′-biphenol and hydroquinone, respectively, prepared in our earlier work. Ion exchange capacity (IEC_w, weight-based; IEC_v, volume-based), thermal stabilities, swelling, proton and methanol transport properties of the membranes were investigated in relation to their structures and compared with those of perfluorinated ionomer (Nafion 117). The SPAEEKK-D membrane incorporating the phthalazinone monomer DHPZ showed relatively lower water uptake and methanol permeability compared with earlier SPAEEKK-B and SPAEEKK-H membranes incorporating biphenol and hydroquinone monomers, respectively. Inclusion of phthalazinone in the SPAEEKK-D copolymers led to lower water absorption, enabling increased proton exchange concentrations in the hydrated polymer matrix that resulted in more desirable membrane properties for future direct methanol fuel cell applications. The SPAEEKK-D membranes also showed improved mechanical and thermal properties and oxidative stability compared with the earlier SPAEEKK-B and -H membranes. *© 2007 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 989–1002, 2008

Keywords: direct methanol fuel cell; ionomer; methanol permeability; phthalazinone; proton conductivity

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are promising clean power sources for vehicular transportation, residential and institutional, and also for computers and mobile communication equipment.[1] Perfluorosulfonic acid PEMs, such as Du Pont'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, although this membrane has disadvantages such as high cost, low operation temperatures, and high fuel permeability. Considerable efforts have been made to develop alternative hydrocarbon-based polymer electrolyte membranes to overcome the drawbacks of the current widely used

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Nafion. The objectives of these investigations were to increase the operation temperature of FCs, to lower the fuel crossover, to simplify the production process, and to decrease the cost of PEMs, thereby overcoming the corresponding drawbacks of perfluorinated ionomers, which hinder their practical applications. Chemically and thermally stable fully aromatic hydrocarbon polymers containing pendant acidic functions are considered promising as alternative PEM materials.[2]

Among recently developed polymer electrolyte membranes, sulfonated poly(arylene ether sulfone) (SPAES) and sulfonated poly(arylene ether ketone) (SPAEK) are promising.[3–9] Wang et al.[9] reported the synthesis of biphenyl-based SPAES. The conductivity values at 30 °C for the 40% disodium 3,3′-disulfonate-4,4′-dichlorodiphenyl sulfone (SDCDPS) copolymer and 60% SDCDPS copolymer were 0.11 and 0.17 S/cm, respectively. Meng and coworkers[10–13] synthesized aromatic poly(arylene ether)s containing arylene-ether backbone with sulfonated groups pendant to the main chain, as well as polyphthalazinones with sulfonic acid groups connected rings adjacent to the phthalazinone moiety, which are claimed to reduce hydrolytic and oxidative degradation.

In many other sulfonated polymers, electron-withdrawing sulfonic acid groups on ortho-ether sites are expected to decrease the hydrolysis stability of that ether linkage.[14] To avoid this potential instability, PEM materials have been synthesized whereby the sulfonic acid groups are situated at sites other than ortho to the ether linkage. Miyatake et al.[14] synthesized copolymers containing sulfonated tetraphenylene and fluorinated alkane moieties with sulfonic acid groups attached onto pendant phenyl groups by the postsulfonation reaction of corresponding polymers. In our previous work,[6,15] sodium 6,7-dihydroxy-2-naphthalenesulfonate (DHNS) was used to prepare a series of poly(arylene ether ether ketone ketone) (SPAEEKK) copolymers via nucleophilic polycondensation with commercially available monomer 1,3-bis(4-fluorobenzoyl)-benzene (1,3-BFBB or 1,4-BFBB) and 4,4′-biphenol, hydroquinone, and hexa-fluorobisphenol A (6F-BPA). In the SPAEEKKs derived from DHNS, sulfonic acid groups are attached on a naphthalene ring away from the ether linkage, which is expected to decrease the effect on the hydrolysis of ether linkage.

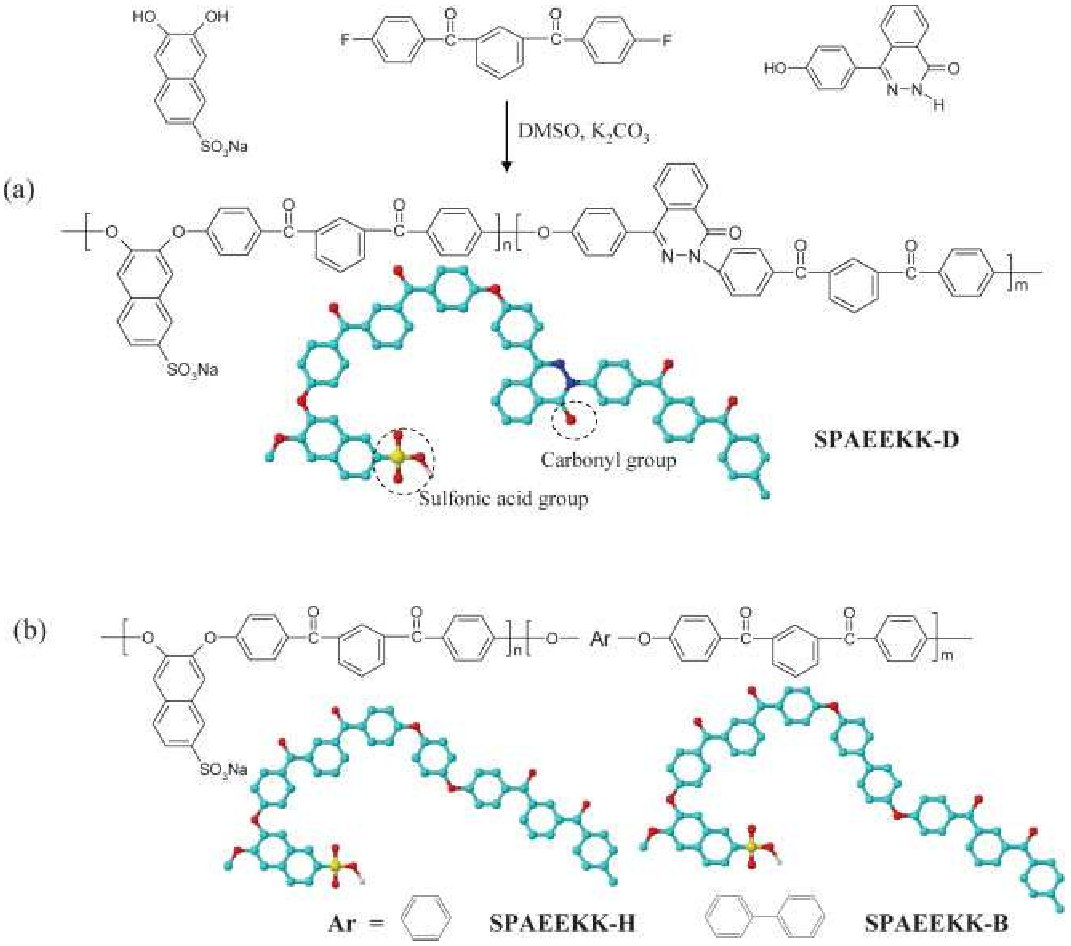
Unless carefully designed, sulfonated aromatic polymers generally have a tendency to swell at high humidity and elevated temperature, although proton conductivities in the range of 10^{-2} to 10^{-1} S/cm have been achieved from these membranes. A number of PEM materials containing phthalazinone units have been reported. Xiao et al.[16] synthesized sulfonated poly(phthalazinone ether sulfone)s utilizing sulfonated 4,4′-difluorodiphenyl sulfone as the sulfonated monomer. It was reported that the low water swelling obtained was due to hydrogen bonding involving the carbonyl groups of the oxyphenyl phthalazinone unit. In our previous article,[5] we described the synthesis of poly(phthalazinone ether ketone nitrile)s. The 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one (DHPZ) monomer can readily undergo a nucleophilic substitution reaction to give polymer because the phthalazinone NH groups behave like phenolic OH groups. Therefore, the phthalazinone monomer is used for preparing high-performance engineering plastics.[17–19]

