

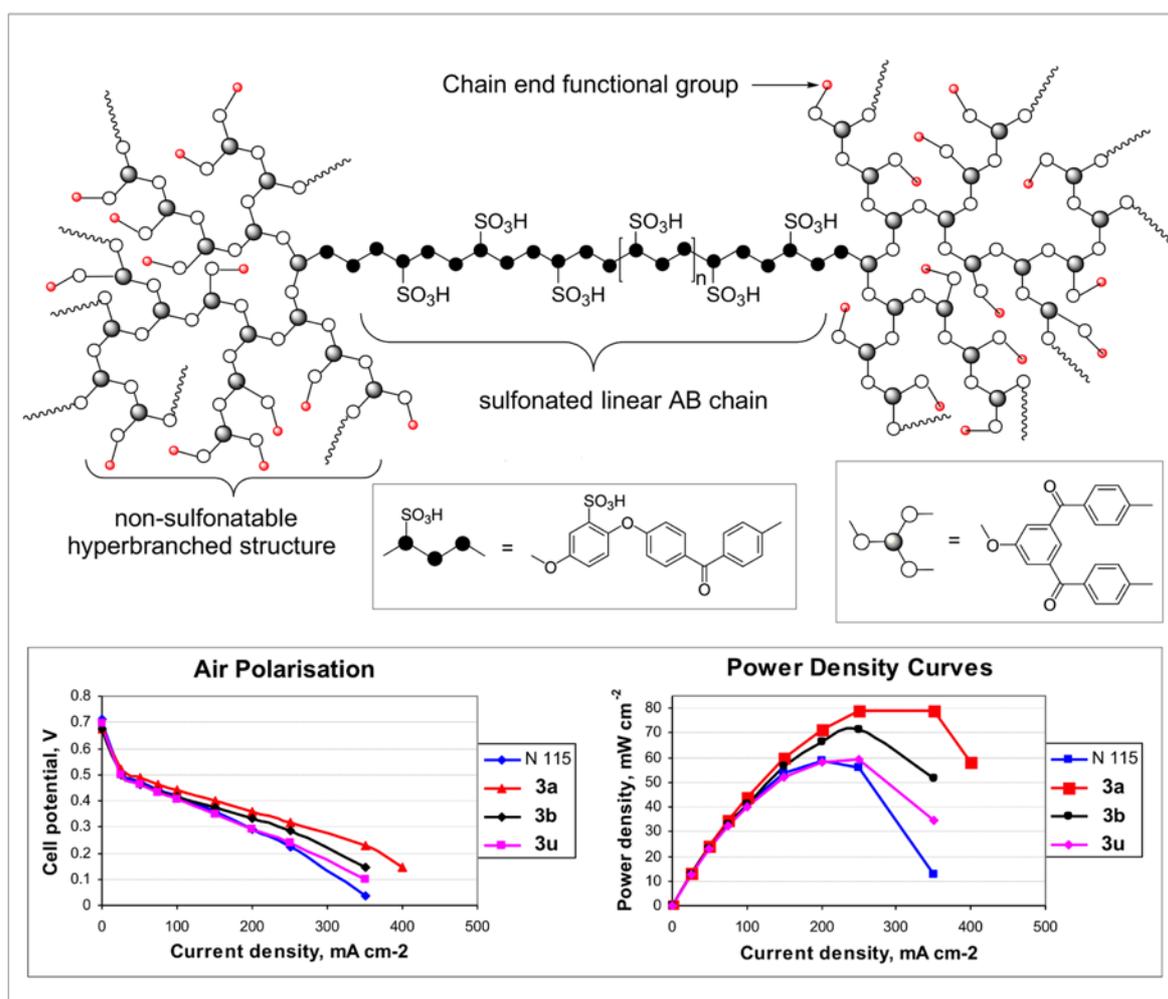
Triblock ionomers based on linear and hyperbranched poly(ether ketone)s: ionomer synthesis, fabrication of proton-transport membranes and evaluation for direct-methanol fuel cell applications

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Triblock ionomers derived from linear and hyperbranched poly(ether ketone)s: ionomer synthesis, fabrication of proton-transport membranes and evaluation for direct-methanol fuel cell applications

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ABSTRACT: Polycondensation of an aromatic ether-ketone AB₂ monomer in the presence of bis(4-fluorobenzoyl)-terminated PEEK affords semi-crystalline triblock copolymers in which the central block is a readily-sulfonatable PEEK chain and the outer blocks are non-sulfonatable hyperbranched moieties. Post-polymerisation sulfonation of each these copolymers in 96% sulfuric acid, after extraction of a cyclic oligomer fraction originating from the AB₂ monomer, yields the corresponding ionomer in which sulfonation has occurred exclusively and quantitatively on the central block. The ion-exchange capacities of these ionomers were in the range 1.4 to 1.8 mmol g⁻¹, and their inherent viscosities were 3.9 to 4.8 dl g⁻¹. The ionomers were successfully solution-cast into tough, transparent, thin-film membranes (ca. 40 μm in thickness) which were evaluated for direct-methanol fuel cell (DMFC) performance in terms of proton conductivity, methanol diffusion coefficient, limiting current density and maximum power density. The triblock ionomers showed substantially higher DMFC performance than a control membrane based on the industry-standard fluorocarbon ionomer Nafion[®] 115, and their methanol diffusion coefficients were two to three times lower.

1. Introduction

The direct-methanol fuel cell (DMFC) using a polymer electrolyte membrane (PEM) has significant potential as a portable power source,¹⁻⁶ as a result of: (i) simple design (Figure 1); (ii) high efficiency; (iii) low emissions to the environment; (iv) easy storage of aqueous methanol; (v) low operating temperatures; (vi) no need for a fuel vaporiser or reformer; and (vii) no membrane-humidification or thermal management requirements. However, the large-scale introduction of DMFC is challenged by a number of issues, notably (i) high methanol

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permeability of industry-standard fluorocarbon membranes such as Nafion[®] 115, leading to high methanol crossover, and (ii) the need for a more efficient catalyst for oxygen reduction. The loss of fuel cell performance due to slow O₂ reduction kinetics can be minimised to a certain extent by reducing the thickness of the membrane to lower its ionic resistance, but this also increases methanol crossover. Higher concentrations of methanol fuel can increase power density and reduce fuel volume, but in general a high concentration of methanol in the aqueous feed leads to excessive swelling of the membrane. Furthermore, unoxidised methanol concentrates at the anode and will again cross over to the cathode. Methanol crossover can poison the cathode catalyst, leading to increased cell-heating, lower oxygen activity, reduced cell voltage and power density, and loss of DMFC efficiency as a result of ‘parasitic’ oxidation of methanol to CO₂ and H₂, at the cathode.⁷⁻¹⁰ Present DMFC technology thus uses a dilute aqueous methanol feed, at 1M to 3M concentration, to limit the extent of methanol crossover.

