



Novel sulfonated poly(arylene ether ketone) copolymers bearing carboxylic or benzimidazole pendant groups for proton exchange membranes

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ABSTRACT

A novel strategy in which the benzimidazole group and sulfonic group are simultaneously attached to an aromatic polymer has been reported in this paper. For this purpose, sulfonated poly(arylene ether ketone) copolymers containing carboxylic acid groups (SPAEK-*x*-COOH, *x* refers to the molar percentage of sulfonated repeating units) are prepared by the aromatic nucleophilic polycondensation of sodium 5,5'-carbonyl-bis(2-fluorobenzene-sulfonate) (SDFBP), 4,4'-difluorobenzophenone (DFBP) and phenolphthalin (PPL). Then the carboxylic acid groups attached to the SPAEK-*x*-COOH are transformed to benzimidazole units through condensation reactions (referred to as SPAEK-*x*-BI). Fourier transform infrared spectroscopy and ¹H NMR measurements are used to characterize and confirm the structures of these copolymers. SPAEK-*x*-COOH membranes exhibit superior mechanical properties with maximum elongations at break up to 133%, meanwhile SPAEK-*x*-BI also shows good thermal and mechanical stability. The proton conductivity, swelling ratio and methanol permeability of the polymers with benzimidazole are lower than those with carboxylic groups, which indicated that there is an acid–base complex between benzimidazole and sulfonic acid groups. A balance of proton conductivity, methanol permeability, thermal and mechanical stabilities can be designed by incorporation of functional groups to meet the requirements for the applications in direct methanol fuel cells.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are receiving tremendous attention as transport, stationary, and portable future power sources because of their low emissions and high energy conversion efficiency [1–2]. The proton exchange membrane (PEM), which serves as a separator of fuels between the anode and the cathode as well as allowing protons to pass through the membranes to complete the entire reaction, is the key component of the PEMFCs [3]. Perfluorinated copolymers, such as Dupont Nafion[®], are the current state-of-the-art PEM materials with features of high conductivity and excellent chemical stability at moderate temperatures (<90 °C) [4]. However, the conductive and mechanical properties are deteriorated above their glass transition temperature (*T_g*) ca. 110 °C. High methanol crossover in direct methanol fuel cells (DMFCs), high cost, and environmental inadaptability limited their large-scale commercial applications [5]. Therefore, it is significant to develop new PEM materials as alternatives with lower cost and considerable performances. Among the potential alternatives, acid-doped

polybenzimidazoles (PBI) [6–7] and sulfonated poly(arylene ether ketone)s (SPAEEKs) [8–9] have been extensively studied.

Membranes based on PBI complexes with inorganic acids have been found to possess high proton conductivity and exhibit good performance in PEMFCs at high temperatures. However, leaching out of small inorganic acid molecules such as phosphoric acid at high temperature is a big problem for long-term stability of such systems. Many approaches were proposed to solve this problem, such as direct sulfonation of commercial PBI membrane [10], introducing alkylsulfonate or arylsulfonate side chain onto reactive N–H sites [11–13] and so on. Meanwhile, SPAEEKs are also considered as promising alternative materials because of their advantages of low cost, easy preparation, good mechanical strength and high chemical and thermal stabilities [14–15]. Like other sulfonated aromatic copolymers, SPAEEKs require a high sulfonation level to achieve sufficient proton conductivity. Unfortunately, too high loading of acidic groups may lead to undesirable large swelling and a dramatic loss of the mechanical strength. One option is to blend highly sulfonated PAEEKs with base polymer such as PBI [16–18]. The blend membrane exhibited high thermal and mechanical properties, low methanol permeability, and good resistance to swelling. These improved properties were believed to be caused by the acid–base interaction between sulfonic acid groups and amine groups. Fu et al. blended the aromatic polymer bearing benzimidazole groups with

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sulfonated poly(ether ether ketone) to obtain high proton conductivity through acid–base interactions [19]. The study demonstrated that polymers bearing benzimidazole pendant groups may become a viable strategy to develop new membranes that could operate at higher temperatures. In the similar manner, the synthesis of copolymers bearing both sulfonic acid groups and benzimidazole pendant groups could be a promising strategy to join a combination of properties in a single material.

In this paper, we report the synthesis and characterization of a series of novel SPAEKs containing simultaneously sulfonic groups and benzimidazole groups. The introduction of basic benzimidazole group was expected to induce a strong inter-chain interaction between the basic amino groups and the sulfonic acid groups. For this purpose, a series of SPAEKs containing simultaneously sulfonic groups and carboxylic groups (SPAEC-*x*-COOH) were designed and copolymerized from sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) (SDFBP), 4,4'-difluorobenzophenone (DFBP) and phenolphthalin (PPL), which has a carboxyl group located between its phenolic groups. The carboxylic group in the SPAEC-*x*-COOH side chain is an active pendant group that could react with 1,2-diaminobenzene to be easily transformed into benzimidazole units. Additionally, these copolymers with carboxylic groups were also characterized. They are of potential interest as they present convenient sites for cross-linking, which is often otherwise achieved through the sulfonic acid group. The proton conductivity, methanol permeability, thermal and mechanical stabilities were then investigated in detail to examine the influence of pendant functional groups, e.g. carboxylic and benzimidazole groups.

2. Experimental

2.1. Materials

Monomer DFBP was obtained from Yanbian Longjing Chemical Company. SDFBP was synthesized according to a procedure described in our previous work [20]. All other reactants and solvents were obtained from Tianjin Tiantai Chemical Company and used as received without further purification.

2.2. Preparation of the sulfonated poly(arylene ether ketone) copolymers with carboxylic acid groups (SPAEC-*x*-COOH)

2.2.1. Monomer synthesis

Phenolphthalein (0.156 mol, 50 g), sodium hydroxide (1.875 mol, 75 g), and zinc (0.58 mol, 32.5 g) were added to 1500 ml water, and the intensely red reaction mixture was heated at 60 °C under continuously stirring until a grayish-white reaction mixture was resulted. Then the product was poured into aqueous hydrochloric acid and filtered to separate the white solid. Then it was dried in a vacuum oven at 120 °C for 48 h and white powder phenolphthalin was obtained in almost quantitative yield. The *mp* is 243.5–244.5 °C; ¹H nuclear magnetic resonance (¹H NMR) (500 MHz, DMSO-*d*₆, ppm): 6.381 (s,1H,CH), 6.660–6.778 (*m*,8H,2C₆H₄OH), 6.981–7.721 (*t*,4H, C₆H₄COOH), 9.223 (s, 2H, OH), 12.792(s,1H,COOH); elemental analysis for C₂₀H₁₆O₄—Calcd.: C, 74.92%; H, 4.99%; O, 20.09%. Found: C, 73.41%; H, 4.66%; O, 21.93%.

