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Multiblock sulfonated–fluorinated poly(arylene ether)s for a proton exchange membrane fuel cell

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Abstract

New proton exchange membranes were prepared and evaluated as polymer electrolytes for a proton exchange membrane fuel cell (PEMFC). Sulfonated–fluorinated poly(arylene ether) multiblocks (MBs) were synthesized by nucleophilic aromatic substitution of highly activated fluorine terminated telechelics made from decafluorobiphenyl with 4,4′-(hexafluoroisopropylidene)diphenol and hydroxyl-terminated telechelics made from 4,4′-biphenol and 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone. Membranes with various sulfonation levels were successfully cast from *N*-methyl-2-pyrrolidinone. An increase sulfonated block size in the copolymer resulted in enhanced membrane ion exchange capacity and proton conductivity. The morphological structure of MB copolymers was investigated by tapping mode atomic force microscopy (TM-AFM) and compared with those of Nafion® and sulfonated poly(arylene ether) random copolymers. AFM images of MBs revealed a very well defined phase separation, which may explain their higher proton conductivities compared to the random copolymers. The results are of particular interest for hydrogen/air fuel cells where conductivity at high temperature and low relative humidity is a critical issue.

Keywords: Proton exchange membrane; Morphology; Multiblock copolymers

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are being explored as the technology of choice for clean and efficient energy conversion systems for automobiles, portable applications, and power generation. The primary demands on the hydrated proton exchange membrane (PEM) are high proton conductivity (around 0.1 $\mathrm{S\,cm^{-1}}$), low fuel and oxygen permeability, and high chemical, thermal and mechanical stability. Conventional PEMFCs operating with perfluorosulfonic acid membranes offer quite good performance below 80 °C. However, to decrease the complexity and increase the efficiency and carbon monoxide tolerance of the PEMFC system, there is a strong need for PEMs capable of sustained operation above 100 °C. Unfortunately, the proton conductivity of perfluorosulfonic acid membranes such as Nafion® suffer greatly at low relative humidity condition (below 80%) and at temperatures exceeding 80 °C. Also, the barrier properties of this membrane are usually insufficient when methanol is used as a fuel. These factors, in addition to the high cost of Nafion®, have triggered extensive research for alternative PEM materials, some relying on other species than water for proton conduction [1].

Sulfonated aromatic polymers have been recently studied [2–8] and in some cases showed satisfactory chemical and electrochemical stability for fuel cell applications. Among these polymers, poly(arylene ether sulfone)s containing sulfonate groups have been extensively investigated for high temperature fuel cell application. They are prepared by direct polymerization of the disulfonated activated halide with a bisphenol using a method similar to 'polysulfone' nucleophilic substitution condensation polymerization conditions. These random copolymers display a hydrophilic/hydrophobic phase separated morphology that varies depending on the degree of sulfonation. The conductivity and water uptake of this series of copolymers also increases with degree of sulfonation [9]. However, once the degree of sulfonation reaches 60 mol%, a semicontinuous hydrophilic phase is observed and the membranes swell dramatically, forming a hydrogel that is not useful as a proton exchange membrane.

Segmented multiblock (MB) copolymers are synthesized in order to create 'tailor-made materials' showing a combination of properties of the based homopolymers. The combination of supramolecular phase separation in MB copolymers with self-ordering occurring on a molecular scale can provide interesting properties compared to random copolymers. Multiblock

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copolymers composed of two or more long, contiguous sequences of chemically dissimilar repeat units, are able to spontaneously assemble into a wide variety of nanostructures, spherical or cylindrical micelles, bicontinuous channels, coalternating layers, and complex combinations [19,20].

Genies et al. reported the synthesis of series of sulfonated block polyimides containing sulfonated and unsulfonated blocks and compared their properties with statistical (random) copolyimides [17]. According to this work, the block polyimides had higher water uptake and proton conductivity than the random ones, and concluded that the location of acid moieties along the polymer chain was important. Holdcroft et al. studied the properties of the graft copolystyrenes where sulfonic acid groups were closely packed along the grafts side chains. The comparison of properties of these graft copolymers to the random analogs showed that the proton conductivity of the graft copolymers increased greatly with ion content, whereas the conductivity of the random copolymers was much lower. The authors attributed this result to the morphology difference of the two systems [18].

Previously, we reported synthesis of multiblock copolymers by reacting hydrophilic fluorine-terminated sulfonated poly(2,5-benzophenone) oligomers with hydrophobic hydroxyl-terminated biphenol poly(arylene ether sulfone) [10]. These multiblock copolymers have great potential as proton-exchange membranes due to the expectation that multiblock copolymers can self-assemble into multiphase domain structures on a nanometer scale due to the repulsive interactions between the incompatible blocks.

