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Synthesis and characterization of poly(aryl ether ketone) copolymers containing (hexafluoroisopropylidene)-diphenol moiety as proton exchange membrane materials[☆]

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Abstract

Sulfonated poly(aryl ether ketone)s (SPAEK) copolymers were synthesized by aromatic nucleophilic polycondensation from 4,4′-(hexafluoroisopropylidene)-diphenol, 1,3-bis(4-fluorobenzoyl)benzene and di-sulfonated difluorobenzophenone. The copolymers exhibited good thermal and oxidative stability. The SPAEK membranes with sulfonic acid content (SC) ranging from 0.6 to 1.16 maintained adequate mechanical strength after immersion in water at 80 °C for 24 h. The proton conductivities of the SPAEK films increased with SC and temperature, reaching values above 3.3×10^{-2} S/cm at 80 °C for $SC\geq0.76$. Tensile strength measurement indicated that SPAEK membranes with SC 0.76, 0.98 and 1.16 are tough and strong at ambient conditions. Consequently, these materials are promising as proton exchange membranes (PEM) for fuel cells operated at medium temperatures.

Keywords: Poly(aryl ether ketone); Proton exchange membrane; Proton conductivity

The proton exchange membrane (PEM) is a key component in the PEM fuel cell (FC), functioning as an electrolyte, transferring protons from the anode to the cathode and providing a barrier for electrons and for fuel and oxygen cross-leaks between the electrodes. Currently, perfluorinated copolymers such as Dupont™ Nafion® are the most commonly utilized PEM materials. Although these materials possess excellent mechanical properties, chemical stability and high proton conductivity, the loss of proton conductivity at temperatures >80 °C and high cost inherent in fluorinated polymers, limit their application in fuel cells operated at elevated temperatures [1,2]. Consequently, alternative, predominantly hydrocarbon PEM materials with high proton conductivity are presently of considerable industrial interest.

The main approach, adopted by many researchers, has involved the attachment of sulfonic acid groups onto various aromatic polymers [1–9] that have high thermal, chemical and oxidative stability, good mechanical properties and low cost. Examples are sulfonated poly(ether ether ketone) (PEEK) [2–5], poly(ether sulfone) (PES) [6–8], polyimides (PI) [9–12], poly(pthalazinone arylene ether) [13], poly(aryl ether nitriles) [14], etc. Usually they are prepared either by post-sulfonation of commercial polymers or by direct synthesis of sulfonated polymer via copolymerization of sulfonated monomers. Among post-sulfonated polymers, sulfonated derivatives of PEEK (SPEEK) [2–5] and of poly(ether ether ketone ketone) (SPEEKK) [2,15] hold much promise as alternatives to fluorinated PEM materials [2]. However, the mechanical integrity of PEMs, based on these aromatic polymers with a high degree of sulfonation (DS), tends to degrade in hot water due to excessive swelling. This is partly because the random distribution of

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sulfonic acid groups along the polymer backbone, introduced by post-sulfonation, is intrinsically heterogeneous. This is due to the different reaction duration for external and internal layers of polymer granules, usually slowly dissolving in acid medium. Post-sulfonation is less likely to favour the formation of uniform phase-separated structures containing ionic domains within long non-sulfonated hydrophobic segments. The high proton conductivity along with strength of hydrated PEM are generally believed to be associated with structures resembling the nanoporous sponge morphology of Nafion membranes, whereby hydrophobic/hydrophilic nanophase separation [2] is observed in the presence of water. Here the sulfonic acid groups form hydrophilic domains contributing to the proton conductivity of the PEMs and the non-sulfonated polymer backbone forms well-networked hydrophobic domains providing their mechanical strength. The synthesis of sulfonated polyaromatic materials by direct copolymerization of disulfonated monomers with other non-sulfonated aromatic monomers [6–14,16–19] may be a better approach to this morphology, allowing at the same time, a better control of the polymer homogeneity and DS. The sulfonated monomers containing two sulfonic acid groups on neighboring phenyl rings (e.g. 5,5′-carbonylbis(2-fluorobenzene-sulfonate) (SDFBP) or 3,3′-disulfonate-4,4′-dichlorodiphenyl-sulfone (SDCDPS)), feature enhanced localized sulfonic acid density in the polymer and consequently results in a greater length of the hydrophobic non-sulfonated backbone segments. This may be beneficial for proton conductivity and mechanical strength of PEMs, as was observed for sulfonated PAEKs [16–19], PES [6–8] and PI [9–12].

