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Poly(aryl ether ketone)s with carboxylic acid groups: synthesis, sulfonation and crosslinking†

Baijun Liu,[ab] Wei Hu,[b] Gilles P. Robertson[a] and Michael D. Guiver[*a]

Carboxylic acid-containing poly(aryl ether ether ketone) (PFEEK–COOH) and poly(aryl ether ether ketone ketone) (PFEEKK–COOH) were synthesized from the monomer 9,9-bis(4-hydroxyphenyl)-fluoren-4-carboxylic acid. The latter polymer, PFEEKK–COOH, was post-sulfonated to yield SPFEEKK–COOH whereby the site and the degree of sulfonation (DS from 0 to 3) could be controlled. The reaction progress and structures of the resulting sulfonated polymers were identified by 1D and 2D NMR techniques. The carboxylic acid group was used as to crosslink SPFEEKK–COOH by reaction with poly(vinyl alcohol) (PVA) to prepare crosslinked membranes. The proton conductivity of a crosslinked SPFEEKK–COOH-1.6/PVA membrane was ~0.15 S cm^{-1} at 65 °C, while maintaining acceptable dimensional stability in water. Thermal stability, water uptake and proton conductivity of carboxylated, carboxylated/sulfonated, and crosslinked membranes were investigated.

Introduction

Fuel cells, which are devices for transforming chemical energy directly into electricity, are considered to be promising clean power sources. A proton-exchange membrane (PEM) is a key component in the fuel cell membrane electrode assembly (MEA) for transferring protons from the anode to the cathode while providing a barrier to fuel crossover between the electrodes in proton-exchange membrane fuel cells (PEMFCs) and in direct methanol fuel cells (DMFCs).[1,2] There is no doubt that perfluorinated sulfonic acid (PFSA) copolymers, such as Nafion, have some excellent properties for fuel cell devices as well as some negative aspects. The search for non-fluorinated hydrocarbon polymers having high proton conductivity, low fuel crossover, excellent chemical and electrochemical stability, low cost and lower environmental impact as alternatives to PFSAs is an ongoing area of intensive research.[3] To date, many sulfonated high-temperature hydrocarbon-based polymers, such as polyimides,[4,5] polyphenylene,[6,7] polybenzimidazole[8] and poly(phenylquinoxaline)[9] have been investigated. Poly(aryl ether)-type polymers (PAEs), such as poly(aryl ether ketone)s (PAEKs) and poly(aryl ether sulfone)s, are a class of high performance engineering thermoplastics known for their excellent combination of chemical stability, physical and mechanical properties.[10] Most of the sulfonated PAE-type polymers were developed based on post-sulfonated polymers or on copolymers produced from sulfonated monomers.[3] In comparison with some polymers prepared by the post-sulfonation method, copolymers obtained by direct copolymerization of sulfonated monomers have advantages in the controllability of sulfonic content by monomer ratio adjustment. However, relatively few sulfonated monomers have been developed so far,[3] for reasons such as control of sulfonation and monomer purification. Although some post-sulfonated polymers may exhibit poor controllability over both DS and sulfonation site, there are a number of post-sulfonated polymer systems with well-defined structure through rational design of the monomers that comprise the polymer structure.[11]

Ionomeric hydrocarbon-based polymers with sulfonic (–SO$_3$H), phosphonic (–PO(OH)$_2$),[12–14] and carboxylic (–COOH) acid groups[15–17] are attracting increasing attention for their potential applications as proton-exchange membranes in fuel cells. The number of carboxylated polymers investigated as PEM materials are rather limited due to their lower acidity compared with –SO$_3$H. However, PEM materials containing –COOH, particularly those that have chemical stability, are of potential interest as they present convenient sites for crosslinking,[18,19] which is often otherwise achieved through the –SO$_3$H group.

Maintaining dimensional stability for high proton-conductivity membrane materials under humidification is one of the key issues that needs to be addressed in the design of effective PEM materials. The introduction of sites for crosslinking membranes by covalent or other interaction may be an effective avenue for controlling dimensional swelling. In polymers with an optimal degree of crosslinking, improved properties such as solvent resistance, thermal stability, mechanical strength and oxidative stability are often observed.[20–22] Lee et al. recently reported PEMs crosslinked by an esterification reaction between –COOH and –OH.[18,19] In the present study, two types of poly(aryl ether ketone)s containing carboxyl acid group attached to fluorenyl were prepared. The polymer PAEEKK was post-sulfonated under mild reaction conditions for different time periods to yield sulfonated derivatives (SPFEEKK–COOH) with DS ~0 to 3 per repeat unit and at three specific sulfonation sites. The resulting SPFEEKK–COOH could be crosslinked at the –COOH site with poly(vinyl alcohol) (PVA). Selected properties of these

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carboxylated, carboxlated/sulfonated, and crosslinked polymers have been investigated, which are expected to be suitable PEMs in direct methanol fuel cells.

Results and discussion

Synthesis of monomer and polymers containing a –COOH group

A carboxylic acid-containing monomer, 9,9-bis(4-hydroxyphenyl)-fluorenone-4-carboxylic acid, was synthesized in pure monomer-grade form using an improved two-step reaction, as shown in Scheme 1. A synthesis and purification procedure to produce the monomer on a scale of hundreds of grams was briefly described in a patent by us[23] and is described in more detail here. The structure of the monomer was confirmed by elemental analysis and NMR spectra. The fully assigned ^{1}H and ^{13}C NMR spectra of the monomer are shown in Fig. 1.