In this article, we report new multiblock copolymers containing perfluorinated poly(arylene ether) as the hydrophobic segment and highly sulfonated poly(arylene ether sulfone) as hydrophilic segment, with the aim of providing polymeric materials with a highly phase-separated morphology. The phase of the hydrophobic block should enable good mechanical stability under a fully hydrated state whereas the hydrophilic block should provide high proton conductivity. The objective of this work is to produce thermally and hydrolytically stable, flexible membrane films with low methanol permeability and high proton conductivity. We also report a morphology study of these MB copolymers using AFM. All copolymers were characterized in terms of water-uptake and ion-exchange capacity.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich and used as received unless otherwise noted. *N*-Methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO) and *N*,*N*-dimethylacetamide (DMAc) were dried over calcium hydride, distilled under vacuum and stored under nitrogen before use. THF was dried and distilled over sodium. 4,4′-Biphenol was obtained from Eastman Chemical and sublimed before use. The specialty monomer 4,4′-dichlorodiphenylsulfone (DCDPS) was purchased from Aldrich and recrystallized from toluene. The sulfonated comonomer, 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone (SDCDPS) was synthesized in-house from 4,4′-dichlorodiphenylsulfone (DCDPS) according to a method which is reported elsewhere [15]. Decafluorobiphenyl was purchased from Aldrich Chemical Co. and dried under vacuum at 60 °C for 24 h before use. 4,4-Hexafluoroisopropylidenediphenol (bisphenol AF or 6F-BPA), purchased from Aldrich, was purified by sublimation and dried under vacuum.

2.1.1. Membrane preparation

A solution of copolymer in NMP (2 wt%) was prepared and filtered. The filtered solution was cast onto a glass plate and dried on a hot plate. The membranes were detached from the glass plates after they were immersed into deionized water for 5 min. To convert the membranes into the acid form they were immersed into 0.5 M sulfuric acid solution and boiled for 2 h. Finally, the membranes were thoroughly washed with boiling deionized water for 2 h and stored in deionized water.

2.2. Characterization

Conductivity measurements were performed on the acid form of the membranes using a Solatron SI 1280B Impedance analyzer. An impedance spectrum was recorded from 100 KHz to 0.01 Hz. The resistance of the film was taken at the frequency that produced the minimum imaginary response. All the impedance measurements were performed at 30 °C above water with relative humidity ranging from 100 to 20%.

IR spectra were taken on a Perkin–Elmer FT-IR Spectrum GX instrument using an ATR cell. Tapping mode atomic force microscopy (TM-AFM, Digital Instruments, Nanoscope IV) was performed in air. All treated samples were allowed to equilibrate by exposure to 100% relative humidity at 30 °C for at least 24 h before testing. The samples were then imaged immediately at ambient condition.

Molecular weights were determined by gel permeation chromatography (GPC) (Waters, Breeze system) system consisting of three HT styrogel columns and a refractive index detector using NMP as the mobile phase at 60 °C. Approximate molecular weights were calculated from a calibration plot constructed with polystyrene standards.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Unity 400 instrument operating at 399.952, 100.578 and 145.783 MHz, respectively, in $CDCl_3$ or DMSO-d_6.

Percent water absorption of the membranes at 30 °C was determined by the following procedure; the wet membranes were equilibrated at 30 °C for 24 h, removed and blotted to remove surface water droplets, then quickly weighed. The dry weight of membrane was determined by weighing the membranes after vacuum drying at 120 °C for 24 h. The percent water absorption was calculated using the equation, water absorption $(\%) = (W_{\mathrm{wet}} - W_{\mathrm{dry}})/W_{\mathrm{dry}} \times 100$ where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively.

Glass transition temperatures (T_g) were determined by differential scanning calorimetry, using a Perkin–Elmer DSC 7 instrument at a heating rate of 20 °C min^{-1}, under a stream of

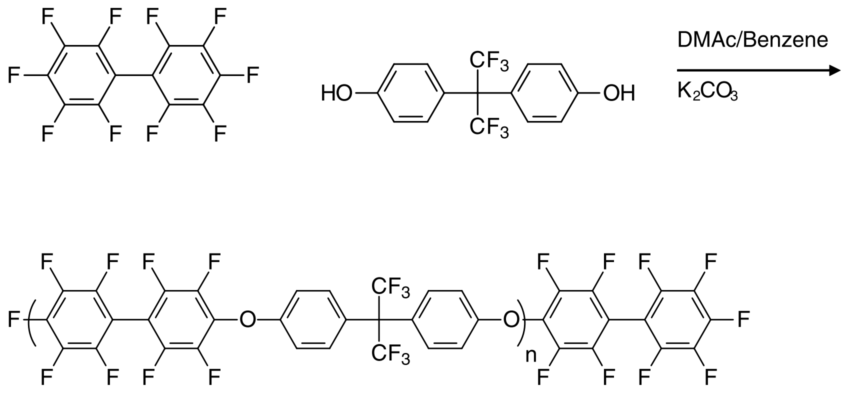

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Fig. 1. Decafluorobiphenyl-terminated poly(arylene ether)s.