The present work reports the synthesis of a series of SPAEKs copolymers (Scheme 1) exhibiting high proton conductivity and thermal and oxidative stability, and which remain mechanically strong in hot water. The incorporation of the hexafluoroisopropylidene diphenyl moiety into the polymer not only enhances the polymer solubility without loss of thermal stability [20], but also promotes the hydrophobicity of non-sulfonated backbone segments of SPAEKs. The group of McGrath recently reported the preparation of sulfonated polysulfones, containing the hexafluoroisopropylidene diphenyl moiety [8]. Our group also recently reported the synthesis of similar sulfonated PAEKs [18]. However, the copolymers discussed in the present work differ from the ones previously studied by replacement of the non-sulfonated monomer 4,4′-difluorobenzophenone (DFDP) with 1,3-bis(4-fluorobenzoyl)benzene (1,3-FBB). The purpose of this is to increase the statistical length of non-sulfonated segments in order to improve the mechanical strength of the membranes. Independently from the present work, another group recently reported the preparation of similar polymers in a patent application [21], but none of the polymer properties has been disclosed.

1. Experimental section

1.1. Materials

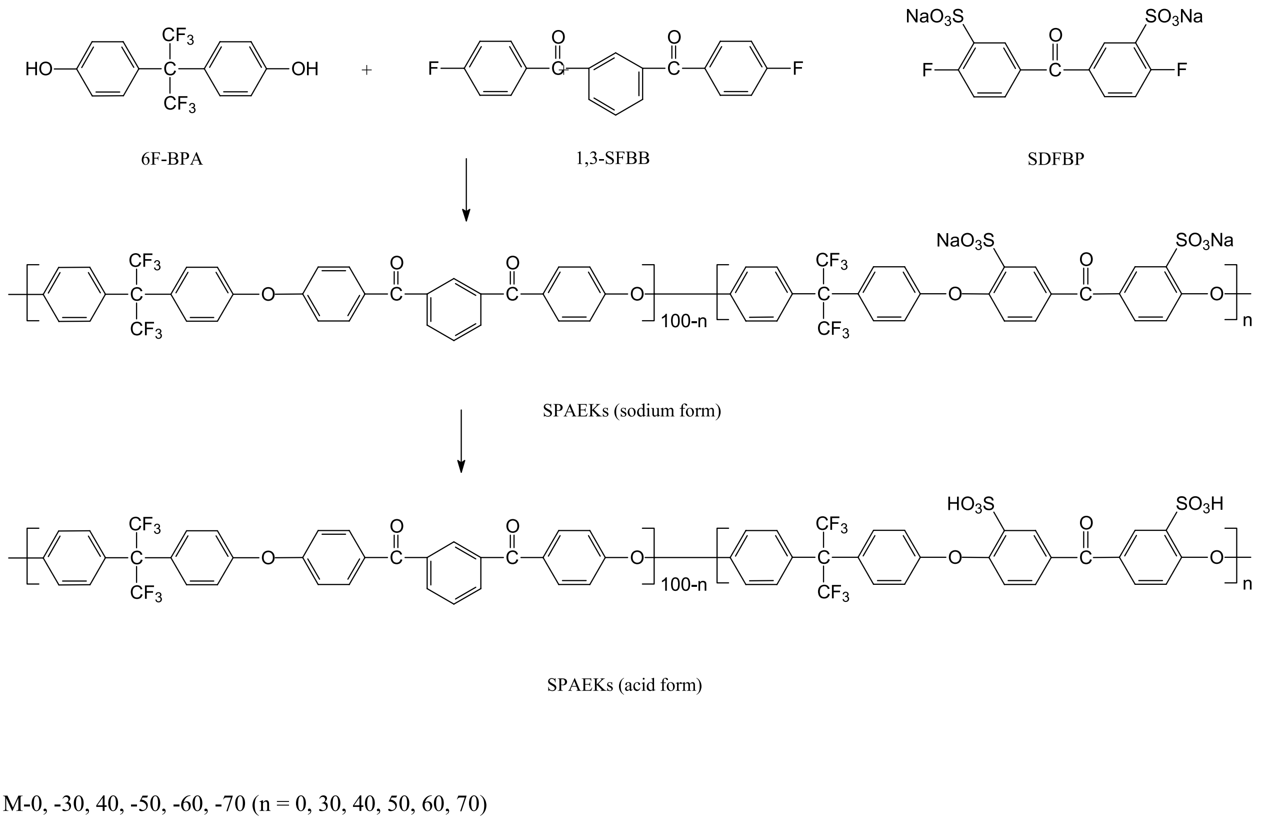
Fuming sulfuric acid (30% SO_3), dimethylacetamide (DMAc), anhydrous potassium carbonate, 4,4′-difluorobenzophenone (DFBP) and 1,3-bis(4-fluorobenzoyl)benzene (1,3-FBB) were obtained from Aldrich Chemical Corp. MEMBRA-CEL™ dialysis tubing (MWCO 3500) was obtained from Serva Electrophoresis (Germany). 4,4′-(hexafluoroisopropylidene)-diphenol (6F-BPA) was obtained from SCM Corp. Monomer sodium 5,5′-carbonylbis(2-fluorobenzene-sulfonate) (SDFBP-Na) (yield: 70%) was prepared following the procedures, disclosed elsewhere [16,17]. The fully sulfonated structure was confirmed by FTIR and ^{1}H NMR analyses. IR (cm^{-1}): 1662 (C=O), 1592 (C=C), 1085 (Ar-SO_3Na). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.36 (dd, 9.40, 8.35 Hz, 2H), 7.74 (m, 2H), 8.07 (dd, 6.8, 2.0 Hz, 2H).

