Macromolecules **2007,** *40,* 983−990

Synthesis of Sulfonated Polybenzimidazoles from Functionalized Monomers: Preparation of Ionic Conducting Membranes

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Received June 23, 2006; Revised Manuscript Received September 7, 2006

ABSTRACT: In the present work, a new sulfonated tetraamine and the corresponding sulfonated polybenzimidazoles (sPBI) were synthesized. For the sake of determining the best polymerization conditions, a study involving model compounds was first performed. A strong acid medium was used as polymerization solvent, which allowed to obtain high molecular weight sPBI. A series of polymers with ion exchange capacity (IEC) ranging from 0 to 2.6 mequiv/g were synthesized using a non-sulfonated tetraamine as a comonomer. The chemical structure of those polymers was confirmed by nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) as well as by titration. Thermogravimetric analysis (TGA) and viscosity measurement were performed as well. On the other hand, different architectures of the copolymers were prepared, i.e., random, sequenced copolymers, and blends of the homopolymers. The membranes prepared from the sPBI display low water uptake. The ionic conductivities measured in the hydrated state at room temperature ranged from 10^{-6} to 4×10^{-4} S cm^{-1}.

Introduction

Because of the growing demand for clean energy sources, fuel cell technology has been the focus of the scientific community during the past decade. Such devices have a high energetic efficiency and almost no environmental impact. Among the different types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) has the most promising future as power source for car application. But large-scale development of the PEMFC is still limited by the necessary improvement of some key components, and especially the proton exchange membrane (PEM). Despite its high cost and relatively low stability at high temperature, the perfluorosulfonic acid polymer membrane[1] from Dupont, named Nafion, studied for more than 20 years, is still the most used.

More recently, sulfonated aromatic polymers such as polyimides,[2,3] polysulfones,[4] polybenzoxazoles,[5] and poly(ether ether ketone)s,[6−9] which display good thermal and chemical stability, have been intensively studied as alternative fuel cell membranes. Two different ways can be considered to obtain sulfonated polymers. The first one consists generally in the sulfonation of available polymers[10−13] or newly developed polymers.[14] Although it is a convenient method, difficulties are in general encountered to control precisely the amount of grafted sulfonic groups and their location along the polymer backbone. The second one which was first applied to polyimides[2] and more recently to other polymers[5,6,15−17] involves the polymerization of sulfonated monomers. In this case, the control of the polymer structure is easier. On the other hand, by using a non-sulfonated comonomer, it is possible to design polymers offering a good combination of properties such as conductivity, solubility, and mechanical properties.

Polybenzimidazoles are one of these interesting highly stable aromatic polymers.[18] The benzimidazole ring is a heterocyclic ring with an amphoteric character. Taking advantage of the basic character, PBI was doped with strong acids such as phosphoric acid to prepare ionic conducting membranes.[18−22] In this case, a stable association between the benzimidazole ring and the strong acid is formed, giving a new class of proton conducting polymer membranes. Indeed, these membranes are of particular interest for uses at high temperature (until 180 °C). In this case, the proton transport is driven by the acid molecules and does not need water, and the conductivity remains very high even at high temperature and low humidification rate. The major drawback of this system is, however, the possible acid drawing off during the fuel cell operation and also the weak ionic conductivity at low temperature ($T < 60$ °C). Most of these membranes are based on the commercially available PBI with the trade name Celazole. From the substitution of the hydrogen of the N−H bond of the benzimidazole ring, Gieselman et al. have synthesized PBI with aliphatic or aromatic sulfonic pendant groups.[23] This method was also used by some other research groups to prepare sPBI as ionic conducting materials.[24,25]

The synthesis of sPBI via the polymerization of sulfonated monomer was first explored by Arnold et al.,[26,27] which was then used by Einsla et al.[28] and more recently by Qing et al.[17,29−31]

The aim of the present study is the synthesis of novel sPBI from an original sulfonated tetraamine. Hereafter, we describe the synthesis of a novel sulfonated monomer, the bis-3-amino-4-[3-(triethylammoniumsulfonato)phenylamino]phenyl sulfone (BASPAPS). This sulfonated tetraamine monomer was reacted with aromatic mono or -dicarboxylic acid compounds to give the benzimidazole model compound and the sulfonated PBI, respectively. A non-sulfonated tetraamine compound, bis-3,4-diaminophenyl sulfone (BDAPS), was used as a comonomer to synthesize copolymers with different IEC. By varying the ratio BASPAPS/BDAPS, different sPBI were prepared as random copolymers or sequenced copolymers with an average sulfonated block length of 5 or 10 repeat units. Polymer blends were also prepared. The sulfonation rate expressed as the IEC

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10.1021/ma0614139 CCC: $37.00

of the polymers synthesized ranged from 0 to 2.6 mequiv H^+/g. The well-controlled structure of the polymers was confirmed by NMR spectroscopy. The molecular weights were high enough to prepare tough membranes from a solution casting method. The preliminary properties of water uptake and conductivity of these membranes are described.