2.2.2. Polymer synthesis

A typical synthetic procedure to prepare SPAEC-40-COOH copolymers is as follows. PPL (50 mmol), SDFBP (20 mmol), DFBP (30 mmol), and anhydrous potassium carbonate (75 mmol) were placed in a three-neck round-bottomed flask equipped with a mechanical stirrer, a Dean-Stark trap with a reflux condenser, and a nitrogen inlet. DMSO and toluene were then introduced as the

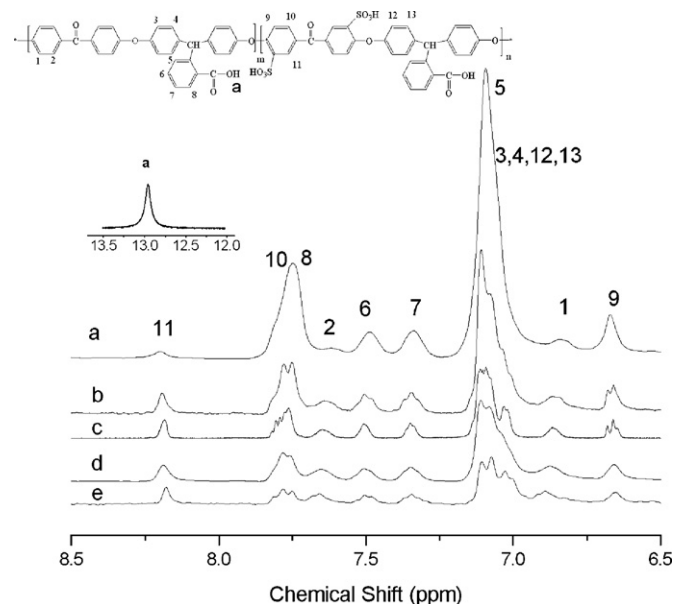


Fig. 1. ¹H NMR spectra of SPAEC-*x*-COOH copolymers in DMSO-*d*₆. (a) SPAEC-20-COOH; (b) SPAEC-40-COOH; (c) SPAEC-50-COOH; (d) SPAEC-60-COOH; (e): SPAEC-70-COOH.

solvent system to offer a solid concentration of 25 wt.%. The reaction mixture was then heated until the toluene began to reflux. The temperature was maintained at 140 °C for 3 h. The temperature was gradually increased to 180 °C to carry out water and toluene from the reaction mixture for 6 h. The viscous reaction mixture was cooled to room temperature and poured into water. The product was isolated by coagulation in HCl solution. The precipitated copolymer was then washed several times with ethanol, and dried in a vacuum oven for 24 h. Yield: 94%. FT-IR: 1709 cm⁻¹ (ν_{sym} of free C=O), 1649 cm⁻¹ (ν_{sym} of bonded C=O) and 1028 and 1083 cm⁻¹ (asymmetric and symmetric stretching vibrations of sulfonate groups). ¹H NMR is shown in Fig. 1.

2.3. Preparation of sulfonated poly(arylene ether ketone) copolymers bearing benzimidazole pendant groups (SPAEC-*x*-BI)

In the following, the synthetic procedure for sulfonated poly(arylene ether ketone) copolymers bearing benzimidazole pendant groups at the example of SPAEC-40-BI is presented: 0.5565 g of the dried SPAEC-40-COOH polymer and 0.1296 g 1,2-diaminobenzene were dissolved in 20 ml of dimethylformamide in a three-neck flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet, followed by an addition of 1.0 g of lithium chloride and 2.86 ml of triphenylphosphite (TPP) into the flask. The solution was stirred at 100 °C for 3 h and then at 150 °C for 10 h under nitrogen atmosphere and poured into 1000 ml of methanol to precipitate the polymer. The precipitate was collected by filtration and dried in a vacuum oven at 100 °C overnight. Yield: 96%. FT-IR: 3417 cm⁻¹ (ν_{sym} of N–H), 1649 cm⁻¹ (ν_{sym} of bonded C=O in the main-chain), 1394 cm⁻¹ (ν_{sym} of C–N), 1028 and 1083 cm⁻¹ (asymmetric and symmetric stretching vibrations of sulfonic acid groups).

2.4. Characterization

Inherent viscosities of the copolymers were measured in DMF at 25 °C with a polymer concentration of 5.0 g l⁻¹. FT-IR spectra of powder samples were recorded between 4000 and 400 cm⁻¹ on a Bruker Vector 22 FT-IR spectrometer. ¹H NMR spectra (in DMSO-*d*₆) were recorded on a 500 MHz Bruker Avance 510 spectrometer. The

chemical shift of tetramethylsilane was used as the internal reference standard. The thermal properties of the SPAEK-x-COOH and SPAEK-x-BI copolymers were performed on a Pyris-1 (Perkin Elmer) thermogravimetric analyzer (TGA). About 5–10 mg samples were kept at 150 °C in the furnace for 20 min under N₂ flow to remove any residual water or solvent remaining, then cooled to 80 °C and then reheated to 700 °C at a heating rate of 10 °C min⁻¹.

2.5. Preparation of membranes

The SPAEK-x-COOH and SPAEK-x-BI membranes were cast onto glass plates from their DMF solution (10 wt.%). Then placed in a vacuum oven at 80 °C for 6 h and at 120 °C for another 12 h to remove the residual solvent completely. Dry membranes were peeled off from the substrate and immersed into 1.0 M HCl solutions overnight. Finally, the membranes were stored in deionized water for 12 h to remove any excess HCl and dried under vacuum for 24 h.