Polymerization of the carboxylic acid-containing monomer with activated difluoro monomers, such as 1,4-bis(4-fluorobenzoyl) benzene or 4,4′-difluorobenzophenone, was conducted by typical nucleophilic polymerization in dimethyl sulfoxide (DMSO) in the presence of K_2CO_3. No crosslinking occurred, even after prolonged polymerization time, at temperatures in the range of 160 to 210 °C. High molecular weight polymers containing pendant carboxylate were readily obtained within several hours, which suggested that the monomer was of sufficient purity and high reactivity (Table 1). The obtained polymers in potassium carboxylate form were transformed to the acid form (PFEEK–COOH and PFEEKK–COOH), as shown in Scheme 2. Both PFEEK–COOH and PFEEKK–COOH could form strong, flexible and transparent films by solution casting from DMSO.

Sulfonation reaction of PFEEK–COOH and PFEEKK–COOH

Sulfonation is an electrophilic reaction, and the ultimate substitution position of –SO₃H groups on the benzene rings is generally determined by the existing substituents on the benzene rings. Generally, sulfonation reactions occur more readily on benzene rings with activated substituents (electron donating), such as methyl (–CH₃) and methoxy (–OCH₃), than on ones with deactivated substituents (electron withdrawing), such as trifluoromethyl (–CF₃) and carbonyl (–CO–). By adjustment of polymer structure, post-sulfonation reactions can produce polymers with well-controlled sulfonation positions, under mild reaction conditions and short reaction times.[11] An advantage of polymer post-sulfonation is that it is relatively simple in comparison with copolymerization of sulfonated monomers because the latter are based on sulfonated monomers, which may need multistep synthesis and purification. The presence of excessive ionic character from salts such as –SO₃⁻M⁺ and –O⁻M⁺ may lead to poor reaction mixture solubility, especially at the
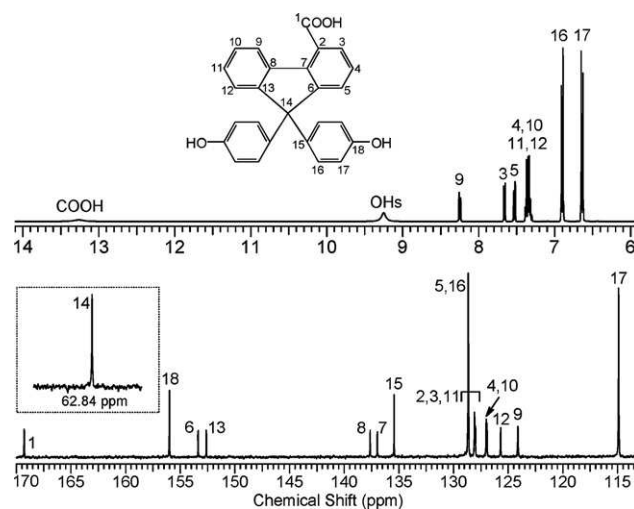
Fig. 1 ^{1}H and ^{13}C NMR spectra of 9,9-bis(4-hydroxyphenyl)-fluoren-4-carboxylic acid.

Table 1 Viscosity and thermal properties of the polymers

Polymer	η^a/dL g^{-1}	T_g/°C^b	T_D/°C^c	$T_{5\%}$/°C^d
PFEEK–COOH	0.9	281	229	283
PFEEKK–COOH	0.7	273	217	277
SPFEEKK–COOH (DS~1.6)	1.4	—	327	350
SPFEEKK–COOH (DS~2.0)	1.5	—	342	356
SPFEEKK–COOH-2.0/PVA-1	—	—	242	266
SPFEEKK–COOH-2.0/PVA-2	—	—	243	271
SPFEEKK–COOH-1.6/PVA	—	—	241	284

^{a} Inherent viscosity. ^{b} Glass transition temperature. ^{c} Onset temperature of decomposition. ^{d} Temperature at 5% weight loss.

initial stages of polymerization of the growing chain, leading to difficulties in obtaining high-molecular weight polymers. This situation is less prone to occur in polymerizations based on unsulfonated monomers.

Several fluorenyl-containing polymers have recently been reported for PEM applications, which showed some promising properties, such as high proton conductivity and low methanol crossover.[24–30] In particular, Miyatake and Watanabe recently reported several sulfonated poly(aryl ether sulfone)s containing fluorenyl moieties through a post-sulfonation method.[27–29] In their work, chlorosulfonic acid was used and both the amount of sulfonation reagent and copolymer make-up were employed to
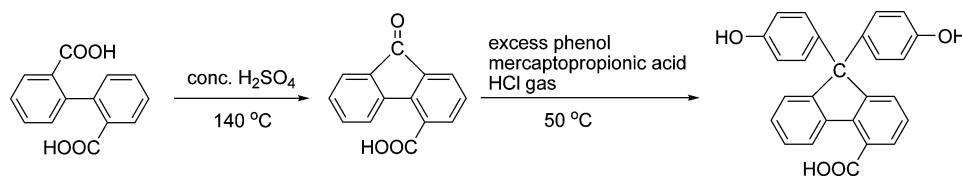
Scheme 1 Synthesis of 9,9-bis(4-hydroxyphenyl)-fluoren-4-carboxylic acid.
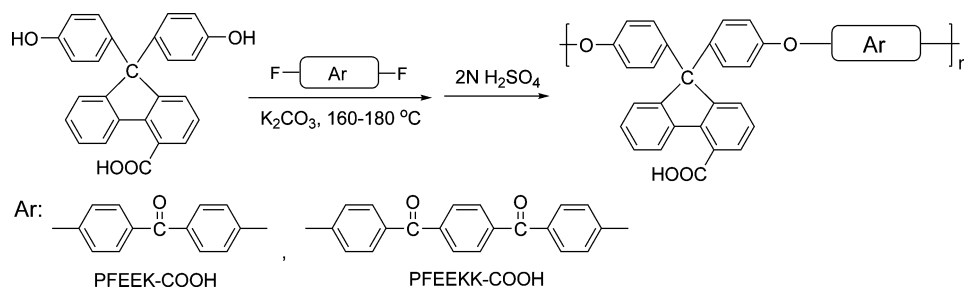
Scheme 2 Synthesis of poly(aryl ether ether ketone)s containing carboxylic groups.

control DS. However, the ionomers were insoluble in CH_2Cl_2 and precipitated out of the solution soon after the polymer and chlorosulfonic acid solutions were mixed, which could have a negative impact on the progress of sulfonation.

