Synthesis and Characterization of Ionic Conducting Sulfonated Polybenzimidazoles

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ABSTRACT: By copolymerization of the disodium-2,2′-disulfonate-4,4′-oxydibenzoic acid (SODBA), the 4,4′-oxybis(benzoic acid) (OBBA) with the bis 3,4-(diaminophenyl)sulfone (BDAPS), a series of high molecular weight sulfonated polybenzimidazoles (sPBI) were prepared by varying the ratio of monomers SODBA/OBBA. Polymers with ion exchange capacity (IEC) ranging from 0 to 3.2 meqH$^+$/g were obtained. The chemical structure of the sPBI was confirmed by NMR, Fourier-transform infra-red (FTIR). Although the sPBI display a very poor solubility in organic solvents, they are, in the ammonium salt form, soluble in polar aprotic solvents such as DMF, NMP, or DMSO. Tough and ductile membranes from solution casting method were prepared. The water uptake and the ionic conductivity were determined at 30 and 90 °C. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1732–1742, 2010

KEYWORDS: fuel cell; membrane; polycondensation; polyelectrolyte; sulfonated polybenzimidazole

INTRODUCTION Over the last decade, considerable interests have been focused on the new clean energy sources. Because of their high energy efficiency, the hydrogen fuel cell is one of the most attractive technologies. However, before to be integrated as power source in the future electric vehicles, the performances and the durability at high temperatures (>100 °C) of one major component of this fuel cell, namely, the electrode membrane assembly (MEA) still needs to be improved. In other words, the design of ionic conducting polymers with improved properties is of a major importance. Indeed, if the sulfonated perfluoro polymer membranes[1] display very good electrochemical properties, its stability appears rather limited at high temperatures. On the other hand, a number of aromatic polymers, such as polyimides,[2,3] polysulfones,[4,5] polybenzoxazoles,[6] poly(ether ether ketone)s,[7,8] were intensively studied as an alternative solution. The design of ionic conducting membranes from these polymers deals mainly with sulfonic acid groups containing macromolecular structures, which can be obtained either by postsulfonation[9–12] or by polymerization of sulfonated monomers.[2,13–17] Although the first method is very convenient because many polymers potentially interesting are commercially available, however, it is rather difficult to control precisely the amount of grafted sulfonic acid groups and their position along the macromolecular backbone. Conversely, for the second approach, the sulfonation extent of polymers is, in general, easier to control because the sulfonic acid groups form part of the chemical structure of at least one of the monomers involved in the polymerization reaction. Also, depending on the type of polymers synthesized, this route allows obtaining block copolymers presenting both hydrophilic and hydrophobic sequences.[18] Concerning the synthesis of sPBI these different approaches were considered. The sulfonation was carried on either by a thermal treatment of sulfuric acid doped PBI,[19–22] or by N alkylation of the imidazole ring.[23–28] sPBI preparation by the polymerization of sulfonated monomers was first reported by Uno et al.[29] and later by Arnold and coworkers,[30,31] but without connection with fuel cell membranes. More recently, other research groups have used this approach for the synthesis of sPBI for fuel cell membrane application.[32–39] In a similar way, McGrath and coworkers[40] have synthesized sulfonated poly (arylene ether benzimidazole) copolymers via a nucleophilic aromatic polycondensation. Finally, an original route to obtain protonic conducting PBI membranes consists in doping PBI with acid compounds such as phosphoric acid[14,41–45] giving ionic conducting membranes with good performances at high temperatures.

As a part of our continuing research on the synthesis of ionic conducting aromatic heterocyclic polymers, the synthesis of sPBI from SODBA and BDAPS monomers was addressed in this work. In varying the ratio SODBA/ODBA monomers, different sPBI were prepared as random copolymers or

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sequenced copolymers with an average sulfonated block length of 5 or 10 repeat units. Polymer blends involving the unsulfonated PBI and the 100% sPBI were also investigated.

EXPERIMENTAL

Materials

4,4′-Oxydibenzoic acid (ODBA) from Atochem was washed with hot tetrahydrofuran (THF) before use. The 30% fuming sulfuric acid and the sodium chloride were purchased from Aldrich. The bis-3,4-diaminophenylsulfone (BDAPS) was kindly provided by Konishi Chemical Ind. Co. and recrystallized in acetonitrile before use. Benzoic acid and 1,2-benzenediamine were purchased from Aldrich and purified by sublimation. Dimethylsulfoxide (DMSO) was purchased from VWR Chemical Co. Eaton reagent was prepared from phosphorous pentoxyde and methanesulfonic acid (Aldrich).

Methods

NMR spectra were recorded on a Bruker AC250, with frequencies of 250 MHz and 62.9 MHz for ^{1}H and ^{13}C analysis, respectively. The solvent used was DMSO-d_6 with tetramethylsilane (TMS) as internal reference. Fourier transformed infra-red (FTIR) spectra were performed on a NICOLET 20SX spectrophotometer. Samples were prepared as KBr pressed pellets. Thermogravimetric analyses (TGA) were achieved with a TA instrument 2950 TGA. The analyses were done with a heating rate of 10 °C/min, from 20 to 600 °C. The inherent viscosity was determined at 30 °C from a 0.5 g/dL polymer solution in H_2SO_4 using an Ubbelhode viscometer. Size exclusion chromatography (SEC) was performed on a Waters apparatus equipped with 2 Plgel Mixed-D columns and refractive index detector. DMF containing 0.05 mol/L of LiBr was used as the solvent at a flow rate of 1.0 mL/min at 70 °C. Polymer solution was filtered through a 0.45-μm PTFE. Calibration was made with polystyrene standards. The titration of polymer acid functions was done as follows: A piece of 30 mg of polymer membrane were immersed during 24 h in 20 mL of a 2 M NaCl aqueous solution. Then titration was performed with a 0.05 M NaOH aqueous solution, using the Radiometer Analytical Titramaster 880 ABU52 instrument. Water uptake of membranes was measured by immersing for 24 h three samples (around 20 mg each) of membrane in a water bath. Afterward, each sample was taken out, quickly wiped with tissue paper and weighed on a microbalance. The water uptake can then be calculated as the ratio (in weight) of adsorbed water on the dry sample weight. The water uptake values reported correspond to the average value of the three samples. For the conductivity measurement, films were previously hydrated for 24 h at ambient temperature in liquid water, sandwiched between two platinum electrodes and then placed in a sealed cell under controlled atmosphere. The complex impedance method was used to measure the proton conductivity of membranes. Frequency dependence of the cell impedance was measured at 5 mV over the frequency range from 100 Hz to 10 MHz with a Schlumberger SI 1255 frequency response analyser.