2.6. Mechanical properties of membranes

The mechanical properties of SPAEK-x-COOH and SPAEK-x-BI membranes were investigated using a SHIMADZU AG-I 1KN instrument at room temperature at a constant crosshead speed of 2 mm min⁻¹. The uniaxial tensile measurements were conducted on membrane samples of 4 mm width and 15 mm length. Prior to the measurements, the membrane samples were stabilized at ambient temperature and humidity, which was around 35% relative humidity.

2.7. Water uptake, swelling ratio, ion-exchange capacity (IEC), methanol permeability and proton conductivity of membranes

The water uptake (WU) and water swelling of the membrane were determined by measuring the change in the weight between the dry and swollen membranes. A detailed procedure was reported previously [21].

The IEC values of SPAEK-x-COOH and SPAEK-x-BI membranes were determined by classical titration. The membrane sample was immersed in 1 M NaCl solution for at least 24 h to exchange the H⁺ ions from Na⁺. The exchanged protons within the solutions were titrated with 0.05N NaOH solutions using phenolphthalein as an indicator. Each sample must be measured three times until it had reached to a constant value. The IEC values were recorded in unit of millimole NaOH per gram of the membrane samples (mequiv. g⁻¹) as an average value for each sample.

Methanol diffusion coefficient was measured using a home-made glass diffusion cell, which consisted of two compartments and divided by a membrane sample. 100 ml pure methanol was placed on one side of the diffusion cell (cell A) and 100 ml water was placed on the other side (cell B). Both compartments were continuously stirred using submersible magnetic stirrers. The concentration of the methanol in cell B was measured by using SHIMADZU GC-8A chromatograph. Peaks areas were converted to the methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated by following formula (1):

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (1)$$

where A , L and V_B are the effective area, the thickness of membrane and the volume of receptor reservoir, respectively. C_A and C_B are the methanol concentration in the donor and receptor reservoirs, respectively. DK and t_0 are the methanol diffusion coefficient and the time lag, respectively.

The proton conductivity was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation

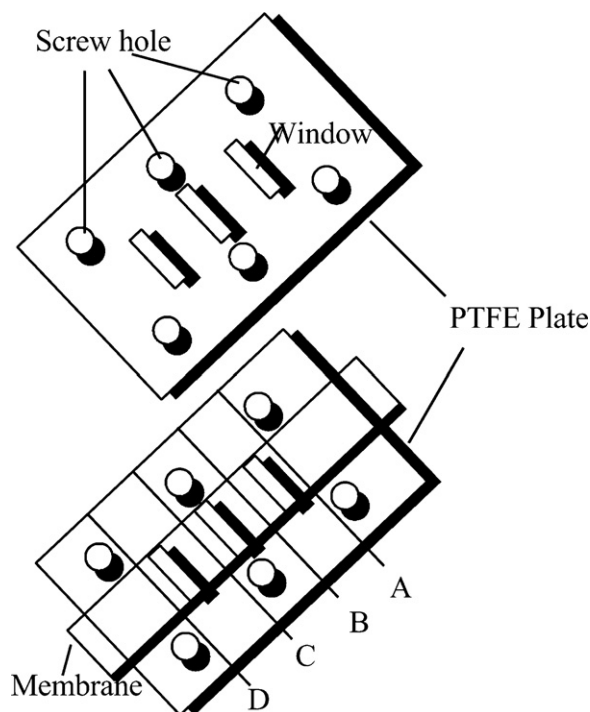


Fig. 2. Schematic diagram of cell for testing membrane proton conductivity.

and 0.0 V dc rest voltage using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). The membranes were cut into 1 cm wide, 4 cm long and were fixed in a measuring cell made of two outer gold wires (A, D) to feed current to the sample and two inner gold wires (B, C) to measure the voltage drops. The cell is shown in Fig. 2. All the membranes were mounted between two polytetrafluoroethylene (PTFE) plates. The cell was immersed into water during measurement. All conductivity measurements reported in this paper were conducted in plane. Before measurement, the films were full hydrated in water for 24 h. The proton conductivity was calculated by following Eq. (2):

$$\sigma = \frac{L}{RA} \quad (2)$$

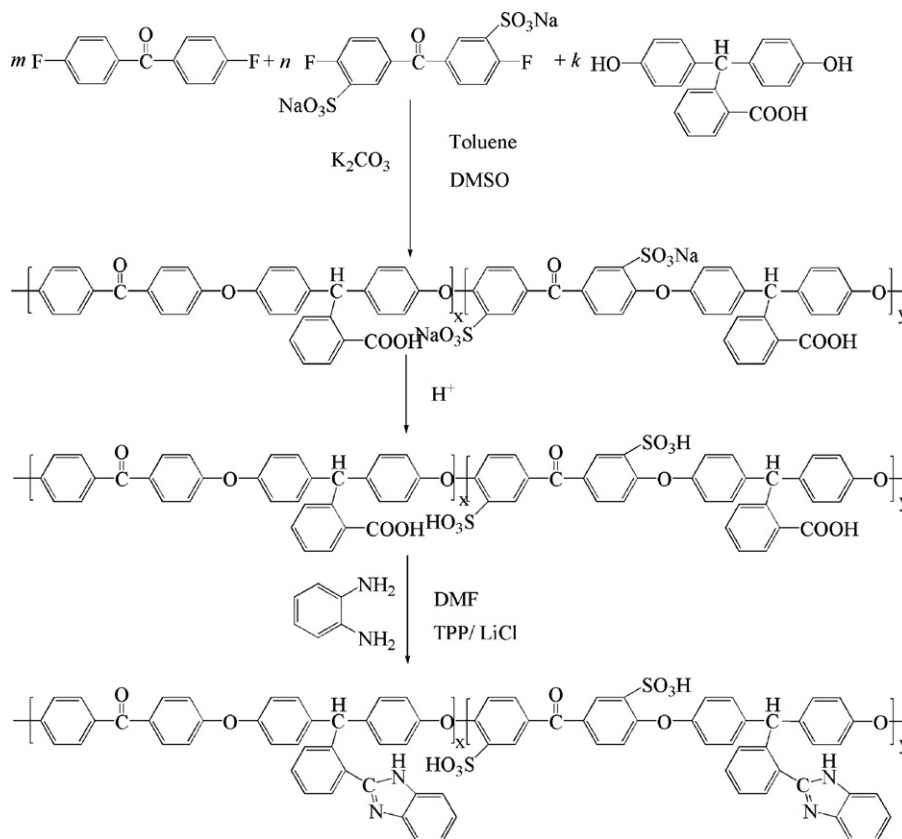
where σ is proton conductivity in S cm⁻¹, L is the distance between the two electrodes, R is resistance of the membrane and A is the cross-sectional area of membrane.