In the present work, a new series of poly(arylene ether ether ketone ketone) copolymers containing the phthalazinone unit (SPAEEKK-D) were prepared from commercially available monomers BFBB, DHNS, and DHPZ. Although there are a number of studies on PEM materials containing the phthalazinone unit, we are not aware of any that have attempted to compare its effect on polymer properties in comparison with other monomer units. Since many PEM materials containing phthalazinone moieties have been reported, we wished to determine whether the phthalazinone moiety exerted a beneficial effect on the overall properties of the PEM material. Consequently, this study examines the structure–property relationships of phthalazinone units in the new SPAEEKK-D copolymers and compares these with other previously reported SPAEEKK-type copolymers that have identical structure with the exception that phthalazinone was replaced by hydroquinone or biphenol-derived units. Therefore, this study provides a direct comparison of the contribution of each type of monomer unit. Among fuel cell-related properties, we primarily focus on water uptake, various IECs, proton conductivity, methanol permeability, and mechanical properties drawing comparison between polymers of similar sulfonated monomer content.

EXPERIMENTAL

Materials

2,8-Dihydroxynaphthalene-6-sulfonate sodium salt (2,8-DHNS-6) was purchased from Rintech, and



Scheme 1. (a) Chemical structure of SPAEEKK copolymers (SPAEEKK-D) used in this study, by ACD/ChemSketch; (b) Chemical structure of copolymers derived from 2,8-DHNS-6, 1,3-BFBB, and HQ (designated SPAEEKK-H) and BP (designated SPAEEKK-B) in ref. 6.

4-(4-hydroxyphenyl)-2,3-phthalazin-1-one (DHPZ) was kindly provided by Prof. Xigao Jian, Dalian Polymer New Material, People's Republic of China. 2,8-DHNS-6 and DHPZ were recrystallized from a mixture of ethanol/water (50/50 v/v) and DMAc, respectively. 1,3-Bis(4-fluorobenzoyl) benzene (1,3-BFBB) was purchased from Aldrich and was recrystallized from ethanol before usage. All other chemicals such as methanol, toluene, DMAc, and K_2CO_3 (obtained from Aldrich) were of reagent grade and used as received.

Copolymerization

Scheme 1 shows the chemical structure of sulfonated poly(arylene ether ether ketone ketone) copolymers used in this study. The copolymers derived from 2,8-DHNS-6, 1,3-BFBB, and HQ (The polymer was designated as SPAEEKK-Hxx) and BP (SPAEEKK-Bxx) were reported in previous work.[6]

A typical synthetic procedure to prepare sulfonated statistical copolymer derived from DHPZ (SPAEEKK-Dxx) is described as follows. 10 mmol 1,3-BFBB, 4 mmol 2,8-DHNS, 6 mmol DHPZ, and 15 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 DMSO and 10 mL toluene were charged into the reaction flask under argon atmosphere. The reaction mixture was heated to 130–140 °C. After dehydration and removal of toluene, the reaction temperature was gradually increased to 160–170 °C. When the solution viscosity had apparently increased, the mixture was cooled to 100 °C and coagulated into a large excess of ethanol or water with vigorous stirring. The precipitated copolymer was washed several times with water and dried in a vacuum oven at 90 °C for 24 h. The resulting polymer was designated SPAEEKK-D40, (*n*) 40 refers to the 2,8-DHNS-6 content of aromatic phenol monomers.

An amount of 1 g of copolymer in the sodium salt form was dissolved in 20 mL of DMAc and filtered with a 0.45-μm Teflon syringe filter. The filtered solution was poured onto a glass plate and dried at about 60 °C under a constant purge of nitrogen for about 2 days. The acid form membranes were obtained by immersing corresponding sodium form membranes in 2 N H_2SO_4 for 24 h at room temperature and then in deionized water for another 24 h, during which water was changed several times. The thickness of all membrane films was in the range 50–100 μm. The dry membrane thickness was measured using a micrometer (all membrane thicknesses reported here are in the dry state).

Characterization of the Membranes

IR and NMR Measurement

IR spectra were measured on a Nicolet 520 Fourier transform spectrometer with membrane samples in a diamond cell. ^{1}H NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at a proton frequency of 399.95 MHz. 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.

TGA and DSC Analysis and Viscosity

The degradation process and the thermal stability of the sample were investigated using thermogravimetry (TGA) (TA Instruments, TGA 2950). Polymer samples for TGA analysis were preheated to 150 °C at 10 °C/min under a nitrogen atmosphere and held isothermally for 40 min for moisture removal. The TGA measurements were then carried out under a nitrogen atmosphere using a heating rate of 10 °C/min from 50 to 700 °C.

The bound (nonfreezing) and the freezing water of the SPAEEKK-D membranes in a fully hydrated state were determined by DSC, using a reported procedure.[20]

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

Oxidative Stability and Water Uptake

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 30 and 80 °C. The expended time that the membrane started to break into pieces (t_1) and final membrane degradation time (t_2) of polymer membranes into the reagent were used to evaluate oxidative resistance. Water uptake was measured after drying the membrane in acid form at 100 °C under vacuum overnight. After measuring the weights of dry membranes, the sample films were soaked in deionized water at 30 and 80 °C and periodically weighted on an analytical balance until a constant water uptake weighed was obtained. The water uptake was calculated as a percentage using the following equations;

$$\text{Water Uptake (wt \%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

$$\text{Water Uptake (vol \%)} = \frac{(W_{\text{wet}} - W_{\text{dry}})/\delta_{\text{w}})}{(W_{\text{dry}}/\delta_{\text{m}})} \times 100 \quad (2)$$

where W_{dry} and W_{wet} are the weights of dry and wet samples, respectively; δ_{m} is the membrane density in the dry state, and δ_{w} is the density of water (1 g/cm^3). Copolymer density was measured from a known membrane dimension and weight after drying at 80 °C for 2 h. The dimensional swelling ratio was calculated in the *x* direction from films 5–10 cm long as:

$$\text{Swelling Ratio (\%)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100 \quad (3)$$

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

Ion Exchange Capacity, Proton Conductivity, and Methanol Permeability

The ion exchange capacity (IEC$_{\text{w}}$, in mequiv/g) was determined using the classical titration technique. We also calculated a weight based IEC$_{\text{w}}$ from the copolymer structure, which were typically higher than the experimental value measured from titration technique as shown in Table 1.[9] All IEC$_{\text{w}}$ are reported on the basis of the dry polymer. A volume-based IEC [IEC$_{\text{v}}$ (dry)

Table 1. Composition and Properties of SPAEEKK Copolymers

Polymer	Content of 2,8-DHNS (mmol)	EW Expected (g/mol SO_3)	IEC_w Expected (mequiv/g)	IEC_w Measured (mequiv/g)	$T_{d5\%}$ (°C)[a]	T_d (°C)[b]	λ $[H_2O]/[SO_3H]$ Based on IEC_w (30 °C)	η_{inh} (dL/g)[c]
SPAEEKK-D40	4	1303	0.77	0.75	429	347	4.5	1.31
SPAEEKK-D50	5	1043	0.96	0.95	421	336	5.7	1.21
SPAEEKK-D60	6	869	1.15	1.14	417	305	6.2	1.35
SPAEEKK-D70	7	745	1.34	1.31	389	299	7.0	1.45
SPAEEKK-D80	8	652	1.53	1.49	385	295	9.7	0.98
SPAEEKK-H50	5	915	1.09	1.00	353	306	7.6	1.12
SPAEEKK-H60	6	784	1.28	1.21	341	300	7.5	1.19
SPAEEKK-H70	7	690	1.45	1.40	342	297	8.1	1.34
SPAEEKK-H80	8	620	1.61	1.59	345	305	8.9	1.63
SPAEEKK-B50	5	991	1.00	0.98	339	294	7.0	2.74
SPAEEKK-B60	6	834	1.20	1.15	348	292	8.8	1.01
SPAEEKK-B70	7	723	1.38	1.37	339	292	9.8	1.78
SPAEEKK-B80	8	639	1.56	1.54	347	300	9.5	2.62
SPAEEKK-6F (70)[d]	7	769	1.30	1.29	387	313	9.1	2.45

[a] Acid form.