nitrogen. Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TGA 7 thermogravimetric analyzer at 10 °C min^{-1} in air and nitrogen.

Water contact angle measurement was carried out using a Rame–Hart goniometer. Samples were treated with boiling 0.5 M sulfuric acid solution for 2 h and washed with boiling deionized water and stored in deionized water. The fully hydrated membranes were napkin dried to remove surface water before mounting on the stage. Numbers reported are advancing contact angles.

*2.3. Synthesis of telechelic hydrophobic oligomer **1***

A typical polymerization procedure was as follows; decafluorobiphenyl (3.007 g, 9.0 mmol) and 6F-BPA (2.689 g, 8.0 mmol) were dissolved in DMAc (40 mL) (to make a 14% (w/v) solid concentration) and benzene (4 mL) in a reaction flask equipped with a nitrogen inlet and magnetic stirrer. The reaction mixture was stirred until completely soluble and then an excess of K_2CO_3 (3.31 g, 24 mmol) was added. The reaction bath was heated to 120 °C during 2 h and kept at this temperature for 4 h. The mixture was precipitated into 200 mL of acidic water/methanol (1:1 in volume fraction). It was then filtered and successively washed with deionized water. Drying of the product at 80 °C under vacuum gave essentially a quantitative yield of white polymer **1**. ^{1}H NMR ($CDCl_3$): δ 7.10(d, 2H), 7.45(d, 2H). ^{19}F NMR ($CDCl_3$): −64.0 (CF_3), −137.5, −152.4 (Ar–F), −137.2, −149.8, −160.2 (Ar–F). ^{13}C NMR ($CDCl_3$): 115.4, 128.8, 132.0, 157.1 (6F-BPA), 118.4, 122.1, 125.8, 129.7 (–CF_3), 103.1, 134.7, 140.1, 143.3, 146.4 (fluorobiphenyl). Molecular weight: M_n = 8.0 K, M_w = 15.9 K with a polydispersity of 1.97.

*2.4. Synthesis of telechelic hydrophilic oligomer **2***

The desired hydroxyl-terminated 100% disulfonated poly (arylene ether sulfone) (BPS) was synthesized from 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone (SDCDPS) and 4,4′-biphenol. Low molecular weight BPS polymers were targeted using an excess of the biphenol as the end-capping group. Into a 100 mL three-necked flask equipped with a mechanical stirrer, nitrogen inlet and a Dean–Stark trap, biphenol (0.3724 g, 2.0 mmol) and 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone (disodium salt) (0.8733 g, 1.77 mmol) were added. Potassium carbonate (0.55 g, 4 mmol) was added and sufficient NMP (7 mL) was introduced to make a 14% (w/v) solid concentration. Toluene (5 mL) was used as an azeotroping agent. The reaction mixture was heated under reflux at 150 °C for 4 h to dehydrate the system. The temperature was then slowly raised to 180 °C to distill off the toluene. The reaction mixture was allowed to proceed at this temperature for 18 h and at 195 °C for another 4 h. It was then cooled to 90 °C and hydroxyl-(phenoxide) terminated product was used without isolation in the next step.

*2.5. Synthesis of multiblock copolymer **3***

The mutiblock copolymers were synthesized from the fluorine-terminated hydrophobic oligomers **1** and the telechelic hydroxy-terminated hydrophilic oligomers **2**. As a typical example, to a preformed solution of polymer **2** with a calculated molecular weight of 5000 g mol^{-1} was added a solution of oligomer **1** (molecular weight of 5000 g mol^{-1}) (1.2921 g, 0.2413 mmol) in NMP (10 mL) followed by 5 mL of benzene. The addition of the **1** solution was done in several portions during 1 h. The reaction mixture was stirred at 90 °C for 2 h and at 110 °C for 24 h. The viscosity of the mixture increased dramatically during the course of the reaction to the point that more NMP (40 mL) was required to lower the viscosity and improve efficiency of stirring. The reaction product was precipitated into 600 mL of water/methanol (1:1 in volume fraction). The product was filtered and first treated in boiling deionized water for 24 h and then treated in boiling THF for 4 h before being dried at 80 °C for 48 h in a conventional oven. The reaction yield was 90–95% (Figs. 1 and 2).