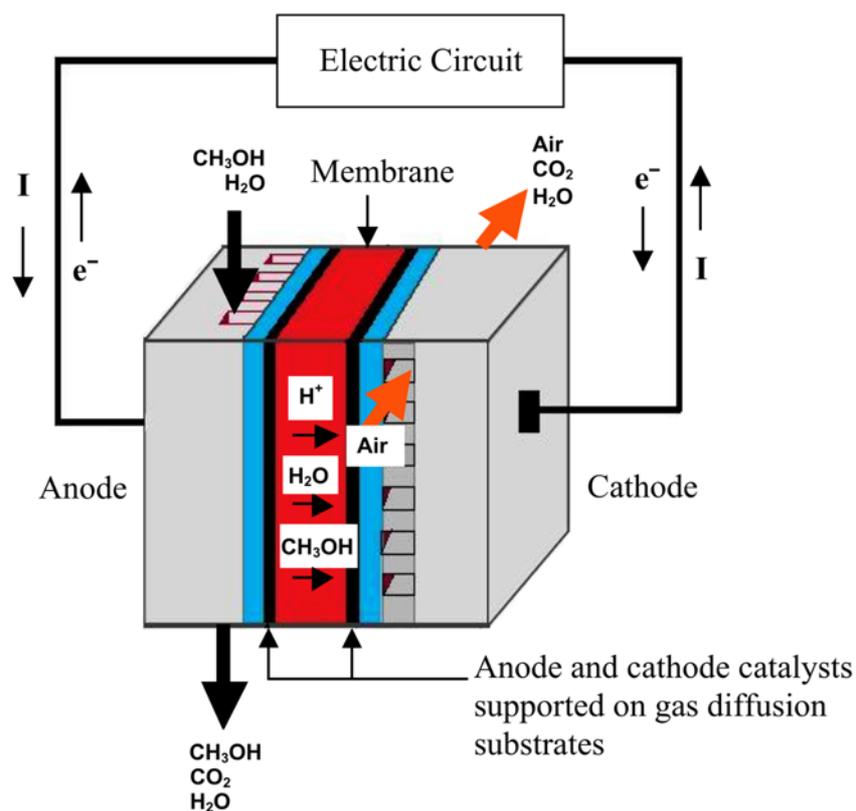


Figure 1. Schematic representation of a direct-methanol fuel cell, showing transport of protons, water and methanol through the ionomer membrane, with oxidation of methanol to CO₂ and water.⁷

The function of the polymer-electrolyte (ionomer) membrane is to transport protons from the anode to the cathode during fuel cell operation and, therefore, the polymer electrolyte membrane is a critical component of the membrane-electrode assembly (MEA). Nafion[®] ionomers (Chart 1a) were initially developed by DuPont,¹¹ as membranes for electrochemical chlor-alkali technology, and the high electronegativity of fluorine makes the sulfonic acid groups superacidic ($\text{pK}_a \approx -6$), leading to very high proton conductivities. Moreover, the C-F bonds are stable at the anode/cathode potential, even in the presence of small amounts of hydrogen peroxide which are formed during fuel cell operation. These properties, combined with reasonably good mechanical stability, mean that Nafion membranes are well-suited for PEMFC applications. Other commercial perfluorosulfonated membranes include Flemion[®] (Asahi Glass), Aciplex[®] (Asahi Chemical), and XUS[®] (Dow Chemical)¹² (Chart 1b). Partially fluorinated membranes such as Ballard's sulfonated poly(trifluorostyrene) BAM3G[®] system (Chart 1c) have also been introduced.¹³

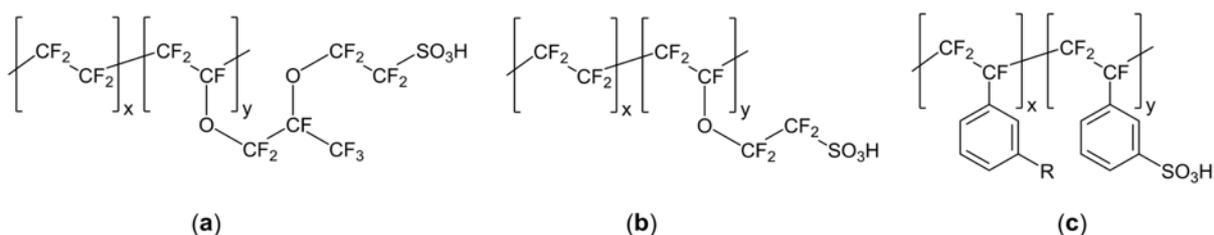


Chart 1. Fluorocarbon ionomers: (a) DuPont Nafion[®], (b) Dow XUS[®] and (c) Ballard BAM3G[®]

Although these fluorinated membranes exhibit good fuel cell performance below 90 °C, their proton conductivities suffer at temperatures above this due to dehydration, and the low glass transition temperatures of fluorocarbon polymers also result in loss of mechanical strength under these conditions.¹⁴ Ionomeric derivatives of many alternative polymers with potentially greater thermo-mechanical durability have therefore been investigated as alternative membrane materials. For example, aromatic poly(ether-ketone)s such as PEEK and PEK (Chart 2) are well-known as high-performance thermoplastics because of their outstanding properties such as high chemical and thermal stability, mechanical strength and very good electrical resistance.¹⁵⁻¹⁶ These polymers are widely used in applications such as coatings, adhesives, molding resins, structural composites and electrically insulating materials.¹⁷⁻²¹ Poly(ether-ketone)s are also known for their semi-crystallinity and consequently high thermomechanical performance and resistance to attack by organic solvents.^{22,23}