Experimental Section

Materials. Bis-4-chlorophenyl sulfone was purchased from Alfa Aesar and purified by sublimation before use. Metanilic acid was used as received from Alfa Aesar. Fuming nitric acid (90%), concentrated sulfuric acid (96%), acetic acid, hydrochloric acid, triethylamine (NEt_3), potassium carbonate, and palladium (10 wt % on activated carbon) were obtained from Aldrich. Eaton reagent was prepared before use with phosphorus pentoxide and methanesulfonic acid (Aldrich). Bis-3,4-diaminophenyl sulfone (BDAPS) was kindly provided by Konishi Chemical Ind. Co. and recrystallized in acetonitrile before use. Benzoic acid (Aldrich) was purified by sublimation while dicarboxydiphenyl ether (Atochem) was washed with tetrahydrofuran (THF) before use. Dimethyl sulfoxide (DMSO) was purchased from VWR Chemical Co., *N*-methylpyrrolidone (NMP), acetonitrile, THF, and ethyl acetate from SDS Chemical Co., and ethanol and methanol from APC Ind.

Methods of Characterization. NMR spectra were obtained on a Bruker AC250, with frequencies of 250 and 62.9 MHz respectively for ^{1}H and ^{13}C analysis. The solvent used was DMSO-d_6, and tetramethylsilane (TMS) was used as internal reference.

Fourier transformed infrared spectra were recorded on a Nicolet 20SX spectrophotometer under nitrogen flux. Samples were prepared as KBr pressed pellets or as thin polymer film.

Thermogravimetric analyses (TGA) were recorded from a TA Instruments 2950 TGA. Samples were polymer powder. The dynamic analyses were performed under helium with a heating rate of 10 °C/min, between 20 and 700 °C.

The inherent viscosity was determined from 0.5 g/dL polymer solution in 96% H_2SO_4 using a Ubbelhode viscometer at 30 °C.

The acid titration of the sulfonated polymers was done as follows: a 30 mg piece of polymer membrane was immersed for 24 h in 20 mL of 1 M NaCl aqueous solution. Then titration was performed with a 0.02 M NaOH aqueous solution, using the Radiometer Analytical Titramaster 880 ABU52 instrument.

Water uptake of the membranes was also measured by immersing for 24 h three samples (around 20 mg each) of membrane in a water bath at ambient temperature (20 °C). 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 previously hydrated for 24 h at ambient temperature in liquid water were sandwiched between two mercury electrodes in a sealed cell. The complex impedance method was used to determine the proton conductivity of the membranes. The frequency dependence of the cell impedance was measured at 5 mV over the frequency range from 100 Hz to 1 MHz with a Schlumberger SI 1255 HF frequency response analyzer.

Synthesis of Precursors and Monomer. *Bis-4-chloro-3-nitrophenyl Sulfone (**1**).* 50 g (0.17 mol) of sublimated bis-4-chlorophenyl sulfone and 250 mL of 96% H_2SO_4 were added to a 1 L three-necked round-bottom flask equipped with a reflux condenser, a liquid addition funnel, and a mechanical stirrer. The reaction mixture was stirred at room temperature until complete solubilization of bis-4-chlorophenyl sulfone. The mixture was then cooled to 2−3 °C in an ice water bath. A sulfonitric solution was prepared with 32 mL of 90% fuming HNO_3 (0.44 mol) and 50 mL of 96% H_2SO_4 and then added dropwise from the addition funnel. The addition took place over a 4 h period while maintaining the temperature around 2−3 °C to avoid side reactions. Upon completion of addition, the solution temperature was very slowly increased to room temperature and let stand overnight. The final heterogeneous reaction mixture containing pale yellow precipitate was slowly poured in 3 L of deionized water. The yellow precipitate was filtered, washed twice with water, and with 200 mL of 1 M K_2CO_3 solution to eliminate the residual acid. Then the crude product was washed again with water until neutral pH and finally dried for 5 h under vacuum at 80 °C. One recrystallization in acetic acid resulted in 57 g (89% yield) of pale yellow needles. IR peaks (cm^{-1}): 1538, 1360 (NO_2), 1340, 1173 (SO_2), 1047 (Ph−Cl). ^{1}H NMR (δ, ppm, in DMSO-d_6, 21 °C): 8.76 (2H, d, J_{HH} = 2.3 Hz), 8.33 (2H, dd, J_{HH} = 8.4, 2.3 Hz), 8.08 (2H, d, J_{HH} = 8.6 Hz). ^{13}C NMR (δ, ppm, in DMSO-d_6, 21 °C): 147.80, 139.30, 133.55, 132.55, 131.45, 125.39.

*Bis-3-nitro-4-[3-(triethylammoniumsulfonato)phenylamino]-phenyl Sulfone (**2**).* 25 g of (1) (66 mmol), 28.7 g of metanilic acid (165 mmol), 45 mL of triethylamine (230 mmol), and 120 mL of DMSO were added in a 500 mL three-necked round-bottom flask equipped with a reflux condenser, a nitrogen inlet/outlet, and a magnetic stirrer. The red solution obtained was heated to 120 °C for 6 h and then precipitated in 500 mL of ethyl acetate. The yellow powder obtained was filtered and then recrystallized twice in ethanol. 44 g (84% yield) of expected product as a yellow crystal compound was isolated. IR peaks (cm^{-1}): 3335 (N−H), 1506, 1352 (NO_2), 1330, 1157 (SO_2), 1226, 1191, 1036 (SO_3^-). ^{1}H NMR (δ, ppm, in DMSO-d_6, 21 °C): 9.93 (2H, s), 8.57 (2H, d, J_{HH} = 2.3 Hz), 7.90 (2H, dd, J_{HH} = 9.1, 2.3 Hz), 7.53 (4H), 7.39 (2H, t, J_{HH} = 8.0 Hz), 7.28 (2H, dt, J_{HH} = 8.0, 2.3 Hz), 7.05 (2H, d, J_{HH} = 9.1 Hz), 3.05 (12H, q, J_{HH} = 7.3 Hz), 1.14 (18H, t, J_{HH} = 7.1 Hz). ^{13}C NMR (δ, ppm, in DMSO-d_6, 21 °C): 149.68, 145.44, 137.30, 133.20, 131.90, 129.08, 128.17, 126.57, 125.48, 123.60, 122.43, 117.66, 45.62, 8.51.