[b] Extrapolated onset for first weight loss (acid form).

[c] η_{inh} (dL/g) was measured at 30 °C in DMAc.

[d] Derived from 1,4-BFBB, DHNS, and 6F-BPA.[15]

and IEC_v (wet)] of SPAEEKK-D, -H, and -B membranes were calculated and listed on Table 3.

Proton conductivity was measured using a Solartron 1260 impedance analyzer over the frequency range of 10 to 10^7 Hz. The proton conductivities reported here were measured in the longitudinal mode using the four-point technique. Prior to the proton conductivity measurements, membranes were immersed in boiling water for 2 h and were then soaked in water at 60 °C for 3 days to hydrate, with several changes of water. Methanol permeability was measured using a glass diffusion cell. Methanol concentrations were determined by NMR spectra. The methanol permeabilities of SPAEEKK-H and -B membranes that were not reported in ref. 6 were measured to compare the effect of polymer structure under same conditions. Proton conductivity and methanol permeability were measured using a reported procedure.[15]

RESULTS AND DISCUSSION

Synthesis and Characterization of SPAEEKK-D Copolymers

All monomers used in this study for the preparation of SPAEEKK copolymers are commercially available and inexpensive. The functional monomer DHNS is a diphenol with pendant sodium sulfonate groups. 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 copolymerization with BFBB in our previous study.[6] As mentioned earlier, the DHPZ monomer and either BP or HQ or 6F BPA readily copolymerizes with BFBB monomer by a nucleophilic substitution reaction to give SPAEEKK, because the phthalazinone NH groups behave like phenolic OH groups. The series of SPAEEKK-D copolymers were prepared by nucleophilic substitution reactions with DHPZ as the diphenol-type monomers, DHNS and BFBB as activated dihalides, and K_2CO_3 as a weak base. All the obtained SPAEEKK-D had good solubility in aprotic solvents such NMP, DMAc, and DMSO. All the polymer series were cast into strong transparent and flexible membranes. 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.

Polymerization compositions and properties of SPAEEKK-D are summarized in Table 1. The hereby measured data of SPAEEKK-H, SPAEEKK-B, and SPAEEKK-6F in Table 1 are consistent with those reported in our previous study.[6,15] The previously reported results on SPAEEKK-H, -B, and -6F are combined for comparison.

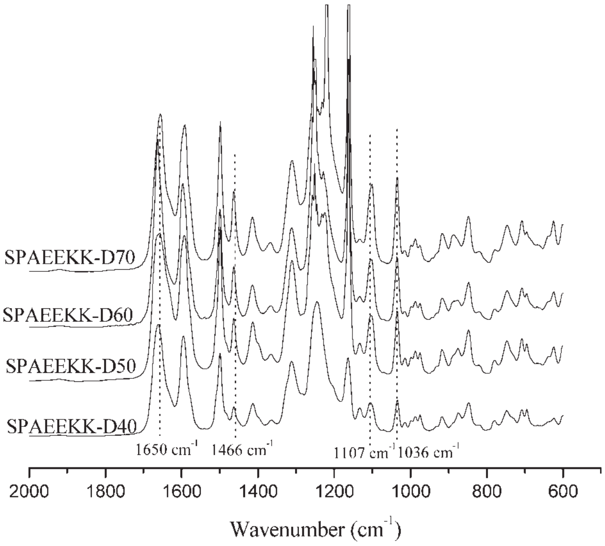


Figure 1. FTIR spectra of SPAEEKK-D copolymers.

The chemical structures of SPAEEKK-D copolymers were characterized by FTIR and ^{1}H NMR. The FTIR spectra of SPAEEKK-D copolymers are shown in Figure 1. Characteristic bands of the aromatic sodium sulfonate symmetric and asymmetric stretching vibrations are observed at 1036 and 1107 cm^{-1} for all the copolymers, and the intensity of these characteristic absorption bands increase with DHNS containing sulfonic acid group, which confirm successful introduction of sulfonate groups into polymers. In similarity with the previous FTIR results[6] of SPAEEKK-H and -B, the splitting of characteristic absorption bands of 1,4-aromatic ring substitution at around 1466 cm^{-1} caused by the presence of sodium sulfonated groups were also observed.

The structural properties of the synthesized polymers were also investigated by liquid phase ^{1}H NMR spectroscopy with DMSO-d_6 as the solvent and reference material. A ^{1}H NMR spectrum showing the aromatic region for SPAEEKK-D80 copolymer is displayed in Figure 2(a). The broad spectral lines are a result of the poor mobility of this polymer with a possibly rigid structure and strong hydrogen bonding properties from the —SO_3H groups. Nevertheless, assignment of groups of signals was made easy by simply comparing this spectrum with previously synthesized and fully characterized polymers containing these same monomers.[6] It is worthwhile mentioning that hydrogens H-6 and H-12 appear at different positions due to the asymmetric phthalazinone monomer. The BFBB protons H-6 or H-12 resonate at higher frequencies (6.8–7.5 ppm) due to induction when exposed to an ether linkage ensuing from attachment of the BFBB monomer to the —OH group of the phthalazinone monomer. The same BFBB protons, designated H-6′ or H-12′, will appear at lower frequencies (7.5–8.1 ppm) when BFBB is linked to the nitrogen atom of the phthalazinone monomer. In previous articles, we frequently reported experimental sulfonic acid contents (SCs) based on NMR signal intensity ratios (integral ratios). The SC calculations for this polymer are made impractical due to this asymmetry of the phthalazinone monomer and its repercussions on chemical shifts of some protons.

