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Publisher's version / Version de l'éditeur:
https://doi.org/10.1002/fuce.200900076
Fuel Cells, 10, 1, pp. 45-53, 2010

DOI: 10.1002/fuce.200900076

Sulphonated Biphenylated Poly(aryl ether ketone)s for Fuel Cell Applications

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Received April 13, 2009; accepted September 21, 2009

Abstract

New series of fully aromatic poly(ether ketone)s with a biphenyl pendant groups were synthesised. A direct comparison of sulphonation reaction among monophenylated poly(ether ether ketone) (Ph-PEEK), biphenylated poly(ether ether ketone) (BiPh-PEEK) and PEEK (Victrex) was thoroughly investigated. Several advantages of the pendant-phenyl poly(ether ketone)s compared with commercial PEEK were identified, including ready control over the site of sulphonation and degree of sulphonation (DS), and mild and rapid sulphonation. The basic membrane physical properties comprising of thermal and mechanical properties, dimensional stability and proton conductivity were studied. One new membrane, sulphonated biphenylated poly(ether ether ketone) (BiPh-SPEEKDK) having a good combination of membrane properties was fabricated into a membrane electrode assembly (MEA), and it showed excellent direct methanol fuel cell (DMFC) performance.

Keywords: DMFC, Fuel Cells, MEA, Membrane, Proton Exchange Membrane

1 Introduction

Proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) using proton conductive polymer electrolyte membranes (PEMs) as one of the key components are promising future power devices in automotive, stationary and portable electronic applications [1, 2]. Known for their excellent oxidative and dimensional stabilities, high proton conductivity and ideal microstructure, Nafion-type membranes having the perfluorosulphonic acid chemical structure are the state-of-the-art proton conductive membranes currently utilised in PEMFC and DMFC systems. It is of great industrial and academic interest to develop alternatives to Nafion-type membranes, due to the well-known drawbacks of the perfluorinated membranes such as high cost, high fuel crossover, low operation temperature and environmental recycling uncertainties [3, 4].

During the last decade, many PEMs were developed by introducing proton conductive groups including sulphonic acid ($-SO_3H$), phosphonic acid ($-PO(OH)_2$) and carboxylic acid (–COOH) groups into high performance polymers [5–7]. However, most of the scientific literature claiming to show good properties are only concerned with the PEM synthesis and basic membrane characterisation, while far less literature concerns work on membrane electrode assembly (MEA) and cell performance of hydrocarbon-based PEM materials [8]. Due to their excellent thermal and mechanical properties, poly(aryl ether ketone)s (PAEKs) have been extensively studied as high-performance engineering materials [9]. Sulphonic acid groups are often incorporated into PAEKs through post-sulphonation of existing PAEKs. For example, commercial Victrex PEEK could be sulphonated in concentrated sulphuric acid, although a long reaction period was required [10, 11]. The sulphonation reactions of low molecular weight aromatic molecules have been well investigated and several established principles could be followed. In contrast, the sulphonation of high-molecular-weight macromolecules may be more complicated. In order to achieve high degree of sulphonation (DS) or control over DS, more vigorous reaction conditions such as strong sulphonation reagents and elevated temperatures are often used, which sometimes lead to loss of selectivity on the site of sulphonation and also unwanted side reactions [12]. Since post-sulphonation is a relatively simple procedure that is amenable to scale-up, it is necessary to carefully investigate the sulphonation reaction applied to pendant-phenyl aromatic polymers that can be specifically and rapidly sulphonated at the terminal biphenyl site under rela-

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tively mild conditions. These enable PEM materials to be made having well-defined regular chemical structures under mild sulphonation conditions using concentrated sulphuric acid by the so-called post-sulphonation way. These homopolymer-like PEMs are different from widely reported post-sulphonated copolymers because the sulphonated biphenyl-containing repeat units are regular as compared with many other random copolymers obtained by post-sulphonation of the main chain. The ion exchange capacity (IEC) is controlled primarily by the ketone monomer segment. This advantage in the structure is reflected in their improved PEM properties, such as dimensional stability in hot-water and DMFC performance.

Kvalnes [13] reported the synthesis of p-biphenyl-hydroquinone in 1934, and no polymers except a polyester [14] was prepared based on this monomer. In a previous short communication [15], we reported MEA performance of a sulphonated biphenylated PAEK (BiPh-SPAEK) in order to study the relationship between the performance and the structure. In the present study, detailed work including the synthesis of p-biphenyl-hydroquinone using an improved synthetic route, and the polymerisation of fully aromatic poly(ether ketone)s based on the above monomer is reported for the first time. The site-selective sulphonation reaction and kinetics of the biphenylated poly(ether ether ketone) (BiPh-PEEK) were studied. The properties relative to PEMs applications were investigated and the DMFC performance based on one membrane is also presented.

2 Experimental

2.1 Materials

4,4′-Difluorobenzophenone (99%), 1,4-benzoquinone (98%) and zinc powder (99%) were obtained from Sigma–Aldrich Ltd., and used as a received. 1,4-Bis(4-fluorobenzoyl)benzene (98%) and 4,4′-bis(4-fluorobenzoyl)biphenyl (98%) were obtained from Jilin University, and recrystallised from chlorobenzene before use. Anhydrous potassium carbonate (Sigma–Aldrich Ltd., 99%) was ground into fine powder and stored in a vacuum oven at 120 °C before use. All other chemicals were received from commercial sources and used without further purification.

2.2 Synthesis of *p*-Biphenyl-hydroquinone

p-Biphenyl-hydroquinone was synthesised via a coupling reaction of p-biphenyl diazonium with 1,4-benzoquinone followed by a reduction reaction, as shown in Scheme 1, and the synthetic procedure was similar to a previously reported one of (3-methyl)phenylhydroquinone [16].

p-Biphenyl-quinone: yield, 65%; m.p., 191 °C. Elem. Anal. Calcd. for $C_{18}H_{12}O_2$ (260.29 g mol^{-1}): C 83.06%, H 4.65%. Found: C, 83.12%; H, 4.62%.