3. Results and discussion

3.1. Synthesis of SPAEK-x-COOH and SPAEK-x-BI copolymers

The phenolphthalin monomer was prepared by the reduction of phenolphthalin with zinc powder in aqueous NaOH solution, followed by neutralization with dilute hydrochloric acid, according to a procedure proposed by Wang et al. [22].

As shown in Scheme 1, novel sulfonated poly(arylene ether ketone)s containing carboxylic groups were synthesized by a nucleophilic aromatic substitution (S_NAr) polycondensation of activated aromatic halides with phenolphthalin under standard conditions. The degree of sulfonation (D_s), which is the number of sulfonated groups per repeating unit, was controlled by adjusting the ratio of DFBP (monomer m) to SDFBP (monomer n). The resulting copolymer was denoted as SPAEK-x-COOH, where x represents the mol% of sulfonated repeating units. The polymerization results and analytical data are displayed in Table 1. The intrinsic viscosity of the



Scheme 1. Synthesis of SPAEK-*x*-COOH and SPAEK-*x*-BI copolymers.

copolymers was above 0.7 dL g^{-1} in DMF at 25°C , indicating that high molecular weights were obtained.

^1H NMR spectroscopy provided unambiguous structure elucidation and was also used to quantify the experimental D_s [23,24]. The aromatic regions of ^1H NMR spectra of SPAEK-*x*-COOH copolymers dissolved in $\text{DMSO-}d_6$ are shown in Fig. 1. A sharp peak about 8.2 ppm was separated from the other aromatic groups, and was assigned to the hydrogen atoms adjacent to the sulfonic groups (H_{11}). Therefore, the D_s can be measured by comparing the intensity of this signal H_{11} with the intensities of the remaining aromatic signals. The calculated values of D_s are in good agreement with those expected from the copolymer compositions and shown in Table 1.

The SPAEK-*x*-BI were also prepared by a condensation reaction between 1,2-diaminobenzene and SPAEK-*x*-COOH copolymers using TPP as a dehydration agent and lithium chloride for enhancing the dissolution of the product in DMF. In order to avoid the formation of the amide structure by cross-linking, the reaction was conducted by a two-stage process: firstly at a lower temperature of 100°C for 3 h to create a single C–N bond between the

carboxylic acid group of SPAEK-*x*-COOH and one amino group of 1,2-diaminobenzene, and then, at 150°C for 10 h to form the C=N bond between the carboxylic carbon atom and the other amino group of 1,2-diaminobenzene.

Spectroscopic characterization methods (^1H NMR and FT-IR) confirmed the structure of the polymers. The typical FT-IR spectra of SPAEK-60-COOH and SPAEK-60-BI copolymers are shown in Fig. 3. It should be noted that the C=N or C–N stretching bands was overlapped by other function groups in the main-chain of SPAEK-

Table 1
The analysis data of SPAEK-*x*-COOH and SPAEK-*x*-BI membranes.

Polymer	<i>m</i> (mmol)	<i>k</i> (mmol)	<i>m</i> / <i>k</i>	D_s^a	D_s^b	η_{sp}/c^c
SPAEEK-20-COOH	80	20	8:2	0.4	0.16	0.58
SPAEEK-40-COOH	60	40	6:4	0.8	0.61	1.66
SPAEEK-50-COOH	50	50	5:5	1.0	0.90	2.62
SPAEEK-60-COOH	40	60	4:6	1.2	0.95	1.94
SPAEEK-70-COOH	30	70	3:7	1.4	1.36	0.81

^a Degree of sulfonation obtained from monomer ratio.

^b Degree of sulfonation obtained from ^1H NMR data.

^c η_{sp}/c was measured at a concentration of 0.5 g dL^{-1} in DMF at 25°C .

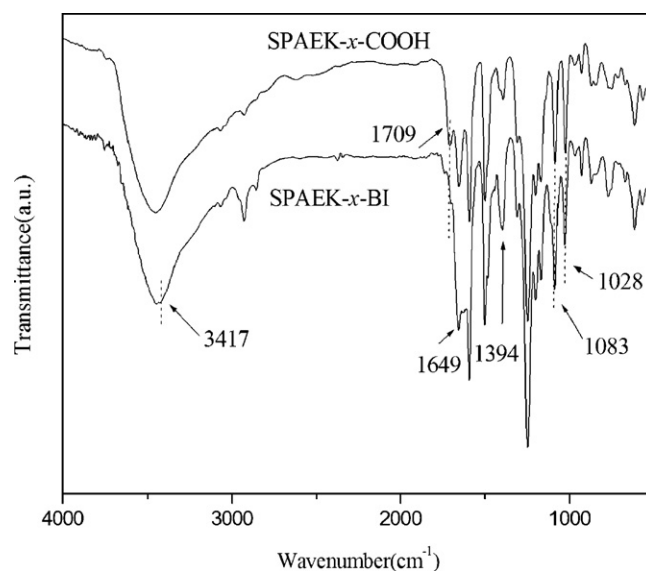


Fig. 3. FT-IR spectra of SPAEK-*x*-COOH (top) and SPAEK-*x*-BI (bottom), *x* refers to 60.