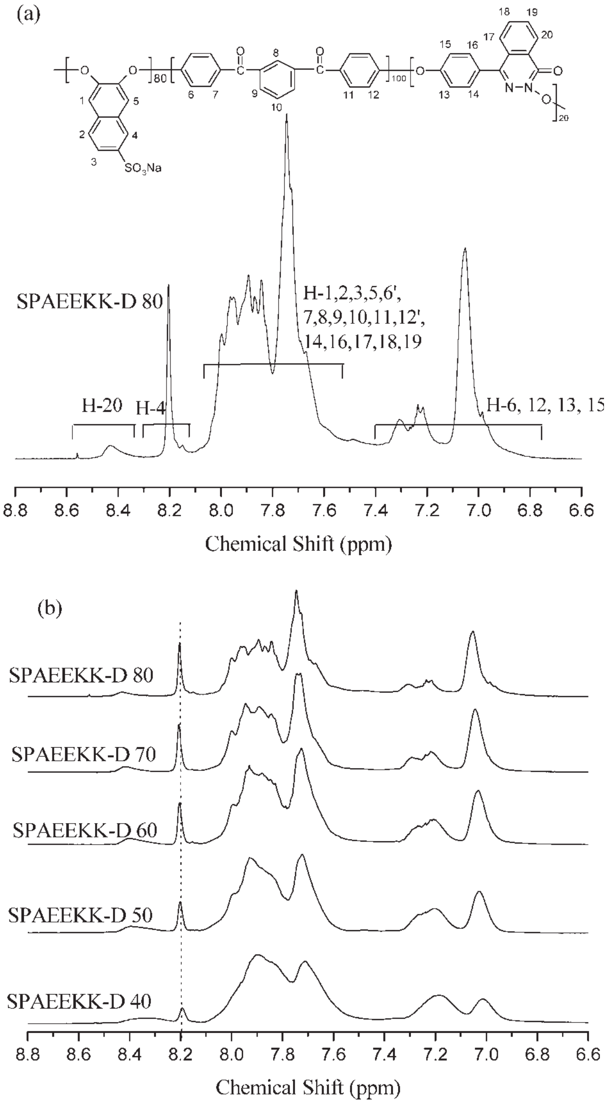


Figure 2. (a) ^{1}H NMR spectra of SPAEEKK-D80, (b) ^{1}H NMR spectra of SPAEEKK-D copolymers with content of sulfonated monomer.

However, it is clear from Figure 2(b), which shows stacked spectra of a series of synthetic copolymers, that they do have the desired altered ratios of monomers. As expected, the intensities of the signals specific to one monomer such as H-4 from the DHNS monomer and H-20 from the phthalazinone monomer are increasing or decreasing according to the monomer ratios used in the preparation of the copolymers.

Thermal Properties of SPAEEKK Copolymers

The sodium form membranes were converted into their corresponding acid form by immersing the membranes 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. The TGA curves measured under flowing nitrogen are shown in Figure 3. The first weight loss region (occurring between temperatures of T = 250–450 °C) is believed to be the result of the loss of the sulfonic acid. In the second weight loss region (at temperatures >500 °C), the polymer residues were further degraded at T = 550 °C, which corresponds to the decomposition of the main chains of the SPAEEKK. Table 1 shows the $T_{d5\%}$ and onset weight loss temperature (T_d) of SPAEEKK-H, -B, -D, and -6F in acid form. $T_{d5\%}$ and T_d of SPAEEKK-H and -B are observed between 339 and 353 °C, and 292 and 306 °C, respectively. SPAEEKK-D containing DHPZ show somewhat higher $T_{d5\%}$ than SPAEEKK-H, -B containing HQ or BP, and similar to SPAEEKK-6F containing 6F-BPA. All SPAEEKK copolymers show sufficient thermo-oxidative stabilities, since PEMs are usually not exposed to temperatures exceeding 200 °C in air during the process of MEA preparation. Therefore, all SPAEEKK copolymers have adequate thermal stabilities for PEM application.

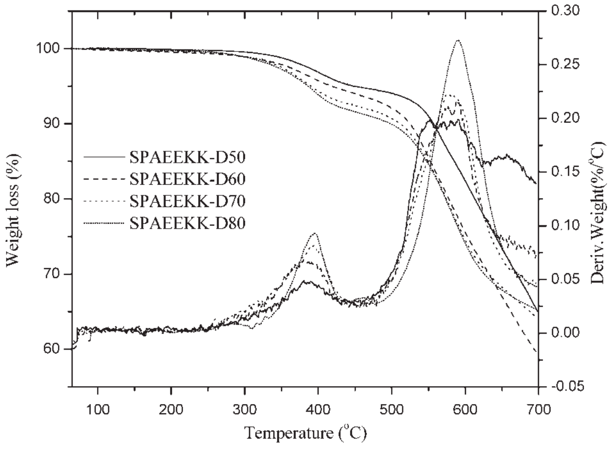


Figure 3. TGA of SPAEEKK-D copolymers.

Water Uptake

The hydrophilic nature of the SPAEEKK copolymers was examined with water uptake measurements. Water is the main vehicle by which protons are transported through the membrane; therefore, it is an essential requirement to promote proton conductivity. All the sulfonated copolymers were swollen to some extent by deionized water at 30–80 °C, but were not soluble. The water uptake and swelling results are shown in Figure 4. The water uptake (wt %) for each copolymer increased with increasing sulfonated monomer and temperature. The water uptake (wt %) of the SPAEEKK-D series membranes increased linearly up to 70 wt % sulfonated monomer content (IEC_w = 1.31 mequiv/g), but then a sudden increase was observed above 80 wt % sulfonated monomer content as shown in Figure 4(a). The hydration of the polymer and the transport of protons in PEM are known be critical factors and are often described using the number of water molecules per sulfonic acid group (λ).[21] Table 2 shows the λ of each state of water based on IEC_w. The state of water in the SPAEEKK-D copolymer was measured using a reported procedure by a DSC thermodiagram.[20] The value of λ estimated from the number of total water molecules increased with DHNS content. In addition, the fraction of freezing water increased dramatically for DHNS $\geq$80 wt %. An increase in the free volume capable of containing water molecules and an increase in the continuous hydrophilic domain structure can significantly increase the water uptake of the copolymer.[22(a)] The percolation threshold for water uptake occurred at DHNS 70% (SPAEEKK-D70). It is reported that an important reason for the higher methanol permeability for Nafion is its higher fraction of freezing bound and free water versus nonfreezing bound water compared with that of the poly(arylene ether)-based copolymers.[22(b)] The fraction of freezing water of Nafion is higher than that of the SPAEEKK copolymers as listed in Table 2.

Figure 4(b,c) shows the water uptake and swelling ratio of SPAEEKK copolymer made