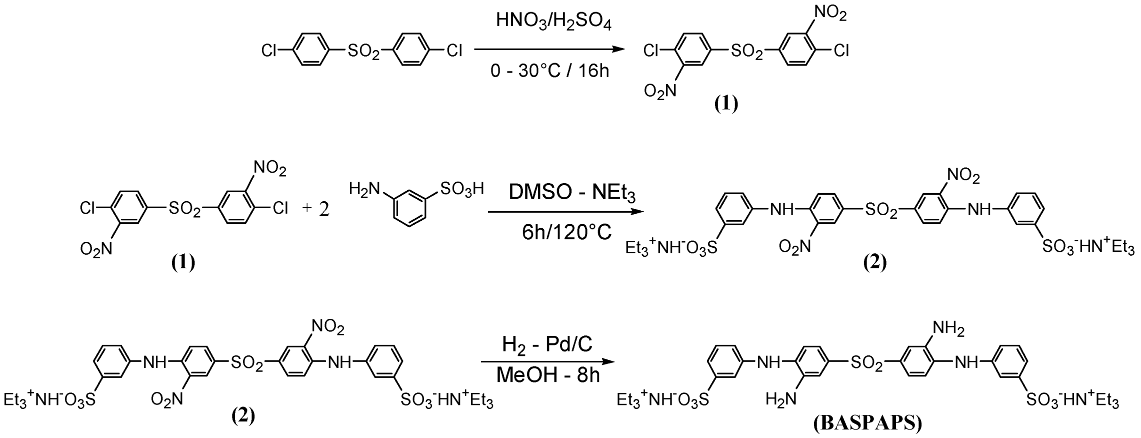
Bis-3-Amino-4-[3-(triethylammoniumsulfonato)phénylamino]-phenyl Sulfone (BASPAPS). 10 g of (**2**), 0.25 g of Pd/C(10%), and 120 mL of methanol were introduced into a hydrogenation autoclave fitted with a manometer. The reactor was previously flushed three times with hydrogen in order to remove any trace of oxygen and then filled to 40 bar with hydrogen. The reduction was achieved at room temperature for 12 h. The solution was then hot-filtered and the solvent evaporated, giving 9.1 g (97% yield) of a red powder. IR peaks (cm^{-1}): 3406, 3357, 3275, 1307 (N−H), 1338, 1145 (SO_2), 1219, 1176, 1034 (SO_3^-). ^{1}H NMR (δ, ppm, in DMSO-d_6, 21 °C): 8.92 (2H, s), 7.54 (2H, s), 7.28 (2H, t, J_{HH} = 1.8 Hz), 7.22−7.08 (8H, m), 6.99 (2H, dd, J_{HH} = 8.2, 2.1 Hz), 6.89 (2H, dt, J_{HH} = 7.3, 2.1 Hz), 5.31 (4H, s), 3.05 (12H, q, J_{HH} = 7.3 Hz), 1.12 (18H, t, J_{HH} = 7.1 Hz). ^{13}C NMR (δ, ppm, in DMSO-d_6, 21 °C): 149.07, 142.70, 139.85, 134.36, 133.32, 128.69, 117.69, 117.64, 117.04, 115.79, 115.01, 112.79, 45.87, 8.73.

Eaton Reagent Preparation. 3 g of phosphorus 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 until there was complete dissolution of P_2O_5.

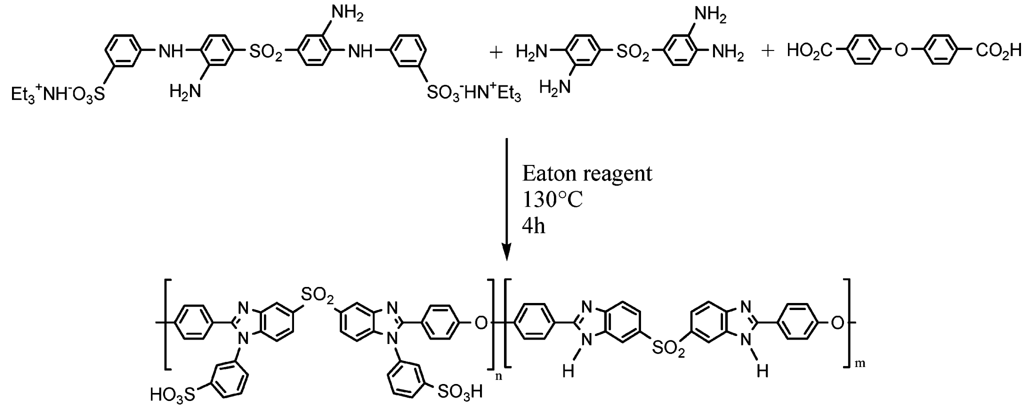
This mixture was used as a solvent for both polymerization and synthesis of benzimidazole model compounds and was prepared just before use.