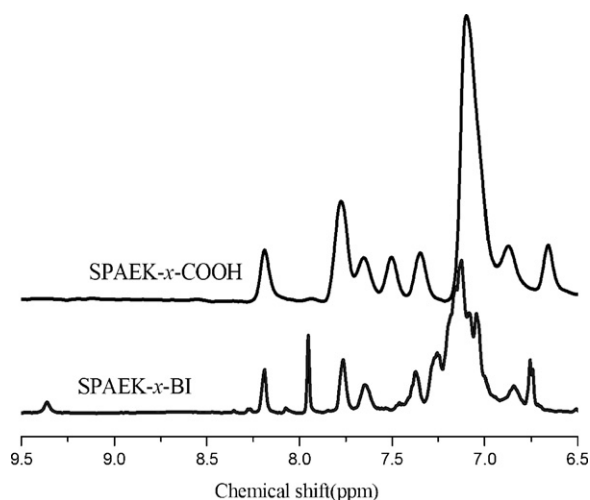


Fig. 4. ^1H NMR spectra of SPAEK- x -COOH (top) and SPAEK- x -BI (bottom) (in DMSO-d_6), x refers to 60.

60-BI and not distinguished from SPAEK-COOH. However, the strong absorption at 1709 cm^{-1} due to the $\text{C}=\text{O}$ asymmetric stretching of the carboxylic acid groups in SPAEK-60-COOH almost disappeared in SPAEK-60-BI, indicating the conversion of almost all of the carboxylic acid groups into benzimidazole groups. Absorption bands around 1028 and 1083 cm^{-1} can be assigned to symmetric and asymmetric stretching vibrations of sulfonic acid groups.

In the ^1H NMR spectra, the successful incorporation of benzimidazole pendant groups into SPAEK copolymers was further confirmed by the additional resonances at 9.36 ppm corresponding to the protons on the nitrogen atoms, and the peaks at 7.95 ppm due to the protons on the aromatic rings of benzimidazole pendant groups (Fig. 4).

3.2. Thermal stability

The thermal properties of the SPAEK- x -COOH and SPAEK- x -BI copolymers were investigated by TGA under N_2 atmosphere at a

heat rate of $10^\circ\text{C min}^{-1}$. As shown in Fig. 5, SPAEK- x -COOH copolymers exhibited a typical two-step degradation pattern. The first weight loss region (occurring between temperatures of 250 and 400°C) was believed to be associated with the elimination of sulfonic acid groups and the second weight loss step starting at about 450°C corresponded to the main polymer chain of decomposition. Meanwhile, the desulfonation temperatures of SPAEK- x -BI copolymers were higher than those of their corresponding SPAEK- x -COOH copolymers, indicating the incorporation of benzimidazole groups can improve the thermal stability of a polymer. It is well-known that the sulfonic groups can form polysalt with basic benzimidazole groups and this leads to the stabilization of the aromatic sulfonic acid groups, which might be the reason for the higher desulfonation temperatures [25,26].

3.3. Mechanical properties

It is essential for PEMs to possess adequate mechanical strength to withstand fabrication of the membrane electrode assembly [27]. The mechanical properties of the SPAEK- x -COOH and SPAEK- x -BI membranes are summarized in Table 2. The stress-strain data are shown in Fig. 6. The SPAEK- x -COOH membranes exhibited excellent mechanical properties with tensile stress at maximum load of 47 – 52 MPa , Young's moduli of 1.1 – 1.5 GPa , and elongations at break of 12 – 13% . Compared with those of other series of sulfonated poly(arylene ether ketone) membranes [27–30], the introduction of the carboxylic groups, that is, the inter-chain hydrogen bond or ionic bond, could significantly enhance the mechanical properties of the membranes. For instance, SPAEK-50-COOH was found to have a large elongation at break of 133% and a high modulus of 1268 MPa . The high modulus and elongation properties of SPAEK- x -COOH afforded flexible, creaseable films. The Young's modulus and tensile stress at maximum load of SPAEK- x -BI membranes were found to be higher as compared to the corresponding SPAEK- x -COOH membranes. However, it behaved more like an engineering thermoplastic with an elongation to break of 6 – 9% . This could be explained by the fact that inter- or intramolecular ionic interaction between acidic and basic functional groups lead membranes to be of higher cross-linking density [22,25].

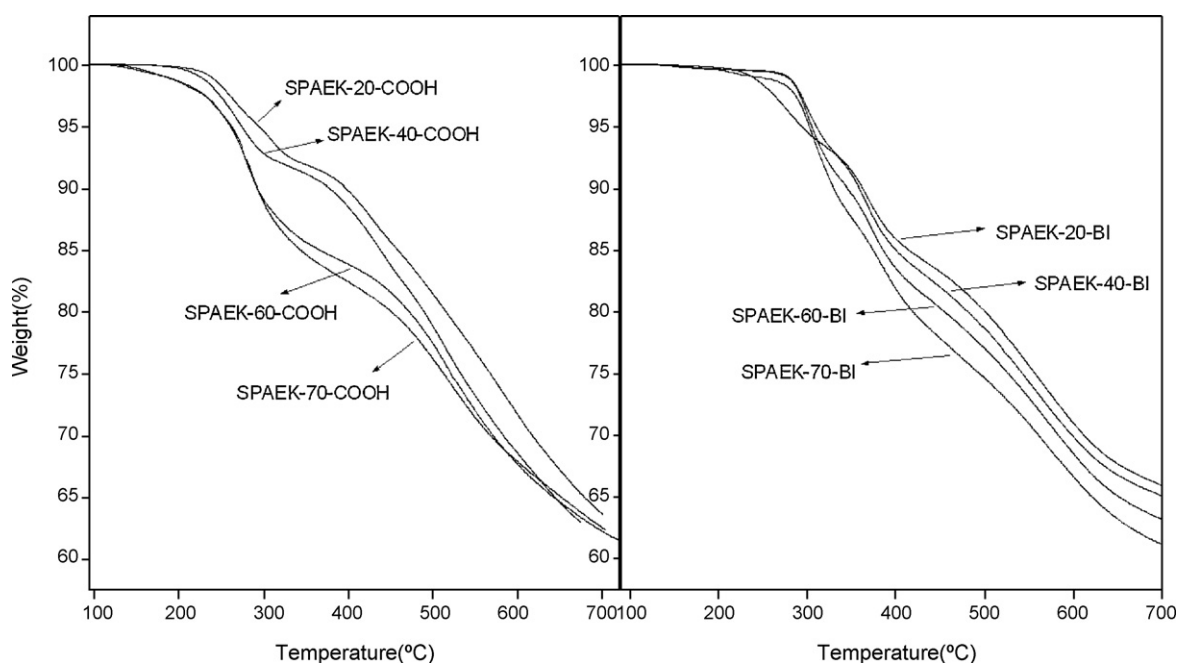


Fig. 5. TGA thermograms of SPAEK- x -COOH and SPAEK- x -BI copolymers in N_2 .