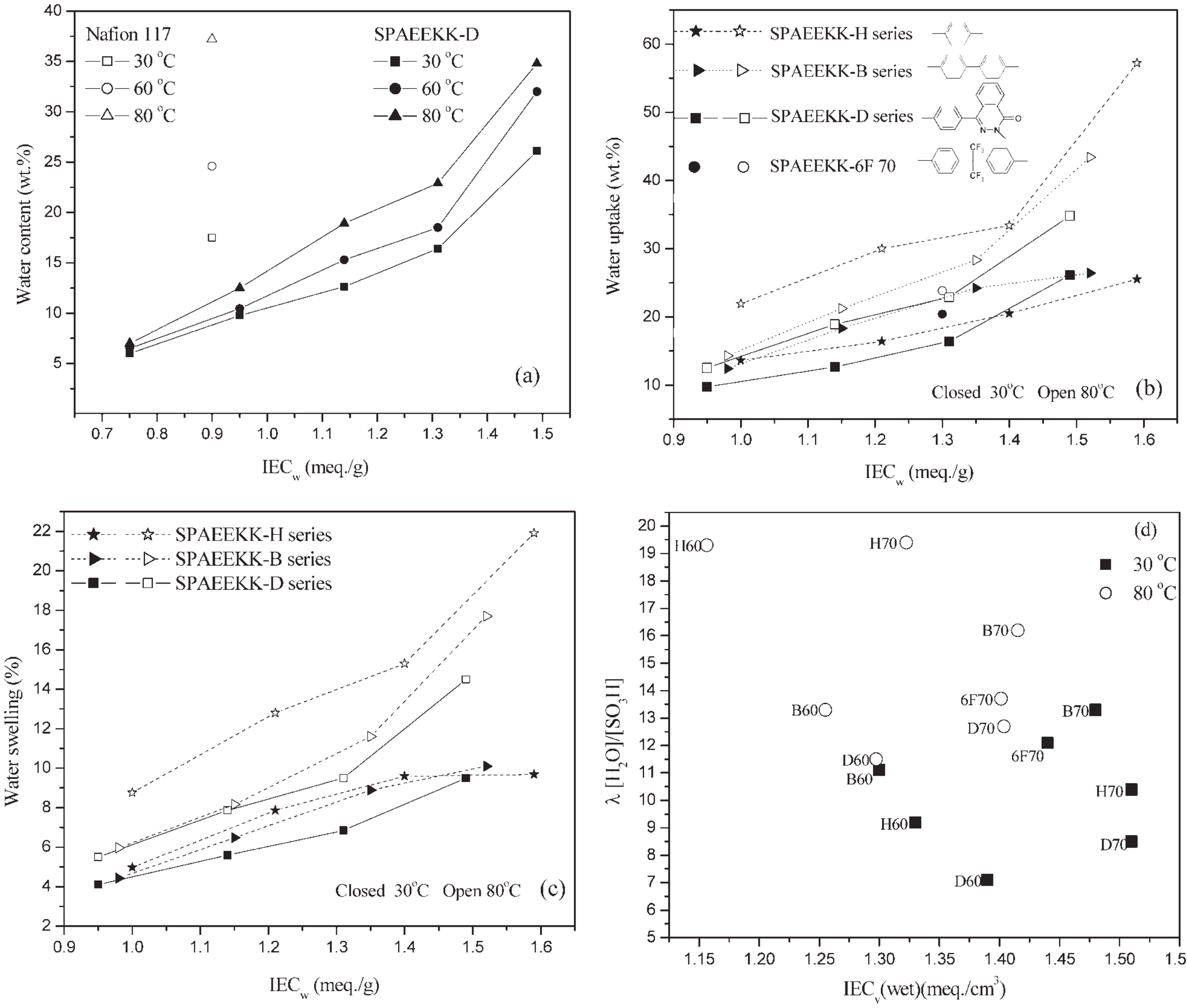


Figure 4. (a) Water uptake of SPAEEKK-D and Nafion 117; (b) Effect of SPAEEKK structure on membrane water uptake and (c) water swelling as a function of IEC and temperature; (d) λ based on IEC$_v$ (wet) as a function of IEC$_v$ (wet) for different SPAEEKK copolymer structures.

from BP, HQ, 6F BPA, and DHPZ. The water uptake of the SPAEEKK membrane derived from 6F-BPA is lower than those of the previously reported SPAEEKK membranes derived from 4,4′-biphenol or hydroquinone monomer at high temperature, because of the hydrophobic nature of the 6F-BPA connecting units.[6] The water uptake of copolymers containing HQ at 80 °C were higher than those of comparable sulfonated copolymer with similar IEC values. Conversely, DHPZ systems had the lowest water uptake. The low water uptake originates from the hydrogen bonding between hydrogen atoms of sulfonic acid and carbonyl groups of oxyphenyl phthalazinone unit.[16] Copolymers containing DHPZ also show a lesser dimensional swelling than those containing HQ, BP with the same DHNS ratio.

Table 3 shows the density, IEC, water uptake, and proton conductivity of the SPAEEKK copolymers. The changes in length scale (reflected in volume measurements) are expected to directly impact observed properties such as proton conductivity and permeability. Therefore, choosing quantities that are weighted by volume rather than weight serve as a more reasonable comparison basis, while polymer density affects water uptake (wt %).[24] When IEC$_w$ (mequiv/g) is changed to IEC$_v$ (dry) (mequiv/cm^3) and water uptake (wt %) is changed to water uptake

Table 2. Characterization of Water Uptake and λ of Each State of Water in the SPAEEK-D Membranes

Polymer	Water Uptake % (at 30 °C)			λ $[H_2O]/[SO_3H]$ Based on IEC_w			Selectivity[a]	E_a (kJ/mol)
	Total	Free	Bound	Total	Freezing	Bound		
SPAEEKK-D40	6.1	0.9	5.2	4.5 (1)[b]	0.7 (0.15)[c]	3.8 (0.85)[d]	3.23	15.68
SPAEEKK-D50	9.8	2.8	7.0	5.7 (1)	1.6 (0.28)	4.1 (0.72)	3.29	8.66
SPAEEKK-D60	12.6	3.5	9.1	6.2 (1)	1.7 (0.28)	4.5 (0.72)	3.59	9.15
SPAEEKK-D70	16.4	4.5	11.9	7.0 (1)	1.9 (0.27)	5.1 (0.73)	4.69	8.87
SPAEEKK-D80	26.1	8.6	17.5	9.7 (1)	3.2 (0.33)	6.5 (0.67)	1.96	9.85
Nafion 117	23	17.1	5.9	14.0 (1)	10.4 (0.74)	3.6 (0.26)	0.31	8.04

[a] The ratio of proton conductivity to methanol permeability ($\times 10^5$ S · s cm^{-3}) at 30 °C.

[b–d] Fraction of each state of water ([b][λ of total water]/[λ of total water]; [c][λ of freezing water]/[λ of total water]; [d][λ of bound water]/[λ of total water]).

(vol %), the resulting change in λ is shown in Table 3. The values of λ based on IEC (wet) are higher that those of λ based on IEC_w and IEC_v (dry). Figure 4(d) shows temperature dependence of λ based on IEC_v (wet). The IEC_v (wet) was used in Figure 4(d) as a basis for comparison, because it reflects the concentration of ions within the polymer matrix under hydrated conditions. The λ values increase with temperature, although IEC_v (wet) values decrease. Especially, the λ of SPAEEKK-H60 and -H70 increase from 9.2 and 10.4 to 19.3 and 19.4, respectively. Both proton conduction and methanol permeation take place through the same pathway in the membranes, such as the hydrophilic cluster channels. From these λ results, we can expect that the methanol permeability of SPAEEKK-H series membrane should be higher, although the proton conductivity is high.

The water uptake directly affects the sulfonic acid concentrations within the polymer matrix under hydrated conditions, which can be gauged by comparing wet volume-based IEC [IEC_v (wet)] values with IEC_w values. Although the SPAEEKK-D have lower IEC_w compared to SPAEEKK-H or SPAEEKK-B or both due to monomer unit size, the IEC_v (wet) of SPAEEKK-D are higher than that of SPAEEKK-H or SPAEEKK-B or both. For example, the IEC_w and IEC_v (wet) of SPAEEKK-D60 are 1.14 mequiv/g and 1.39 mequiv/cm^3, respectively. The IEC_w of SPAEEKK-B60 is 1.15 mequiv/g, which is similar to SPAEEKK-D60. However, the IEC_v (wet) of SPAEEKK-B60 is 1.30 mequiv/cm^3,

Table 3. Effect of Different Monomers on Density, IEC, Water Uptake, and Proton Conductivity at 30 °C

	Density (g/cm^3)	Water Uptake (wt %)	Water Uptake (vol %)	IEC_w (mequiv/g)	IEC_v (dry)[a] (mequiv/cm^3)	IEC_v (wet)[b] (mequiv/cm^3)	λ $[H_2O]/[SO_3H]$ based on		Conductivity (mS/cm)
							IEC_v (dry)	IEC_v (wet)	
SPAEEKK-D60	1.45	12.6	18.3	1.14	1.65	1.39	4.2	7.3	13.7
SPAEEKK-D70	1.42	16.4	23.3	1.31	1.86	1.51	4.9	8.6	24.3
SPAEEKK-H60	1.34	16.4	21.9	1.21	1.62	1.33	5.6	9.2	16.3
SPAEEKK-H70	1.38	20.5	28.3	1.40	1.93	1.51	5.9	10.4	27.5
SPAEEKK-B60	1.42	18.3	25.9	1.15	1.63	1.30	6.2	11.1	15.0
SPAEEKK-B70	1.46	24.2	35.3	1.37	2.00	1.48	6.7	13.3	25.2
SPAEEKK-6F70	1.45	21.4	31.0	1.29	1.87	1.43	6.4	12.1	18.6
Nafion 117	1.85	23.0	42.5	0.91	1.68	1.18	7.6	20.0	78.9

[a] IEC_v (volume-based) = (Dry membrane density × IEC_w).