In contrast with the sulfonation of fluorenyl-containing poly(aryl ether sulfone)s,[27–29] concentrated H_2SO_4 was utilized as both the sulfonation reagent and solvent for the sulfonation of the present carboxylated polymers (Scheme 3). The carboxylated/sulfonated poly(aryl ether ether ketone)s were readily soluble in concentrated H_2SO_4 and no precipitation occurred during the sulfonation process. Using mild sulfonation conditions of 95–98% sulfuric acid at room temperature, the resulting polymers containing both –COOH and –SO$_3$H groups had well-defined structure. It is of interest to observe that there are three specific sulfonatable sites per repeat unit, which is quite different from the structural characterization reported for the post-sulfonation of fluorenylated PES without –COOH groups in the ClSO$_3$H–CH$_2$Cl$_2$ system.[27–29] In their studies of the post-sulfonation of fluorenyl-containing poly(arylene ether)s, no sulfonation on the main chain was reported as occurring.

The good solubility of both carboxylated polymers and post-sulfonated ones in DMSO made it possible to monitor the sulfonation reaction by NMR. Fig. 2 shows the reaction kinetics of PFEEKK–COOH in H_2SO_4 at a concentration of 3.0 g polymer per 100mL H_2SO_4 at room temperature. It is noted that the reaction rate was fast within the first 10 days and was especially rapid during the first day, and a DS of 2.0 was achieved after a five-day reaction. The reaction rate was much slower after 10 days, and DS close to 3.0 was achieved after a 45-day reaction.

NMR analysis of the polymers

All the polymer spectra were fully characterized by 1D (^{1}H, ^{13}C) and 2D (COSY, HSQC, HMBC) NMR. Fig. 3 and 4 show
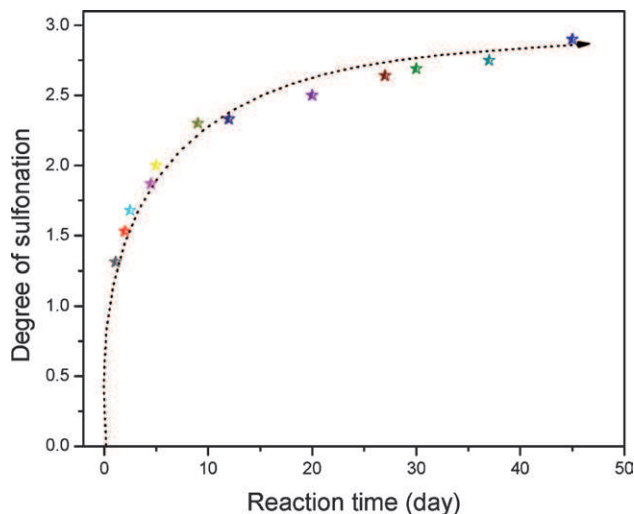
Fig. 2 Sulfonation reaction of PFEEKK–COOH in 95–98% H_2SO_4 at a concentration of 3.0 g polymer per 100mL H_2SO_4 at room temperature.

stacked ^{1}H and ^{13}C spectra, respectively, of unsulfonated PFEEK–COOH and PFEEKK–COOH along with sulfonated PFEEKK–COOH (DS~3). The ^{1}H NMR spectrum of SPFEEKK–COOH (DS~2) is also displayed in Fig. 3C but its corresponding ^{13}C spectrum is not shown in Fig. 3 due to its complexity resulting from random sulfonation at the equivalent X and Y sites as described later. The NMR signals of the fluorenyl monomer (Fig. 1) and of the unsubstituted polymers (Fig. 3 and 4) were easily assigned. Characterization of the sulfonated polymers was arduous as up to three –SO$_3$H groups could be introduced onto the polymer. Nevertheless, we were successful in identifying the sulfonation sites and the rate of reaction using 1D and 2D NMR techniques. The distinctive
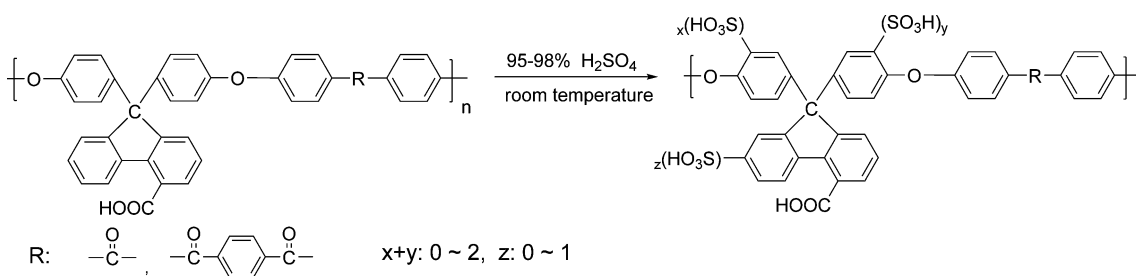
Scheme 3 Sulfonation of poly(aryl ether ether ketone)s containing carboxylic group.
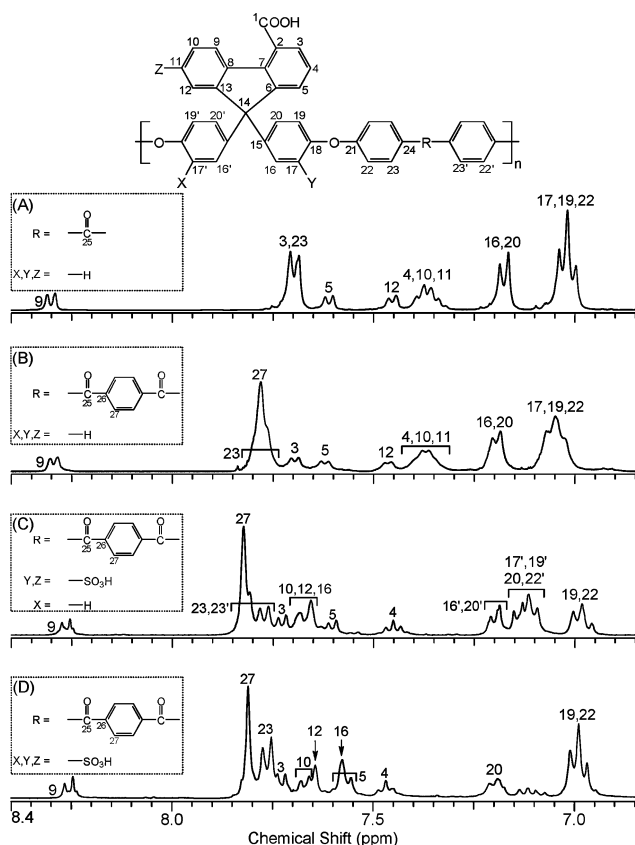
Fig. 3 ^{1}H NMR spectra of PFEEK–COOH (A), PFEEKK–COOH (B), SPFEEKK–COOH (DS~2.0) (C) and SPFEEKK–COOH (DS~3.0) (D).