^{1}H NMR (DMSO-d$_6$): δ(ppm) = 7.76, d (8.4 Hz), 2H; 7.72, d (8.4 Hz), 2H; 7.63, d (8.8 Hz), 2H; 7.49, t (7.2 Hz), 2H; 7.40, t (7.2 Hz), 1H; 7.01 d (2.8 Hz), 1H; 6.99, d (8 Hz), 1H; 6.93, dd (8 Hz, 2.8 Hz), 1H.

^{13}C NMR (DMSO-d$_6$): δ(ppm) = 187.66, 186.58, 144.63, 141.30, 139.17, 137.28, 136.03, 131.91, 131.76, 129.98, 128.96, 127.88, 126.69, 126.40.

p-Biphenyl-hydroquinone: yield, 75%; m.p., 177 °C. Elem. Anal. Calcd. for $C_{18}H_{14}O_2$ (262.30 g mol^{-1}): C 82.42%, H 5.38%. Found: C 82.22%, H 5.61%.

^{1}H NMR (DMSO-d$_6$): δ(ppm) = 8.89, s, 1H; 8.85, s, 1H; 7.71–7.63, m, 6H; 7.47, t (7.6 Hz), 2H; 7.36, t (7.2 Hz), 1H; 6.81, d (8.4 Hz), 1H; 6.76, d (2.8 Hz), 1H; 6.63, dd (8.4 Hz, 2.8 Hz), 1H.

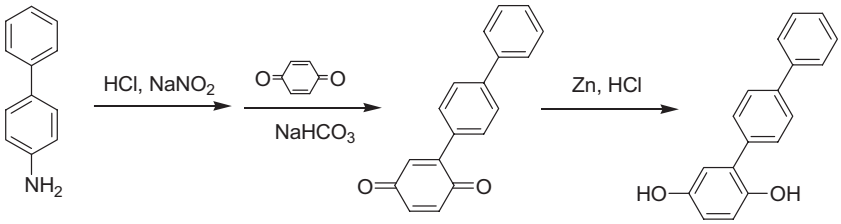
^{13}C NMR (DMSO-d$_6$): δ(ppm) = 150.12, 146.86, 139.93, 138.12, 137.88, 129.47, 128.91, 127.53, 127.27, 126.48, 126.14, 116.84, 116.24, 115.03.

2.3 Synthesis of the Starting Polymers

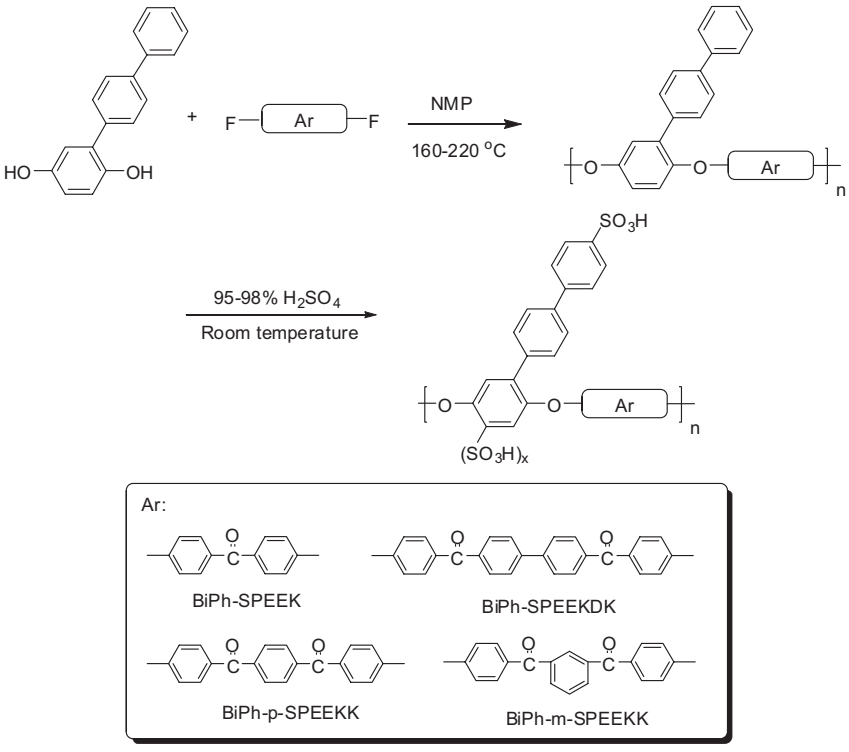
All the polymers were synthesised via a nucleophilic aromatic substitution polycondensation [16]. A typical synthesis of p-biphenylated PEEK (BiPh-PEEK) is given as follows: To a 100 mL three-necked flask equipped with a magnetic stirrer, an argon inlet and a Dean–Stark trap with a condenser, were added p-biphenyl-hydroquinone (2.623 g, 0.01 mol), 4,4′-difluorobenzophenone (2.182 g, 0.01 mol), anhydrous K_2CO_3 (1.794 g, 0.013 mol), N-methylpyrrolidone (NMP) (23 mL) and toluene (15 mL). The system was allowed to reflux for 3 h, and then the toluene was removed. The reaction temperature was increased to 190 °C. After 6 h, an additional 10 mL of NMP was added into the viscous reaction mixture. After a short period, the viscous solution was poured into 200 mL of water to precipitate out the polymer. The polymer was ground into fine powder using a blender. The polymer powder was refluxed in deionised water and ethanol several times to remove the salts and solvents, and dried at 120 °C for 24 h.

All the other polymers were prepared using the same synthesis and purification routine, and their chemical structures are shown in Scheme 2.

BiPh-PEEK: Elem. Anal. Calcd. for $(C_{31}H_{20}O_3)_n$ (440.49 g mol^{-1}): C 84.53%, H 4.58%. Found: C 83.27%, H 4.43%.



Scheme 1 Synthesis of p-biphenylhydroquinone.



Scheme 2 Synthesis of Y-shaped polymers with a p-biphenyl pendant group and their sulphonation.

^{1}H NMR ($CDCl_3$): δ(ppm) = 7.83, d (8.8 Hz), 1H; 7.77, d (8.8 Hz), 1H; 7.73, d (8.8 Hz), 1H; 7.66, d (8.8 Hz), 1H; 7.58–7.52, m, 6H; 7.39, t (7.2 Hz), 2H; 7.34–7.25, m, 2H, 7.18–7.06, m, 4H; 6.95, d (8.8 Hz), 1H; 6.91, d (8.8 Hz), 1H.