[b] IEC_v (wet) = IEC_v (dry)/{1 + [0.01 × Water Uptake (vol%)]}.[24]

Table 4. Mechanical Properties and Oxidative Stability of the Sulfonated Copolymers

Polymer	Tensile Stress (MPa)	Young's Modulus (GPa)	Elongation at Break (%)	Oxidative Stability t_1 (h) 30 °C	Oxidative Stability t_1 (h) 80 °C	Oxidative Stability t_2 (h) 30 °C	Oxidative Stability t_2 (h) 80 °C
SPAEEKK-D60	43	2.22	5.0	42	3	50	4
SPAEEKK-D70	58	2.02	9.5	40	2.5	47	3
SPAEEKK-H60	74	2.52	4.3	34	2	39	2.5
SPAEEKK-H70	68	2.69	3.8	32	1.5	37	2
SPAEEKK-B60	43	1.48	19.5	37	2.5	44	3
SPAEEKK-B70	65	1.87	10	35	2	42	2.5
SPAEEKK-6F70	39	1.15	10.6	34	2	40	3
Nafion 117[a]	38	0.18	301	–	–	–	>6

[a] Data from ref. 25.

which is lower than SPAEEKK-D60. In the case of SPAEEKK-H60, the IEC_w is 1.21 mequiv/g, which is higher than SPAEEKK-D60, while the IEC_v (wet) of SPAEEKK-H60 is 1.33 mequiv/cm^3, which is lower than SPAEEKK-D60. The sulfonic acid concentration of the dry SPAEEKK-D polymer was retained when in the hydrated state, while SPAEEKK-H or SPAEEKK-B or both have high swelling properties and the sulfonic acid concentration of SPAEEKK-H or SPAEEKK-B or both was diluted under equilibration with water.

Mechanical Properties and Oxidative Stability

It is essential for PEMs to possess adequate mechanical strength and oxidative stability. Here, the tensile test of SPAEEKK-D, -H, and -B membranes was conducted and the results are listed in Table 4. For comparison, the Nafion 117 was also tested under same conditions.[25] Nafion membrane showed a Young's modulus of 0.18 GPa, elongation at break of 301%, and the tensile stress of 38 MPa as listed in Table 4. The SPAEEKK-D, -H, -B, and -6F membranes in the dry state had tensile stress of 39–74 MPa, Young's moduli of 1.15–2.69 GPa, and elongation at break of 3.8–19.5%. As shown in Table 4, these materials showed much higher tensile strength and the lower elongation than Nafion 117.

The oxidative stability of the polymers was evaluated by immersion of the four different series of SPAEEKK membranes in Fenton's reagent at 30 and 80 °C. All membranes did not dissolve in Fenton's reagent before 2.0 h treatment at 80 °C, although the membranes were broken into pieces in Fenton's reagent at t_2. However, the SPAEEKK-H60 and -70 membranes dissolved and disappeared in Fenton's reagent after 2 and 3 h, respectively.

As listed in Table 4, the SPAEEKK-D membranes exhibited improved oxidative stabilities compared with the earlier copolymers SPAEEKK-H, -B, and -6F.

Proton Conductivity and Methanol Permeability

Proton conductivities as a function of temperature and IEC_w are displayed in Figure 5(a,b). For SPAEEKK-D copolymers, it is obvious that the proton conductivities increase with increasing IEC_w values as they do with the water uptake. The SPAEEKK-D60, -D70, and -D80 show room temperature proton conductivities higher than 10^{-2} S/cm.

Figure 5(c) shows the newly measured proton conductivities of SPAEEKK-B60, -B70 and SPAEEKK-H60, -H70 reported earlier.[6] The proton conductivities of these membranes we reported previously were measured in the transverse direction (across the membranes).[6] Therefore, the proton conductivities of SPAEEKK-B and -H copolymers were remeasured in the longitudinal mode to enable direct comparison to the new SPAEEKK-D copolymers prepared in this study.

It was also previously reported that the proton conductivities of these membranes increase with temperature and attain a certain value, then begin to decrease, presumably because of dehydration of membrane films at elevated temperature. This is a reasonable and expected result, because the cell to measure proton conductivity was open to air by a pinhole, and humidity from boiling water was constantly sup-