Model Compound Synthesis. *Bis[2-phenyl-1-(3-sulfophenyl)-5-benzimidazole] Sulfone (Figure 2).* 0.513 g of (BASPAPS) (0.637 mmol), 0.156 g of benzoic acid (1.274 mmol), and 9 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 benzoic acid which could affect the reagent stoichiometry. The temperature was slowly increased to 130 °C. The reaction mixture was then kept for 3 h. The dark reaction mixture obtained was then poured in 100 mL of water. The resulting precipitate was filtered and washed carefully twice with water to give 0.41 g (84% yield) of a gray powder. IR peaks (cm^{-1}): 1630, 1586, 1570, 1445, 1286 (benzimidazole), 1332, 1154 (SO_2), 1211, 1178, 1036 (SO_3H). ^{1}H NMR (δ, ppm, in DMSO-d_6, 87 °C): 8.42 (2H, s), 7.93 (2H, d, J_{HH} = 8.4 Hz), 7.81 (2H, d, J_{HH} = 7.5 Hz), 7.68 (2H, s), 7.59 to 7.32 (16H, m). ^{13}C NMR (δ, ppm, in DMSO-d_6, 87 °C): 154.53, 150.88, 139.89, 139.54, 137.25, 134.51, 130.79,

Scheme 1. Synthesis of BASPAPS



Scheme 2. Synthesis Scheme of Sulfonated Polybenzimidazole by Copolymerization of BASPAPS, BDAPS, and DCDPE



129.65, 129.44, 128.54, 127.65, 127.60, 127.01, 124.47, 122.94, 118.28, 112.26.

Polymer Synthesis. *Homopolymer and Random Copolymers.* The typical procedure is as follows. In a first step, the water content of the monomers was determined by TGA and taken in account for the weighing of sample in order to avoid an unbalanced ratio of the monomers. In a 100 mL three-necked round-bottom flask equipped with a nitrogen inlet/outlet and a mechanical stirrer, 1.4459 g (1.7941 mmol) of BASPAPS, 0.4642 g (1.7941 mmol) of dicarboxydiphenyl ether (DCDPE), and 25 g of Eaton reagent were introduced. After complete dissolution of the monomers at 80 °C, the temperature was gradually increased to 130 °C. The mixture was maintained 4 h at 130 °C and diluted as increases the viscosity. Then the reaction mixture was poured in 300 mL of water, and the precipitate was filtrated and washed several times in boiling water (typically three times) until neutral pH of the washing water. The gray powder obtained was dried overnight at 120 °C under high vacuum to give 1.3 g of polymer (94% yield).

Random copolymers were synthesized introducing the three monomers in the same time at the beginning of the reaction, as shown in Scheme 2.

The non-sulfonated homopolymer was synthesized in such the same manner. The polymerization temperature was about 110 °C.

Sequenced Copolymers. The synthesis of sequenced copolymers involves a two-step reaction. The first one concerns the preparation of sulfonated oligomers end-capped with diamine functions. The second step involves the polymerization of these oligomers with non-sulfonated monomers. As general procedure, the synthesis of the 50% sulfonated copolymer with an average sequence length of 5 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, 2.4991 g (3.1010 mmol) of BASPAPS, 0.6419 g (2.4808 mmol) of DCDPE, and 40 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 3 h. The reaction mixture was then cooled to 80 °C, and 0.8635 g of BDAPS (3.1010 mmol), 0.9629 g of DCDPE (3.7212 mmol), and 25 g of Eaton reagent were added. After complete solubilization, the solution was heated at 130 °C for 3 h. Solvent was gradually added to maintain the solution viscosity at a level not too high. The post-work-up was the same as for the homopolymers.

Membrane Preparation. 0.5 g of polymer was dissolved at 150 °C in 25 mL of NMP-containing triethylamine. The solution was stirred overnight and then filtered through a Whatman 30 μm filter before being cast onto a clean glass substrate. The solvent was evaporated at 60 °C overnight under nitrogen flux and then heated gradually to 200 °C and maintained at this temperature for 1 h. After cooling to room temperature, the membrane was unstuck from the glass plates by immersion in water. To remove the residual solvent, the membrane was dried under high vacuum for 5 h at 120 °C and then immersed in water and methanol. The membrane was then acidified in a HCl (0.5 M) solution overnight and rinsed three times in water to remove the remaining free HCl out of the membrane. Thin flexible membrane was obtained with a thickness between 20 and 60 μm.

Polymer Blend Membranes. Two NMP solutions (2 wt %) were prepared: one containing the sulfonated homopolymer sPBI100 (in the $HNEt_3^+$ form[32]) and the other one containing the non-sulfonated polymer nsPBI. In a second step, these two solutions were mixed in such proportion to reach the IEC desired and stirred overnight. The membrane was prepared in the same manner as that described above.