^{13}C NMR ($CDCl_3$): δ(ppm) = 194.05, 161.54, 161.10, 152.63, 148.45, 140.59, 140.29, 135.75, 135.24, 132.18 (m), 129.29, 128.75, 127.45, 126.95, 123.17, 122.45, 120.30, 117.15, 116.31.

BiPh-m-PEEKK: Elem. Anal. Calcd. for $(C_{38}H_{24}O_4)_n$ (544.59 g mol^{-1}): C 83.81%, H 4.44%. Found: C 82.51%, H 4.21%.

^{1}H NMR ($CDCl_3$): δ(ppm) = 8.16–8.07, m, 1H; 7.98–7.08, m, 2H; 7.87–7.85, m, 2H; 7.78–7.75, m, 2H; 7.58–7.52, m, 7H; 7.39, t (7.2 Hz), 2H; 7.31–7.28, m, 2H; 7.17–6.95, m, 6H.

BiPh-p-PEEKK: Elem. Anal. Calcd. for $(C_{38}H_{24}O_4)_n$ (544.59 g mol^{-1}): C 83.81%, H 4.44%. Found: C 82.80%, H 4.32%.

BiPh-PEEKDK: Elem. Anal. Calcd. for $(C_{44}H_{28}O_4)_n$ (620.69 g mol^{-1}): C 85.14%, H 4.55%. Found: C 84.16%, H 4.46%.

2.4 Sulphonation Reactions and Membrane Making

Mild and simple reaction conditions were used for incorporating sulphonic acid groups. A typical procedure is as follows: to a 100 mL flask, 5 g of BiPh-PEEK and 50 mL of concentrated sulphuric acid were added. After stirring at room temperature for 5 h, the homogeneous viscous solution was precipitated into a mixture of water and ice to get a silk-like solid. The solid was washed with water until the water reached neutral pH. The sulphonated BiPh-SPEEK was dried in a vacuum oven at 100 °C for 48 h.

An amount of 0.5 g of the above dried polymer was dissolved in 15 mL of DMAc and the solution was filtered through a filter paper. The filtered solution was poured onto a glass plate and dried in an oven at 50 °C under a constant slow purge of nitrogen for one week. The resulting flexible membrane was dried in a vacuum oven at 120 °C for 24 h. The thickness of all membrane films was in the range of 50–100 µm.

The same procedure was followed for all the other polymers.

BiPh-SPEEK (DS = 2): Elem. Anal. Calcd. for $(C_{31}H_{20}O_9S_2)_n$ (600.62 g mol^{-1}): C 61.99%, H 3.36%, S 10.68. Found: C 61.07%, H 3.89%, S 10.13.

^{1}H NMR (DMSO-d_6): δ(ppm) = 7.84–7.73, m, 4H; 7.73–7.66, m, 4H; 7.66–7.58, m, 4H; 7.54–7.52, m, 1H; 7.23, s, 1H; 7.18–7.06, m, 4H.

BiPh-p-SPEEKK (DS = 1): Elem. Anal. Calcd. for $(C_{38}H_{24}O_7S)_n$ (624.66 g mol^{-1}): C 73.07%, H 3.87%, S 5.13. Found: C 72.37%, H 4.09%, S 5.43.

^{1}H NMR (DMSO-d_6): δ(ppm) = 7.86–7.76, m, 8H; 7.66–7.58, m, 8H; 7.39–7.23, m, 3H; 7.15–7.08, m, 4H.

BiPh-p-SPEEKK (DS = 2): Elem. Anal. Calcd. for $(C_{38}H_{24}O_{10}S_2)_n$ (704.72 g mol^{-1}): C 64.76%, H 3.43%, S 9.10. Found: C 62.78%, H 3.76%, S 8.83.

^{1}H NMR (DMSO-d_6): δ(ppm) = 7.82–7.79, m, 8H; 7.67–7.58, m, 8H; 7.55, s, 1H; 7.22, s, 1H; 7.14–1.10, m, 4H.

BiPh-m-SPEEKK (DS = 1): Elem. Anal. Calcd. for $(C_{38}H_{24}O_7S)_n$ (624.66 g mol^{-1}): C 73.07%, H 3.87%, S 5.13. Found: C 72.29%, H 4.18%, S 5.52.

^{1}H NMR (DMSO-d_6): δ(ppm) = 7.99–7.55, m, 16H; 7.35–7.04, m, 7H.

BiPh-SPEEKDK (DS = 2): Elem. Anal. Calcd. for $(C_{44}H_{28}O_{10}S_2)_n$ (780.82 g mol^{-1}): C 67.68%, H 3.61%, S 8.21. Found: C 66.92%, H 3.98%, S 7.98.

^{1}H NMR (DMSO-d_6): δ(ppm) = 7.98–7.90, m, 4H; 7.90–7.80, m, 8H; 7.74–7.67, m, 4H; 7.67–7.60, m, 4H; 7.63, s, 1H; 7.26, s, 1H; 7.17, d (8.0 Hz), 4H.

2.5 Characterisation and Measurements

^{1}H and ^{13}C NMR spectra of the sulphonated polymers 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. The elemental analysis was carried out with a PerkinElmer 2400 Series II CHNS/O elemental analyzer. Inherent viscosities (η_{inh}) were measured using an Ubbelohde viscometer at a polymer concentration of 500 mg dL^{-1} in DMAc solutions at 30 °C.

A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for evaluating thermal stability of the polymers. Polymer samples for TGA analysis

were preheated at 150 °C for 40 min under nitrogen atmosphere to remove moisture. These samples were then heated for 10 min^{-1} from 50 to 800 °C under nitrogen atmosphere. A TA Instruments differential scanning calorimeter (DSC) model 2920 was used for measuring T_g. Samples for DSC analysis were initially heated at a rate of 10 min^{-1} under nitrogen atmosphere to the temperature below their decomposition temperature, followed by quenching them to room temperature. Thereafter, the samples were heated at a rate of 10 °C min^{-1} under nitrogen atmosphere to evaluate T_g.