SODBA Monomer Synthesis

In a 500 mL three-necked round-bottom flask equipped with a magnetic stirrer, a condenser, a nitrogen inlet/outlet and containing 150 mL of 30% fuming sulfuric acid, and 75 g of ODBA (0.29 mol) were added. The resulting reaction mixture was then heated 2 h at 110 °C. The final brown homogeneous solution was cooled down to room temperature before to be slowly poured in NaCl saturated aqueous solution. The resulting precipitate was filtered off and recrystallized twice in water. After drying under vacuum for 20 h at 120 °C, 102 g of expected product as white needle-like crystals were obtained. Yield: 76%. IR (KBr, cm^{-1}): 3474, 2941, 1719 (CO_2H), 1251, 1084, 1031 (SO_3Na), 1155 (Ph—O—Ph), 936, 898, 767, 704 (1,2,4-trisubstituted benzene), 619 (C—S). ^{1}H-NMR (DMSO-d_6, 20 °C, ppm): 8.44 (d, $J = 2.1$ Hz, 2H), 7.96 (dd, $J = 8.4$, 2.1 Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H). NMR ^{13}C (DMSO-d_6, 20 °C, ppm): 166.36, 156.93, 137.50, 132.31, 129.75, 125.45, 120.46.

Eaton Reagent Preparation

A total of 3 g of phosphorous pentoxide (P_2O_5) and 20 mL of methanesulfonic acid were placed in a 50 mL flask with a magnetic stirrer. The mixture was stirred at 40 °C till complete dissolution of P_2O_5. This mixture was used as a solvent for both polymerization and synthesis of benzimidazole model compounds, and prepared just before use.

Model Compounds Synthesis

2,2′-Disulfo-4,4′-bis(2-benzimidazole)-diphenylether (1)

1.297 g of SODBA (2.806 mmol), 0.607 g of 1,2-benzenediamine (5.612 mmol), and 10 g of Eaton reagent were placed into a 50 mL three-necked round-bottom flask equipped with a reflux condenser, a nitrogen inlet/outlet, and a magnetic stirrer. The nitrogen flow was very weak to avoid the sublimation of 1,2-benzenediamine. The reaction mixture was heated to 130 °C and kept at this temperature for 2 h. The reaction solution was then poured in 100 mL of water, resulting in a very thin precipitate. Because of difficulties encountered for the filtration of the very thin formed powder, centrifugation was preferred to isolate the compound, which was then washed carefully with water and centrifuged again to give 1.04 g of a clear pink powder that was dried under vacuum at 120 °C for 15 h. Yield: 66%. IR (KBr, cm^{-1}): 3430 (NH), 1633, 1599, 1286 (benzimidazole), 1253, 1085, 1029 (SO_3), 616 (C—S), 1155 (Ph—O—Ph). ^{1}H-NMR (DMSO-d_6, 20 °C, ppm): 8.72 (d, $J = 2.2$ Hz, 2H), 8.13 (dd, $J = 8.5$, 2.2 Hz, 2H), 7.63 (q, $J = 3.0$ Hz, 4H), 7.25 (q, $J = 3.2$ Hz, 4H), 7.13 (d, $J = 8.5$ Hz, 2H). ^{13}C-NMR (DMSO-d_6, 20 °C, ppm): 156.96, 150.63, 139.52, 138.72, 129.03, 127.03, 124.20, 123.14, 122.56, 115.06.

4,4′-Bis(2-benzimidazole)-diphenylether (2)

1.789 g of ODBA (6.928 mmol), 1.498 g of 1,2-benzenediamine (13.856 mmol), and 13 g of Eaton reagent were placed into a 50 mL three-necked round-bottom flask equipped with a reflux condenser, a nitrogen inlet/outlet, and a magnetic stirrer. The nitrogen flow was very weak to avoid the sublimation of 1,2-benzenediamine. The temperature was slowly increased to 130 °C and the reaction mixture was kept for 1 h. The clear reaction mixture obtained was then poured in 100 mL of water. The precipitate obtained was filtered off and washed twice with water, and once in ethyl acetate. After drying under vacuum 20 h at 120 °C, 2.50 g of expected product as clear brown powder was obtained. Yield: 90%. IR (KBr, cm^{-1}): 3417, 3144 (NH), 1626, 1605, 1539, 1292 (benzimidazole), 1145, 1068 (Ph—O—Ph). ^{1}H-NMR (DMSO-d_6, 20 °C, ppm): 8.30 (d, J = 8.4 Hz, 4H), 7.67 (q, J = 3.0 Hz, 4H), 7.35 (d, J = 8.4 Hz, 4H), 7.28 (q, J = 3.0 Hz, 4H). ^{13}C-NMR (DMSO-d_6, 20 °C, ppm): 157.88, 150.86, 139.20, 128.82, 125.67, 122.47, 119.50, 115.18.

2,2′-Diphenyl-5,5′-sulfonyldibenzimidazole (3)

2.064 g of BDAPS (7.416 mmol), 1.811 g of benzoic acid (14.832 mmol), and 15 g of Eaton reagent were placed into a 50 mL three-necked round-bottom flask equipped with a reflux condenser, a nitrogen inlet/outlet, and a magnetic stirrer. The temperature was slowly increased to 120 °C and the reaction mixture was kept for 1 h. The clear reaction mixture obtained was then poured in 300 mL of water. The precipitate obtained was filtered off and washed twice with boiling water. After drying under vacuum 20 h at 120 °C, 3.12 g of expected product as white powder was obtained Yield: 93%. IR (KBr, cm^{-1}): 3427 (NH), 1631, 1600, 1287 (benzimidazole), 1253, 1183 (SO_2), 616 (C—S). ^{1}H-NMR (DMSO-d_6, 30 °C, ppm): 8.35 (s, 2H), 8.29 (d, 4H), 7.91 (m, 4H), 7.67 (m, 6H). ^{13}C-NMR (DMSO-d_6, 30 °C, ppm): 154.54, 141.04, 138.99, 136.04, 131.32, 129.38, 128.60, 127.26, 121.83, 115.67, 115.61.

Polymer Synthesis

Homo Polymers and Random Copolymers

The typical procedure used to obtain the 50% sulfonated random copolymer is as follows. First the water content of the monomers was determined to avoid the unbalance ratio of the monomers. In a 100 mL three-necked round-bottom flask equipped with a nitrogen inlet/outlet and a mechanical stirrer, 0.960 g of SODBA (2.076 mmol), 0.536 g of ODBA (2.076 mmol), 1.156 g of BDAPS (4.152 mmol), and 25 g of Eaton reagent were introduced. After complete dissolution of the monomers at 80 °C, the temperature of the reaction mixture was gradually increased to 130 °C and maintained for 14 h. Addition of 20 g of solvent was necessary during the reaction to keep the viscosity of solution not too high. Then the reaction mixture was poured in 300 mL of water giving a fiber-like precipitate. The polymer was then crushed. The resulting polymer particles were filtered off and washed several times in boiling water (typically three times) until to get neutral pH of the washing water. The white powder obtained was dried overnight at 120 °C under vacuum to give 2.21 g of polymer (98% yield). The nonsulfonated homopolymer was synthesized following the similar operating conditions. Only the polymerization temperature was changed (110 °C instead of 130 °C).