Results and Discussion

Monomer Synthesis. The synthesis of the new sulfonated tetraamine monomer BASPAPS (Figure 1) was achieved in three steps with an overall yield of 72%. Nevertheless, the different purifications allowed to obtain easily BASPAPS with a polymer

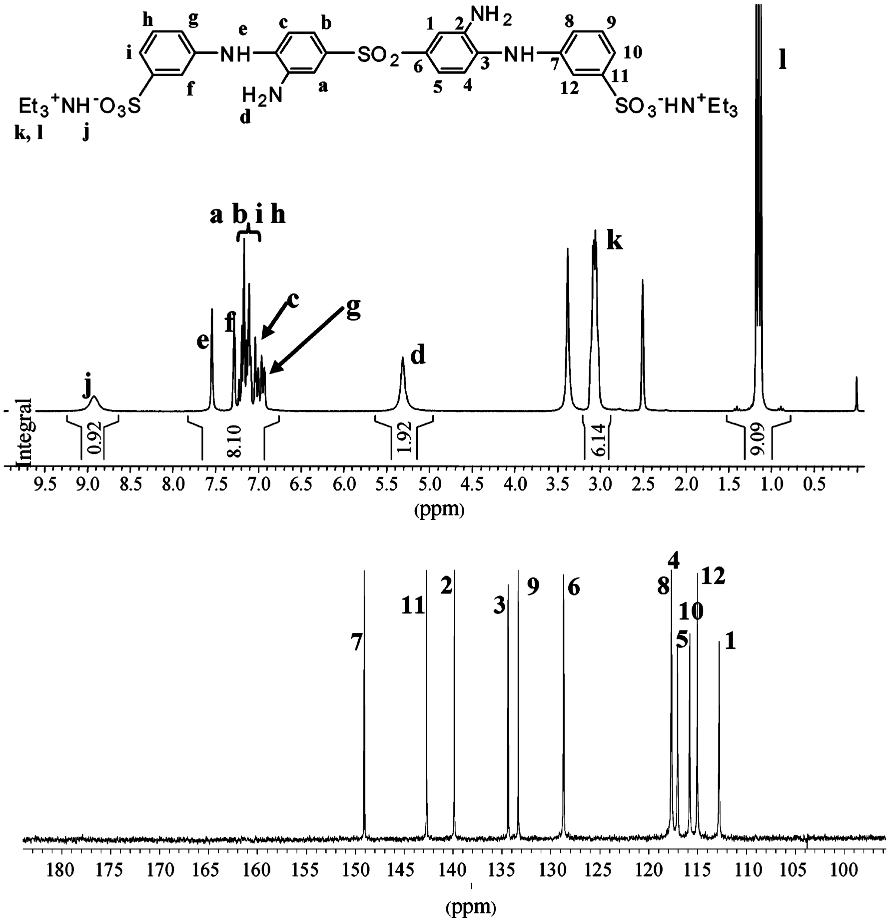


Figure 1. ^1H and ^{13}C NMR spectra of BASPAPS.

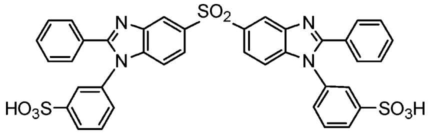


Figure 2. Chemical structure of benzimidazole model compound.

grade purity. Its structure was confirmed by FT-IR, ^1H NMR, and ^{13}C NMR analysis (Figure 1). To limit the water absorption of BASPAPS which could induce problems for the sample weighing, the sulfonic groups were maintained on triethylammonium form until polymerization, which is much less hygroscopic than the acidic form.

Model Synthesis. The synthesis of model compound represented in Figure 2 was achieved by reacting BASPAPS with benzoic acid. This synthesis was performed in order to define better the experimental conditions for the preparation of high molecular weight fully cyclized PBIs and also to get precise data regarding the chemical shifts of ^1H and ^{13}C NMR which can be used further for the analysis of polymer spectra. Among the ^{13}C NMR data as mentioned earlier, it is interesting to notice the chemical shift around 155 ppm, characteristic of the N═C—N carbon of the benzimidazole ring, confirming that the expected structure was obtained. We observed also a peak around 151 ppm, which is related to the aromatic carbon bounded to the sulfonic group. On the other hand, the characteristic vibration bands of benzimidazole assigned by Musto et al.[33,34] at 1630 cm^{-1} (C═N/C═C stretching), 1586 cm^{-1} (ring vibration characteristic of conjugation between benzene and imidazole rings), 1445 cm^{-1} (in-plane ring vibration of 2,6-disubstituted benzimidazole), and 1286 cm^{-1} (imidazole ring breathing) were observed in the FT-IR spectra. Moreover, the fact that no carbonyl peaks between 1750 and 1650 cm^{-1} were indentified can be considered as good evidence of complete cyclization into imidazole rings.[35]

In a further work, this compound will be used as a model compound[36] to study in a first stage the chemical degradation of sPBI membranes in water at different temperatures.

Polymer Synthesis. Originally, PBI synthesis was carried out in poly(phosphoric acid)[37,38] (PPA) which is known as a very good solvent for condensation reactions. However, the high viscosity of this solvent sets a real problem of handling. For this reason, we found it was more convenient to use the Eaton reagent,[39]which is a low-viscosity liquid solvent, for the synthesis of our PBI. Moreover, the reaction mixture is more easily kept homogeneous[40] during the polymerization reaction. PBI powder or fiber was obtained simply by pouring the solution in H_2O, with no need of washing with a basic solution to remove completely the remaining free acid, as is necessary for poly(phosphoric acid). 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 BASPAPS, BDAPS, and DCDPE according to this procedure. PBI with different composition varying between 0 and 100% of sulfonated tetraamine were synthesized, giving IEC between 0 and 2.57mequiv/g. For two of them, three different polymer architectures were prepared: random copolymer and sequenced copolymers with sulfonated block length containing 5 or 10 repeat units.