The proton conductivities of the membranes were estimated from AC impedance spectroscopy data, obtained over a frequency range of 1–10^7 Hz with oscillating voltage of 100 mV, using a Solartron 1260 gain phase analyzer. Specimens in the form of 20 mm × 10 mm strips were soaked in deionised water for 48 h prior to the test. These were clamped in a frame between two platinum electrodes, and then placed in a temperature-controlled cell exposed to air by a pinhole, where it was equilibrated at given temperature at 100% RH at ambient pressure for 30 min. Measurements in four-point mode were carried out. 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, and 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.

The mechanical properties of the thin films were evaluated at room temperature on an Instron 5565 instrument at a strain rate of 10 mm min^{-1}, and a 500 N load cell was used. The samples were prepared by cutting into a dumbbell shape (DIN-53504-S3A).

The water uptake was calculated from: water uptake $(\%) = \frac{\omega_{wet} - \omega_{dry}}{\omega_{dry}} \times 100\%$ where ω_{dry} and ω_{wet} are the weights of dried and wet samples, respectively.

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

IEC of the sulphonated polymers was measured using a typical titration method. The films in acid form were equilibrated with 100 mL of 1 M NaCl for 24 h. The amount of the H^+ released from the membranes was determined by titration of 0.1 M NaOH aqueous solution and phenolphthalein as an indicator.

MEA fabrication and fuel cell operating conditions were conducted according to Los Alamos National Laboratory protocols [15]. The cell was preconditioned under H_2/air fuel cell operation at 0.7 V for 2 h. We used Pt–Ru black (1:1 atomic ratio, HiSPEC 6000, Alfa Aesar) for anode and Pt black (HiSPEC 1000, Alfa Aesar) for cathode and 5% commercially available Nafion dispersion. The catalyst ink was painted onto the membrane until the catalyst loading reached 8 mg cm^{-2} for anode and 6 mg cm^{-2} for cathode. Active area is 5 cm^2. The cell was held at 80 °C; 1 and 2 M aqueous methanol solution was fed to the anode with a flow rate of 1.8 mL min^{-1}; 90 °C humidified air was fed at 500 sccm without back pressure.

3 Results and Discussion

3.1 Synthesis of Fully Aromatic PEKs with Biphenyl Pendant Groups

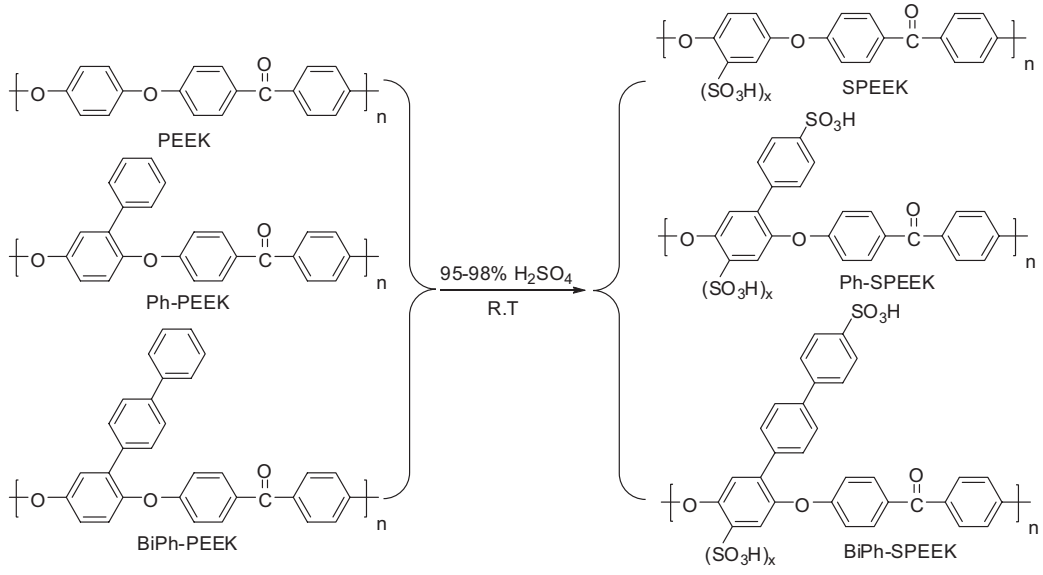
There is a need to develop structurally new PAEKs with functional groups or activated reaction sites for their further application in new fields [17]. In the present study, a new family of fully aromatic PAEKs with a bulky biphenyl pendant groups was prepared and their further functionalisation to introduce sulphonic acid groups was investigated.

Until now, many monomers including bisphenols and activated dihalongenated monomers have been developed for the preparation of PAEKs via nucleophilic substitution polycondensation [17]. Those monomers usually result in PAEKs possessing good thermal and chemical stability. In our study, a biphenol monomer containing a biphenyl pendant, BiPh-PH, was synthesised using a previously reported method of our group [16]. This monomer was polymerised with four different activated difluoro monomers, in NMP and K_2CO_3 at 160–190 °C, to provide four PAEK homopolymers.

3.2 Sulphonation Reaction of BiPh-PEKs

Sulphonated polymers prepared by post-sulphonation reaction often show poor controllability over DS and substitution sites. Generally, strong sulphonation reagents (such as fuming sulphuric acid and chlorosulphonic acid) have been used to incorporate acid groups into polymer chains, which may lead to the poor selectivity of substitution sites and the possibility of side reactions and chain degradation. In addition, DS is usually adjusted by the reaction time, which results in the difficulty in its precise control. Recently, we reported some polymers having good site selectivity and which have fully sulphonated substitutions within a short reaction time by post-sulphonation method [18]. This is in strong contrast to the sulphonation of PEEK, which occurs over a long reaction period of hundreds of hours.

Sulphonation is an electrophilic aromatic substitution reaction in which a hydrogen atom on an arene is replaced by a sulphonic acid. The several benzene rings with various electron withdrawing or electron donating substituents present in the structure of PAEKs add complexity to the sulphonation reaction. For the sulphonation reaction of PEEK (Victrex), it is well known that the monosubstitution occurs on the benzene ring connecting two ether linkages. In order to make direct comparisons of the sulphonation kinetics of PEEK with the pendant-phenyl and pendant-biphenyl PEEKs, identical sulphonation conditions such as polymer concentration, sulphonation reagent concentration, stirring speed, reaction temperature, and the polymer structures are given in Scheme 3. DS values, estimated from ^1H NMR spectroscopic analysis as a function of reaction time, are shown in Figure 1.