Sequenced Copolymer

The synthesis of sequenced copolymers involves a two-step reaction: (1) Concerns the preparation of sulfonated oligomers endcapped with diamine functions. (2) Corresponds to chain extension by allowing the reaction of the sulfonated oligomers with the nonsulfonated monomers. As general procedure, the synthesis of the 50% sulfonated copolymer with a targeted average length sequence of five sulfonated repeat units is reported hereafter.

In a 100 mL three-necked round-bottom flask equipped with a nitrogen inlet/outlet and a mechanical stirrer, 1.098 g of SODBA (2.375 mmol), 0.793 g (2.850 mmol) of BDAPS, and 18 g of Eaton reagent were first introduced. After complete dissolution of the monomers at 80 °C, the temperature was increased to 130 °C and maintained for 14 h. The reaction mixture was then cooled to 80 °C and 0.736 g of ODBA (2.850 mmol), 0.661 g of BDAPS (2.375 mmol), and 12 g of Eaton reagent were added. After complete solubilization of the added monomers, the solution was heated again at 130 °C and kept at this temperature for 14 h. The work up to isolate the polymers was the same as for the random copolymers.

Membrane Preparation

Polymer (1.0 g) was dissolved at 150 °C in 15 mL of DMSO containing triethylamine. The solution was stirred overnight, filtered through a Whatman 30 μm filter, and then casted onto a clean glass substrate. The solvent was evaporated at 60 °C overnight under nitrogen flux, and then at 200 °C for 1 h (the temperature was gradually increased from 60 to 200 °C). After cooling back to room temperature, membrane was lifted off the glass plates by immersion in water. To remove the solvent trace, the membrane was dried under vacuum for 5 h at 120 °C, and then immersed in water and methanol. The membrane was then acidified in a 2 M HCl solution for overnight and rinsed thrice with water. A series of thin flexible membranes having a thickness ranging from 20 to 60 μ were obtained following this procedure.

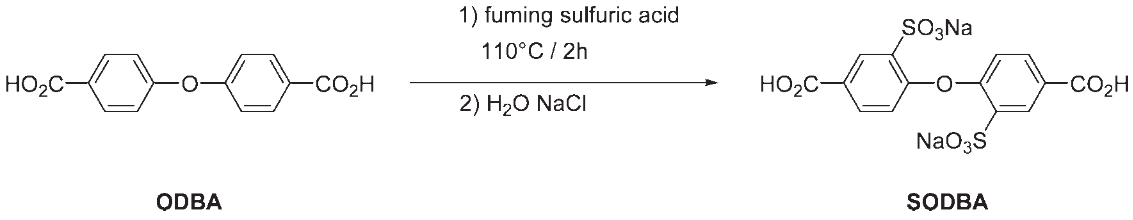
Polymer Blend Membranes

A series of DMSO solution containing both sulfonated homopolymer sPBI100 in the ammonium form and the nonsulfonated polymer nsPBI were prepared. By varying the ratio of the two polymers, blends having different relative IEC were obtained. To prepare membranes from these blend solutions similar aforementioned conditions were used. Transparent membranes were obtained.

RESULTS AND DISCUSSION

Monomer Synthesis

SODBA has been synthesized (Scheme 1) as previously reported by Einsla et al.[6] Only the final work up was slightly different. So the precipitation of the reaction medium in saturated NaCl solution was found a convenient method to isolate the expected product. After two crystallizations in water, polymer grade SODBA monomer was obtained with a quite good yield. The chemical structure of SODBA was confirmed by FTIR and NMR analysis. In comparison with the FTIR spectrum of ODBA, those of SODBA clearly display three new absorption bands at 1251, 1084, 1031 cm^{-1} assigned to the O=S=O stretching vibration of the SO_3Na group. As



SCHEME 1 Synthesis of SODBA.

mentioned in the Einsla's publication, the ^{1}H-NMR showed three peaks in the aromatic region at 8.4, 7.9, and 6.8 ppm. Now taking in consideration the observed coupling effects between the different protons, we can affirm that the sulfonation occurred on the two aromatic rings in the ortho position of the ether bond. The ^{13}C-NMR spectrum was also in good accordance with the expected chemical structure.