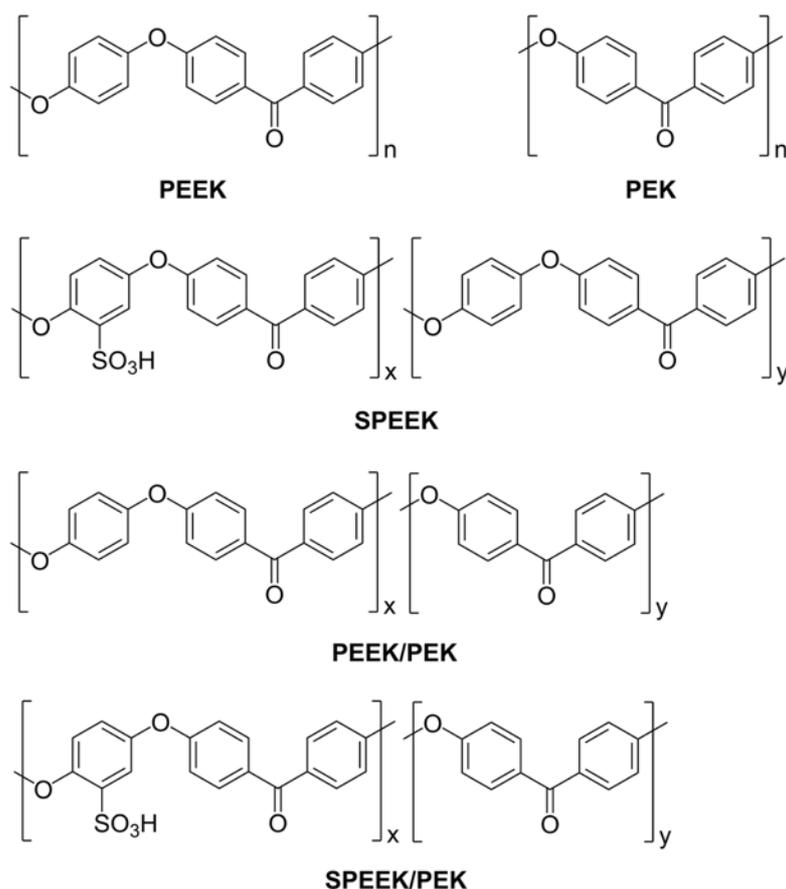


Chart 2. Some aromatic polyetherketones and their derived sulfonic acid ionomers

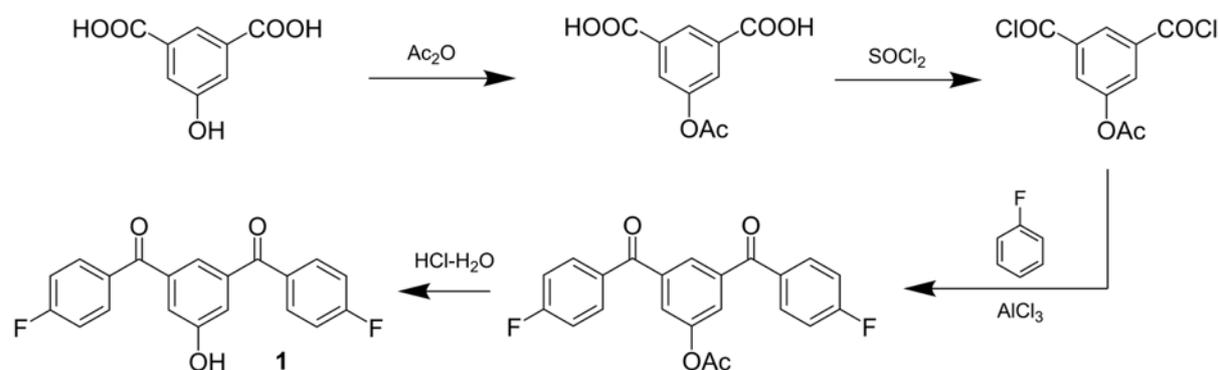
Poly(arylene ether ketone)s have been produced as sulfonic acid ionomers, either by post-polymerisation modification or by direct synthesis of the polymers from pre-sulfonated monomers.²⁴ Such sulfonic acid ionomers may, for example, be obtained by post-polymerisation sulfonation of poly(ether ketone)s in which the readily-sulfonatable 1,4-dioxybenzene residue is present.²⁵⁻²⁷ (Chart 2). Well-defined sulfonation of homopolymers such as the commercial poly(ether ether ketone) PEEK is, however, not easy to achieve, and in order to obtain a specific ion exchange capacity it is generally better to start with a copolymer of specified composition. Thus, PEEK/PEK (Chart 2) dissolved in 96% sulfuric acid will sulfonate only at the PEEK residues, so that the ion-exchange capacity of the resulting ionomer is pre-determined by the composition (x:y ratio) of the starting copolymer.²⁸ Nevertheless, at the high sulfonation levels required for good proton conductivity, such ionomers often swell uncontrollably in the presence of water and may even dissolve completely in aqueous media at high temperature. We have previously reported the development of "microblock" ionomers as a route to aromatic ionomers with high conductivity and limited swellability,^{29,30} but although performing well in fuel cell and electrolyser applications these materials require the synthesis

of relatively complex "extended" monomers. In the present work we have investigated an alternative and much simpler synthetic approach to the swelling problem, namely the synthesis of triblock ionomers by "end-capping" bis(4-fluorobenzoyl)-terminated PEEK with a non-sulfonatable, hyperbranched poly(ether ketone), formed *in situ*, followed by sulfonation of the central PEEK block. A series of such triblock ionomers were here investigated as membranes for direct-methanol fuel cell applications.

2. Results and Discussion

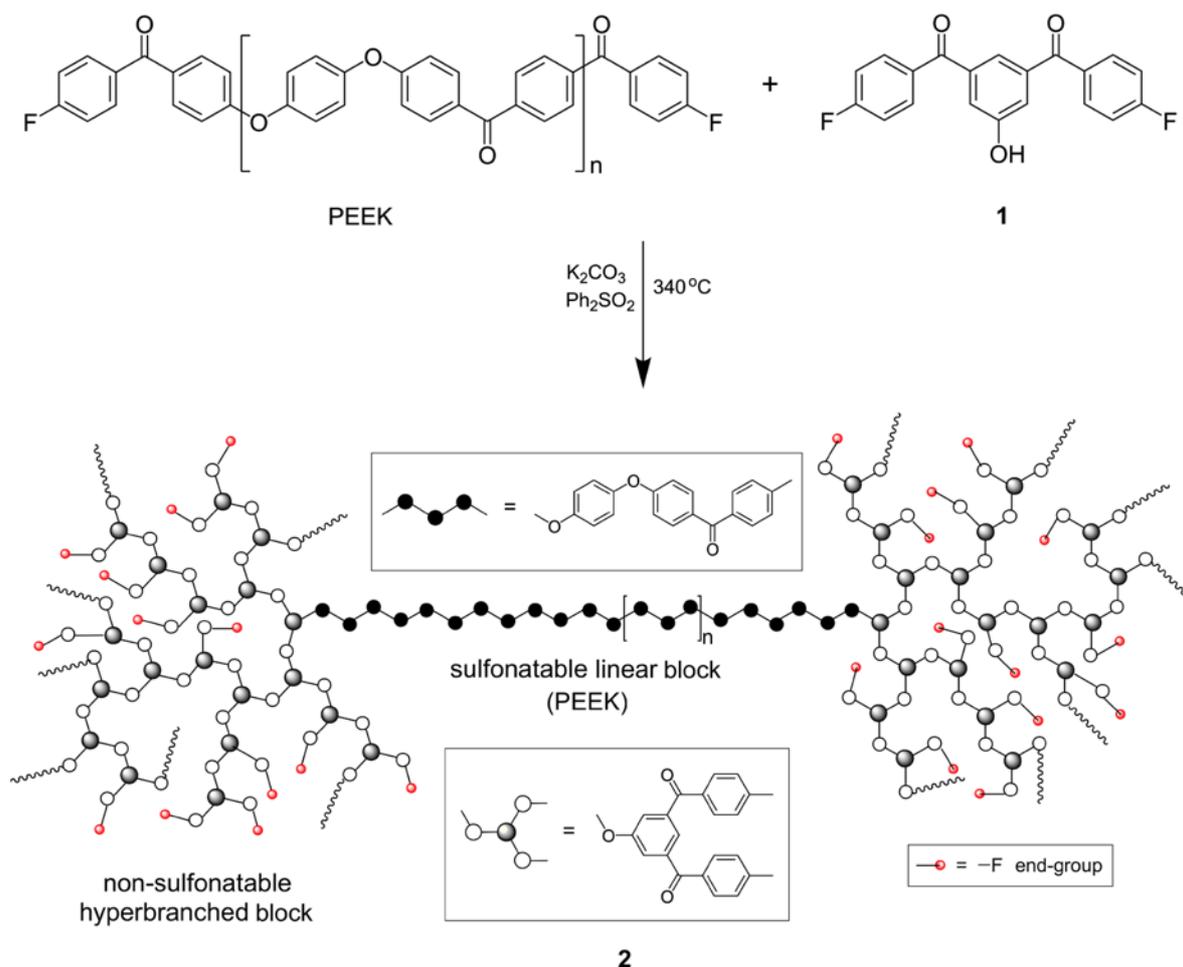
2.1 Synthesis of copolymers and ionomers