1.2. Polymerization

Typically the procedure [17,18,22] of copolymerization by polycondensation, is as follows. Monomers 1,3-FBB, SDFBP-Na (combined total 0.5 mmol), 0.5 mmol 6F-BPA and 0.55 mmol potassium carbonate were added into a 50 mL three-neck flask, equipped with a Dean-Stark trap and an argon inlet. Eighteen milliliter DMAc and 15 mL toluene were used as solvents. The mixture was refluxed for 2 h at 130 °C until water was removed from the reaction mixture by azeotropic distillation and then excess toluene was distilled off. The temperature of the reaction mixture was slowly raised to 160 °C and maintained at that temperature for 24 h. Before stopping the reaction, 5 mL DMAc was added to dilute the reaction solution. Then the cooled polymer was precipitated into ethanol, washed with acetone and then with water. The recovered polymers were dried at room temperature for 2 days and under vacuum at 80 °C for 24 h. The yields of all polymers were $>90\%$.

1.3. Membrane preparation

The SPAEK membranes (sodium salt form) were cast onto glass plate from their DMAc solution (15 wt%) after filtration using a fine glass frit filter funnel and dried at 50 °C for 2 days and then at 120 °C under vacuum for 24 h. The SPAEK membranes (in sodium salt form) were transformed to their acid form by soaking in deionized water for 1 day at room temperature, and then by immersion in 1.0 N HCl solution for 24 h. The obtained acid form membranes were washed by immersion in deionized water for 24 h, following a previously described protocol [18]. The thickness of all membrane samples was in the range of 70 and 100 μm.



Scheme 1. Synthesis of sulfonated poly(aryl ether ketone) copolymers (M series). M-0, -30, 40, -50, -60, -70 (*n*=0, 30, 40, 50, 60, 70).

1.4. Characterization

Inherent viscosities of the copolymers were measured at 30 °C on 0.6 g L^{-1} solutions in DMAc. FTIR spectra of the powder samples were recorded on a Nicolet 520 Fourier transform spectrometer using a diamond cell. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova 400 NMR spectrometer operating at a resonance frequency of 399.95 MHz for ^{1}H. For each analysis, polymer solutions were prepared in deuterated dimethylsulfoxide (DMSO-d_6). The chemical shift of tetramethylsilane was used as the internal reference standard.