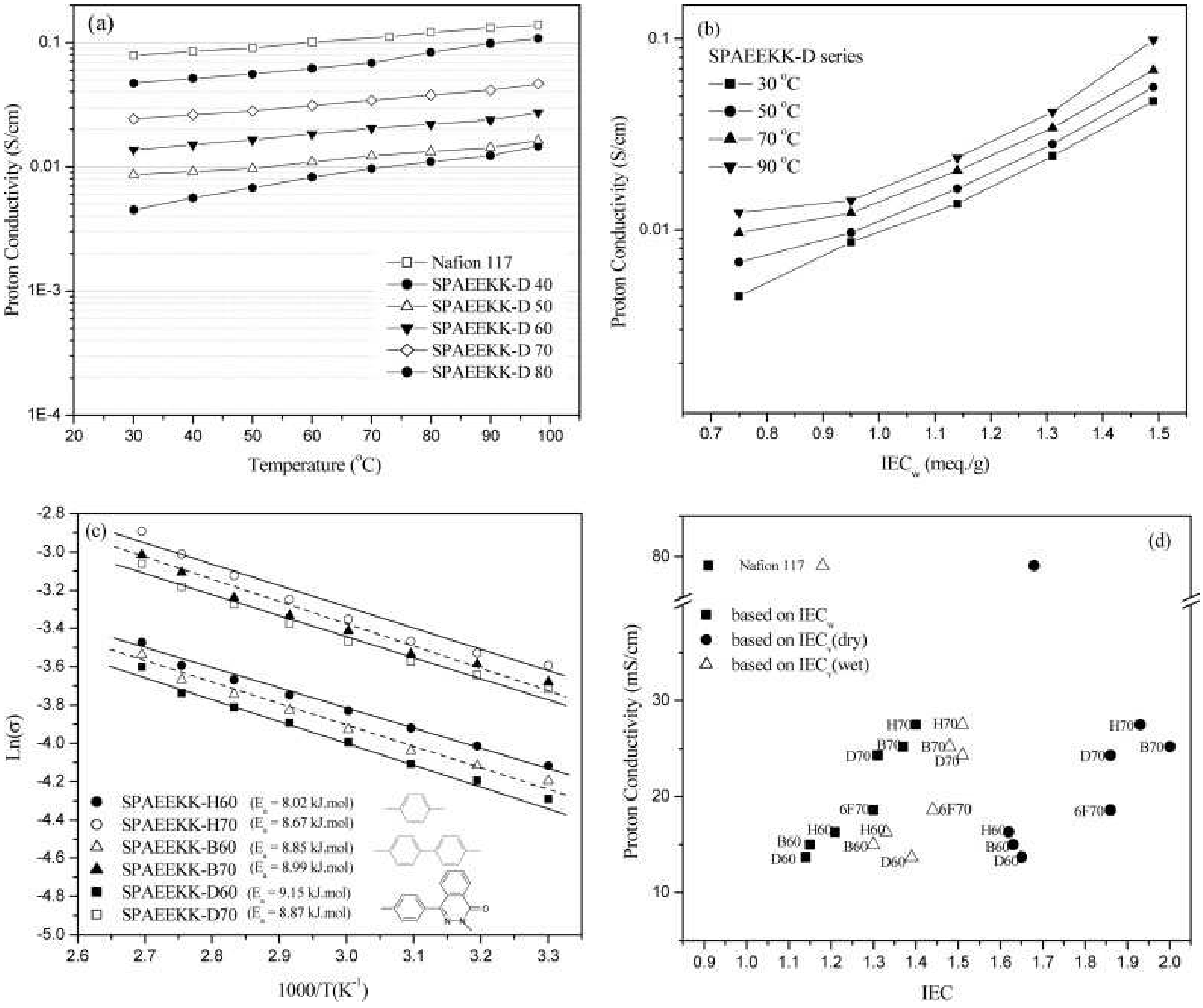


Figure 5. Proton conductivities of SPAEEKK-D versus (a) temperature and (b) IEC; (c) Effect of structure on membrane proton conductivities as a function of temperature (DHNS 60 and 70%: Proton conductivities of the SPAEEKK-B and H copolymer were remeasured in the longitudinal mode for comparison); (d) Proton conductivity at 30 °C as a function of IEC.

plied to the area around the cell. However, SPAEEKK-H60, -H70 and -B60, -B70 show proton conductivities increasing with temperature as shown in Figure 5(c), because the proton conductivities were remeasured with films submersed in water in the present work.

Figure 5(c) displays the effect of temperature on proton conductivity. The activation energy (E_a) for proton conductivity was obtained from the Arrhenius equation as follows:

$$\sigma = \sigma_o \exp(-E_a/RT) \quad (4)$$

where σ is the proton conductivity (in S/cm), E_a is the activation energy (in kJ/mol), R is the universal gas constant (= 8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (in K). As expected, the increase of temperature results in an increase in proton conductivity based on the simplified diffusion mechanism and thermal motion of protons in channels within membranes.

SPAEEKK-H copolymers show higher proton conductivities than SPAEEKK-B and -D at the same sulfonated content value, since they have higher IEC$_w$ values, which is shown and listed for comparison in Table 1 and Figure 5(d). The λ based on IEC$_v$ (wet) of SPAEEKK-D, number of water molecules per sulfonic acid group in hydrated

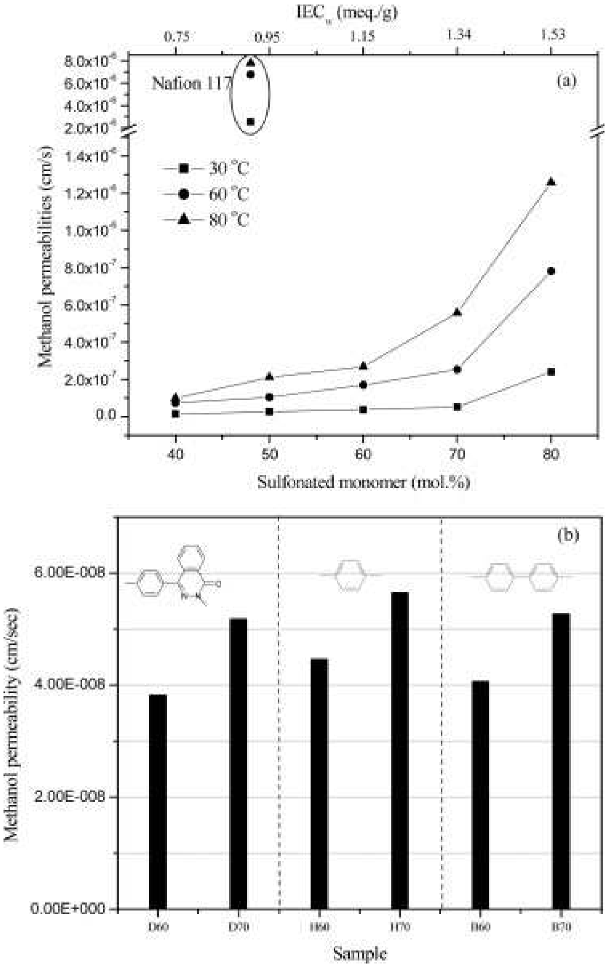


Figure 6. (a) Methanol permeabilities of SPAEEKK-D as a function of sulfonated monomer content at different temperatures; (b) Effect of SPAEEKK structure on membrane methanol permeabilities at 30 °C (DHNS 60 and 70%).

state, is lower than that of SPAEEKK-H, although the IEC$_v$ (wet) of SPAEEKK-D series is same as that of SPAEEKK-H series due to high density and low water uptake (wt %) of SPAEEKK-D. This is one factor affecting the proton conductivity of SPAEEKK membranes, although other factors affect also the proton conductivity.

Compared with the SPAEEKK-D membranes, the SPAEEKK-B membranes have a similar density and IEC$_w$ as shown in Table 3. However, the water uptake (wt % and vol %) of SPAEEKK-B is higher than that of SPAEEKK-D. The SPAEEKK-D membranes derived from DHPZ show a relatively lower water uptake due to the hydrogen bonding between hydrogen atoms of sulfonic acid and carbonyl groups of the oxyphenyl phthalazinone unit. This hydrogen bonding is reported to be strong between 20 and 100 °C.[16]

Figure 6(a) shows the methanol permeabilities of SPAEEKK-D and Nafion 117 as function of sulfonated monomer at different temperature. The methanol permeability for each copolymer increased with increasing sulfonated monomer and temperature. The methanol permeability of the SPAEEKK-D series membranes increased approximately linearly up to 70 wt % sulfonated monomer content, but a sudden increase was observed above 80 wt % sulfonated monomer content. This is referred to as the "percolation threshold." This trend in methanol behavior was the same as that observed for the water uptake behavior.

The methanol permeability of SPAEEKK-D60 and -D70 membranes (2.6×10^{-7} and 5.5×10^{-7} cm/s, respectively at 80 °C) was lower than that of Nafion 117 (1.3×10^{-6} cm/s at 80 °C). The methanol permeabilities of SPAEEKK-B60, -B70, SPAEEKK-H60, -H70 were measured to compare the effect of membrane structure under same conditions with SPAEEKK-D membranes. The methanol permeabilities of these membranes are shown in Figure 6(b). SPAEEKK-D membranes show relatively lower methanol permeability than SPAEEKK-B at the same sulfonated content value and IEC value.

Figure 7(a) shows the proton conductivity and methanol permeability of the SPAEEKK-D membranes measured as a function of IEC$_w$ values. As reported previously,[23,26] it appears that both proton conduction and methanol permeation take place through the same pathway in the membranes, such as the hydrophilic cluster channels. As shown in Figures 4(a) and 7(a), the percolation behavior was observed in the water uptake and the methanol permeability, but was not observed in the proton conductivity of the SPAEEKK-D membranes. A possible explanation for this behavior is related to the proton and methanol transport mechanisms.[8] It is known that methanol permeates through hydrophilic ionic channels and that protons are transported by hopping between ionic sites due to hydrogen bonding as well as through ionic channels.[15] The protons transport through the membrane via bound and free water using the Grötthus and the vehicle mechanisms, respectively. Therefore, the proton conductivity of the SPAEEKK membranes increases linearly with increasing sulfonation level.