Structural Characterization. On the basis of NMR data of the model compound, we were able to clearly analyze the ^{13}C spectra of the polymers and confirm their expected structure. As an example, we represent the spectrum of the sulfonated

Table 1. Chemical Composition and Characterization of SPBI

				IEC (mequiv/g)			
					measured by		
acronym	structure	% BASPAPS	% BDAPS	calculated	NMR	titration	η_{inh} (dL/g)
nsPBI	homopolymer	0	100	0	0	0	1.78
sPBI50rand	random	50	50	1.61	1.54	1.48	3.51
sPBI50seq5	sequenced, 5[a]	50	50	1.61	1.71	1.45	2.82
sPBI50seq10	sequenced, 10[a]	50	50	1.61	1.61	1.67	2.26
sPBI75rand	random	75	25	2.15	2.00	2.08	2.62
sPBI75seq5	sequenced, 5[a]	75	25	2.15	2.14	2.14	2.29
sPBI75seq10	sequenced, 10[a]	75	25	2.15	2.14	2.26	2.28
sPBI90rand	random	90	10	2.41	2.37	2.50	2.68
sPBI100	homopolymer	100	0	2.57	2.57	2.52	2.23

[a] Number of sulfonated repetitive units per sulfonated sequence in the polymer.

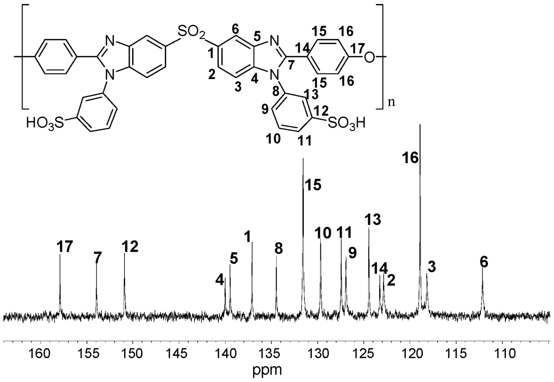


Figure 3. ^{13}C NMR spectrum of the homopolymer from BASPAPS (sPBI100).

homopolymer in Figure 3. The peak appearing at 155 ppm corresponds to the carbon of the imidazole ring while the one appearing at 151 ppm corresponds to the carbon bearing sulfonic acid group.

In the FT-IR spectra of sPBI100 (sulfonated homopolymer), characteristic bands of benzimidazole ring are observed at 1610, 1597, 1563, 1468, and 1443 cm^{-1}. The bands at 1206, 1178, and 1037 cm^{-1} clearly indicate the presence of the sulfonic acid groups.[23,25]

IEC Determination. As illustrated in Table 1, we have observed a good agreement between the theoretical IEC calculated from the feed monomer ratio (BASPAPS/(BASPAPS + BDAPS)) and the determined IEC from NMR analysis.

From the ^{1}H NMR spectrum of each homopolymer (nsPBI and sPBI100), we were able to identify peaks related to the sulfonated repeat unit or to the non-sulfonated one. As illustrated in Figure 6, the peak around 8.45 ppm was attributed to one aromatic proton of the sulfonated repeat unit, whereas the multiplet at 8.2 ppm was assigned to three protons of the non-sulfonated repeat unit. As seen in Figure 4, these two peaks are well distinguished, and it is possible to determine the extent of sulfonation (s%) of the copolymers using the following equation:

$$s\,(\%) = \frac{\text{area} \times 8.45}{(\text{area} \times 8.45) + (\text{area} \times 8.2) \div 3}$$

For example, we have determined the value of 47% for the copolymer sPBI50rand, which corresponds to an IEC of 1.54 mequiv/g while the corresponding calculated value was 1.61 mequiv/g (s = 50%). This good concordance between the calculated and measured values (see Table 1) allows to consider this experimental determination of the IEC as a reliable method.

The IEC of the copolymers synthesized was also determined by titration. The method commonly used to determine IEC of sulfonated polymers such as PEEK[6] involves in a first stage the immersion in a 1 M NaCl solution of the membrane in the acid form. The membrane is converted to the sodium form by exchanging its H^{+} ions with the Na^{+} from the solution. In the second stage, the membrane is removed from the solution, and the exchanged H^{+} ions within the solution are titrated with NaOH.

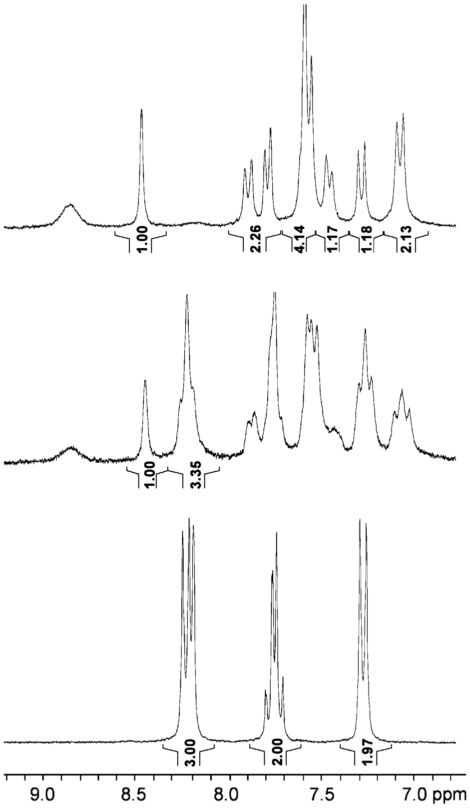


Figure 4. ^{1}H NMR spectra of the homopolymers sPBI100 (a), nsPBI (c), and the copolymer sPBI50stat (b).