Scheme 3 Sulphonation of the fully aromatic PEEKs.

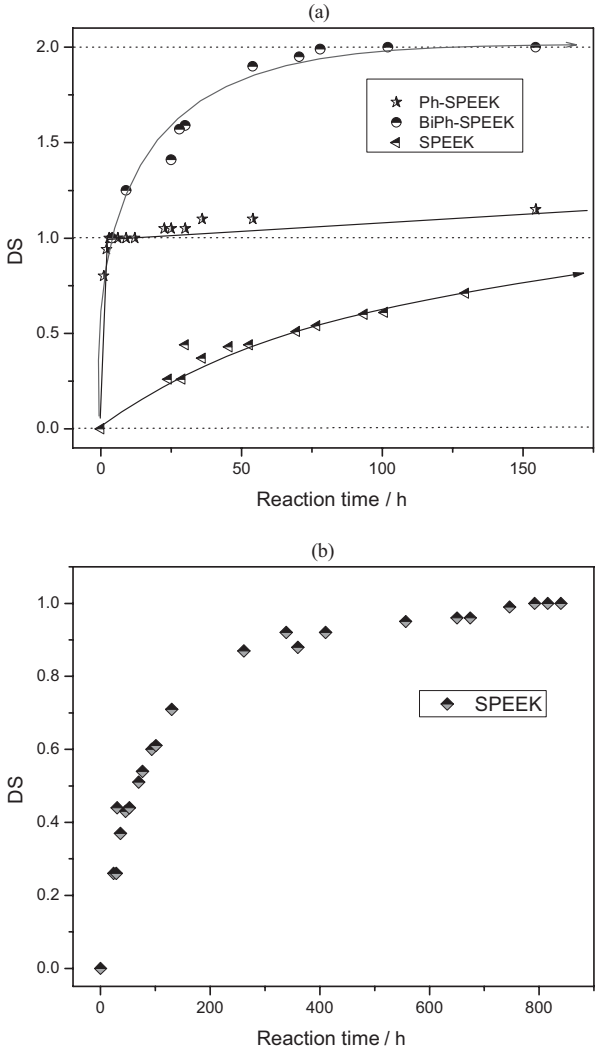


Fig. 1 Kinetics of sulphonation reaction: (a) a comparison among BiPh-SPEEK, Ph-SPEEK and SPEEK; (b) SPEEK for a long reaction time.

DS values of 1.0 for Ph- and BiPh-SPEEK were achieved within 3 h., in strong contrast with the >30 days required for SPEEK with the same DS, as shown in Figure 1(b). NMR spectroscopic analysis of Ph- and BiPh-SPEEK indicated the site of sulphonation is on the pendant benzene rings at the initial stage, whereas the main-chain sulphonation for all the three polymers occurred much more slowly. The sulphonation rate of the main-chains was greatly affected by the substituents on the pendant rings. For example, main-chain sulphonation of the BiPh-SPEEK was the most rapid, with a DS of 2.0 achieved after 75 h, while for the same reaction time period, the DS value of Ph-SPEEK was less than 1.3. A possible explanation for the behaviour of the latter polymer is that the position of the deactivated $-SO_3H$ is located on the conjugated system sufficiently close to the main-chain reaction site to reduce the activity of the backbone. Also, this could explain why only one sulphonic acid substituent was attached onto the pendant biphenyl group of BiPh-SPEEK. The above results and analysis were supported by the observed NMR spectra, as shown in Figure 2. All the other sulphonated PAEKs based on different arylene ketone backbones studied in this work showed the same tendency, and BiPh-p-SPEEKK (DS = 1 and 2, Figure 3), BiPh-m-SPEEKK (DS = 1) and BiPh-SPEEKDK (DS = 2) having suitable DS values were selected for further studies.

3.3 Thermal and Mechanical Properties of the Membranes

As an important class of high-performance polymers, fully aromatic PEKs typically possess extremely attractive thermal properties including high glass transition temperature (T_g) and high thermal degradation temperature, enabling them to be utilised at high operating temperatures. Only one transition temperature was observed in the DSC curves before decomposition temperature, both for starting BiPh-PAEK

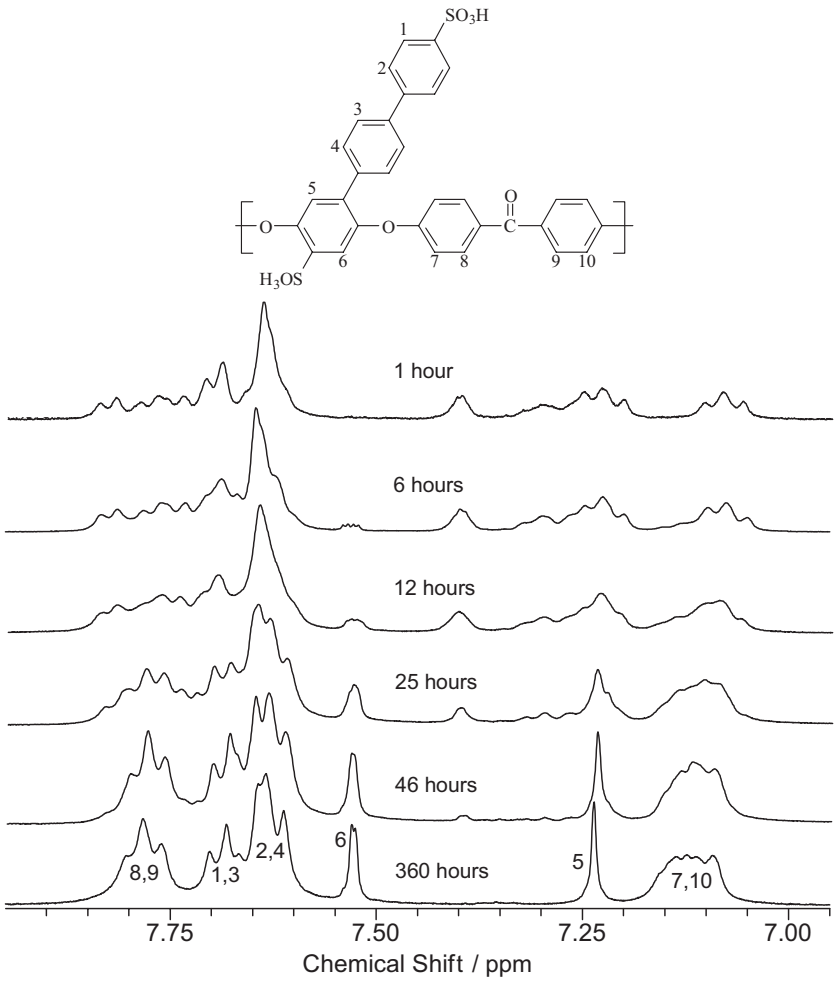


Fig. 2 ^{1}H NMR spectra of BiPh-SPEEK at different reaction times.