Fig. 4 ^{13}C NMR spectra of PFEEK–COOH (A), PFEEKK–COOH (B) and SPFEEKK–COOH (DS~3.0) (C).

proton H9, present on all studied derivatives, always appeared in the high frequency area (8.3 ppm) due to the strong electron de-shielding effect on H9 of the nearby carboxylic acid's anisotropic induced magnetic field. The intensity of the H9 signal was later used to estimat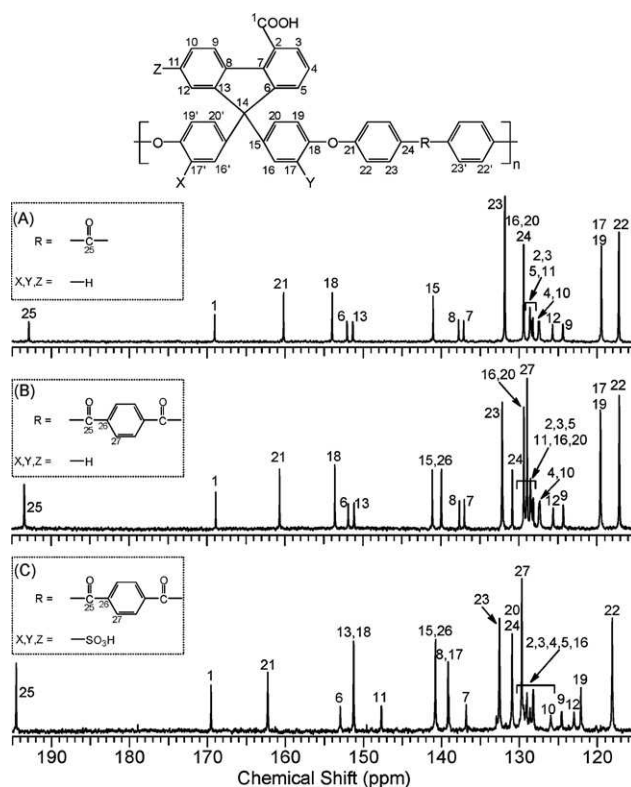e the degree of sulfonation on the main polymer chains. ^{1}H and COSY spectra showed very small changes in chemical shift values for the hydrogen atoms of spin system H3–H4–H5 present in the fluorenyl monomer and in the fluorenyl moiety of all the synthetic polymers, including the sulfonated ones. The electron-withdrawing carboxylic acid deactivates the benzene ring, hence protecting it against sulfonation. On the other hand, the spin system H9–H10–H11–H12 of the other fluorenyl benzene ring is clearly altered by the sulfonation reaction. ^{1}H NMR spectra of Fig. 3 show a distinct shift of H10 and H12 to higher frequencies resulting from the substitution of H11 by an electron-withdrawing –SO$_3$H group. In addition to that, the carbon signal from C11 shifted nearly 20 ppm towards higher frequencies (147.8 ppm) as a result of its new linkage with the electronegative sulfur atom; C11 also shows a heteronuclear 3-bond coupling in the HMBC spectrum with the distinct proton H9 at high frequency. Analysis of the ^{1}H NMR spectra of the sulfonation reactions indicated a faster sulfonation rate on the fluorenyl ring when compared with the reactivity at the main chain. This was readily observed by the fast transition of H10–H12 to higher frequencies. Polymer main-chain sulfonation occurs specifically at the *ortho* position of the ether