Commercially available PEEK is known to be terminated by 4-fluorobenzoyl groups,³¹ because the polymer synthesis is "end-stopped" with 4,4-difluorobenzophenone,³² both to control molecular weight and to avoid leaving thermally unstable phenolic end groups in the polymer. Consequently, it seemed feasible to generate triblock copolymers with a central PEEK block and hyperbranched end blocks by direct reaction of commercial PEEK with the known AB₂ monomer 3,5-bis(4-fluorobenzoyl)phenol, **1**. The latter was synthesized (Scheme 1) by a modification of the literature procedure.³³ Thus, 5-hydroxyisophthalic acid was first acetylated using acetic anhydride at 90 °C to afford 5-acetoxyisophthalic acid, which was then derivatised to the corresponding acid chloride by treatment with thionyl chloride. This was converted to 1-acetoxy-3,5-bis(4-fluorobenzoyl)benzene by Friedel-Crafts acylation followed by hydrolysis to afford 3,5-bis(4-fluorobenzoyl)phenol, **1**, in 43% overall yield. The product melted sharply at 154 °C (lit. 153 °C).³⁴



Scheme 1. Synthesis of the AB₂ monomer 3,5-bis(4-fluorobenzoyl)phenol (**1**)

Polycondensation of monomer **1** in the presence of bis(4-fluorobenzoyl)-terminated PEEK was then carried out at high temperature (340 °C) in diphenylsulfone as solvent, with potassium carbonate as the acid-acceptor (Scheme 2). After cooling, grinding, and extraction of the solvent with refluxing methanol and the potassium salts with hot water, the resulting linear-hyperbranched triblock copolymer **2** was obtained in 75% yield.



Scheme 2. Synthesis of the linear-hyperbranched triblock copolymer **2**

Two different linear-hyperbranched triblock copolymers, **2a** and **2b**, were synthesised by this method, with molar ratios of monomer-**1**:PEEK(repeat unit) being 50:50 and 60:40 respectively. Copolymer **2a** was semi-crystalline, showing both a glass transition temperature (146 °C) and a crystalline melting point (340 °C) by DSC, but **2b**, containing a higher proportion of the hyperbranched component, was amorphous, with a T_g of 173 °C. At room temperature, both copolymers were soluble in concentrated sulfuric acid. Their inherent viscosities in 96% sulfuric acid were 0.96 and 0.59 dL g⁻¹, respectively.

It is known that polycondensations of an AB₂ monomer can lead to formation not only of a hyperbranched polymer, but also to a homologous series of soluble macrocyclic oligomers identifiable by MALDI-TOF MS.³⁴ In the present work, the two semi-crystalline copolymers **2a** and **2b** were extracted exhaustively with refluxing chloroform, and the extracts were analysed for the presence of such macrocycles. As shown in Figure 2, macrocycles containing up to 15 repeat units of monomer **1** were indeed identified in these soluble fractions, each extract typically representing about 15 wt% of the total product.

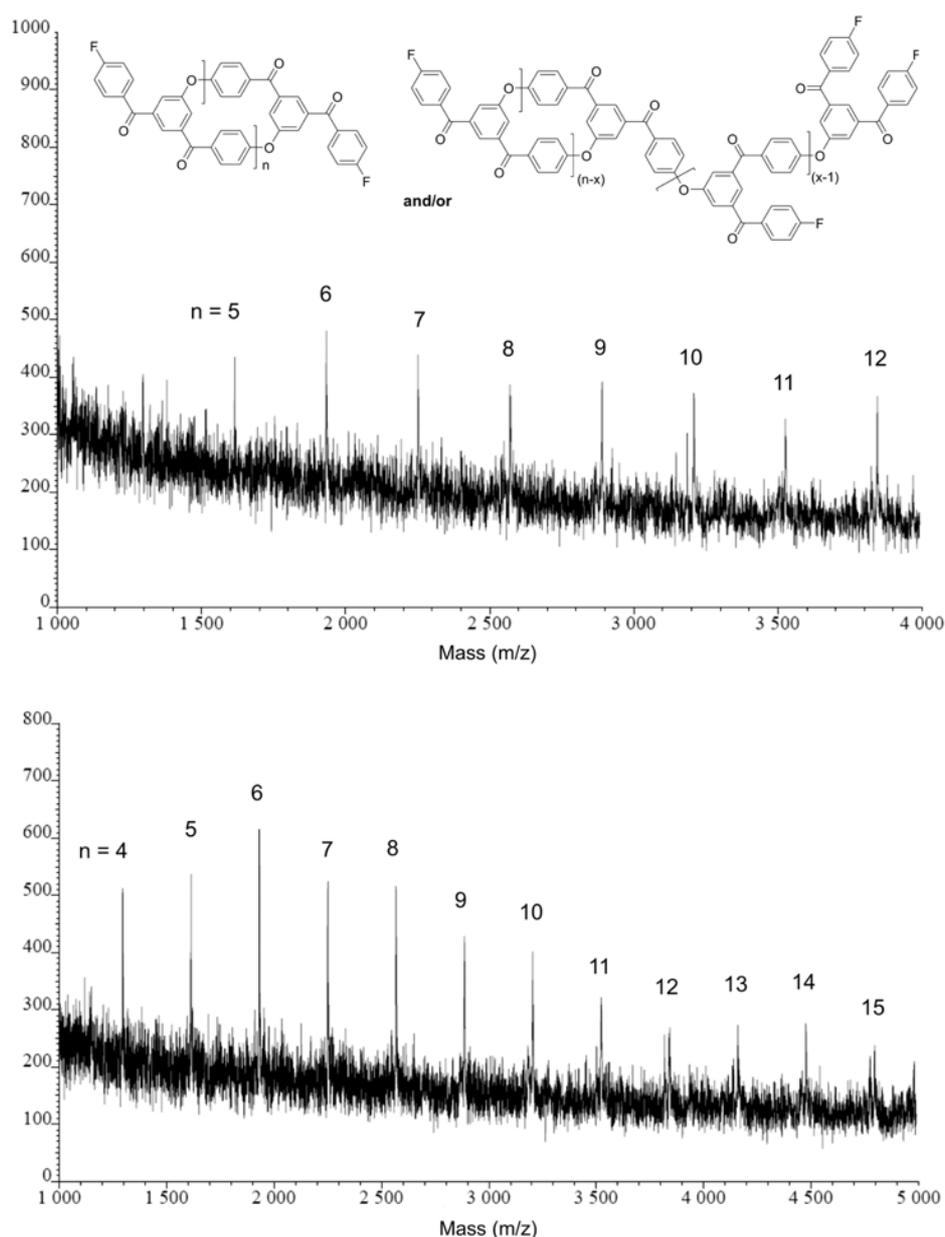
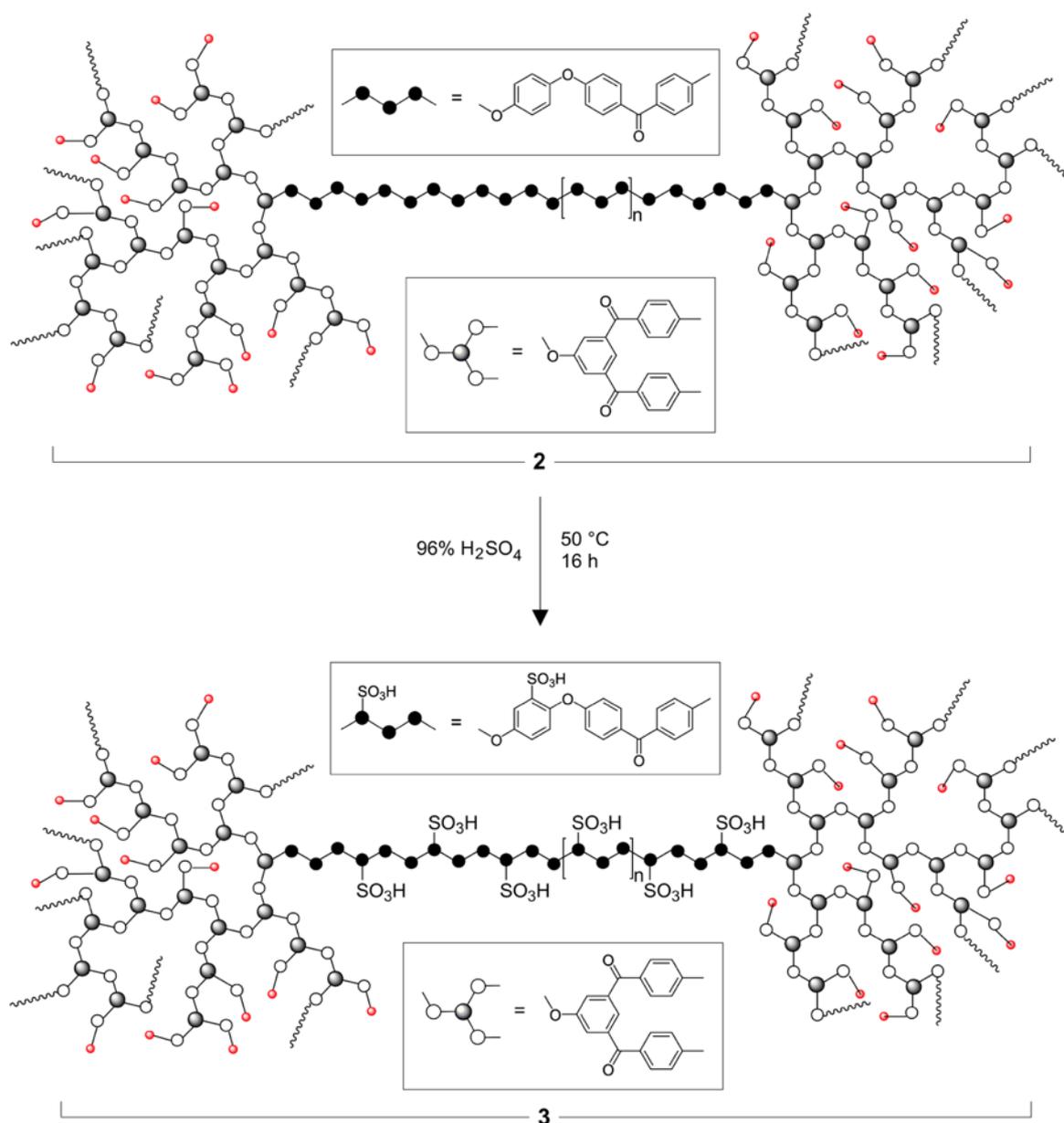