The potential performance of DMFC membrane is often evaluated using the ratio of the proton conductivity to the methanol permeabil-

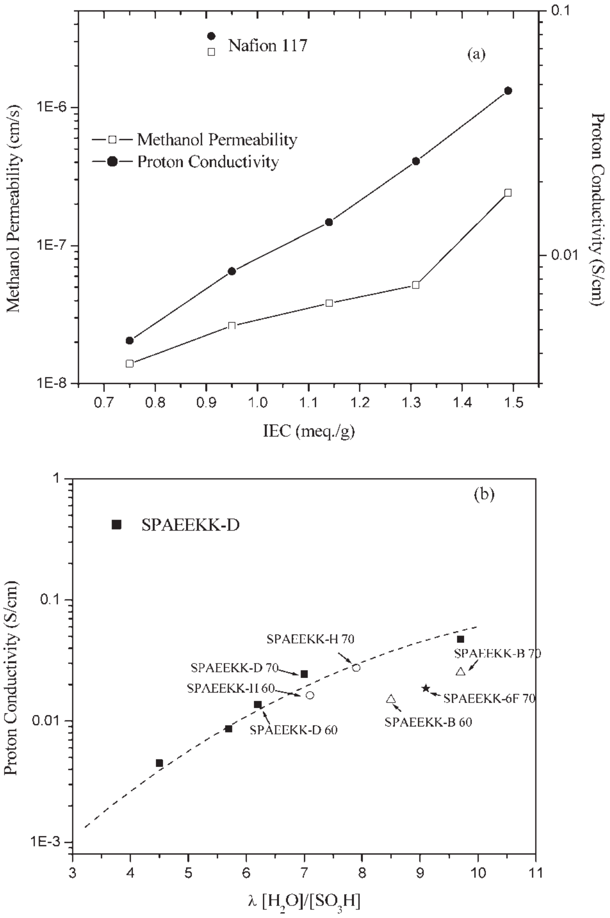


Figure 7. (a) Proton and methanol transport of SPAEEKK-D membranes as functions of IEC_w; (b) Proton conductivity at 30 °C as functions of λ based on IEC_w.

ity, which is known as the selectivity.[8] The selectivity of SPAEEKK-D membranes increased for DHNS content up to 70% and decreased thereafter with increasing DHNS content as listed in Table 2. The maximum selectivity of SPAEEKK-D membrane occurred near the percolation threshold (SC 70 wt %).

Figure 7(b) shows the proton conductivity as a function of water. The water uptake is given in units of $\lambda = [H_2O]/[SO_3H]$. The proton conductivities of SPAEEKK-D increase with increasing λ. The proton conductivities of copolymer derived from BP (SPAEEKK-B60, B70), HQ (SPAEEKK-H60, H70), and SPAEEKK-6F70 are given for comparison. SPAEEKK-D show lower proton conductivities than SPAEEKK-B's and -H's at the same sulfonated content value since they have higher equivalent weights, which are listed in Table 1. The range of proton conductivities of SPAEEKK polymer containing DHNS 60% and 70% are from 0.014 to 0.016, and 0.024 to 0.027 S/cm, respectively. The SPAEEKK-D shows lower λ than SPAEEKK-H, -B, and -6F.

Figure 8(a) shows the strong trade-off relationship between proton conductivities and methanol permeabilities for the SPAEEKK-D membrane series and Nafion 117 at 30 and 80 °C. Figure 8(b) shows a similar plot that compares the four different SPAEEKK copolymers. The methanol permeability of SPAEEKK-6F membrane derived from 1,4-BFBB is significantly higher than that of SPAEEKK-D, -H, and -B membranes derived from 1,3-BFBB as shown in Figure 8(b). As can be seen, all the SPAEEKK membranes revealed methanol permeability in the range of 1.4×10^{-8} to 4.5×10^{-7} cm/s at 30 °C, which constitutes a considerable reduc-

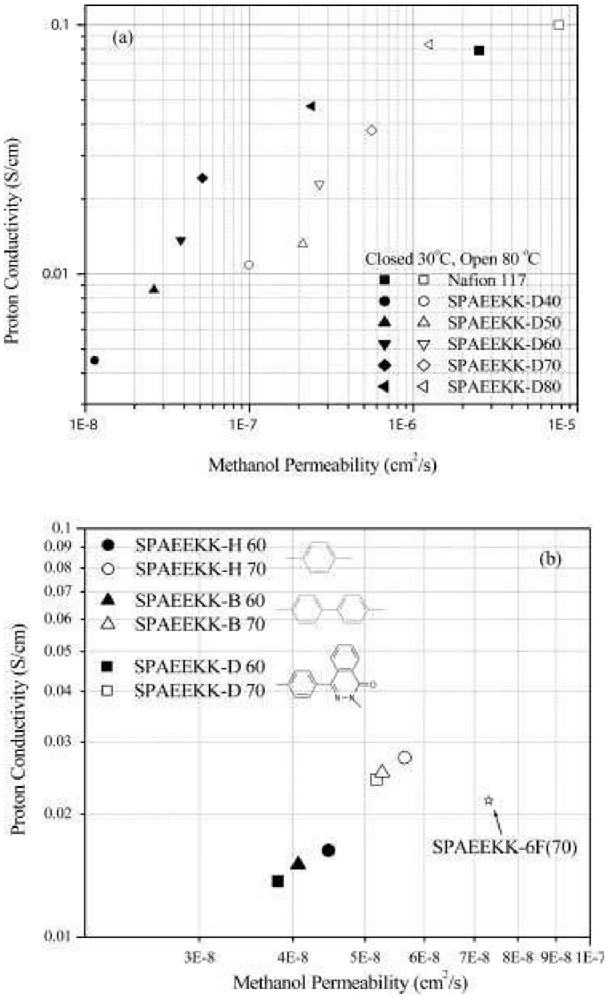


Figure 8. Proton conductivities and methanol permeabilities of (a) SPAEEKK-D membranes and (b) SPAEEKK-D, -B, -H series membranes.

tion compared with Nafion with value of 2.4 $\times 10^{-6}$ cm^2/s.

CONCLUSIONS

This article examines the effect and relative contribution of phthalazinone units in poly(arylene ether ether ketone ketone) (SPAEEKK-D) copolymers in comparison with similarly-structured copolymers derived from other monomer units such as hydroquinone (HQ) and 4,4′-bisphenol (BP).

The SPAEEKK-D membranes incorporating DHPZ phthalazinone monomer had the lowest relative water uptake compared with other polymers of similar IEC allowing relatively high ion concentrations in the hydrated polymer matrix. The low water uptake is believed to originate from the hydrogen bonding between hydrogen atoms of sulfonic acid and carbonyl groups of the phthalazinone unit. The SPAEEKK-D copolymers containing phthalazinone moieties showed decreased methanol permeability. The SPAEEKK-D membranes also showed improved mechanical and thermal properties and oxidative stability over the SPAEEKK-B and -H copolymer membranes.

The various advantages of the polymers under study, such as low monomer cost, high thermal and oxidative stability, low water uptake, and low methanol permeability, suggest that SPAEEKK-D copolymer incorporating phthalazinone moieties derived from the DHPZ monomer are more attractive as PEM materials for fuel cells application compared with those derived from the other monomer units. Incorporating the phthalazinone monomer as a building block appears to provide some benefit for improving the properties of PEM materials. Further development of the SPAEEKK-D copolymer electrolytes for DMFC is being investigated. We anticipate good performance of SPAEEKK-D copolymer and will report the performance in the future.

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