linkages and exclusively on the fluorenyl monomer residue as shown by the large chemical shift displacements of C17 (20 ppm shift to 138.0 ppm) and H16 (0.38 ppm shift to 7.58 ppm) towards higher frequencies. The reaction rate on the main chain was monitored by comparing the intensity of the invariable H9 with the intensities of the distinct low frequency H19–H22 resulting from the presence of a –SO$_3$H at the Y position. The X and Y positions of the polymer in Fig. 4 are equivalent since a spatial representation of the molecule would show the fluorenyl group perpendicular to the main chain due to C14. Sulfonation therefore takes place at both sites randomly. Fig. 3C shows SPFEEKK–COOH DS 2 where Y and X have been labeled exclusively as –SO$_3$H and –H for practical reasons only; signals of Fig. 3C which are labeled with numbers bearing a prime (*e.g.* 22′) indicate atoms on or near an unsulfonated ring. Fig. 3D and 4C show the simple ^{1}H and ^{13}C NMR spectra resulting from symmetric, highly substituted repeat units of SPFEEKK–COOH (DS~3). The actual DS is slightly lower than 3 (~2.9) because residual unsubstituted H17′–H19′ and H22′ could still be observed in the 7.05–7.15 ppm region even after a long reaction time. SPFEEK–COOH polymer spectra are not reported here because the polymer's physical properties were less attractive than the SPFEEKK–COOH derivatives. Nevertheless, thorough NMR analysis of the sulfonation reactions on the fluorenyl and main chain of SPFEEK–COOH polymer samples revealed the exact same site-specific reactivity leading to a DS~3 polymer as seen in SPFEEKK–COOH. The main difference was in the sulfonation reaction rate. The fluorenyl group underwent rapid sulfonation as seen before and

observed once again by ^{1}H NMR of specific (H10–H12) signal displacements towards higher frequencies. On the other hand, the main-chain sulfonation was significantly accelerated. The sulfonation rate on the main chain could not be monitored by ^{1}H NMR, as it was in the case of SPFEEKK–COOH, due to the complexity of overlapping signals at low frequencies. However, a clear and simple spectrum of the symmetric DS~3 repeat units was observed after only 5 days. This interesting result may be explained by a more reactive PFEEK–COOH towards nucleophilic sulfonation reaction since electron delocalization over a longer ketone–aryl–ketone in PFEEKK–COOH when compared with a single ketone in PFEEK–COOH results in decreased nucleophilicity at the *ortho*-ether sites of the fluorenyl moieties.

Crosslinking of SPFEEKK–COOH and PVA

A number of PEMs that were crosslinked through the sulfonic acid group were previously reported.[2,3] While it is an effective method, the crosslink utilizes some of the proton-conducting sulfonic acid groups, thereby reducing conductivity. This can be partly alleviated by starting with highly sulfonated polymers that may even be water soluble. The crosslinking reaction to yield ester linkages between –COOH groups of sulfonated polymers and –OH groups of PVA is reported in several articles.[18,19] It is well known that a good solvent for both polymer and crosslinking reagent is especially important in order to get a compatible system. In this study, DMAc and PVA (75% hydrolysis and average M_w of 3000) were selected as solvent and crosslinking reagent, respectively. An improved procedure including membrane making and then crosslinking was employed for the thermal crosslinking reaction of this new blend (Scheme 4). All films before and after curing were clear and transparent, which suggested the compatibility of the SPFEEKK–COOH/PVA system. PVAs with high molecular weight and high percentage hydrolysis were not suitable for this system because of their poor solubility in DMAc. Low molecular diols, such as 1,4-butanediol and 1,5-pentanediol, showed good solubility in DMAc and could form transparent films with SPFEEKK–COOH. However, they did not exhibit good characteristics as crosslinking agents, since they could not be well retained in the film when treated at crosslinking temperature.

Properties of the membranes

The carboxylated polymers, PFEEK–COOH and PFEEKK–COOH, had high T_g values of 281 and 273 °C, respectively (Table 1). As shown in Fig. 5, the thermal stabilities of the membranes were evaluated in air by TGA. Similar to the many examples of sulfonated poly(arylene ether ether ketone)s, the present carboxylated polymers showed obvious two-stage thermal decomposition. The first stage at around 220 °C may be associated with the loss of –COOH groups, and the second one around 500 °C may be caused by the decomposition of the polymer backbone. It was clear that the first-stage weight loss increased in magnitude with the incorporation of –SO$_3$H groups. The crosslinked SPFEEKK/PVA was thermally stable up to 200 °C in air, and its first-stage weight loss may be from the combination of the loss of carboxylic/sulfonic acid groups and the degradation of PVA.

Water uptake and dimensional stability of PEMs are closely related to proton conductivity. The water within the membrane provides a carrier for the proton, and maintains high proton conductivity. Increasing the –SO$_3$H groups in the polymer structure enhances the proton conductivity but is often
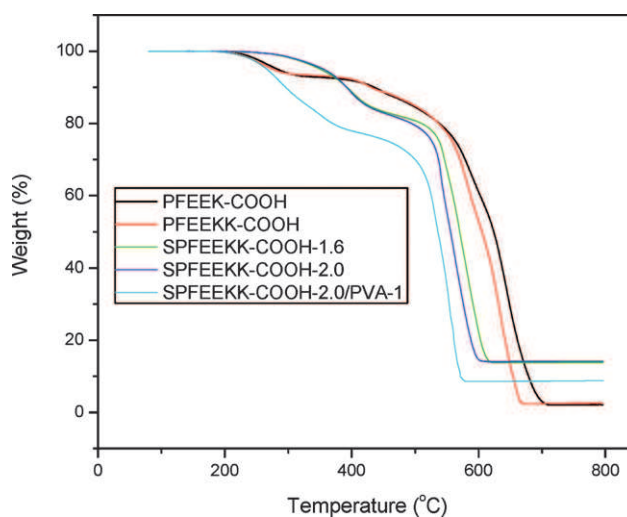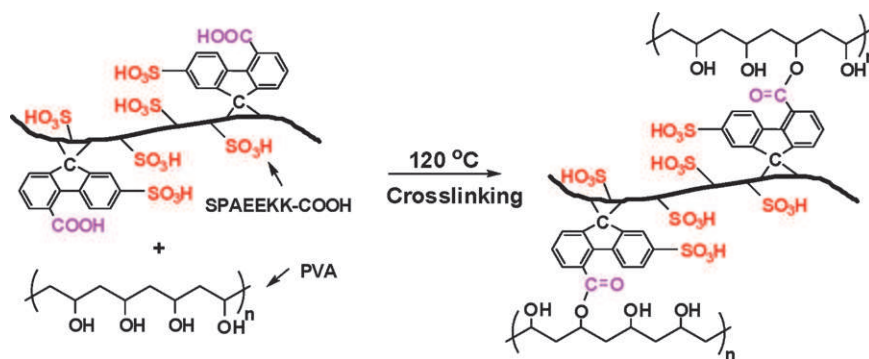

Fig. 5 TGA curves of PFEEEK–COOH, PFEEKK–COOH, SPFEEKK–COOH (DS~1.6 and 2.0) and cross-linked SPFEEKK-2.0/PVA-1 in air.