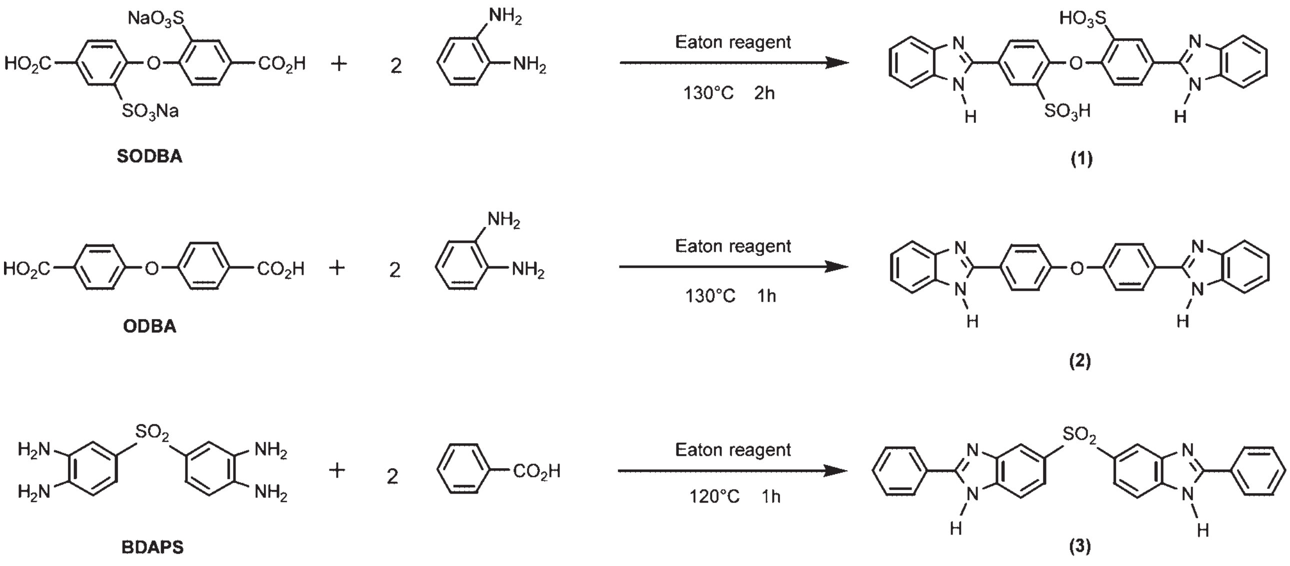
Model Synthesis

The synthesis of model compounds from the three monomers used for the preparation of sPBI and shown Scheme 2 was performed to define the better experimental conditions to obtain high molecular weight fully cyclized PBI. Thereby, it was shown from ^{13}C-NMR study of reaction products, that benzimidazole ring formation in the Eaton's reagent occurs quantitatively at temperature not much that 130 °C. For that, the peak appearance at 156 ppm characteristic of the —NH—C=N— (benzimidazole ring) was followed as well as the total disappearance of peaks around 170 ppm relative to carbonyl of both amide and carboxylic functions. These model compounds were also of particular interest to get data regarding the chemical shifts of ^{1}H and ^{13}C-NMR, which were helpful for the analysis of polymer spectra. On the other hand, we have determined their molecular weights by SEC to estimate the difference between the measured and the true value and to use it for the determination of a corrected number average molecular weight of both sulfonated oligomers and sulfonated polymers. For any of these model compounds, a melting temperature was shown by DSC. Only a T_g at 181 °C for model compound **3** was observed.

Polymer Synthesis

Originally, PBI synthesis was carried out by melt polymerization of aromatic bis diamines with aromatic dicarboxylic acids or derivatives.[46] More recently, Inoue et al.[47] used polyphosphoric acid (PPA), which is known to be a very good solvent for different condensation reactions. However Tomlin et al.[48] reported some problems regarding the synthesis of high molecular weight PBI in PPA. Before the condensation, polymerization is very far advanced, they pointed out the crystallization of low molecular weight oligomers out of PPA. Moreover, PPA is a highly viscous solvent setting a real problem of handling.

For these reasons, we found it was more convenient to use the Eaton reagent[49] for the synthesis of our sPBI as described by Kim et al.[50] In contrast with PPA, Eaton reagent is a low viscous solvent. Furthermore, the polymer can be separated more easily simply by pouring the reaction solution in H_2O, with no need of repeated washing with a basic solution to remove completely the remaining solvent, as it is necessary when polyphosphoric acid is used. The polymers obtained through this process have their sulfonic groups on the acid form. A series of sPBI, listed in Table 1, were prepared from SODBA, ODBA, and BDAPS. So sPBI with an IEC ranging from 0 to 3.20 mequiv./g were obtained. Random copolymers (Scheme 3) were considered as well as



SCHEME 2 Synthesis of model compounds.

TABLE 1 Composition of sPBI Synthesized

				IEC (mequiv./g)		
					Measured by	
Acronym	Structure	% SODBA	% ODBA	Calculated	NMR	Titration
nsPBI	Homopolymer	0	100	0	0	0
sPBI50rand	Random	50	50	1.84	1.84	1.80
sPBI50seq5	Sequenced, 5[a]	50	50	1.84	1.85	2.06
sPBI50seq10	Sequenced, 10[a]	50	50	1.84	1.89	1.98
sPBI75rand	Random	75	25	2.57	2.57	2.46
sPBI75seq5	Sequenced, 5[a]	75	25	2.57	2.55	2.62
sPBI75seq10	Sequenced, 10[a]	75	25	2.57	2.55	2.47
sPBI90rand	Random	90	10	2.96	2.91	2.86
sPBI100	Homopolymer	100	0	3.20	3.20	3.12

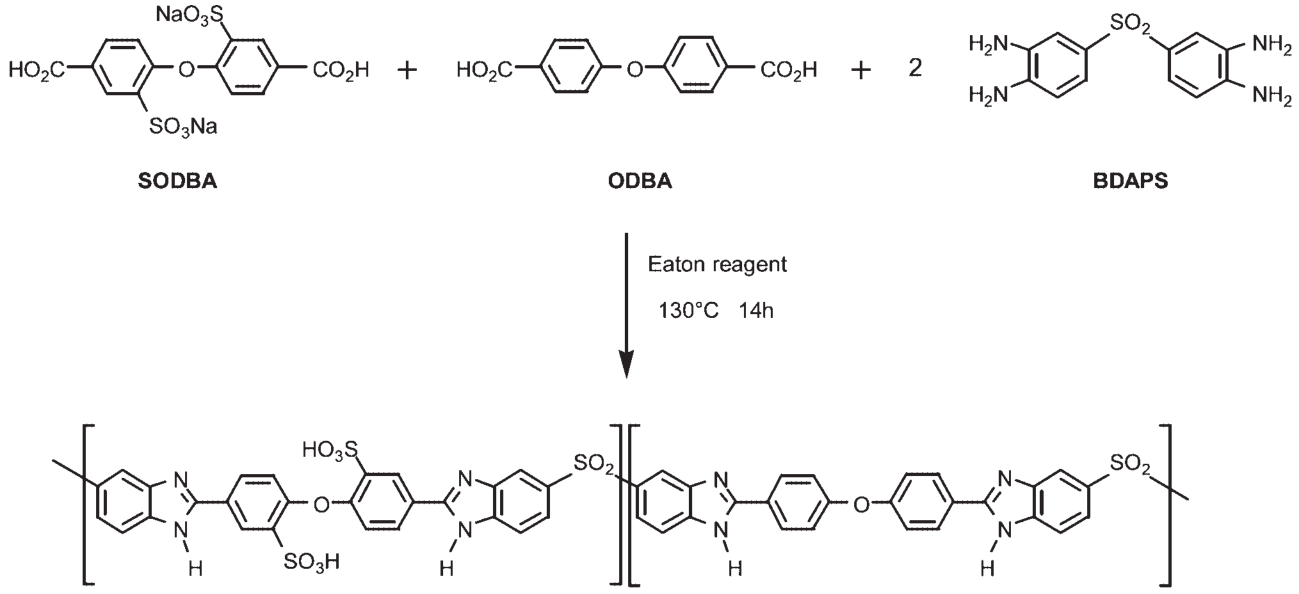
[a] Average number of repeat units of sulfonated sequence of the polymer.

sequenced ones with sulfonated block length of 5 or 10 repeat units (Scheme 4). Afterward, the acronyms s-oligo5 and s-oligo10 were chosen to identify the oligomers having respectively, an average of 5 or 10 sulfonated repeat units. To confirm the structure of the sequenced copolymers, SEC analyses were performed on the sulfonated oligomers prepared in the first step of the synthesis. Considering that the molecular weight values obtained from polystyrene calibration curves were too much different from those expected, we have decided to determine the molecular weight of the model 1 by the same method and in the same conditions to calculate the ratio $M_{n_{exp}}/M_{n_{theo}}$ which was found to be 2.6 and use it to determine an $M_{n_{corr}} = M_{n_{exp}}/2.6$ of the two sulfonated oligomers (see Table 2).