All attempts to adapt this method to our sPBI gave experimental IEC much lower than the theoretical value. The same behavior was observed by Roziere et al. with *N*-benzysulfonate-grafted PBI.[41] Soaking their sPBI in a 1 M NaCl solution, they could exchange only 33% of the total amount of H^{+} in their polymers. This observation seems to indicate that the acid protons of sPBI are more difficult to exchange than for the other kind of sulfonated polymers. The hypothesis that an acid−base complex between benzimidazole and the sulfonic acid groups of the polymer is formed could explain why the acid protons seem to be less accessible to the exchange with Na^{+}.

To overcome this uncompleted exchange problem, the membrane was kept in the solution for the titration. Under such conditions, the titration curve changed dramatically, presenting

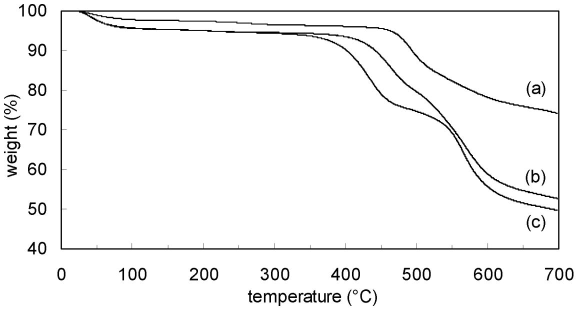


Figure 5. TGA curves of nsPBI (a), sPBI50stat (b), and sPBI100 (c) at 10 °C/min.

two inflection points. The first one corresponds to the titration of the "free H^+" exchanged previously in the solution. The second one was attributed to the H^+ catched in the membrane. So the IEC can be determined from the second equivalent volume, as reported in Table 1. The IEC values measured from this method were in good agreement with the theoretical values, varying not more than 10%.

Solubility and Viscosity. The solubility of the non-sulfonated PBI synthesized is quite similar to the solubility of pristine PBI described in the literature.[18] Homogeneous solutions of 5−10 wt % can be easily obtained in polar aprotic solvent (DMSO, NMP, DMAc, DMF), from which very tough films can be prepared. On the other hand, the solubility was found much lower for sulfonic acid groups containing PBI. DMSO can be considered as the only solvent able to give a polymer solution from which acid membranes can be directly prepared. Another way to obtain sPBI DMSO solutions was to transform the sulfonic group acid group into its ammonium form by adding triethylamine which prevents the SO_3H−benzimidazole interactions. In this way, it is possible to solubilize the polymer not only in DMSO but also in NMP and DMAc. Polymer solutions up to 2 wt % were prepared, which is still low compared with nsPBI but much higher than what could be obtained by direct solubilization in DMSO.

Some inherent viscosity measurements of the different polymers were performed in DMSO at 30 °C with a concentration of 0.5 g/dL. The value obtained for nsPBI was 2.9 dL/g, which could be considered as evidence of the high molecular weight of this polymer. Concerning the sulfonated polymers, inherent viscosities as high as 7.3 and 9.0 dL/g were determined for sPBI100 and sPBI75rand, respectively. In the case of sPBI50rand, the solution viscosity was so high that it was impossible to measure it. Such behavior was previously observed by Roziere et al. with *N*-benzysulfonate-grafted PBI.[41] To account for this behavior, the interactions between the SO_3H acid group and the benzimidazole basic group were taken into consideration. To overcome this problem, we performed the measurements from solutions of the sPBI in sulfuric acid, as reported in Table 1. The viscosities obtained were comparable to those of high molecular weight PBI measured from polar solvent solutions.[42]

Thermal Degradation. The thermal stability of the synthesized PBI was studied under helium at a heating rate of 10 °C/min. Three different weight losses can be observed in Figure 5. The first one occurs until 100 °C and corresponds to the elimination of absorbed water. Because of the water swelling effect of the sulfonic acid groups, this first weight loss is more important when the PBI is sulfonated. The second weight loss observed for the sPBI between 350 and 450 °C is related to the desulfonation reaction. In the study of the sulfonated homopolymer (sPBI100), the amount of lost material at this step is about 20% of the total weight of the dry polymer, which is exactly the ratio in weight of SO_3H groups grafted on the polymer backbone.

Table 2. Ionic Conductivity and Water Uptake of the SPBI Membranes

sample name	IEC (mequiv/g)	water uptake[a] wt %	water uptake[a] λ (H_2O/SO_3H)	conductivity[b] (S/cm)
nsPBI	0	7.0		1.9×10^{-6}
sPBI50rand	1.61	13.3	4.6	8.2×10^{-7}
sPBI50seq5	1.61	13.9	4.8	6.5×10^{-6}
sPBI50seq10	1.61	16.9	5.8	1.3×10^{-5}
sPBI50blend	1.61	15.9	5.5	3.9×10^{-6}
sPBI75rand	2.15	18.9	4.9	2.5×10^{-5}
sPBI75seq5	2.15	18.2	4.7	1.3×10^{-4}
sPBI75seq10	2.15	21.9	5.7	1.4×10^{-4}
sPBI75blend	2.15	20.4	5.3	2.4×10^{-4}
sPBI90rand	2.41	26.6	6.0	1.7×10^{-4}
sPBI90blend	2.41	24.3	5.5	2.8×10^{-4}
sPBI100	2.57	27.0	5.8	3.6×10^{-4}

[a] After 24 h at 20 °C in liquid water. [b] Measured at room temperature with 100% relative humidity (RH).