Scheme 4 Plausible schematic representation of sulfonated poly(aryl ether ether ketone ketones)s crosslinked by ester linkages.

accompanied by excessive water uptake and dimensional change of the membranes. As shown in Table 2, carboxylated polymers, PFEEK–COOH and PFEEKK–COOH possessed extremely low water uptakes ($\leq 5\%$) and swelling ratio ($< 5\%$) at room temperature. After sulfonation, the water uptake of SPFEEK–COOH-2.0 increased to 240%. At 65 °C, SPFEEKK-2.0 was completely dissolved into water. Crosslinking is an effective method for reducing dimensional change for PEMs that operate under a humid environment. After crosslinking, the membranes had significantly lower water uptake and swelling ratios than the corresponding membranes before crosslinking. For example, the room-temperature water uptake for the crosslinked SPFEEKK–COOH-2.0-PVA-1 and -2 was reduced three-fold to $\sim$80%. Although both SPFEEKK–COOH-2.0 and PVA were soluble in hot water, the crosslinked membranes were not soluble in hot water. In addition, the ratio of PVA and SPFEEKK–COOH-2.0, which are associated with the density of crosslinking, would impact the water uptake and swelling ratio. It is noted that the dimensional instability of crosslinked membranes at elevated temperature ($\sim$100 °C) occurs due to the high DS values from the amount of sulfonation. The crosslinked membrane based on SPFEEKK–COOH-1.6, which contained the lowest amount of –SO$_3$H groups, showed acceptable dimensional stability, with the swelling ratio having a value of 30% at 65 °C. Although the incorporation of aliphatic PVA polymer through ester linkages leads to a reduction in thermooxidative stability, the crosslinked SPFEEKK/PVA membranes maintain dimensional shape after 15 minutes of treatment with Fenton's reagent (3% H$_2$O$_2$ containing 2 ppm FeSO$_4$) at 80 °C. The thermooxidative stability may be sufficient for the crosslinked SPFEEKK/PVA membranes to be utilized in DMFCs.

Proton conductivity is strongly related to the content of acid groups and is a crucial parameter for the practical application of PEMs in fuel cells. Carboxylated polymers exhibit much lower relative proton conductivity compared with sulfonated polymers because of their lower relative acidity caused by a low degree of dissociation (Table 2 and Fig. 6). At room temperature, proton conductivity of PFEEK–COOH and PFEEKK–COOH was 6.6×10^{-4} and 5.8×10^{-4} S cm^{-1}, respectively. When sulfonated, the proton conductivity of these carboxylated polymers (SPFEEKK–COOH-2.0) increased to 7.5×10^{-2} S cm^{-1} at room temperature, which was even higher than that of Nafion 117. However, it was not suitable for fuel cell applications due to its poor dimensional stability in water. The proton conductivity of crosslinked SPFEEKK–COOH-1.6/PVA that
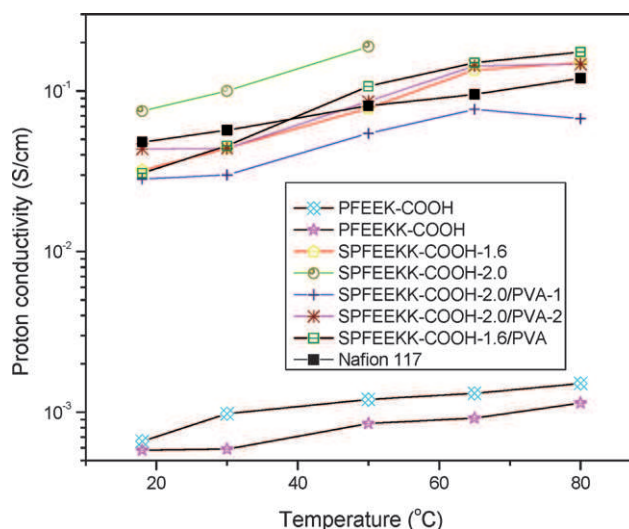
Fig. 6 Proton conductivities of PFEEK–COOH, PFEEKK–COOH, SPFEEKK–COOH (DS$\sim$1.6 and 2.0) and crosslinked SPFEEKK/PVA membranes.

showed acceptable dimensional stability in water was around 0.15 S cm^{-1} at 65 °C.

Experimental

Characterization and measurements

^{1}H and ^{13}C NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at frequencies of 399.95 MHz for ^{1}H and 100.575 MHz for ^{13}C at 35 °C. An indirect detection probe was used for the acquisition of 1D and 2D spectra. Deuterated dimethylsulfoxide (DMSO-d$_6$) was selected as the solvent and the DMSO signals at 2.50 ppm (^{1}H NMR) and 39.51 ppm (^{13}C NMR) were used as the chemical shift references. Inherent viscosities (η_{inh}) were measured using an Ubbelohde viscometer at a polymer concentration of 0.5g dL^{-1} in DMSO solutions at 30 °C.