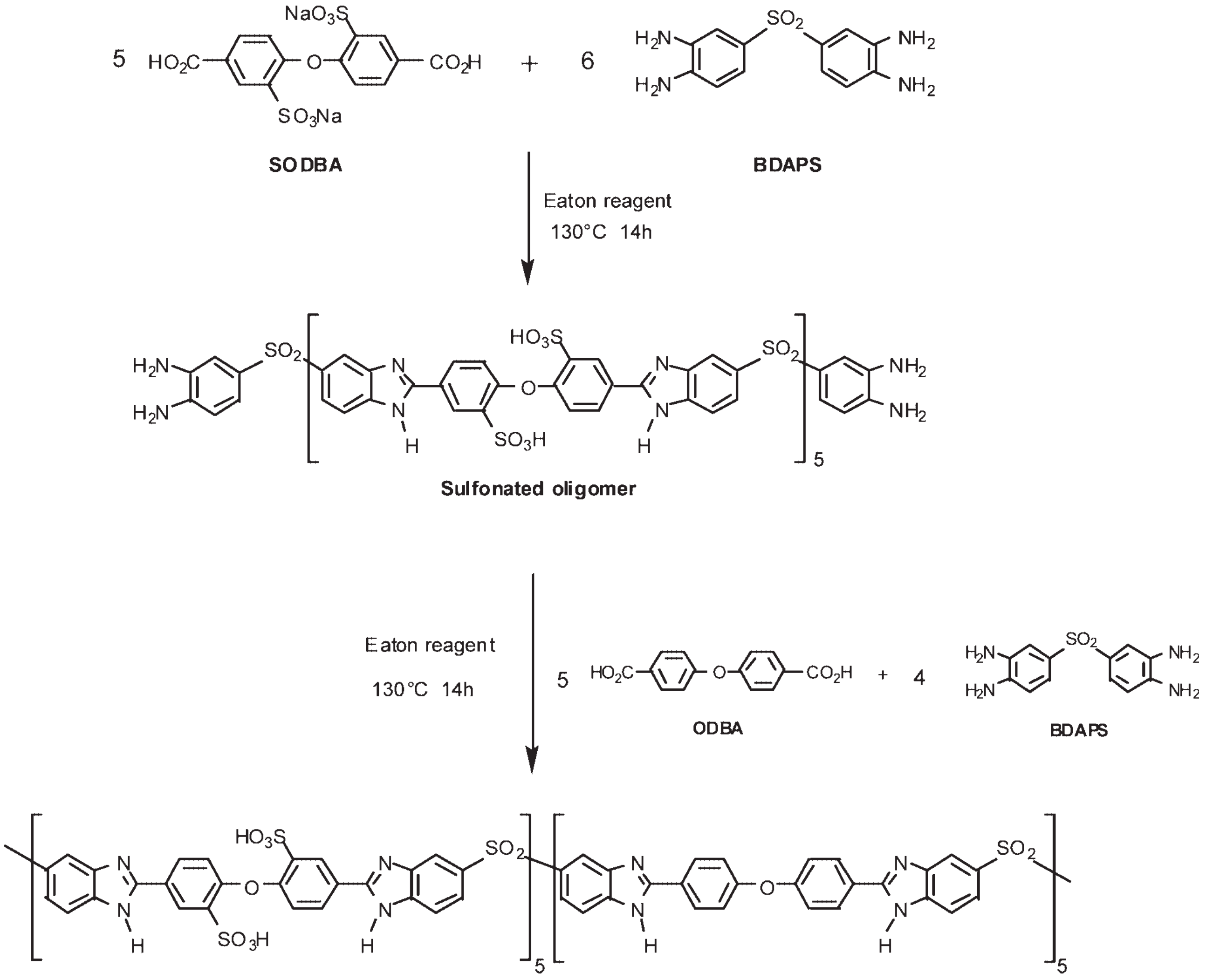
The inherent viscosity (η_{inh}) measurement of the sPBI was also carried out. To prevent ionic interactions concentrated sulfuric acid was used as solvent. The values listed Table 3 are consistent with high molecular weight polymers. An investigation by SEC was also possible using sPBI in lithium sulfonate form because soluble in DMF. The number-average molecular weights ($M_{n_{exp}}$) obtained, varied from 77,000 to 227,000. As for the sulfonated oligomers, such high values cannot be considered as representative values of molecular weights of these polymers. On the other hand, the corrected M_n values calculated from the relation used for the oligomers are more credible (see Table 3).

NMR Structural Characterization

From NMR data of the model compounds, we were able to clearly analyze the ^{13}C spectra of polymers and confirm their structure. As an example, the spectrum of the sulfonated homopolymer sPBI100 is reported Figure 1. As aforementioned, the peak appearing at 154 ppm is characteristic of



SCHEME 3 Synthesis of sPBI by copolymerization of SODBA, ODBA with BDAPS.



SCHEME 4 One pot two-step synthesis route of sequenced copolymer.

one carbon of the imidazole ring, whereas this appearing at 139 ppm corresponds to the carbon bonded to sulfonic acid group. It is of particular interest to notice that the benzimidazole ring on this sPBI possesses two isomers, depending on the position of the *N*—H. This group can be either in para position or in meta position of the sulfone bridging group. Because of the presence in the chain of both isomers, most of the carbon peaks appear in the spectrum as large peaks.

Information regarding the chemical structure of the sPBI can also be obtained from ^{1}H-NMR analysis (Fig. 2). Although the aromatic protons $H_{1,2,3}$ and $H_{1',2',3'}$ of the nonsulfonated and sulfonated units have similar chemical shifts at 8.2 and 7.8 ppm, those corresponding to the protons $H_{4',5',6'}$ of the sulfonated phenyl ring are well distinguished from $H_{4,5}$ of the nonsulfonated phenyl ring. So, the chemical shift of H_5 was found to be at 7.3 ppm, whereas this corresponding to $H_{5'}$ appears at 7.15 ppm. These specific resonance frequencies allowed us to determine the chemical composition of the sulfonated copolymers. The proportion of sulfonated repeat units to the total number of repeat units, also expressed as the sulfonation degree (SD) is given by the equation:

$$\mathrm{SD} = \frac{(\text{Area } 7.15)}{(\text{Area } 7.15) + (\text{Area } 7.3)2} \times 100 \quad (\text{expressed in } \%)$$

The calculated SD of the copolymer sPBI75, for example, was found to be 75%, in good accordance with the target value.