Figure 2. MALDI-TOF mass spectra of the chloroform extracts from copolymers **2a** (above) and **2b** (below). Peak labels correspond to the values of n for the macrocycles and/or macrocycle-polymer systems shown. Sodium trifluoroacetate was used as cationising agent, and peak-masses thus represent $[M + Na]^+$.

Once the soluble, macrocyclic fractions had been removed, the linear-hyperbranched copolymers **2a** and **2b** were sulfonated by dissolving in 96% sulfuric acid and heating at 50 °C for 16 h. Porous yellow beads of the resulting ionomers were produced on adding the cooled solutions dropwise to water. The beads were washed with water until acid-free and then dried under vacuum at 100 °C for 4 h, affording ionomers **3a** and **3b** (Scheme 3). In order to establish the effects on membrane performance of allowing the macrocyclic component to remain in the ionomer, an original, *unextracted* sample of copolymer **2a** was also sulfonated to give a third ionomer, **3u**.



Scheme 3. Sulfonation of the central (PEEK) block of copolymers of type **2**, affording triblock ionomers **3**

The above procedure is known to fully sulfonate PEEK homopolymer (generating one sulfonic acid group per hydroquinone residue),³⁵ but as the hyperbranched blocks contain at least one carbonyl group on every aromatic ring, the latter blocks will not undergo sulfonation under such conditions.²⁸ This implies that removal of the macrocyclic fraction (also non-sulfonatable, being derived from the same monomer (**1**) as the hyperbranched block) should afford an ionomer with an increased ion-exchange capacity (IEC). Thus, *measuring* its ion-exchange capacity would enable the relative proportions of sulfonated and non-sulfonated blocks to be established and compared with the original monomer-composition. It is clear from Table 1 that the measured ion-exchange capacities for **3a** and **3b** are indeed significantly higher than the values calculated from the molar ratios of monomer **1** to PEEK used in the syntheses of their precursor-polymers **2a** and **2b**. These ratios were 50:50 and 60:40 respectively, but the measured IEC values indicate ratios in the final, extracted versions of these copolymers of 39:61 and 51:49 respectively. In both cases the proportion of material derived from monomer **1** has decreased substantially after extraction, consistent with removal of a macrocyclic fraction derived from this monomer.

For comparison of the DMFC performance of membranes derived from the PEEK-centred triblock ionomers of type **3** with that of a membrane based on partially-sulfonated PEEK itself ("SPEEK"),³⁶ a sample of SPEEK (Table 1) with with an IEC similar to that of ionomer **3u** was synthesised according to the latter reference.

Table 1: Characterisation data for ionomers **3a**, **3b**, **3u** and SPEEK

Ionomer	Experimental values					Theoretical values	
	η_{inh} (dL g ⁻¹) ^a	T_g (°C)	IEC (mmol g ⁻¹)	EW (g mol ⁻¹)	DS	IEC (mmol g ⁻¹)	EW (g mol ⁻¹)
3a	3.90	194	1.741	574	1.19	1.493	670
3b	3.62	222	1.438	695	1.24	1.183	846
3u	4.77	196	1.599	625	1.07	1.493	670
SPEEK	2.41	199	1.491	671	0.49	2.715	368

^a Measured in NMP at 25 °C. IEC – Ion Exchange Capacity; EW – Equivalent Weight; DS – Degree of Sulfonation relative to composition of unextracted copolymer.

2.2 Membrane fabrication and testing

Ionomers **3a**, **3b**, **3u** and SPEEK (Table 1) were cast from NMP solution into tough, flexible, transparent membranes, with specified thicknesses in the range 38 to 70 μm . They were fabricated into membrane-electrode assemblies (MEAs) by the method described in an earlier paper,³⁷ and their characteristics in direct methanol fuel-cell tests are summarised in Table 2.