A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for evaluating thermal stability of the polymers. The samples for TGA analysis were preheated at 150 °C for 40 min to remove moisture, and then heated at 10 °C min^{-1} from 80 to 800 °C in air. The resulting curves were shifted to make the starting weight as 100%. A TA Instruments differential scanning calorimeter (DSC) model 2920 was used for

Table 2 Water uptake, swelling and proton conductivity of the membranes

Polymer	WU (%)^a 18 °C/65 °C	SR (%)^b 18 °C/65 °C	σ^c/S cm^{-1} 18 °C/65 °C
PFEEK–COOH	4/5	2/3	$6.6 \times 10^{-4}/1.3 \times 10^{-3}$
PFEEKK–COOH	3/4	1/2	$5.8 \times 10^{-4}/9.2 \times 10^{-4}$
SPFEEKK–COOH-1.6	64/125	19/36	$3.2 \times 10^{-2}/1.3 \times 10^{-1}$
SPFEEKK–COOH-2.0	240/—	64/—	$7.5 \times 10^{-2}/—$
SPFEEKK–COOH-2.0/PVA-1	80/$\sim$500	17/$\sim$100	$2.8 \times 10^{-2}/7.7 \times 10^{-2}$
SPFEEKK–COOH-2.0/PVA-2	88/$\sim$2000	30/$\sim$200	$4.8 \times 10^{-2}/1.4 \times 10^{-1}$
SPFEEKK–COOH-1.6/PVA	50/91	16/30	$3.0 \times 10^{-2}/1.5 \times 10^{-1}$

^{a} Water uptake in weight%. ^{b} Swelling ratio in volume%. ^{c} Proton conductivity.

measuring m.p. (monomer) and T_g (polymers). m.p. was taken from the first run at a heating rate of 10 °C min^{-1}. T_g was evaluated from the second heating run at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere, after an initial heat–quench cycle.

The proton conductivity was estimated from AC impedance spectroscopy data, obtained over a frequency range of 1 to 107 Hz with oscillating voltage of 100 mV, using a Solartron 1260 gain phase analyzer. Specimens in the form of 20 × 10 mm strips were soaked in deionized water for at least 24 h prior to the test. Each specimen was placed in a temperature-controlled cell open to the air at 100% RH at ambient pressure. Measurements, in two-point mode, were carried out after sample conditioning in the closed cell overnight or longer. The conductivity (σ) of the samples in the longitudinal direction was calculated, using the relationship $\sigma = L/(R \times d \times W)$, where L is the distance between the electrodes, d and W are the thickness and width of the sample stripe respectively. R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re (Z) axis.

Water uptake and swelling ratio measurements

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

The water uptake content was calculated by: water uptake (wt.%) = $(W_{wet} - W_{dry})/W_{dry} \times 100\%$, where W_{dry} and W_{wet} are the weights of dried and wet samples, respectively.

The swelling ratio was calculated by: swelling ratio (%) = $(L_{wet} - L_{dry})/L_{dry} \times 100\%$, where L_{dry} and L_{wet} are the lengths of dry and wet samples, respectively.

Chemicals and materials

Diphenic acid, phenol and mercaptopropionic acid were obtained from Sigma-Aldrich Ltd, and used as received. 1,4-Bis(4-fluorobenzoyl)benzene (Jilin University) and 4,4'-difluorobenzophenone (Sigma-Aldrich Ltd) were recrystallized from chlorobenzene before use. Anhydrous potassium carbonate (Sigma-Aldrich Ltd) was ground into a fine powder using a high-speed blender and thoroughly dried in a vacuum oven before use. Poly(vinyl alcohol) (PVA) with an average molecular weight of 3000 g mol^{-1} and hydrolysis of 75% was obtained from Sigma-Aldrich Ltd. All other chemicals were obtained from commercial sources, and used without further purification.

Synthesis of 9-fluorenone-4-carboxylic acid.

A mixture of diphenic acid (500 g, 2.06 mol) and concentrated sulfuric acid (1.25 L) was stirred at 140 °C for 35 min. The red solution was cooled and poured into 15 L of deionized water to precipitate the product. The resulting precipitate was boiled in fresh water several times. The resulting yellow 9-fluorenone-4-carboxylic acid (463 g, 81% yield) was dried and used for the next step without further purification (Scheme 1). m.p. 226 °C (DSC).

^{1}H NMR (DMSO-d$_6$) (in ppm): 8.23 (d, 8.0 Hz, 1H), 7.93 (dd, 8.0, 1.6 Hz, 1H), 7.75 (dd, 8.0, 1.6Hz, 1H), 7.62 (d, 8.0 Hz, 1H), 7.60 (td, 8.0, 1.6 Hz, 1H), 7.44 (d, 8.0 Hz, 1H), 7.40 (td, 8.0, 1.6 Hz, 1H).

^{13}C NMR (DMSO-d$_6$) (in ppm): 192.09, 167.90, 142.53, 142.18, 135.98, 135.32, 134.48, 133.56, 129.91, 129.24, 128.17, 126.49, 125.69, 123.72.

Synthesis of 9,9-bis(4-hydroxyphenyl)-fluoren-4-carboxylic acid.

9-Fluorenone-4-carboxylic acid (538 g, 2.4 mol), excess phenol (1.13 kg, 12 mol) and mercaptopropionic acid (catalytic amount) were stirred while bubbling in anhydrous HCl gas under inert atmosphere at 50 °C for 6 h. Following completion of the reaction, excess phenol was removed by steam distillation. The filtrate was thoroughly washed with boiling water to give crude 9,9-bis(4-hydroxyphenyl)-fluoren-4-carboxylic acid (yield ≥90%). Crude monomer (400 g) was placed into a 20 L beaker with 8 L of water and heated to 60 °C. Sodium bicarbonate (400 g) was added in portions until effervescence ceased. The total volume was made up to 14 L by addition of water and then the mixture was heated to boiling. After overnight cooling and crystallization, the product in the sodium carboxylate form was filtered using a Buchner funnel. The crystalline monomer was redissolved in 14 L of hot water, and decolorizing charcoal was added and stirred at ∼80 °C for 1 h. The mixture was filtered through Celite and the resulting clarified solution was neutralized by adding concentrated hydrochloric acid. Then the suspension was heated to boiling to coagulate the precipitate. After filtering, washing and drying, the purified product was obtained (Scheme 1). This product was further purified using the same purification procedure (adjusting for bicarbonate quantity), resulting in ∼60% yield from crude monomer. m.p. 304 °C (DSC).