3. Results and discussion

As depicted in Fig. 3, multiblock copolymers were prepared by the reaction of the dialkali metal salt of bisphenol-

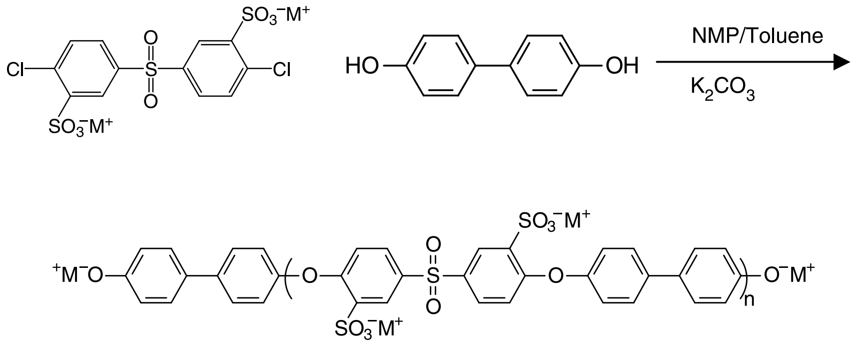

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Fig. 2. Synthesis of hydroxy-terminated sulfonated poly(arylene ether sulfone).

terminated disulfonated poly(arylene ether sulfone)s with decafluorobiphenyl-terminated poly(arylene ether)s in a polar aprotic solvent. The reaction was rapid and produced copolymers with light yellow color in high yield. The dialkali metal salts of bisphenol-terminated disulfonated poly(arylene ether sulfone) were generated using 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone and excess amount of biphenol in the presence of potassium carbonate at 180 °C (Fig. 2). By controlling the amount of biphenol monomer, samples with target molecular weight of 2, 3, 5 and 15 K was prepared. The sulfonated copolymers were used in the next step without isolation. Similarly, decafluorobiphenyl-terminated poly(arylene ether)s were synthesized using 6F-BPA and excess amount of decafluorobiphenyl in DMAc–benzene mixed solvent (Fig. 1). It is known that perfluoroaromatic monomers are highly reactive toward the nucleophilic aromatic substitution reaction and high molecular weight polymers form at relatively low temperature and short periods of time [11–13]. Several fluorinated oligomers were synthesized with molecular weights ranging from 2 to 60 K. Low molecular weight samples formed white powder-like products after isolation, whereas the high molecular weight sample formed white fibrous material. The molecular structure of polymer **1** was confirmed by ^{19}F NMR in $CDCl_3$, and compared with 6F-BPA and decafluorobiphenyl. Fluorine NMR spectrum of high molecular weight polymer **1** showed two aromatic fluorine signals around −138 and −152 ppm and one around −64 ppm for aliphatic CF_3 groups (Fig. 4). Fluorine NMR spectra for low molecular weight fluorine-terminated **1** revealed more details about terminal groups. Peaks at −150 and −160 ppm were assigned to fluorine groups on the terminal phenyl ring of low molecular weight oligomers of **1** and were used to determine their absolute number average ($\bar{M}_n$) molecular weight (Fig. 5).

Reaction of the fluorinated oligomer **1** with preformed sulfonated **2** proceeded rapidly evidenced by the sharp increase in viscosity of reaction solution mixture in the first 1–2 h. Dilution of reaction mixture had little effect on lowering the viscosity of the solution. Products after isolation were treated in boiling water and boiling THF separately, in order to purify the product from unreacted starting oligomers. Multiblock copolymers **3** formed transparent films when cast from solution. The films were quite flexible when fully hydrated and became somewhat brittle as they dried out. These films were tested for ion exchange capacity by titrating with sodium hydroxide standard solution after ion exchange with sodium sulfate (Table 1). The multiblock copolymers had high water uptake both in salt and acid form. Conductivity of these materials in their fully hydrated form in liquid water at 30 °C showed values between 0.08 and 0.32 S cm^{-1} (Table 1).