Table 2: Single cell DMFC performance of ionomer membranes with 3M aqueous methanol as fuel at 60 °C

	N115	3a	3b	3u	SPEEK ^a
Membrane thickness, μm	120	38	42	45	70
Methanol diffusion coefficient, $\text{cm}^2 \text{s}^{-1}$	2.38×10^{-6}	6.97×10^{-7}	9.38×10^{-7}	8.34×10^{-7}	7.91×10^{-7}
Limiting MCO current density, ^b mA cm^{-2}	345	310	338	322	195
Open circuit voltage, V	0.71	0.68	0.67	0.70	0.66
Voltage, V, at maximum current density (mA cm^{-2})	0.04 (350)	0.15 (400)	0.15 (350)	0.10 (350)	0.03 (250)
Maximum power density, mW cm^{-2} at current density (mA cm^{-2})	58.6 (200)	79.1 (350)	71.3 (250)	59.3 (250)	40 (150)
Proton conductivity, mS cm^{-1}	100	45	39	35	39
Membrane resistance, Ohm cm^2	0.116	0.084	0.107	0.126	0.178

^a Casting solutions of SPEEK were very hazy and gave opaque membranes, suggesting the presence of significant residual crystallinity in the sample. ^b MCO = Methanol crossover

As shown in Figure 3, the DMFC performance of the MEA based on membrane **3a** was significantly better than that of Nafion[®] 115 at all current densities studied, while the performance

of membrane **3b** was similar to that of Nafion[®] 115 at low current densities ($< 100 \text{ mA cm}^{-2}$). However, membrane **3b** exhibited superior performance at current densities greater than this. The maximum power densities obtained using membranes **3a** and **3b** were 79 mW cm^{-2} at 350 mA cm^{-2} and 71 mW cm^{-2} at 250 mA cm^{-2} , respectively, compared with 56 mA cm^{-2} for Nafion[®] 115. Membrane **3u**, derived from an *unextracted* copolymer, gave the poorest performance of the three block-ionomer membranes, but still showed an improvement over Nafion[®] 115 at high current density.

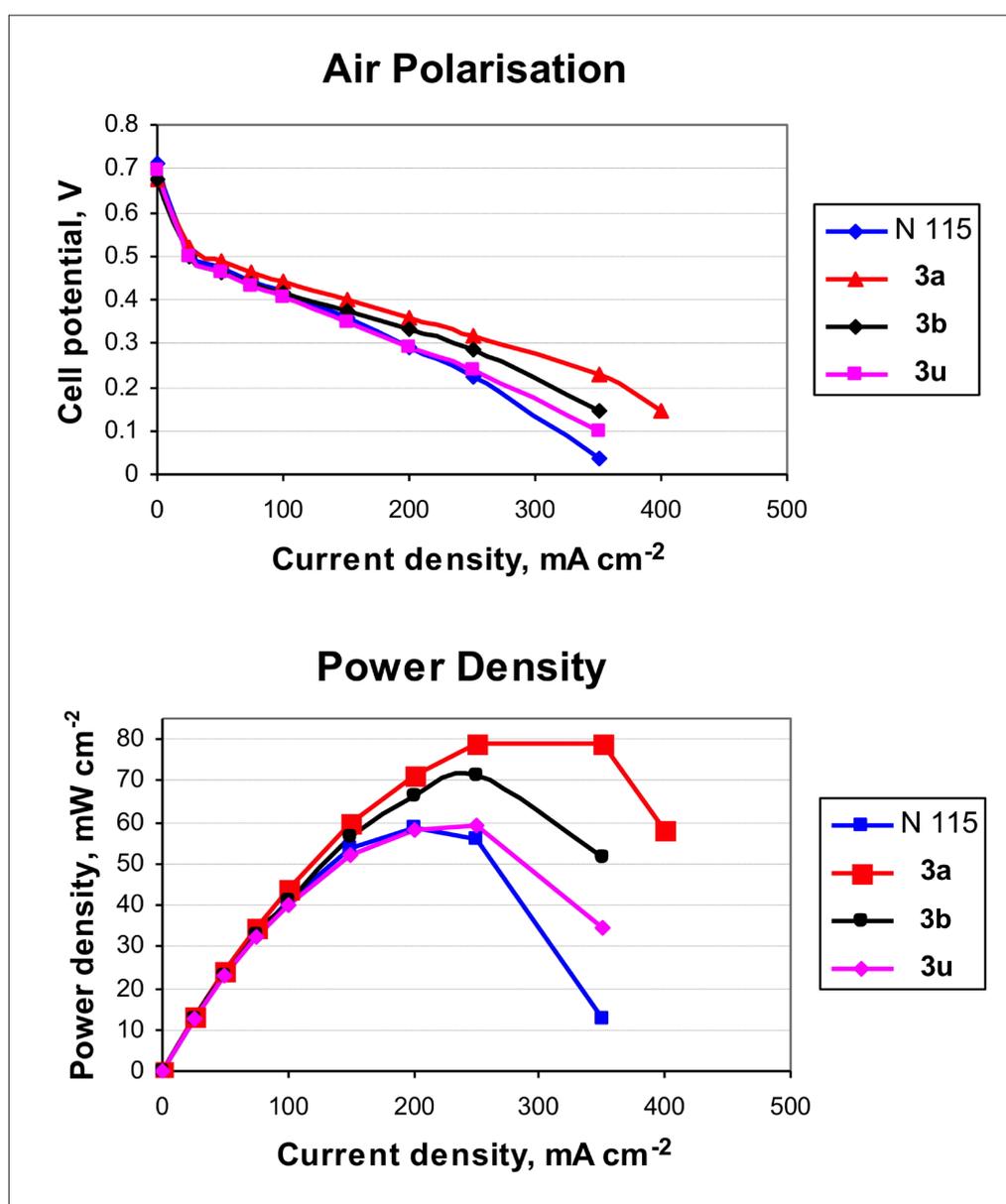


Figure 3: Current–voltage (above) and power density (below) curves for MEAs based on membranes **3a**, **3b**, **3u** and Nafion 115, tested using 3M aqueous methanol as fuel at a cell temperature of $60 \text{ }^\circ\text{C}$.

An important advantage of polyaromatic membranes is their generally lower permeability to methanol compared to Nafion[®] membranes, as a consequence of their different membrane morphologies. Methanol passing through the membrane is directly oxidised in a "parasitic" reaction at the cathode which results in both wastage of fuel and in an overpotential loss which lowers the performance of the cell. In fluorocarbon ionomers the hydrophobic and hydrophilic regions tend to be strongly microphase-separated, with highly connected hydrophilic channels leading to significant "crossover" of methanol. In aromatic ionomers, however, the two phases are much less strongly phase-separated, leading to narrower and less interconnected hydrophilic channels. Water and methanol are more tightly confined in these channels, resulting in significant reduction of methanol permeation across the membrane.³⁸⁻⁴⁰ In the present work, the methanol diffusion coefficients for membranes **3a**, **3b**, and **3u** (Table 5) were found to be two and a half to three times lower than that of Nafion[®] 115 under the same conditions. The high resistance to methanol crossover in the linear-hyperbranched block-ionomer membranes was also exemplified by their limiting methanol-crossover current densities, which were similar to Nafion[®] 115 despite the latter membrane being ca. three times thicker (Table 5). The proton conductivities of **3a**, **3b** and **3u** were in the range 35 to 45 mS cm⁻¹, i.e. only a third to a half of Nafion[®] 115 but, as shown in Figure 4, the net DMFC selectivities (proton conductivity divided by methanol diffusion coefficient) of all three aromatic membranes were markedly higher than that of Nafion[®] 115, especially so for membrane **3a**.