Elemental analysis: C: 79.17%; H: 4.60%; found: C: 78.90%; H: 4.89%.

^{1}H NMR (DMSO-d$_6$) (in ppm): 13.36 (s, 1H), 9.33 (s, 2H), 8.23 (d, 7.6 Hz, 1H), 7.66 (d, 7.6Hz, 1H), 7.53 (d, 7.6 Hz, 1H), 7.35 (m, 4H), 6.89 (d, 8.8Hz, 4H), 6.61 (d, 8.8Hz, 4H).

^{13}C NMR (DMSO-d$_6$) (in ppm): 169.21, 155.92, 153.29, 152.53, 137.55, 136.90, 135.37, 128.58, 128.01, 127.98, 127.91, 126.93, 126.87, 125.62, 124.04, 114.81, 62.76.

Synthesis of polymers containing carboxylic acid (–COOH) group.

A 250 mL three-necked flask equipped with an argon inlet, a mechanical stirrer, and a Dean–Stark trap with a condenser was charged with 9,9-bis(4-hydroxyphenyl)-fluoren-4-carboxylic acid (19.73 g, 0.05 mol), 1,4-bis(4-fluorobenzoyl)benzene (10.91 g, 0.05 mol), anhydrous potassium carbonate (13.82 g, 0.10 mol, 1.5 mol equivalent), DMSO (120 ml) and toluene (30 mL). The mixture was heated to 160 °C under an argon atmosphere, and stirred at reflux temperature for 3 h. After distilling off toluene, the reaction mixture was heated at 180 °C for 6 h to effect polymerization. The viscous solution was poured into ethanol to obtain a fiber-like polymer. The resulting polymer was washed with water, and then ethanol several times to remove residual salts and solvents. The polymer in acid form was obtained after treating the polymer fine powder in 2 N H$_2$SO$_4$ for several days. After washing with water to remove the excess acid, the polymer (PFEEKK–COOH) was dried at 100 °C in a vacuum oven for 24 h.

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The same synthetic procedure was applied to synthesize PFEEK–COOH, as shown in Scheme 2.

Sulfonation reaction for the polymers. Dry powdered polymer (3.0 g, PFEEK–COOH or PFEEKK–COOH) and 95–98% concentrated sulfuric acid (100 mL) were placed in a 250 mL single-necked flask with a cover. The mixture was stirred at room temperature for various reaction times. The resulting homogenous solution was poured into a mixture of ice and water. The precipitate was thoroughly washed with deionized water until neutralized, filtered and dried for 24 h in a vacuum oven at 100 °C. The resulting yellowish sulfonated polymers (SPFEEK–COOH or SPFEEKK–COOH) had different DS values depending on the sulfonation time (Scheme 3).

Preparation of crosslinkable blends and crosslinked films. SPFEEKK–COOH (DS~2.0, 1.00 g) and PVA (0.10 g) were dissolved in 20 mL of DMAc at 50 °C, and then stirred for 6 h at room temperature. After filtering, the clear homogeneous solution was cast on a glass plate and allowed to evaporate slowly in a 50 °C inert environment. The resulting film was crosslinked by treating it in a vacuum oven at 100 °C for 1 h and then at 120 °C for 2 h. The crosslinked film, referred to as SPFEEKK-2.0/PVA-1, was immersed in hot water so it could be readily peeled off the glass plate. A crosslinked film prepared from SPFEEKK–COOH (DS~2.0, 1.00 g) with PVA (0.05 g), referred to as SPFEEKK-2.0/PVA-2 and one prepared from SPFEEKK–COOH (DS~1.6, 1.00 g) with PVA (0.05 g), referred to as SPFEEKK-1.6/PVA, were also prepared using the same procedure (Scheme 4).

Conclusions

New carboxylated poly(aryl ether ketone)s with high T_g values have been prepared from 9,9-bis(4-hydroxyphenyl)-fluoren-4-carboxylic acid and difluorinated monomers. They could be cast into flexible and transparent membranes. The carboxylated polymers were readily post-sulfonated with 95–98% H_2SO_4 at room temperature, and the sulfonation reaction of carboxylated polymers occurred on three specific sites per repeat unit, reaching a DS of ~3. A detailed structural analysis using 1D and 2D NMR techniques revealed the specific sulfonation sites and enabled the kinetics of the reaction to be determined. In contrast with previous post-sulfonation structural studies of other fluorenyl-containing PEMs, detailed NMR measurements in the present study indicate that sulfonation occurs on the *ortho* position of the main-chain ether linkages exclusively on the fluorenyl monomer residue, as well as on one position on the fluorenyl in this polymer. An initial investigation of crosslinking cast carboxylated/sulfonated membranes with PVA through the carboxylic acid was conducted. The crosslinked membranes showed an obvious improvement in the dimensional stability, and water uptake and swelling ratio of crosslinked membranes (DS ~2) were decreased by several times compared with the corresponding carboxylated/sulfonated polymer. The cross-linked SPFEEKK–COOH-1.6/PVA film exhibited both acceptable dimensional stability and high proton conductivity

(~ 0.15 S cm^{-1}) at 65 °C. The crosslinked PEMs are expected to be applicable in the direct methanol fuel cell.

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