TABLE 2 Molecular Weight Determination of Sulfonated Oligomers

Acronym	$M_{n_{\text{theo}}}$ [a]	$M_{n_{\text{exp}}}$ [b]	$M_{n_{\text{corr}}}$
Model 1	562	1,480	562
s-oligo5	3,400	7,170	2,760
s-oligo10	6,520	12,380	4,760

[a] Calculated from the theoretical molecular structure (g/mol).

[b] Determined from SEC analysis (in polystyrene equivalent g/mol).

TABLE 3 Molecular Weight Determination of SPBI

Acronym	η_{inh} (dL/g)	$M_{n_{exp}}$ [a]	$M_{n_{corr}}$	M_w [a]	$M_w/M_{n_{exp}}$
nsPBI	1.78	117,000	45,000	229,000	1.95
sPBI50rand	1.07	77,000	29,600	177,000	2.30
sPBI50seq5	1.84	165,000	63,500	370,000	2.00
sPBI50seq10	1.80	177,000	68,100	367,000	2.10
sPBI75rand	1.27	114,000	43,800	260,000	2.30
sPBI75seq5	2.11	227,000	87,300	417,000	1.80
sPBI75seq10	1.30	111,000	42,700	230,000	2.10
sPBI90rand	1.11	129,000	49,600	238,000	1.90
sPBI100	1.41	153,000	58,800	307,000	2.00

[a] Expressed in polystyrene equivalent g/mol.

The SD determination of each copolymer is reported Table 1 as equivalent ionic exchange capacity (IEC) value. All these values founded are very close to the theoretical IEC values. These results show the interest to use functionalized monomers to well control the extent of functional groups introduced in the polymer chain.

Titration

The IEC of the polymers synthesized can also be determined by titration. Acidified membranes were cut into small pieces and stirred overnight in a 2 M NaCl solution. The mixture was then titrated with a 0.05 M NaOH solution. The protons of the membrane are very difficult to exchange with the Na^+ ions, so it was very important to wait for the stabilization of the pH-meter before each addition of NaOH. One-inflection titration curves are obtained, and it was possible to determine an experimental value of the IEC from the equivalent volume. These values reported Table 1 are quite in good agreement with the values expected from the monomer feed ratio. However, this experimental determination seems less precise than the NMR characterization. This can be explained by the interactions SO_3H-benzimidazole in the membrane that make the H^+/Na^+ exchange difficult.

Thermal Properties

The thermal stability of the sPBI was studied by TGA. As it can be seen Figure 3, the nonsulfonated PBI do not exhibit any significant weight loss before the degradation of the polymer backbone up to 450 °C, whereas for all the sulfonated PBI, a first weight loss between 350 and 470 °C was observed. This first weight loss can be related to the sulfonic acid group loss of the sPBI. This phenomenon corresponds to a desulfonation reaction. Such analysis can be considered as a simple method to determine the extent of sulfonation of a polymer (see Table 4). However, it is less precise than the proton NMR analysis because of the possible overlapping of the end of temperature domain corresponding to the desulfonation and this due to the polymer backbone degradation.

Based on the TGA analysis in dynamic mode, all the sPBI synthesized exhibit good thermal stability, but this cannot be directly linked with the behavior of the material during a

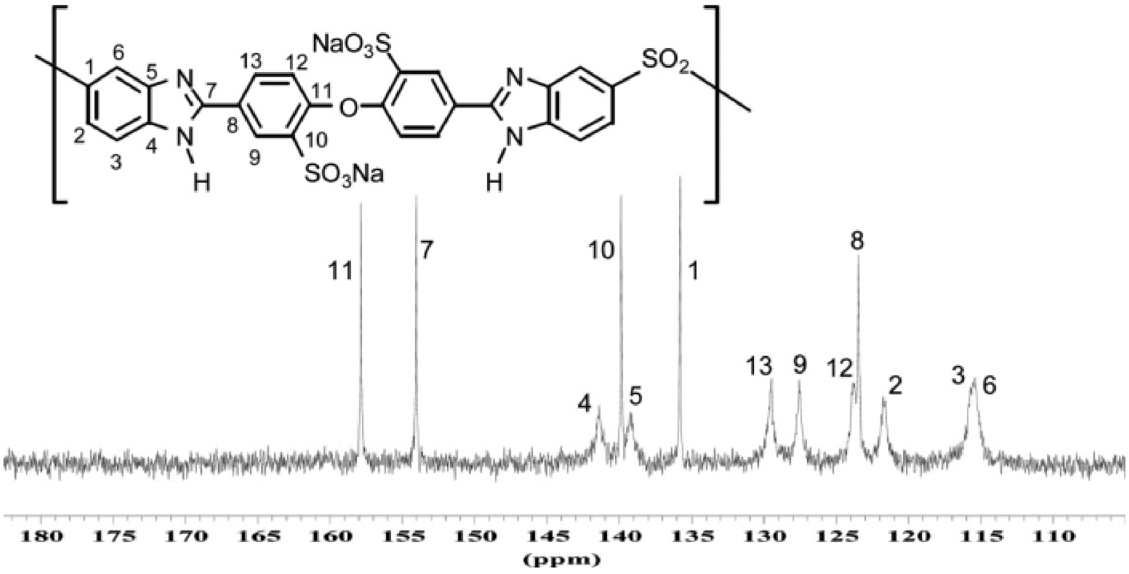


FIGURE 1 ^{13}C-NMR spectra of the sPBI100 homopolymer.