FT-IR has been used to analyze characteristic bands corresponding to the sulfonated groups in sulfonated poly(-arylene ether) sulfones random copolymers [4]. The successful introduction of the sulfonate groups was confirmed by FT-IR spectra (Fig. 6), where strong characteristic peaks at 1027 and 1097 cm^{-1} assigned to symmetric and asymmetric stretching of sulfonate groups were observed for all copolymers. The densities of these two peaks increased as the ratio of sulfonated

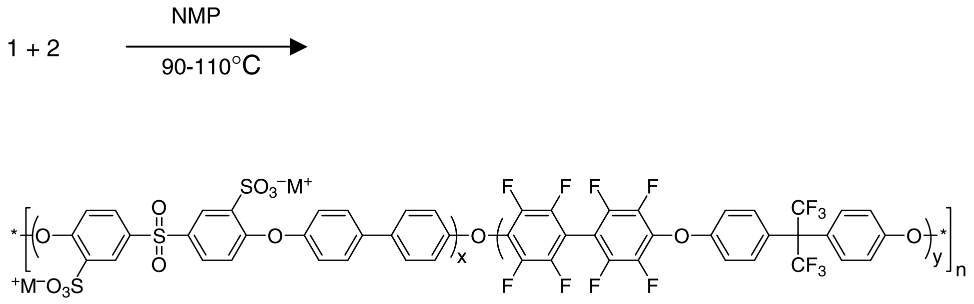

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Fig. 3. Multiblock structure.

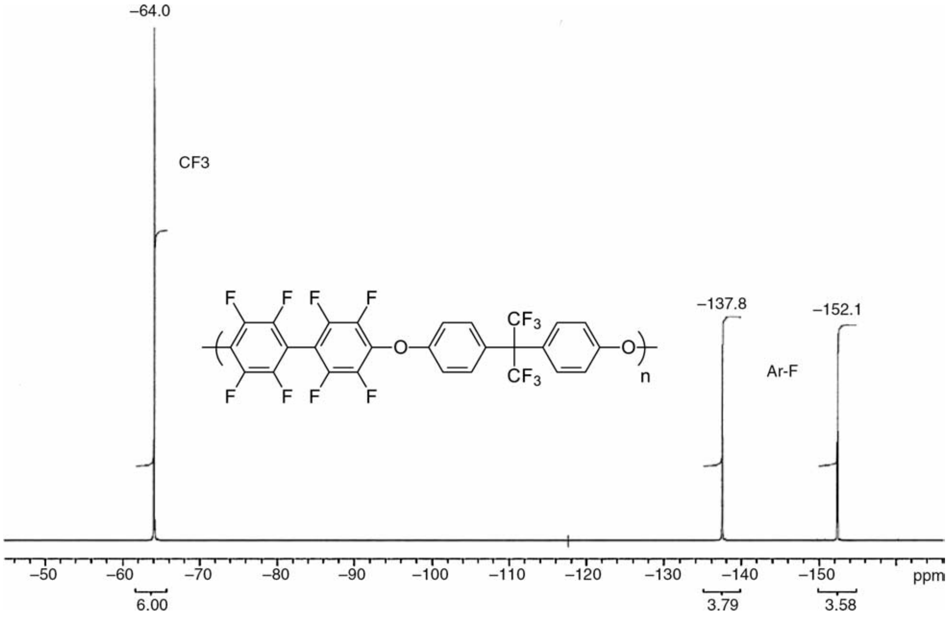

Fig. 4. Fluorine NMR of high molecular weight **1**.

block to fluorinated block increased in the multiblock copolymers.

Glass transition temperature for high molecular weight perfluorinated homopolymer **1** was measured by DSC and determined to be around 175 °C. However, detection of T_g's for the multiblock copolymers was not easy, possibly due to the interference of two separate phases. The thermal stability of the high molecular weight polymer **1** and multiblock copolymers were investigated by TGA. The sulfonated multiblock samples were pre-heated at 150 °C for 20 min in the TGA furnace to remove the moisture. Then, the dynamic TGA experiments were run from 50 to 700 °C at a heating rate of 10 °C min^{-1} under nitrogen or air. High molecular weight perfluorinated **1** showed a 5% weight loss above 475 °C both under nitrogen and air. The TGA traces for the salt and acid form multiblock are compared in Fig. 7. The weight loss for the salt form at around