Table 2
Mechanical properties of SPAEK-x-COOH and SPAEK-x-BI membranes.

Membrane	Maximum stress (MPa)	Elongation at break (%)	Young's modulus (MPa)	Reference
SPAEK-20-COOH	52 ± 3	12 ± 8	1498 ± 72	This work
SPAEK-40-COOH	50 ± 5	90 ± 18	1204 ± 116	This work
SPAEK-50-COOH	50 ± 2	133 ± 2	1268 ± 103	This work
SPAEK-60-COOH	50 ± 4	72 ± 16	1263 ± 84	This work
SPAEK-70-COOH	47 ± 1	25 ± 1	1110 ± 5	This work
SPAEK-20-BI	62 ± 12	6 ± 2	1601 ± 181	This work
SPAEK-40-BI	66 ± 3	8 ± 2	1550 ± 126	This work
SPAEK-60-BI	56 ± 6	9 ± 4	1400 ± 102	This work
SPAEK-70-BI	54 ± 7	7 ± 2	1112 ± 103	This work
TMBP series	49–68	18–33	1010–1640	[27]
BPA series	45–57	18–64	1030–1260	[28]
Diallyl series	43–58	7–10	755–876	[29]
tert-BP series	58–82	4–12	950–1180	[30]

3.4. Ion-exchange capacities, water uptake, and water swelling

The IEC values of the copolymers were determined by titrating the acid form membranes in aqueous NaCl solution with standard sodium hydroxide solution. The theoretical IEC values by ^1H NMR in $[(\text{mmol-SO}_3^-) \text{g}^{-1}]$ and measured IEC values by titrating in $[(\text{mmol-SO}_3^- + \text{mmol-COO}^-) \text{g}^{-1}]$ are shown in Table 3. Except for SPAEK-70-COOH, the experimental IEC values of SPAEK-x-COOH membranes determined by the titration method were higher than the theoretical values because of the existence of -COOH groups. Once tethering the basic benzimidazole groups, the measured IEC values largely decreased, which implied the diminishment of COOH groups and the formation of an acid–base complex between benzimidazole and sulfonic acid groups.

The water uptake and dimensional swelling ratio of PEMs are well-known to have a profound effect on membrane conductivity dimensional stability, and mechanical strength. The water within the membrane provides a carrier for the proton and maintains high proton conductivity. However, excessive water uptake can result in membrane fragility and dimensional change, which could lead to weakness or a dimensional mismatch when incorporated into a membrane electrode assembly (MEA) [9]. Water uptake and swelling ratio values of SPAEK-x-COOH and SPAEK-x-BI membranes were evaluated and are listed in Table 3. As depicted in Fig. 7, these values increased with IEC increasing. For both two series of SPAEK membranes, the water uptake increased linearly up to 60 wt.% sulfonated monomer content, but then a sudden increase was observed above 70 wt.% sulfonated monomer content. Such an

abrupt increase in the water uptake and swelling ratios indicated the achievement of the percolation threshold above which ionic channels could be effectively connected within the membrane for facile proton conduction.

It is interesting to find SPAEK-20-BI shows higher water uptake (12.5%) and swelling ratio (6.0%) than those of SPAEK-20-COOH (8.5% and 1.7%, respectively) when the sulfonic acid content is relatively low. The large benzimidazole pendant groups force chains further apart in the copolymers and generate unoccupied volume capable of containing more water molecules. Strong water absorbency makes the water uptake values of SPAEK-x-BI higher than those of SPAEK-x-COOH at same sulfonated monomer content [31]. Due to the less sulfonic acid contents, the negative effect on the water behavior of the acid–base complex between benzimidazole and sulfonic acid groups can be ignored. On the other hand, SPAEK-x-BI membranes bearing benzimidazole pendant groups have higher water uptake but lower swelling ratio values than SPAEK-x-COOH membranes at the same structural composition ($x \geq 40$). The larger water uptake is believed to be associated with the introduction of the large benzimidazole pendant groups. Moreover, the acid–base complex reduces the amount of free sulfonic acid groups available to form hydrogen bond with water molecules [25,26]. It is apparent that the water in SPAEK-x-BI is less tightly bounded within the polymer microstructure than SPAEK-x-COOH, which constrains the hydrophilic domains along the in-plane direction and thus reduces water swelling.

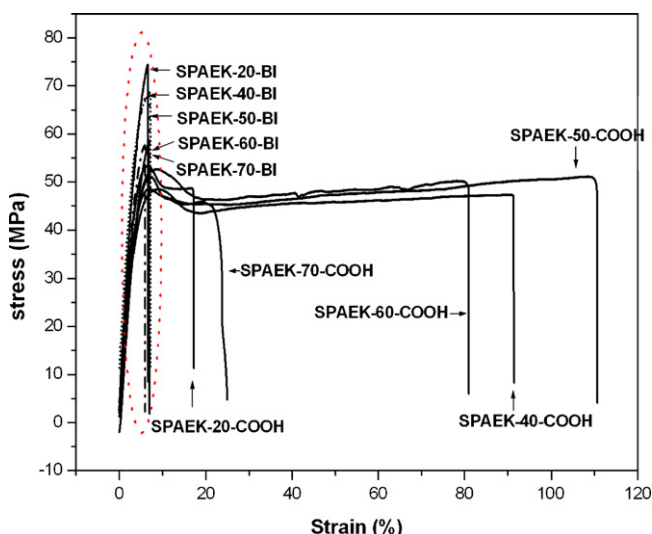


Fig. 6. Stress–strain of SPAEK-x-COOH and SPAEK-x-BI membranes.