A TA Hi-Res TGA 2950 thermogravimetric analyzer (TGA) was employed to study the thermal stability of SPAEK samples. The samples were preheated under air from room temperature to 150 °C at 10 °C/min to remove moisture, cooled to 90 °C, and then reheated from that temperature to 800 °C at 10 °C/min. A TA DSC 2920 differential scanning calorimeter (DSC) was employed to determine the glass transition temperature (T_g) of SPAEK samples. The samples were preheated under nitrogen from room temperature to 160 °C at 10 °C/min to remove moisture, then cooled to 90 °C, and reheated from that temperature to 250 °C at 10 °C/min.

The proton conductivities of the polymer membranes were determined using AC impedance spectroscopy over a frequency range of $1–10^{-7}$ Hz with oscillating voltage 50–500 mV, using a Solatron 1260 gain phase analyzer. Proton conductivities in the longitudinal direction were measured at different temperatures over a period of 1 day for each PEM sample. A sample of membranes 2×1 cm^2 was clamped in a frame, providing electrical contact with two stainless steel electrodes, and placed in an environmental chamber open to air through a pinhole. The membrane in the frame was exposed to water vapour at 100% relative humidity (RH) during the experiments. The proton conductivity was calculated using $\sigma = l/Rdw$, where l is the distance between the electrodes, d and w are the thickness and width of the films, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the axis of abscissas. The impedance data were corrected for the contribution from empty and short circuited cell.

2. Results and discussion

The SPAEKs synthesized in this work were by copolymerization of commercially available monomers 1,3-FBB, 6F-BPA and synthesized di-sulfonated monomer SDFBP under standard conditions. Table 1 shows some properties of these copolymers, which subsequently will be referred to as M-series in order to be distinguished from

Table 1
Synthesized polymers (M series) and their thermal properties

Polymer	SDFBP (mole %)		SC[a]	T_g (°C) acid	T_d (°C)		η_{inh}[b] (dL/g)
	N[c]	N[d]			Acid	Sodium	
M-0	0			161.2	423.9		0.80
M-30	30	–	0.60	178.8	281.8	382.6	1.53
M-40	40	38	0.76	197.7	275.2	405.8	1.56
M-50	50	49	0.98	223.2	284.7	394.2	5.52
M-60	60	58	1.16	235.1	290.8	387.7	2.39
M-70	70	68	1.36	243.5	277.9	417.4	2.05

[a] The sulfonate content (SC).

[b] η_{inh} was measured at a concentration of 0.6 g/dL in DMAc for sodium form of SPAEKs at 30 °C.

[c] The monomer feed percentage of SDFBP.

[d] The percentage of SDFBP measured experimentally by ^{1}H NMR.

recently studied SPAEK-6F [18] films. All samples have high molecular weights (M_w) as evidenced by the high η_{inh} values of >0.8 dL g^{-1}. The high M_w may be associated with the good solubility of the SPAEKs in the reaction medium during polymerization. All 'as-synthesized' SPAEKs in the sulfonate form (Table 1) were of bright yellow color and were soluble in dipolar aprotic solvents (such as DMAc, N-methyl-2-pyrrolidone) (NMP), dimethylformamide (DMF), DMSO.

The sulfonate or sulfonic acid content (SC), expressed as the number of –SO$_3$Na (–SO$_3$H) groups per average repeat unit (R.U.) of the synthesized copolymers was evaluated by ^{1}H NMR. The experimentally determined SCs were found to be in close agreement with the pre-calculated SCs, expected from the monomer feed ratio (Table 1). Fig. 1 shows the aromatic region of a ^{1}H NMR spectrum of SPAEK M-70 (SC 1.36) as an example, illustrating the SC measurement technique. Each signal in the spectrum was assigned to a single or to a group of aromatic protons of sulfonated ($S_{R.U.}$) or non-sulfonated ($NS_{R.U.}$) repeat unit by using simple homonuclear decoupling and 2D COSY NMR experiments. SCs were experimentally calculated, using a method, related to the previously described one [18]. The SCs were obtained by comparing the ^{1}H NMR signal intensity value of $S_{R.U.}$ protons H-24,24′ (8.20–8.35 ppm, 4.29H) with the intensity value of $NS_{R.U.}$ proton signals H-9,9′,13,14,14′ (7.82–8.10 ppm, set to 7.00H). The SC is derived from these signal intensities according to the following equation:

$$SC = 2\left[\frac{S_{R.U.}}{S_{R.U.} + NS_{R.U.}}\right]$$

Therefore

$$SC = 2\left[\frac{(3.5i_{24})}{(3.5i_{24}) + i_{9,13,14}}\right]$$

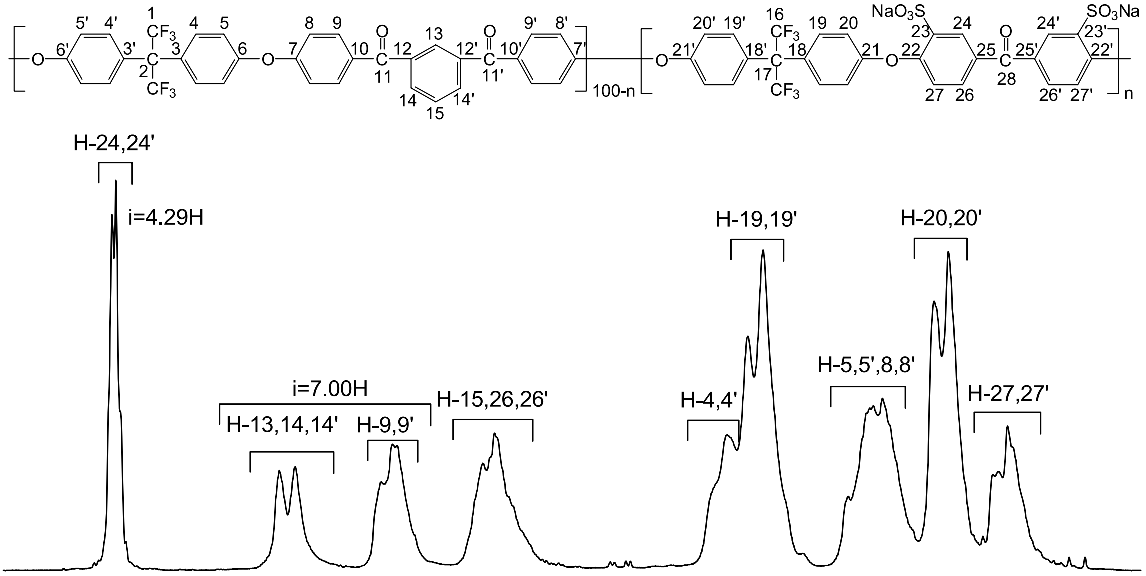


Fig. 1. ^{1}H NMR spectrum of SPAEK M-70 with SC 1.36 ($n=68$).

where $[S_{\mathrm{R.U.}}/(S_{\mathrm{R.U.}}+\mathrm{NS}_{\mathrm{R.U.}})]$ is the ratio of $S_{\mathrm{R.U.}}$ per average polymer R.U.

3.5 is a conversion factor used in the above equation to multiply the intensity value of H-24,24′ (i_{24}) in order to compare intensities for equal number of protons for both $S_{\mathrm{R.U.}}$ and $\mathrm{NS}_{\mathrm{R.U.}}$

i_{24} = intensity of H-24,24′.
$i_{9,13,14}$ = intensity of H-9,9,9′,9′,13,14,14′.
SC = average number of $-\mathrm{SO_3Na}$ per R.U.

For example, the calculation of the SC 1.36 for SPAEK M-70 (Fig. 1) was derived from the ratio of the integral signal intensity of two $S_{\mathrm{R.U.}}$ protons (H-24,24′, $i_{24}=4.29\mathrm{H}$) to that of the integral intensity of seven $\mathrm{NS}_{\mathrm{R.U.}}$ protons (H-9,9,9′,9′,13,14,14′ $i_{9,13,14}=7.00\mathrm{H}$).