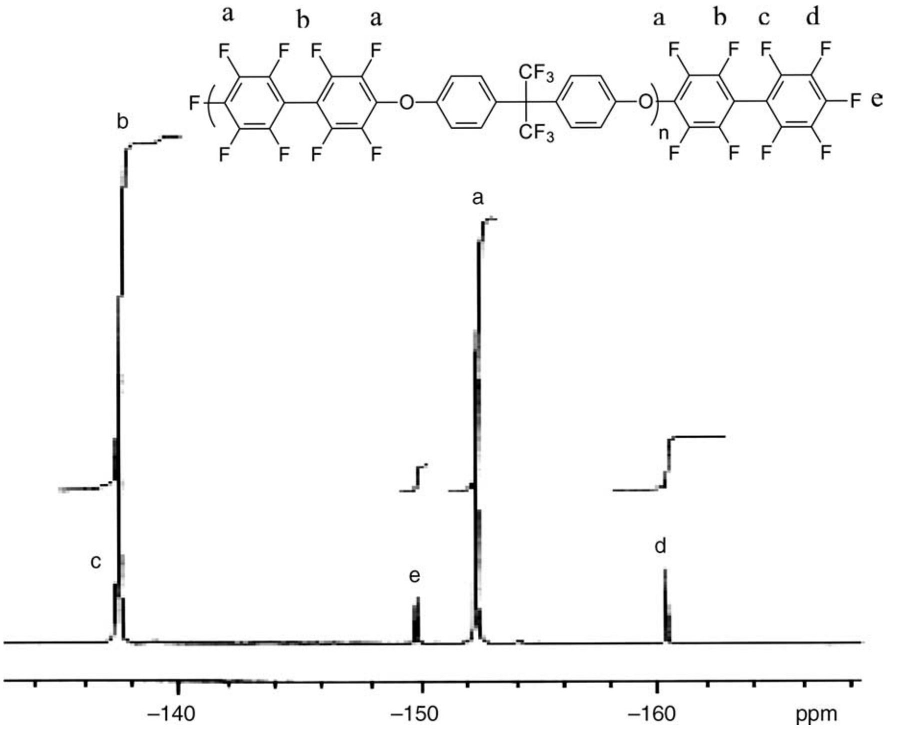

Fig. 5. Fluorine NMR of oligomer **1**.

Table 1
Characterization of multiblock copolymers

Sample	Block size (kg mol^{-1})[a]		IEC (mequiv. g^{-1})[b]		Water uptake (%)	Conductivity[c] (S cm^{-1})
	S	F	Calcd	Exp.		
MB-229	5	2.8	2.05	2.29	470	0.32
MB-150	5	5	1.55	1.50	130	0.12
MB-095	3	5	1.17	0.95	40	0.08
MB3	3	3	1.50	1.47	150	0.16
MB2	2	2	1.42	1.69	110	0.15
Nf-1135	–	–	–	0.89	38	0.10

[a] Target value, (S) represents the sulfonated block and (F) represents the fluorinated block.
[b] Samples were acidified in 0.5 M boiling sulfuric acid for 2 h and boiling deionized water for 2 h.
[c] Measured at room temperature in liquid water.

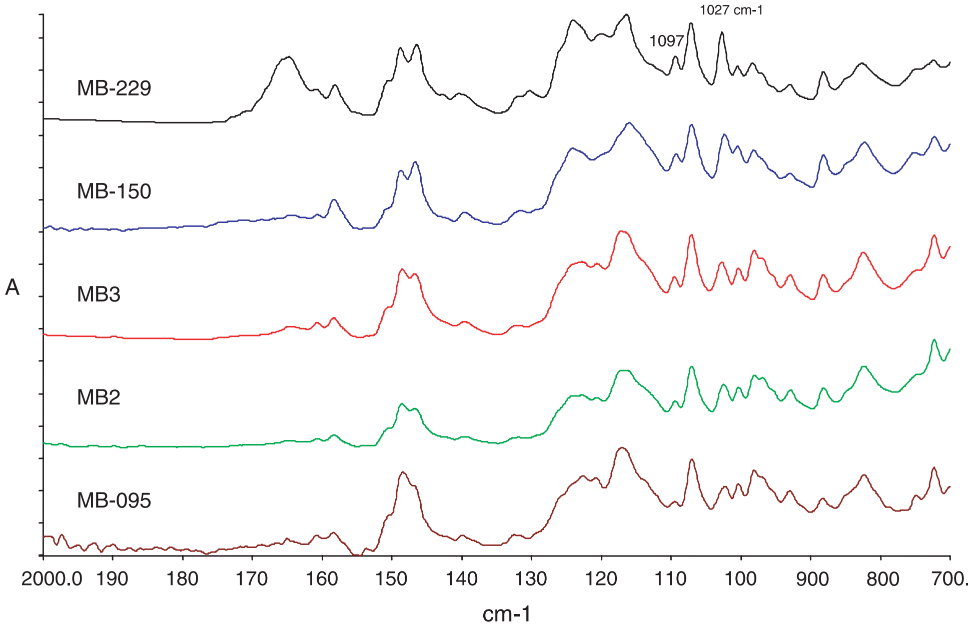

Fig. 6. Influence of the relative size of sulfonated block on FT-IR of MB copolymers (sulfonated block size decreases from top to bottom).