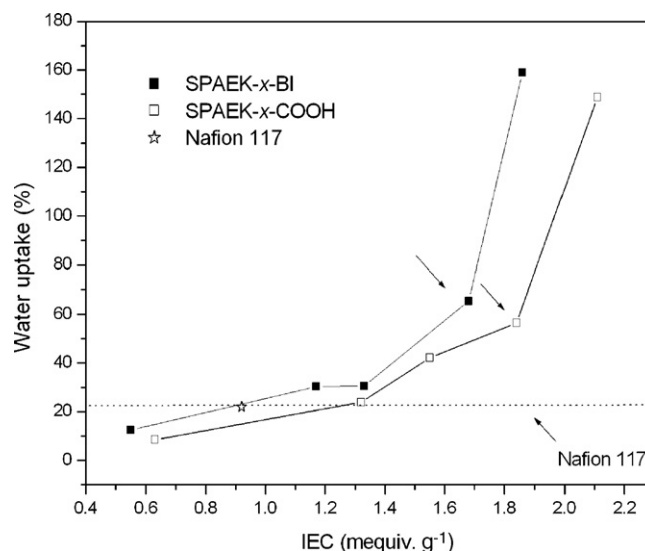


Fig. 7. Water uptake of SPAEK-x-COOH and SPAEK-x-BI membranes.

Table 3

IEC, water uptake, water swelling, proton conductivity and methanol diffusion of the SPAEK-x-COOH and SPAEK-x-BI copolymers.

Membrane	IEC (mequiv. g ⁻¹)		Water uptake (%)	Swelling ratio (%)	Proton conductivity (S cm ⁻¹)		Methanol diffusion (×10 ⁻⁷ cm ² s ⁻¹)
	IEC ^a	IEC ^b			25 °C	80 °C	
SPAEEK-20-COOH	0.31	0.63 ± 0.1	8.5 ± 0.5	1.7 ± 0.1	8.08 × 10 ⁻⁴	0.0022	0.293
SPAEEK-20-BI		0.55 ± 0.1	12.5 ± 0.8	6.0 ± 0.1	8.33 × 10 ⁻⁴	0.0045	0.217
SPAEEK-40-COOH	1.12	1.32 ± 0.2	23.9 ± 1.2	8.4 ± 0.1	0.019	0.086	3.63
SPAEEK-40-BI		1.17 ± 0.2	30.3 ± 0.8	8.2 ± 0.1	0.011	0.051	2.35
SPAEEK-50-COOH	1.58	1.55 ± 0.1	42.1 ± 0.6	13.5 ± 0.1	0.036	0.16	5.75
SPAEEK-50-BI		1.33 ± 0.4	30.5 ± 0.7	11.2 ± 0.1	0.017	0.099	5.68
SPAEEK-60-COOH	1.66	1.84 ± 0.1	56.5 ± 2.0	18.8 ± 0.4	0.069	0.27	8.15
SPAEEK-60-BI		1.68 ± 0.2	65.4 ± 4.0	16.9 ± 0.1	0.044	0.16	7.18
SPAEEK-70-COOH	2.24	2.11 ± 0.2	148.8 ± 4.8	34.3 ± 0.2	0.095	0.24 ^c	12.8
SPAEEK-70-BI		1.86 ± 0.2	159 ± 2.0	24.3 ± 0.1	0.046	0.14 ^c	11.5
Nafion® 117		0.92	22 ± 3	13 ± 2	0.076	0.146	23.8

^a IEC obtained from ¹H NMR.^b IEC obtained from the titration.^c Measured at 60 °C due to excessively swollen at 80 °C.

3.5. Proton conductivity and methanol permeability

Proton conductivities as a function of temperature are displayed in Figs. 8 and 9 for SPAEK-x-COOH's and SPAEK-x-BI's, respectively. With the exception of SPAEK-20-COOH and SPAEK-20-BI, all the other samples showed room temperature proton conductivities higher than 10⁻² S cm⁻¹, which is the lowest value for practical interest for use as PEMs in fuel cells. Since the proton conduction of an electrolyte is generally thermally stimulated, it is natural to expect a rise in proton conductivity with temperature. For example, the proton conductivity of SPAEK-50-COOH membrane (IEC = 1.55 mequiv. g⁻¹) increased from 0.036 to 0.16 S cm⁻¹ with temperature increasing from 25 to 80 °C. It also can be seen that proton conductivities of SPAEK-50-COOH, SPAEK-60-COOH and SPAEK-70-COOH at 80 °C surpassed that of Nafion® 117 (0.146 S cm⁻¹ at 80 °C) to a large content, which were also higher than those of other series of SPAEK membranes without functional groups at equivalent IEC values [27–30]. The introduction of carboxylic acid groups in copolymers led to a significant increase in proton conductivity with increasing temperature.

In general, SPAEK-x-BI membranes with higher degree of sulfonation ($D_s \geq 0.8$) exhibited lower proton conductivities than those

of corresponding SPAEK-x-COOH membranes. For example, the proton conductivity of SPAEK-60-BI membrane was 0.044 S cm⁻¹ at room temperature and increased to 0.16 S cm⁻¹ at 80 °C, while the corresponding SPAEK-60-COOH membrane showed higher proton conductivities of 0.069 S cm⁻¹ at 25 °C and 0.27 S cm⁻¹ at 80 °C. The similar observation has also been reported for sulfonated polynaphthalimides with benzimidazole pendant groups [32]. Proton conductivity depends on the presence of sulfonic acid groups and proton dissociation from these acid groups into the surrounding water in the hydrophilic regions of the polymer. The decrease of the proton conductivity for SPAEK-x-BI is mainly influenced by the loss of carboxylic acid groups and formation of an acid–base complex between benzimidazole and the sulfonic acid groups of the polymer, which might consume a certain amount of sulfonic acid groups [32–34]. Furthermore, the decrease of water swelling restricts the hydrophilic domains along the in-plane direction, which also reduces the proton conductivity measured in-plane. However, at the other end, for SPAEK-20-COOH and SPAEK-20-BI, there are less sulfonic acid contents. In spite of the relatively lower IEC, the proton conductivity of SPAEK-20-BI is higher than that of SPAEK-20-COOH. Such an observation correlates well with the water uptake and swelling behavior. The proton transport requires a significant amount of water to coordinate with proton as it moves