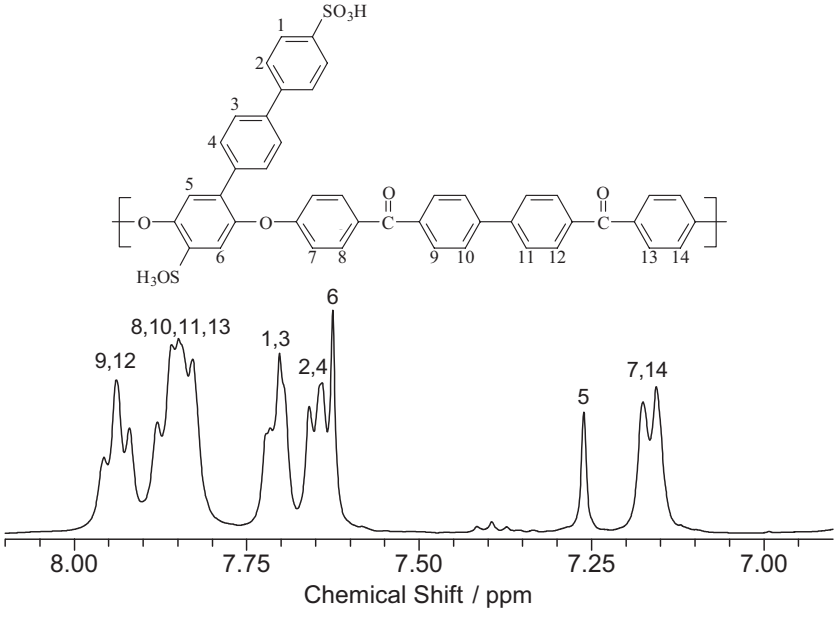


Fig. 3 ^{1}H NMR spectrum of BiPh-SPEEKDK (DS = 2).

polymers and their sulphonated derivatives, which indicated their amorphous nature. As shown in Table 1, the T_g values of the starting BiPh-PAEKs were in the range of 176–193 °C, and the high T_g values were relative with the rigid Y-shaped polymer chains. The bulky and rigid pendants hinder the movement of the segments of molecular chains, which leads to an increase in the glass transition temperatures. In common with previous work, the sulphonated polymers had higher T_g values than the corresponding unsulphonated polymers due to the effect of strong non-bonding interactions of sulphonic acid groups increasing chain rigidity. For example, the T_g of sulphonated BiPh-PEEK (BiPh-SPEEK) was 262 °C, which was 86 °C higher than the corresponding unsulphonated BiPh-PEEK.

All the non-sulphonated PAEKs had outstanding thermal stability, with no weight loss being observed up to 420 °C in air, as shown in Table 1 and Figure 4. All the sulphonated samples exhibited typical two-stage degradation curves. One main decomposition stage around 300 °C is possibly associated with the degradation of the sulphonic acid groups, and the other one around 500 °C is caused by the degradation of the aromatic ether ketone main chains. No obvious degradation could be observed until 250 °C. The combined high T_g with good thermal stability meets the thermal requirements of these sulphonated PAEKs for operating at elevated operation temperatures in fuel cell systems.

The lower acidity of ionomers with $-SO_3H$ groups on aromatic rings compared with perfluorosulphonic acid ionomers requires that a higher content of sulphonic acid groups is needed for maintaining high proton conductivity. However, the polymers having a high content of sulphonic acid groups often exhibit poor dimensional and mechanical integrity under aqueous environment and at elevated temperature [19]. The design of effective PEM materials having both high proton conductivity coupled with good mechanical properties, reasonable water uptake and dimensional stability, is one of the key considerations that require these contradictory requirements to be balanced. After immersion in water for 24 h, the tensile properties of this new class of novel membranes were tested and the results are listed in Table 2. BiPh-SPEEK

Table 1. Viscosities and thermal properties of the polymers.

Polymer	η (dL g^{-1})[a]	T_g (°C)[b] unS	S	$T_{5\%}$ (°C)[c] unS	S	$T_{10\%}$ (°C)[d] unS	S
BiPh-PEEK	2.01	176	262	498	323	510	348
BiPh-p-PEEKK (DS = 1)	2.13	190	253	533	340	556	368
BiPh-p-PEEKK (DS = 2)	2.50	190	297	533	345	556	388
BiPh-m-PEEKK	1.30	186	232	499	344	515	368
BiPh-PEEKDK	1.35	193	281	542	357	558	399

a) Inherent viscosity of sulphonated polymers.
b) Glass transition temperature. S refers to sulphonated polymer, and unS refers to the corresponding starting material.
c) 5% weight loss temperature measured by TGA.
d) 10% weight loss temperature measured by TGA.

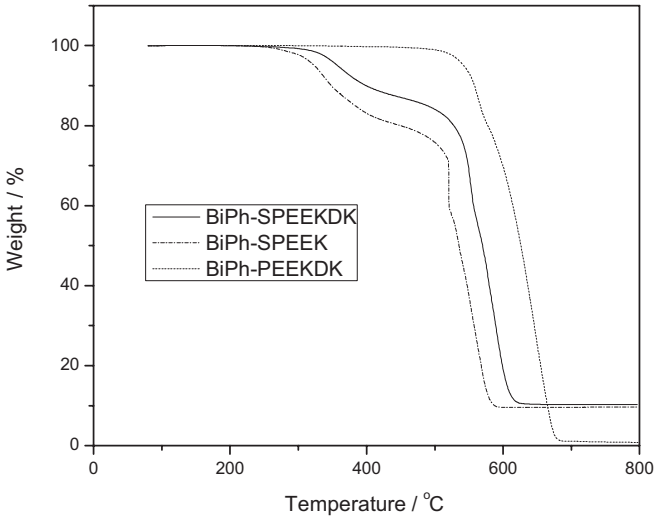


Fig. 4 Examples of TGA curves of non-sulphonated and sulphonated PAEKs in air.