Fig. 2 shows the comparative FTIR spectra of M-0, and M-40, M-70 in sodium salt form with different SC. The absorption band at 1501 $\mathrm{cm^{-1}}$ corresponds to di-substitution on aromatic phenyl for non-sulfonated M-0, whereas the new band at 1482 $\mathrm{cm^{-1}}$ for the M-40, M-70 correspond to tri-substitution on aromatic phenyl due to sulfonation in the phenyl ring. The intensity of the 1482 $\mathrm{cm^{-1}}$ band increases with increasing sulfonated monomer ratio. New absorption bands at 1029 and 1086 $\mathrm{cm^{-1}}$ in M-40 and M-70 were assigned to symmetric and asymmetric stretching vibration O=S=O due to the sodium sulfonate group in the polymers.

The unsulfonated PAEK (M-0) is an amorphous polymer with T_g 161.2 °C, which is very close to that of PEEK (∼150 °C). The T_g of the SPAEK series in the acid form increases with SC. The thermal stabilities of this series of polymers were studied by TGA in air (Table 1). The unsulfonated PAEK(M-0) has high thermal stability and a starting T_d at ∼430 °C in a single step thermal degradation, whereas SPAEKs in the acid form exhibited two distinct thermal degradation steps in accordance with previously made observations [18]: the first weight loss occurring at 270 °C or higher which is associated mainly with the loss of sulfonic acid groups and the second weight loss step starting at about 390 °C, which is related to decomposition of the main chain. All sodium salt form SPAEKs showed higher thermal stability ($T_d > 380$ °C) and single step thermal degradation (Table 1).

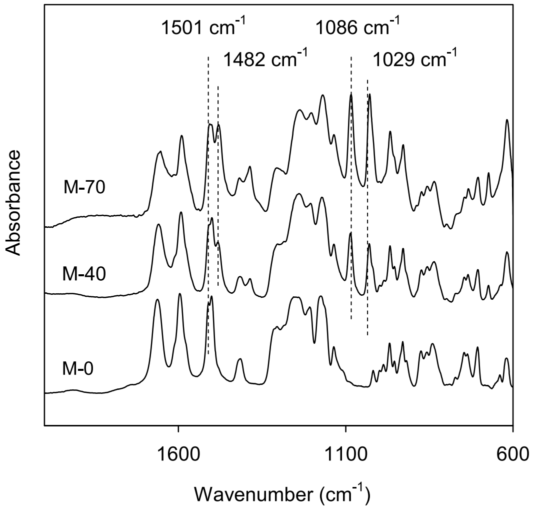


Fig. 2. Comparative FTIR spectra of M series.

Usually, PEMFC conditions imply humid environment and elevated temperatures. Therefore, it is important to determine the water uptake and stability of prepared membranes in water at various temperatures. From Fig. 3, it follows that the M-70 membrane in acid form exhibited excessive water uptake above 150% already at 60 °C and then lost its mechanical strength after immersion in 80 °C water for 24 h. However, the other SPAEK membranes in acid form with SC ≤ 1.16 had adequate mechanical strength before and after immersion in water under the same conditions. For example, M-50 membrane did not exhibit excessive water uptake (51 wt%) and maintained excellent mechanical integrity. Films prepared in the present study series (Table 2) may be compared with the previously studied SPAEK-6F films [18], which exhibited similar water uptake results for the samples with the like SCs. The introduction of the slightly longer hydrophobic segment in this series resulted in no obvious decrease in water uptake compared with SPAEK-6F.

The oxidative stability of the SPAEK series was evaluated by immersing the films into Fenton's reagent (3% $\mathrm{H_2O_2}$ containing 2 ppm $\mathrm{FeSO_4}$) at 80 °C. The M-70 film dissolved within 30 min, whereas the M-60 and -50 films dissolved only after 70 and 220 min, respectively. M-40 and M-30 films remained undissolved after 48 h and retained their mechanical strength, indicating very high oxidative stability [10,11,18]. Significantly, the currently studied M-40 membrane shows better oxidative stability than previously examined SPAEK-40 film [18], which under these conditions lost its strength and dissolved after 390 min.