500 °C was assigned to the degradation of the polymer chain. The acid form MB showed an initial weight loss of around 400 °C and the 5% weight loss occurred around 450 °C which was assigned to the loss of sulfonic acid groups. The second weight loss above 500 °C was assigned to the thermal degradation of the main polymer chain.

Fig. 8 shows the representative surface morphology of Nafion 112, BPSH-40 and MB-150 derived from TM-AFM. BPSH-40 is a poly(arylene ether) sulfone random copolymer containing 40% sulfonated and 60% unsulfonated monomer [14]. All TM-AFM micrographs shown here were taken under partial hydration. Images from Nafion 112 and BPSH-40 suggest that the hydrophilic groups aggregate as isolated domains with some local connection of hydrophilic domains as evidenced by the proton exchange membranes' good conductivity. On the other hand, multiblock copolymer MB-150 showed a very well defined phase separation and a distinct morphological architecture compared to the random

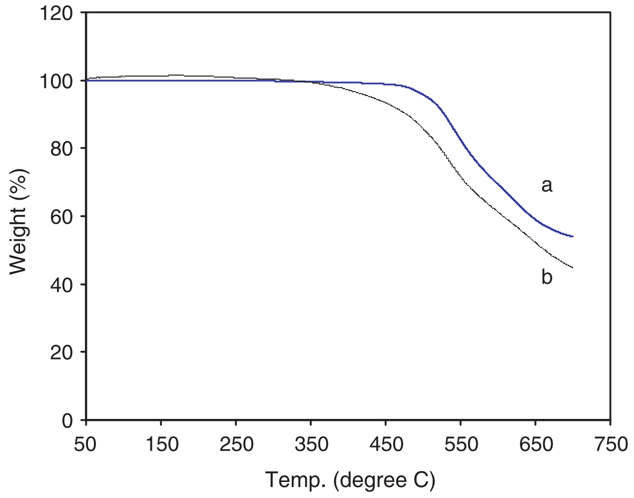

Fig. 7. TGA traces of MB-150 in the salt form (a) and acid form (b) (under N_2).

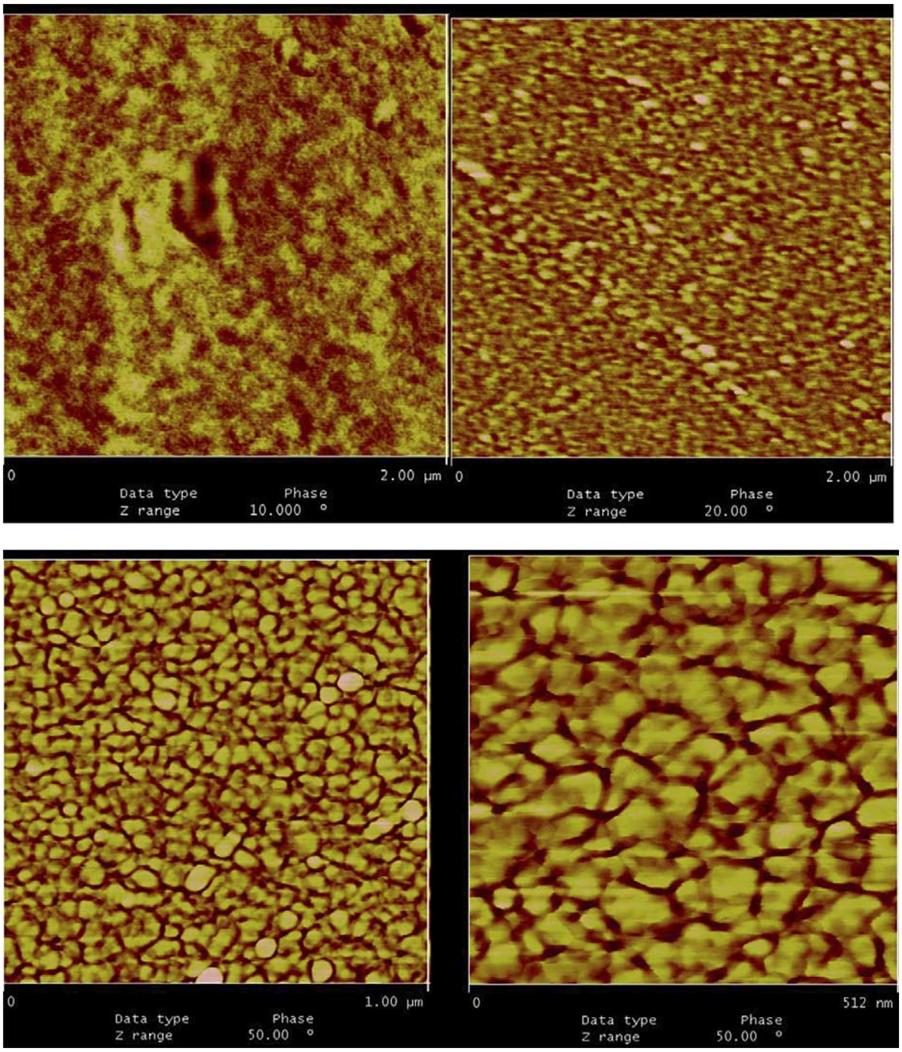

Fig. 8. AFM tapping phase image for Nafion 112 (upper left), BPSH-40 (upper right) and multiblock MB-150 (bottom images).