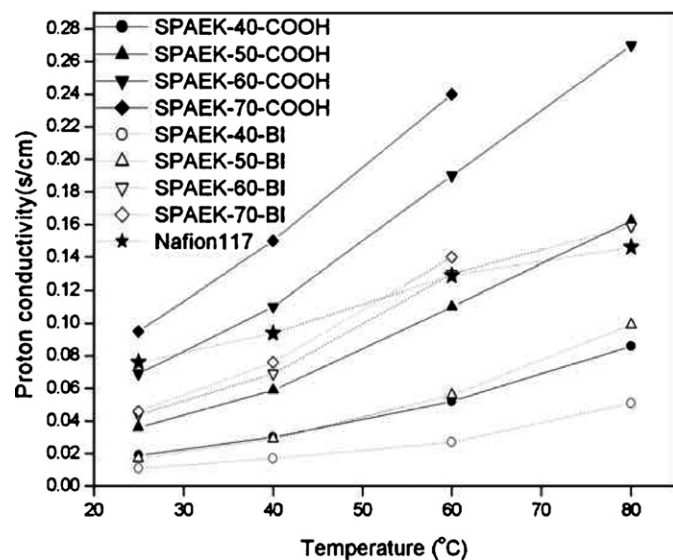


Fig. 8. Proton conductivity of SPAEK-x-COOH and SPAEK-x-BI membranes, x refers to 40, 50, 60, and 70.

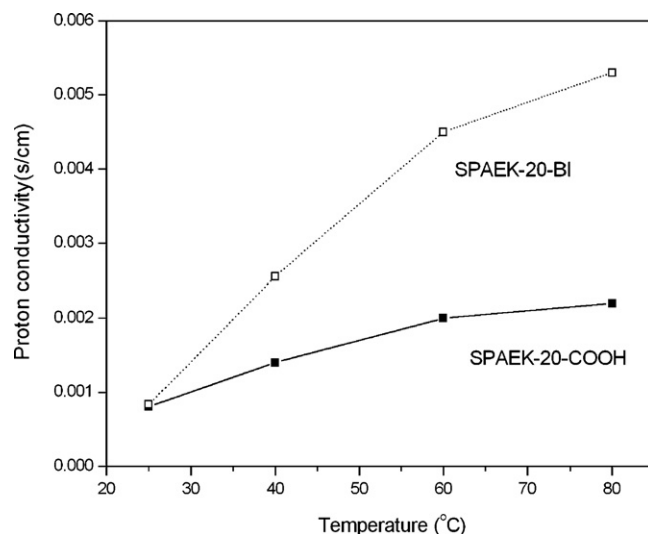


Fig. 9. Proton conductivity of SPAEK-20-COOH and SPAEK-20-BI membranes.

through the membrane. Especially for the low degree of sulfonation, the higher water uptake and swelling facilitates the proton conduction. This observation also demonstrates that the effect of carboxylic acid groups on the conductivity is minimal because of their low relative acidity caused by a low degree of dissociation.

Membranes for the practical usage in DMFC must both possess high proton conductivity and low methanol permeability [21]. The methanol permeability of the SPAEK-*x*-COOH and SPAEK-*x*-BI membranes at room temperature is shown in Table 3. They exhibited methanol permeability in the range of 2.17×10^{-8} to $1.28 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which are all much lower than that of Nafion® 117 ($2.38 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).

Comparing SPAEK membranes with carboxylic and benzimidazole groups having the same structural composition, the methanol permeability is lower for the polymers with benzimidazole. This trend in methanol behavior is the same as that observed for the proton conduction behavior. It has been reported that the proton conduction certainly occurs in the hydrophilic regions of the polymer and the methanol diffuses primarily through the hydrophilic water-rich domains as well [35,36]. The comparison between SPAEK-*x*-COOH and SPAEK-*x*-BI further confirms that there is an acid–base complex between benzimidazole and sulfonic acid groups, which blocks the water-filling domains that are formed by hydrophilic SO₃ clusters and the surrounding water and thus lowers the conductivity and methanol permeability.

Compared with the commonly used Nafion® membranes, SPAEK-*x*-COOH and SPAEK-*x*-BI (*x*=40, 50, and 60) membranes showed comparable water swelling, proton conductivity, thermal and mechanical stabilities, but improved IEC and significantly reduced methanol permeability. Although SPAEK-70-COOH and SPAEK-70-BI exhibited high proton conductivity, which was even higher than that of Nafion®, it was not suitable for fuel cell applications due to its poor dimensional stability in water. Therefore, this research demonstrates the possibility of synthesizing low-cost proton exchange membranes with reduced methanol crossover for fuel cell applications. In general, SPAEK-*x*-COOH and SPAEK-*x*-BI (*x*=40, 50, and 60) membranes are expected to be applicable in DMFCs.

4. Conclusion

A series of novel sulfonated poly(arylene ether ketone)s containing sulfonic groups and carboxylic groups were firstly copolymerized. The carboxylic group in the SPAEK-*x*-COOH copolymers side chain is an active pendant group that could react with 1,2-diaminobenzene to be easily transformed to benzimidazole units. Thus, sulfonated aromatic polymers bearing sulfonic groups and benzimidazole groups were then synthesized and characterized. The incorporation of benzimidazole groups can improve the thermal and mechanical stability of a polymer. At the same time, the introduction of the carboxylic groups can lead a large elongation at break up to 133%. Where the amount of free sulfonic acid groups is high, SPAEK-*x*-BI membranes exhibit lower proton conductivities than those of corresponding SPAEK-*x*-COOH membranes due to the interaction between benzimidazole groups and sulfonic acid groups. However, for the SPAEK with low *D*_s and water uptake, it is supposed that the benzimidazole group tethered to the backbone acts as a medium through the basic nitrogen

for protons transfer between the sulfonic acid groups of SPAEKs. Comparing SPAEK membranes with carboxylic and benzimidazole groups having the same structural composition, the swelling ratio and methanol permeability are lower for the polymers with benzimidazole. Therefore, according to the above results, a balance of proton conductivity, methanol permeability, thermal and mechanical stabilities could be designed by incorporation of functional groups, such as carboxylic and benzimidazole groups. In general, SPAEK-*x*-COOH and SPAEK-*x*-BI (*x*=40, 50, and 60) membranes are expected to be applicable in DMFCs.

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