The proton conductivities (σ) of the SPAEKs series in acid form in the longitudinal direction was measured by AC impedance spectroscopy. All membranes were initially

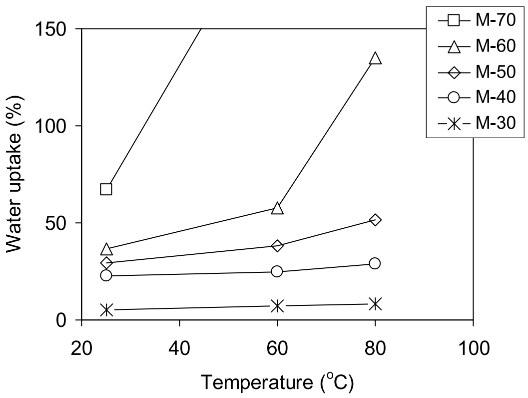


Fig. 3. Water uptake of M series at different temperatures.

hydrated by immersion in deionized water for at least 24 h at room temperature. Some general trends were observed for all samples, as shown in Fig. 4. As well as water uptake, the proton conductivities increased with temperature and with SC. The conductivities of SPAEK membranes (M-40, -50, -60) were in the range of 1.6×10^{-2} to 6.3×10^{-2} S/cm at 25 °C, and 3.3×10^{-2} to 8.5×10^{-2} S/cm at 80 °C, which are considered as high enough for PEM to be promising for fuel cell application. It is noteworthy that at 80 °C, M-50 and M-60 have proton conductivities similar to that of Nafion® 117 (Fig. 4). Along with their hydrothermal stability, this suggests the possibility of application of these materials in PEMFC. Comparing again the current M series with previously examined SPAEK-6F [18], it can be seen that the difference in proton conductivity, observed for the membranes with similar SC was not considerable. Only M-30 was found to have obviously lower proton conductivity than SPAEK-30 [18], which might be attributed to the lower proportion of hydophobic domains formed, due to a higher content of non-sulfonated 1,3-FBB moeity in M series compared with SPAEK-30 (Table 2).

The mechanical strength of the membranes of M-40, -50, -60. -70 and Nafion® 117 were tested by tensile tests at ambient conditions with relative humidity (RH) ~65% (Fig. 5). The initial Young's modulus for the membranes of M40, -50, -60, -70 are 459, 819, 784 and 767 MPa, respectively, which is much higher than the ones of Nafion® 117 (234 MPa) and are similar to the results of SPAEK-6F [18]. In agreement with information reported by DuPont [23], Nafion® 117 membrane at similar ambient conditions showed in our experiment 327% of elongation at break and the maximum stress of 27 MPa at break. As follows from Fig. 5 M40, -50, -60, -70 specimens show elongation at break of 63, 226, 110 and 42%, which surpasses the values previously obtained for SPAEK-6F [18] films. Similar to those membranes, M-40, -50, -60, as can be seen on stress–strain curves (Fig. 5), also show yield behaviour with yield

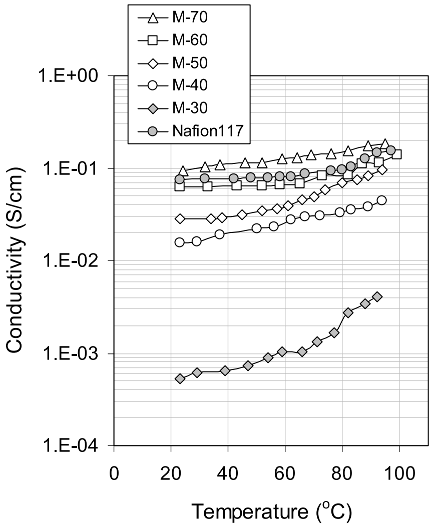


Fig. 4. Proton conductivities of M series films at different temperatures.