copolymers. Existence of well-connected hydrophilic domains is most likely the reason for high proton conductivity of the multiblock copolymers compared with their random copolysulfone counterpart.

Sulfonated poly(arylene ether sulfone) and the fluorinated poly(arylene ether) are two segments with high hydrophilicity and hydrophobicity, respectively. By the introduction of these segments into the multiblock copolymers, a significant change in the surface properties of the copolymer was expected. The surface properties of thin films of the multiblock copolymers cast on a glass plate were investigated by water contact angle measurements. The air side of the multiblock membranes showed a substantial increase water contact angles ($\theta_A = 75 \pm 3°$) compared to non-fluorinated sulfonated poly(ether sulfone) random copolymer ($\theta_A = 60 \pm 3°$) of similar IEC value in their fully hydrated form. The same measurement on the glass side of the MB membranes demonstrated low water contact angle ($\theta_A = 50 \pm 3°$) meaning that the fluorinated segments are able to enrich the air surface side and increase the hydrophobicity of the membranes. Water contact angle θ_A of the air and glass side of cast Nafion was 80° (±3°). This observation indicated the combination of properties in the multiblock copolymers resulting from migration of perfluorinated blocks to air side and sulfonated blocks to glass side. XPS studies of sulfonated poly(ether sulfone) random copolymers containing 6F-

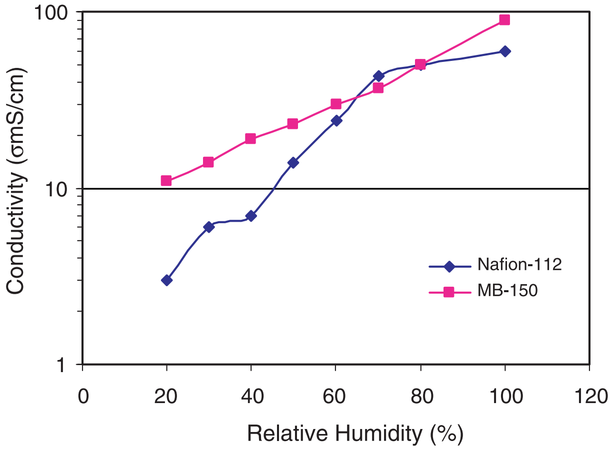

Fig. 9. Influence of relative humidity on proton conductivity at 30 °C.

bisphenol—a monomer instead of biphenol showed that the air-contacting surfaces of these materials have significant surface fluorine enrichment compared to the theoretical bulk fluorine content [16]. The glass-contacting surface was found to have relatively constant fluorine content, consistent with the calculated bulk membrane fluorine content. These results are attributed to the low surface free energy of the hexafluoroisopropylidene moiety, which provides a thermodynamic driving force for the self-assembly at the air–polymer interface.

Fig. 9 displays the effect of relative humidity on proton conductivity for the MB-150 and Nafion 112. As expected, the proton conductivity for both the MB-150 and Nafion decreased exponentially as the relative humidity decreased. However, the MB-150 exhibited higher proton conductivities than Nafion at low relative humidity. This may be attributed to the existence of nano-structure morphology forming sulfonated hydrophilic domains surrounded by fluorinated hydrophobic segments as supported by AFM data.

4. Conclusions

Multiblock copolymers containing hydrophilic disulfonated and hydrophobic fluorinated blocks were successfully prepared by a polycondensation reaction between phenoxide-terminated disulfonated poly(ether sulfone)s and fluorine-terminated poly(arylene ether)s. Several multiblock copolymers were synthesized by varying the size of sulfonated and fluorinated segments. Transparent films cast from NMP solution which had ion exchange capacities up to 2.2 mequiv. g^{-1} and showed water uptake ranging from 40 to more than 400%. AFM phase images showed that the multiblock copolymers form a distinct morphological structure compared with the random copolymers such as BPSH or Nafion. These multiblock membranes showed proton conductivity up to 0.32 S cm^{-1}.

Acknowledgements

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