(DS = 2) with a high $–SO_3H$ content exhibited tensile stress of 5.8 MPa and Young's modulus of 0.03 GPa. These mechanical properties under humidified conditions are judged to be insufficient for utilisation of BiPh-SPEEK (DS = 2) PEM in a fuel cell. However, BiPh-p-SPEEKK (DS = 1), BiPh-m-SPEEKK (DS = 1) and BiPh-SPEEKDK (DS = 2) having a more suitable $–SO_3H$ content exhibited good mechanical properties, with tensile stress of 24.5–43.4 MPa and Young's moduli of 0.54–0.61 GPa and elongations at break of 91–122%. As shown in Figure 5, these three materials have a much higher yield stress and Young's moduli than Nafion 117. By comparison, the respective unsulphonated polymers had tensile stress in the range of 90–100 MPa and Young's moduli of 2.0–2.3 GPa, with elongations at break of 15–30%.

Table 2. Mechanical properties of the SPEK membranes.

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
BiPh-SPEEK (DS = 2)	5.8	0.03	104
BiPh-p-SPEEKK (DS = 1)	43.4	0.54	122
BiPh-p-SPEEKK (DS = 2)	21.9	0.19	159
BiPh-m-SPEEKK (DS = 1)	31.3	0.60	91
BiPh-SPEEKDK (DS = 2)	24.5	0.61	109
Nafion 117	24.5	0.16	316

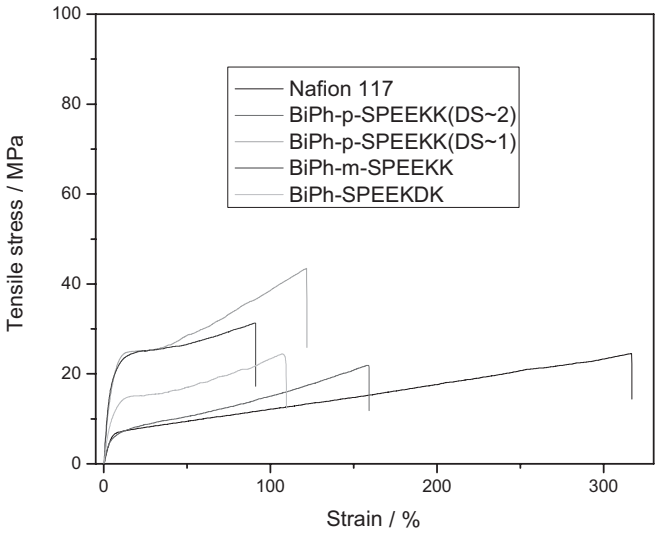


Fig. 5 The stress versus strain curves of the resulting membranes.

3.4 Dimensional Stability and Proton Conductivity of the SPEK Membranes

Sufficient water within the membrane and $–SO_3H$ content is necessary for maintaining high proton conductivity under fuel cell operating conditions of elevated temperature and humidity. However, sufficient $–SO_3H$ content high proton conductivity has a propensity to result in membrane swelling, dimensional instability and mechanical fragility [20]. The design of effective PEMs involves developing materials that balance contradictory properties of high proton conductivity, good mechanical strength and dimensional stability. For example, SPEEK with IEC 1.74 meq g^{-1} had more than 500% water uptake at 80 °C, which might lead to the destruction of cells and the lose of cell performance [15]. Most recently, we found that the homopolymer-like Ph-SPEEKK showed improved dimensional stability and good cell performance at the same level of IEC value [15]. In this study, the water absorption and dimensional change in water at room temperature and 80 °C were evaluated. As shown in Table 3, BiPh-p-SPEEKK (DS = 1) and BiPh-m-SPEEKK (DS = 1) with IEC 1.70 meq g^{-1} had suitable swelling ratios and water absorptions at 80 °C in water, which were also suitable for maintaining their high proton conductivities of 1.1×10^{-1}–1.3×10^{-1} S cm^{-1} at 80 °C. It was noted that the homopolymer-like BiPh-SPEEKDK having more rigid backbones possessed both high proton conductivity (4.5×10^{-2} S cm^{-1} at room temperature and 1.4×10^{-1} S cm^{-1} at 80 °C, respectively) and suitable swelling ratio in hot water even at higher IEC level. Despite the high proton conductivities (~1.0×10^{-1} S cm^{-1}) of BiPh-SPEEK (DS = 2) and BiPh-m-SPEEKK (DS = 2) bearing more $–SO_3H$ groups, they were unsuitable for fuel cell application because of their solubility in hot water.

Table 3. Water uptake and proton conductivity of the SPEK membranes.

Polymer	IEC (meq g^{-1})[a]		WU (%)[b]		SR (%)[c]		σ (S cm^{-1})[d]	
	Calc.	Exp.	18 °C	80 °C	18 °C	80 °C	18 °C	80 °C
BiPh-SPEEK	3.32	3.12	130	s[e]	41	s	1.1×10^{-1}	s
BiPh-p-SPEEKK (DS = 1)	1.60	1.72	34	48	9	14	2.9×10^{-2}	1.1×10^{-1}
BiPh-p-SPEEKK (DS = 2)	2.83	2.61	120	s	38	s	9.0×10^{-2}	s
BiPh-m-SPEEKK	1.60	1.78	35	53	11	19	4.0×10^{-2}	1.3×10^{-1}
BiPh-SPEEKDK	2.55	2.32	57	95	18	35	4.5×10^{-2}	1.4×10^{-1}
Nafion 117	0.91	0.91	19	30	13	20	7.0×10^{-2}	1.2×10^{-1}

a) Ion exchange capability. b) Water uptake.
c) Swelling ratio. d) Proton conductivity.
e) Soluble.