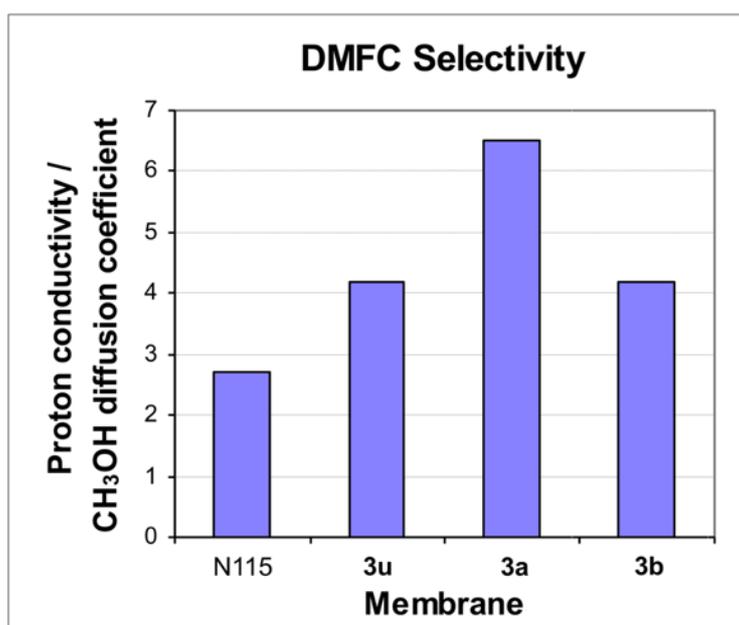


Figure 4: Selectivity for transport of protons relative to methanol in membranes **3a**, **3b**, **3u** and Nafion 115.

Finally, the effects of methanol crossover on DMFC performance for membranes **3u**, **3b** and Nafion[®] 115 were compared by varying the methanol concentration in the fuel over the concentration range 1M to 5M. Although higher concentrations of methanol might be anticipated to provide higher power output, in practice the increasing level of methanol crossover negates this, so that the output of the cell tends to diminish with increasing methanol concentration. This is illustrated in Figure 5, where the cell potentials achieved at two different current densities are plotted against methanol concentration.

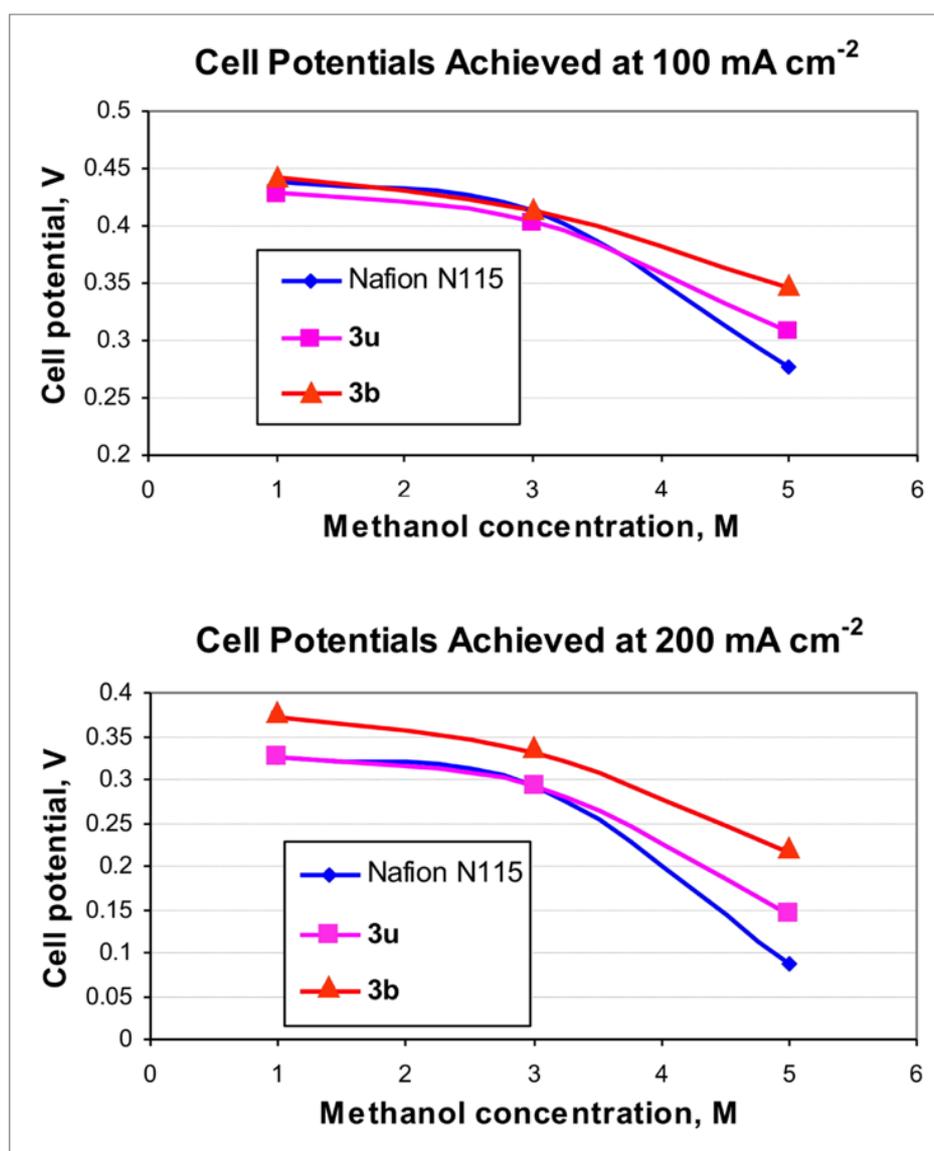


Figure 5: Cell potentials achieved in DMFC by membranes **3u**, **3b** and Nafion 115 as a function of methanol concentration in the aqueous feed, at two different current densities.

In the methanol concentration range 1M to 3M high cell potentials were achieved for all three membranes, but at greater concentrations (5M) increased crossover through the Nafion[®] 115 membrane resulted in a much lower cell potential relative to the two linear-hyperbranched membranes, especially membrane **3b** at the higher current density (Figure 5). The present results clearly demonstrate the potential of linear-hyperbranched sulfonated aromatic polymers as alternatives to Nafion[®] membranes for direct methanol fuel cell applications.