Table 2
Water uptake, swelling ratio and proton conductivities of M series

Polymer	SC measured by NMR	Equivalent weight g/mol SO_3H calcd	Water uptake (%)	Swelling (%)	Water uptake (%)	Swelling (%)	H_2O/SO_3H		σ (S/cm)	
			25 °C		80 °C		25 °C	80 °C	25 °C	80 °C
M-30	–	1052	5	2	8	3	2.9	4.7	5.5×10^{-4}	2.1×10^{-3}
M-40	0.76	835	23	7	29	10	10.5	13	1.6×10^{-2}	3.3×10^{-2}
M-50	0.98	653	29	9	51	18	10.7	19	2.8×10^{-2}	6.9×10^{-2}
M-60	1.16	555	37	15	135	50	11	41	6.3×10^{-2}	8.5×10^{-2}
M-70	1.36	476	67	27	2500	227	18	–	9.4×10^{-2}	1.5×10^{-1}
Nafion 117		1100	19	13	30	20	12	18	7.5×10^{-2}	9.6×10^{-2}

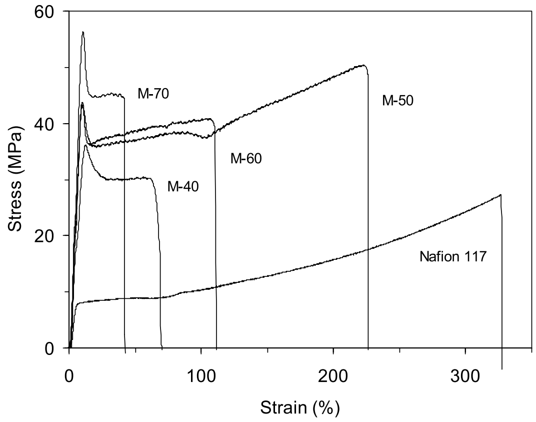


Fig. 5. Stress vs strain curves for M-40, -50, -60, -70, and Nafion® 117 at 25 °C and 65% RH.

strength ranging from 36 to 56 MPa, which clearly indicates the strength and toughness of M-membranes at RH 65%. It is worth mentioning, that the replacement of the DFDP with 1,3-FBB in these copolymers results in membranes with higher values of elongation at break, demonstrating improved plasticity of the new series of polymers. It appears that the mechanical properties of M-40 to M-70 reach a maximum at M-50, which has the greatest elongation at break. Maximum elongation at break is a function of both hydration and SC. Sulfonated polymers containing water of hydration would have interchain H-bonding interactions, which would be mediated by associated water. If the SC is very high, as in the case of M-70, the interchain interactions between SO_3H groups would be reduced because of the high level of hydration surrounding the polymer chains. In an extreme case, highly sulfonated polymers are water soluble. At lower SC, there are fewer interchain H-bonding interactions between SO_3H groups.

3. Summary

A series of SPAEK copolymers were prepared by aromatic nucleophilic copolycondensation of the 4,4′-(hexafluoroisopropylidene)-diphenol (6F-BPA) with various amounts of 5,5′-carbonyl-bis(2-fluorobenzenesulfonate) and 1,3-bis(4-fluorobenzoyl)-benzene. The obtained membranes have good thermal, oxidative and hydrothermal stabilities. The hydrated membranes ($SC \leq 1.16$) show high proton conductivities and good mechanical strength at elevated temperature (80 °C). The SPAEKs membranes with medium $SC \leq 1.16$ did not exhibit excessive swelling in hot water, and at the same time show proton conductivities in the range of $\sim 3 \times 10^{-2}$ to 8.5×10^{-2} S/cm at 80 °C. These values are high enough to consider this series of polymers as promising PEM materials. The tensile test indicates that the SPAEK membranes M-40, M-50 and M-60 (with SC 0.76, 0.98 and 1.16, respectively) are strong and tough and, at least at ambient condition, demonstrate the mechanical properties surpassing that of Nafion.

Acknowledgements

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[23] From Nafion® PFSA membranes product information by DuPont™, the tensile (Young's) modulus is 249 MPa, and maximum tensile strength is 43 MPa in machine direction (MD) and 32 MPa in transverse direction (TD) at 23 °C and 50% RH. Its elongation at break is 225% in MD and 310% in TD at 23 °C and 50% RH.