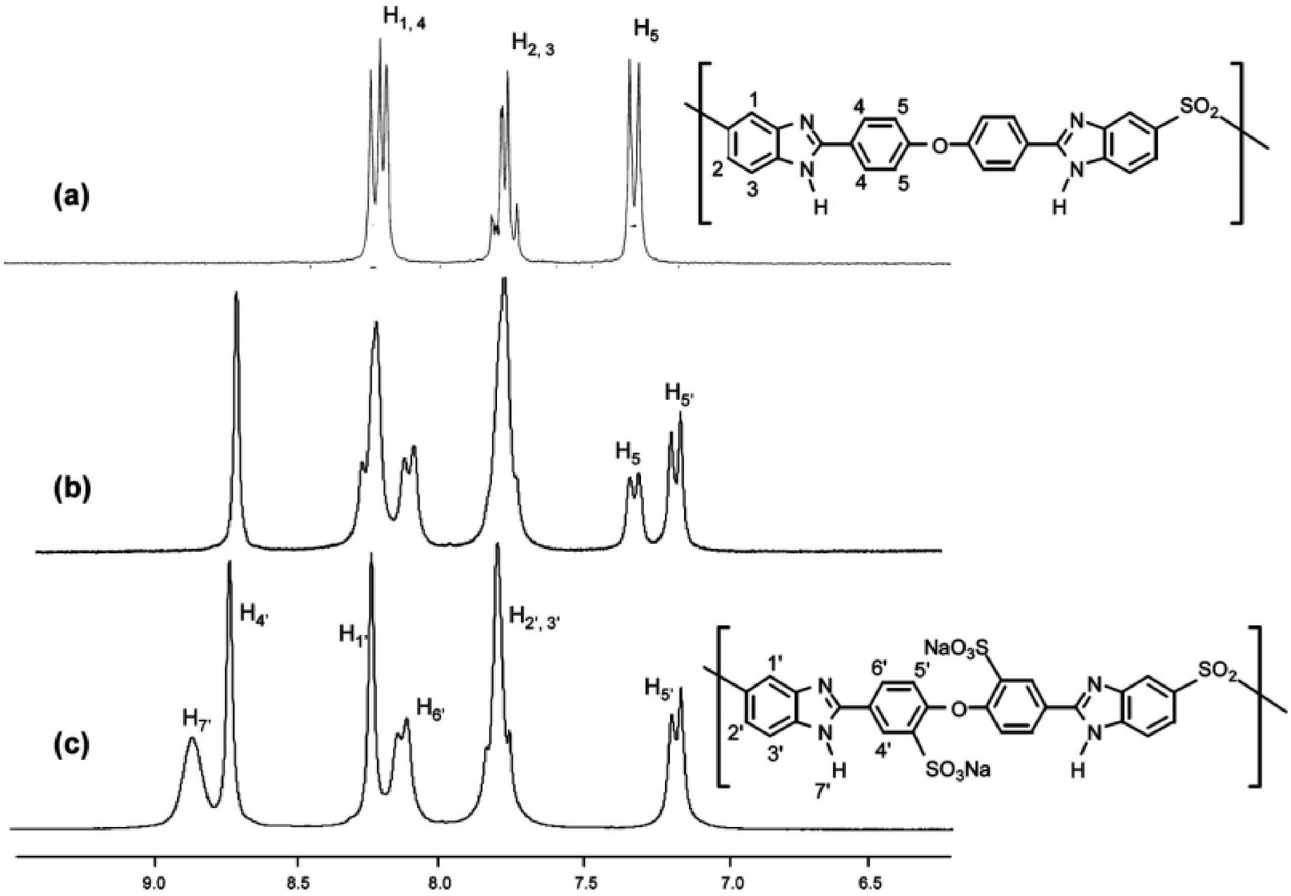


FIGURE 2 ^{1}H-NMR spectra of the homopolymers nsPBI (a), the copolymer sPBI75rand (b), and sPBI100 (c).

long term use at high temperature. To complete these data, an isothermal mode TGA analysis was performed on the sPBI100 at 200 °C under air. The thermogram presented Figure 4 does not display any significant weight loss even after 50 h. This result can be considered as a good indication of the sPBI thermal stability, but of course, do not reflect exactly its thermal behavior in fuel cell operating conditions at this temperature Glass transition temperature (T_g) of the sPBI (random copolymers and homopolymers) was studied by TMA. Unfortunately, no T_g was observed for the sulfonated polymers until to reach the thermal degradation domain

Water Uptake

It is well-known that the proton transport through sulfonated polymer membranes is strongly dependent on their hydration state. As a consequence, the ability of the membranes

TABLE 4 Thermal Properties of the SPBI

Acronym	Sulfonation Rate (%)	$T_{5\%}$ (°C)^{a,b}	Desulfonation (wt %)^b Calculated	Desulfonation (wt %)^b Measured	T_g (°C)
nsPBI	0	482	–	–	336
sPBI50rand	50	418	15	20	
sPBI50seq5	50	424	15	17	
sPBI50seq10	50	421	15	18	
sPBI75rand	75	407	21	24	
sPBI75seq5	75	411	21	24	
sPBI75seq10	75	412	21	24	
sPBI90rand	90	399	24	27	
sPBI100	100	401	26	28	

[a] Temperature at which the 5% weight loss was recorded by TGA.

[b] Sulfonic acid form (SO_3H) of the sPBI.

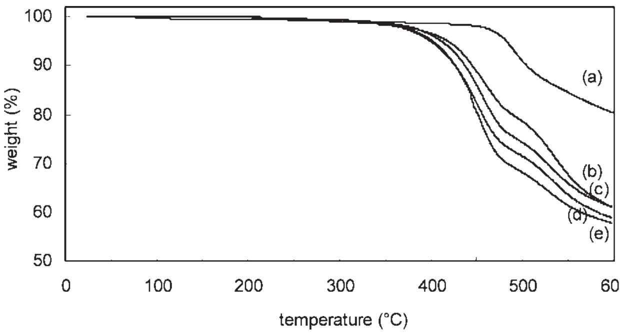


FIGURE 3 TGA analysis of nsPBI (a), sPBI50rand (b), sPBI75rand (c), sPBI90rand (d), and sPBI100 (e).

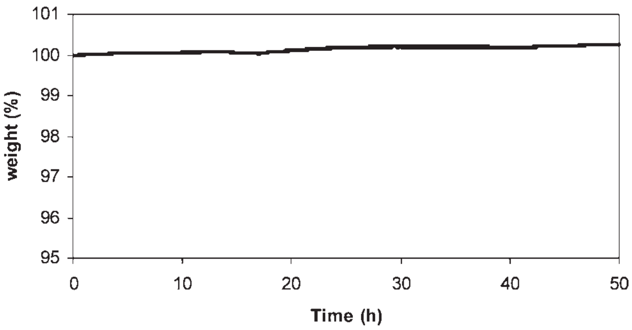


FIGURE 4 Isothermal TGA analysis of sPBI100 at 200 °C under air.

to absorb water is a critical key point. The data obtained from measurements done at 30 °C and 90 °C, are reported Table 5, along with the corresponding values of membrane ionic conductivity.

The water uptake of sPBI membranes are also represented as function of the degree of sulfonation Figure 5. The hydrophilic effect of SO_3H is clearly visible as the water uptake increases with the degree of sulfonation up to 46% for the sulfonated homopolymer sPBI100. However, for the number of H_2O molecules per sulfonic acid group (λ), no significant change was observed with the degree of sulfonation of polymers. All values ranged from 6.7 to 8.7 H_2O/SO_3H, which is quite low in comparison with the value generally obtained with the Nafion ($\lambda = 12$).

In Figure 5, the values are reported obtained for different polymer architectures but having the same degree of sulfonation. Based on these results, one can consider that the blockness of polymers does not change the water uptake properties. On the other hand, after soaking in water at 90 °C, all the membranes absorb less water than at lower temperature. This very particular behavior has already been observed by Qing et al.[32–35] and seems typical of sPBI prepared from sulfonated diacid monomers.