3. Experimental

3.1 Materials

Acetic anhydride (99%), diphenylsulfone (97%), 1-methyl-2-pyrrolidone (NMP), fluorobenzene (99%) and thionyl chloride (>99%) were obtained from Acros Organics. Aluminium chloride (99%), 5-hydroxyisophthalic acid and potassium carbonate (99%) were purchased from Sigma Aldrich. Hydrochloric acid, acetone, methanol and sulfuric acid (96%) were obtained from Fisher Scientific and were used as received. Poly(ether ether ketone) [$M_n = 31$ kD; $M_w = 78$ kD] was donated by Cytec Engineered Materials Ltd. The AB₂ monomer **1** [M.p. 154 °C (lit. 153 °C)³⁴] was synthesised by a method adapted from the literature.³³

3.2 Instrumentation and analysis

Analytical instrumentation and techniques were as described in an earlier publication.³⁷

3.3 Synthesis and characterisation of copolymers and ionomers

Procedure for copolymer synthesis

The synthesis of copolymer **2u** is described here: a mixture of the AB₂ monomer **1** (0.500 g, 1.479 mmol.), PEEK (0.450 g, 1.562 mmol.), potassium carbonate (0.123 g, 0.890 mmol.) and diphenyl sulfone (2.200 g) in a 25 mL Schlenk tube was stirred under a gentle flow of dry nitrogen using a mechanical stirrer and the mixture was heated to 180 °C over 30 minutes using a sand bath attached to a programmable temperature controller. The polycondensation was continued by slowly heating from 180 °C to 340 °C over a period of 2 h and this temperature was maintained for a further 2 h. The hot solution was then poured on to a clean aluminium tray where it solidified on cooling. The solid was milled to a coarse powder, extracted with hot methanol (x 3), hot water (x 3), and again with hot methanol (x 2), and was finally dried at 110

°C for 3 h under vacuum. Yield: 0.716 g (78%). This copolymer (**2u**) was then extracted with chloroform in a Soxhlet for 3 h to remove cyclic oligomers (ca. 17 wt%), and was finally dried under vacuum to give the linear-hyperbranched triblock copolymer **2a**. Copolymer **2b** was synthesised by the same method, but using monomer **1** (0.600 g, 1.775 mmol.), PEEK (0.341 g, 1.184 mmol.), and potassium carbonate (0.148 g, 1.156 mmol).

Characterisation data for copolymer **2a**

DSC: $T_g = 174$ °C, $T_m = 339$ °C; η_{inh} (H₂SO₄) = 0.76 dL g⁻¹; ¹H NMR (CDCl₃/CF₃COOH, δ ppm): 7.11 – 7.21 (12H, m), 7.78 – 7.95 (11H, br, m); ¹³C NMR (CDCl₃/CF₃COOH, δ ppm): 117.4, 122.6, 130.9, 133.9, 152.2, 163.5, 200.1 (C=O); IR (film, cm⁻¹): 1660 (v C=O aromatic), 1597 (v C=C aromatic), 1227 (v C-O-C aromatic), 1159 (v C-F aromatic).

Procedure for ionomer synthesis

A typical procedure, used for the sulfonation of copolymer **2a** and affording ionomer **3a**, is described here. Concentrated sulfuric acid (98%, 6 mL) was stirred with copolymer **2a** (0.400 g) at 50 °C for 16 h. The resulting homogenous solution was cooled to room temperature and added dropwise to deionised water with slow stirring, producing uniform (ca. 3 mm) pale brown beads. The beads were collected by filtration and washed repeatedly with deionised water until the water washings were neutral. The ionomer beads were then air dried for 4 h and vacuum dried at 110 °C for 3 h. Recovery of ionomer **3a** was essentially quantitative. Characterisation data for all the ionomers synthesised in this work are shown in Table 1, and further details for ionomer **3a** are given below.

Characterisation data for ionomer **3a**

DSC: $T_g = 194$ °C; η_{inh} (NMP) = 3.90 dL g⁻¹; ¹H NMR (DMSO-*d*₆, δ ppm): 7.01 – 7.27 (m), 7.51 (d (J = 2.9 Hz), 7.73 – 7.86 (m); ¹³C NMR (DMSO-*d*₆, δ ppm): 117.4 (d, J = 11.7 Hz), 120.3, 122.6, 124.2, 131.2, 131.5, 132.1, 132.6, 133.0, 142.2, 148.4, 162.3, 161.1, 162.4, 193.6 (C=O); IR (film, cm⁻¹): 3465 (v OH br, hydrated SO₃H), 3069 (v CH aromatic), 1662 (v C=O aromatic), 1592 (v C=C aromatic), 1323 and 1082 (v SO₂, SO₃H).

3.4 Membrane fabrication and characterisation

Membrane-casting protocol

The ionomer was dissolved in NMP (15% wt/vol) and the solution was cast onto a clean, A4-sized glass plate and drawn down using an adjustable Gardner knife to give a specific solution film thickness in the range 200 – 500 μm . On evaporation, a dry membrane thickness in the range 40 – 70 μm could then be achieved. The glass plate was placed in a vacuum oven and the rate of heating was controlled so that a final drying temperature of 120 °C was reached over a period of 24 h. The oven was maintained under vacuum at this temperature for a further 3 h and, after cooling to 50 °C, the glass plate and the attached membrane were removed from the oven and soaked in deionised water for 15 min. The membrane could then be peeled readily from the glass surface.

Ion-exchange capacity (IEC), equivalent weight (EW) and degree of sulfonation (DS)

Experimental details for these analyses are given in an earlier publication.³⁷ In the present work, results for ionomers **3a**, **3b**, **3u** and SPEEK are given in Table 1.

3.5 Evaluation of membrane performance in a direct-methanol fuel cell

Anode and cathode electrodes

Commercial grades of a proprietary bonded catalysed substrate (BCS) were used for single cell DMFC tests, as described more fully in an earlier publication.³⁷

Membrane pre-treatment

Membrane samples were soaked in 1M sulfuric acid for 16 h and then thoroughly rinsed with deionised water. The surface water was removed using filter paper.

Membrane-electrode assembly (MEA)

An edge-seal was attached to either side of the membrane by hot-pressing (10 psi) at 90 °C for 2 min. The edge-protected membrane was sandwiched between anode and cathode BCS electrodes (active electrode area = 2 cm^2) and hot-pressed (50 psi) at 150 °C for 3 min. Hot-pressing was used to soften the membrane and Nafion[®] binder in the catalyst layer to promote good adhesion between the membrane and the electrodes.

Electrochemical measurements

Single cell DMFC performance tests such as limiting methanol-crossover current density, membrane resistance and air polarisation (I - V plots) of the membranes were carried out using an Autolab EcoChemie PGSTAT20 potentiostat with a 10A current booster (EcoChemie BSTR10A). The data were analysed using EcoChemie General Purpose Electrochemical Software v.4.9. Aqueous methanol in the concentration range 1M - 5M at a flow rate of 1 mL min⁻¹ and oxygen in the form of air at atmospheric pressure and at a flow rate of 50 mL min⁻¹ were supplied to anode and cathode, respectively, during fuel cell testing. Full details of the protocols for air polarisation testing, methanol-crossover studies, and membrane resistance measurements are given in an earlier publication.³⁷

4. Conclusions

Semi-crystalline triblock copolymers in which the central block is a linear PEEK chain and the outer blocks are hyperbranched moieties may be synthesised by polycondensation of an aromatic ether-ketone AB₂ monomer in the presence of bis(4-fluorobenzoyl)-terminated PEEK. Sulfonation of the central PEEK block in 96% sulfuric acid, after extraction of a cyclic oligomer fraction originating from the AB₂ monomer, yields non-crystalline ionomers with ion-exchange capacities in the range 1.4 to 1.8 mmol g⁻¹. The ionomers were solution-cast from NMP into tough, transparent, thin-film membranes which were evaluated for direct-methanol fuel cell (DMFC) performance in terms of proton conductivity, methanol diffusion coefficient, limiting current density and maximum power density. This new class of membranes shows substantially higher DMFC performance than a control membrane based on the industry-standard fluorocarbon ionomer Nafion[®] 115.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was supported by the Foreign, Commonwealth & Development Office in the UK through a postgraduate Commonwealth Scholarship to Siva Purushothaman, and by Johnson Matthey plc.

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