3.5 DMFC Performance of the Membranes

Although many series of polyarylether-type PEMs have been prepared as potential fuel cell materials, with the exception of sulphonated PEEK and a several other sulphonated polyarylene ether ketones and sulphones, only a few of them were successfully fabricated into MEAs and their data reported [21, 22]. Among those which have modest water uptake, BiPh-SPEEKDK showed the best conductivity. Therefore, DMFC performance of BiPh-SPEEKDK was evaluated and compared with that of industrial standard Nafion®. In general, it is rather difficult to compare the membrane performance in DMFC mode since DMFC performance is determined by the coupled effect of membrane conductivity and methanol permeability and those properties are the function of membrane thickness. We have presented that thicker Nafion membranes give a better performance due to the low methanol crossover while thinner hydrocarbon membranes give better performance due to the low resistance for DMFC applications [23]. Therefore, here we compare the relatively thin BiPh-SPEEKDK (53 μm) membrane with relatively thick version of Nafion (Nafion 117, 180 μm) and equivalent thickness Nafion (Nafion 112, 50 μm).

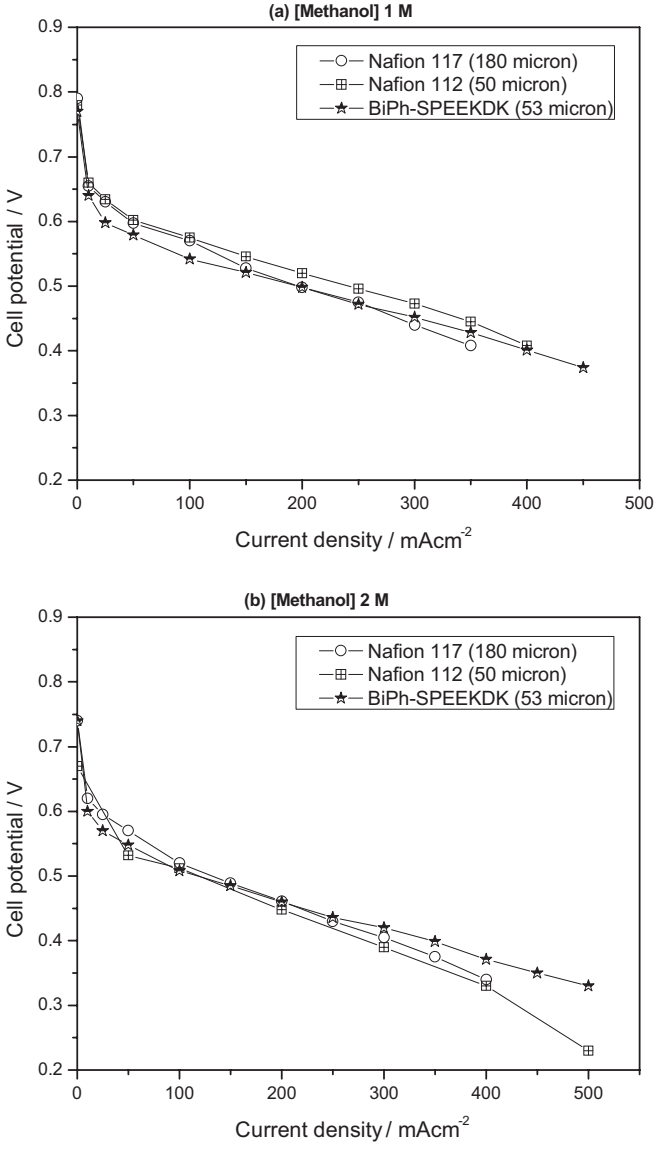


Fig. 6 DMFC performance of BiPh-SPEEKDK and Nafion membranes: (a) methanol feed concentration at 1.0 M and (b) methanol feed concentration at 2.0 M.

As shown in Figure 6, the current density of BiPh-SPEEKDK at 0.5 V at 80 °C in 1 and 2 M methanol reached 195 and 117 mA cm^{-2}, respectively. The DMFC performance of the MEA based on BiPh-SPEEKDK was comparable to or even better than Nafion 112 and 117. Especially, the performance of BiPh-SPEEKDK outperformed the Nafion 112 at 80 °C for the tested conditions in 2 M methanol. The improved performance of BiPh-SPEEKDK could be explained by a combination of lower high frequency resistance (HFR) (95 mΩ cm^2 at 2 M) and lower methanol crossover limiting current (328 mA cm^{-2} at 2 M). Under the same test conditions, Nafion 112 had higher resistance (106 mΩ cm^2 at 2 M) and higher methanol crossover limiting current (527 mA cm^{-2} at 2 M).

4 Conclusion

In this study, several SPEKs with pendant and main-chain sulphonic acid groups were synthesised. The pendant phenyl substituents underwent complete (DS = 1) rapid and mild sulphonation site specifically. A slower main-chain sulphonation reaction, also site-specific, occurred over a much longer time period. Several of the BiPh-SPAEK polymers had an excellent combination of thermal properties, dimensional stability and high proton conductivity. At IEC ~1.70 meq g^{-1}, BiPh-p-SPEEKK and BiPh-m-SPEEKK had suitable swelling ratios (<20% at 80 °C) and high proton conductivities (>1.1×10^{-1} S cm^{-1} at 80 °C). A homopolymer-like sulphonated polymer, BiPh-SPEEKDK, having more rigid backbones possessed both high proton conductivity (4.5×10^{-2} S cm^{-1} at room temperature and 1.4×10^{-1} S cm^{-1} at 80 °C, respectively) and suitable swelling ratio in hot water

even at a high IEC value. An MEA based on the BiPh-SPEEKDK membrane was successfully fabricated, and showed to have attractive DMFC performance compared with Nafion-based MEA at high methanol concentration. The improved performance of BiPh-SPEEKDK could be explained by its high proton conductivity and low methanol permeability.

Acknowledgements

Financial support for this project was provided by the National Natural Science Foundation of China (no. 50973040) and the Science and Technology Development Plan of Jilin Province, China (no. 20090322). Dr. Yu Seung Kim thanks the US DOE Fuel Cell Technologies Program for financial support.

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