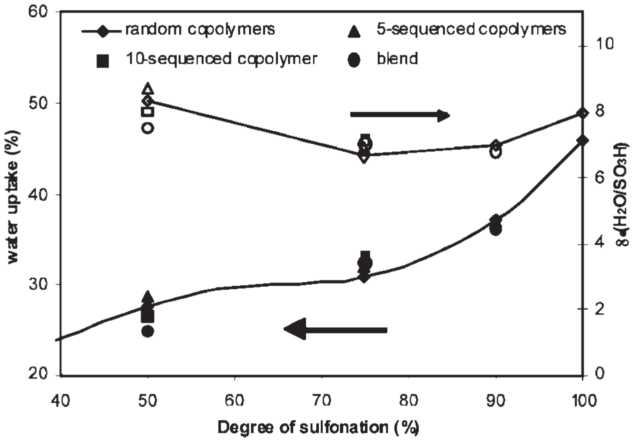


FIGURE 5 Water uptake of sPBI in liquid water at 30 °C, expressed in wt % (black dots) or in number of water molecules per sulfonic acid group (clear dots).

The water uptake property of sPBI100 was also studied at higher temperature in a high pressure reactor and represented Figure 6. The membrane exhibits outstanding capacity to maintain good mechanical stability and moderate swelling up to 180 °C, the limit temperature of the reactor. Up to 140 °C the water uptake remains lower than 50% in weight. Above this temperature, the dramatic increase of water uptake is probably the consequence of weaker ionic interactions between the polymer chains and hence, a better affinity for water. Even at 180 °C, the λ value is only about 13.5, which is comparable with Nafion one at ambient temperature.

Ionic Conductivity

Conductivity is the major parameter used to estimate the propensity of the membrane to proton transport. All measurements were carried out in hydrated state (100% relative humidity), and reported Table 5. As it is currently observed

TABLE 5 Water Uptake and Conductivity of sPBI Membranes

	Water Uptake at 30 °C		Water Uptake at 90 °C		Conductivity (S/cm)	
Acronym	wt %	λ (H_2O/SO_3H)	wt %	λ (H_2O/SO_3H)	30 °C	90 °C
nsPBI	7.0		8.1		1.9E-06	–
sPBI50rand	27.5	8.3	22.1	6.7	–	3.8E-05
sPBI50seq5	28.8	8.7	23.5	7.1	1.4E-05	3.3E-05
sPBI50seq10	26.6	8.0	23.1	7.0	–	1.2E-05
sPBI50blend	24.9	7.5	21.7	6.6	1.7E-05	2.9E-05
sPBI75rand	30.8	6.7	26.3	5.7	1.2E-04	1.8E-04
sPBI75seq5	32.0	6.9	31.6	6.8	4.7E-05	7.1E-05
sPBI75seq10	33.1	7.1	32.3	7.0	7.3E-05	1.2E-04
sPBI75blend	32.6	7.0	31.6	6.8	1.2E-04	1.2E-04
sPBI90rand	37.1	7.0	33.5	6.3	1.8E-04	9.3E-04
sPBI90blend	36.2	6.8	31.5	5.9	–	5.0E-04
sPBI100	45.9	8.0	36.5	6.3	2.0E-04	1.3E-03

–, too low to be correctly measured.

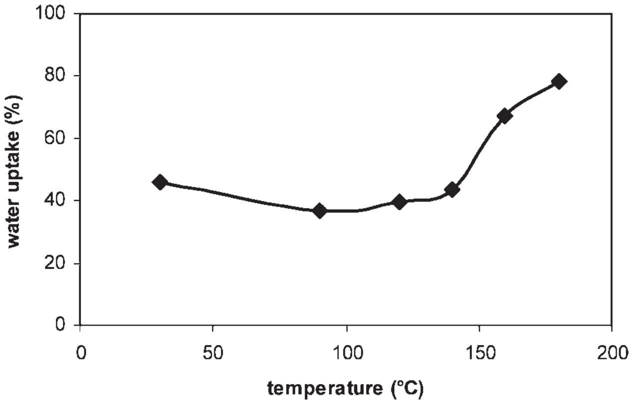


FIGURE 6 Water uptake of sPBI100 in liquid water at high temperature.

for ionomers, the conductivity is dependent on the IEC of the polymers. But surprisingly, conductivities of sPBI at 30 °C are very low compared with other kinds of sulfonated polymers displaying similar IEC. Even the most sulfonated PBI do not exhibit conductivity higher that 0.2 mS/cm. Few other research groups[25,27,28] working on sulfonated PBI already observed such low conduction properties. The interactions sulfonic acid–benzimidazole ring previously described are likely responsible of this phenomenon. The mechanism generally admitted for proton transport in hydrated ionomers is a jump mechanism from one sulfonic acid group to another, assisted by water. In the case of sPBI, the SO_3H are subject to interactions with the benzimidazole units of the polymer backbone and hence, the proton is shared between both groups, yielding to an intermediate form between sulfonic acid/benzimidazole and sulfonate/benzimidazolium. So a fraction of acid functions can be supposed to be not really available for proton transport. Despite the lower water uptake of sPBI membranes at 90 °C, the conductivities measured at this temperature and at 100% relative humidity are higher than at 30 °C. Finally, as expected the conductivity varies with the extent of sulfonation. As we observed for the water uptake, the polymer architecture (random or sequenced polymers) has no real effect on the conductivity of sPBI. It may be supposed that the interactions SO_3H-benzimidazole are so strong that the effect of modifying the size of ionic domains is negligible on the transport properties of the membrane.

CONCLUSIONS

An extensive experimental investigation has been carried out to synthesize ion conducting polybenzimidazole from a sulfonated dicarboxylic acid monomer. The use of this sulfonated monomer allowed to obtain polymers with a well controlled functionalization. As a consequence of the good reactivity of the monomers using Eaton reagent, very high molecular weight sPBI were prepared with an extent of sulfonation varying from 0% to 100%. Tough and flexible membranes were obtained from polymer solution casting. sPBI membranes are thermally stable up to 350 °C, and exhibit outstanding resistance to oxidation in aqueous medium. Their water uptakes at 30 and 90 °C were found to be limited considering the very high IEC of the sPBI. The ionic conductivity of such high IEC sPBI is quite low in comparison with aromatic sulfonated polymers, even at high temperature and high relative humidity. Because a part of sulfonic acid functions interacts with benzimidazole units, the proton transport through membranes is seriously affected. However, the 100% sulfonated PBI (sPBI100) which offers a good balance between oxidative stability, moderate water uptake at high temperature, and conductivity can be considered as a good potentially candidate for high temperature fuel cell membrane application.

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