The last weight loss starting around 450 °C results from the degradation of the polymer backbone. As it is well distinguished from the desulfonation, it is possible to determine quite precisely the weight loss attributed to the degradation of SO_3H and consequently allow to determine the sPBI IEC value.

It is of interest to notice that the degradation of the polymer backbone starting from 450 °C is similar for both homopolymers, sulfonated or not. The *N*-phenyl substituent[43] of the benzimidazole cycle does not seem to affect the thermal stability of PBI.

To corroborate those results, isothermal TGA experiments were recorded during 50 h at 200 °C in air. No significant weight losses were observed for any sPBI.

Membrane Properties. All the measurements were made in the sulfonic acid form of the membrane. The protonation of the membranes after the drying process is complete and confirmed by titration as mentioned in the previous paragraph, as well as by ^1H NMR analysis.

It is well-known that the proton transport through the sulfonated polymer membrane is strongly dependent on its hydration state. As a consequence, the ability of the membrane to adsorb water is a critical key point. The water uptake was measured from the ratio of the weight of water absorbed by the membrane when immersed in water, with respect to the dry membrane weight. It can also be expressed as the number of H_2O molecules per sulfonic group (λ).The data are reported in Table 2 along with the values of conductivity measured in the hydrated state at room temperature. As expected, the water uptake increases with the increasing IEC. However, the λ remains almost constant for all sPBIs. Each sulfonic acid group is solvated by 5−6 water molecules, which is much lower than other proton-conducting sulfonated aromatic polymers.

The values of the ionic conductivity reported Table 2 have been expressed in Figure 6 as a function of the IEC. An important drop of the conductivity is observed from 1.61 mequiv/g, which corresponds to a PBI with 50% of sulfonated units and 50% of non-sulfonated units. The conductivity of the membrane with this composition is very weak. In this case, the sulfonic groups seem completely ineffective for the proton transport. The same behavior was observed by Kosmala et al.[44] when studying acid−base polymer blends of sulfonated PSU with PBI. The conduction of their membranes was very poor when the amount of PBI basic units was higher than those of

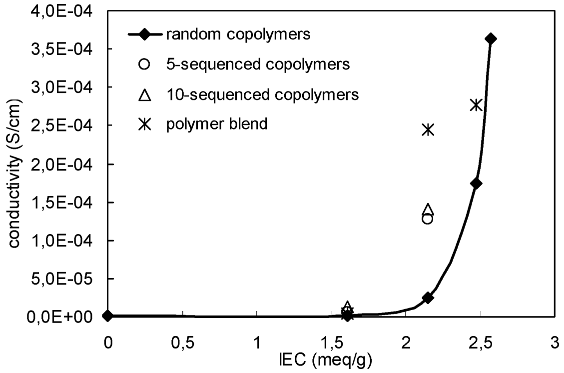
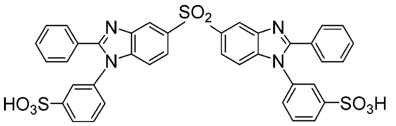
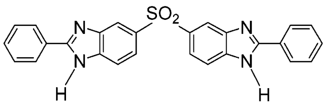


Figure 6. Variation of the proton conductivity vs IEC of sPBIs presenting different architectures.



N-sulfophenylated bisbenzimidazole (A)



bisbenzimidazole (B)

Figure 7. Model compounds tested with the SPARC computer program.

sulfonic acid groups but increased when this proportion is inverted. They concluded that when forming a complex with a basic unit, the acid proton of the SO_3H is no longer available for proton conduction.

The very poor conductivity of our sPBI at low IEC can be attributed to these strong acid−base interactions between the basic benzimidazole of the non-sulfonated unit and the sulfonic acid group. Different research groups[24,45] have already observed such behavior for sPBI, having conductivities of the same order of magnitude, i.e., lower than 10^{-4} S/cm. One evidence of such specific interaction was obtained when low concentrated solution of sPBI100 (in its SO_3H form) was mixed with a low concentrated solution of nsPBI (in the same solvent), which led to a completely insoluble precipitate.

When more SO_3H groups than nonsubstituted benzimidazole rings were introduced in the membrane, an increase of the conductivity was observed. In other words, the basicity of the *N*-sulfophenylbenzimidazole rings seems to be weak enough for not afford very strong acid−base interactions. Because of the insolubility in water of the model compounds, the determination of the basicity from a simple method[46,47] of *N*-sulfophenylbenzimidazole and benzimidazole rings was not possible. However, a good estimation of the pK_a of the different benzimidazoles can be obtained from the computer program SPARC. This program involves algorithms based on fundamental chemical structure theory that combines principles of linear free energy relationship (LFER) and perturbed molecular orbital theory (PMO) to predict ionization pK_a values of molecules strictly from their molecular structure.[48,49] Bisbenzimidazole model compounds (Figure 7) representative of nsPBI (compound B) and sPBI100 (compound A) were studied with this program. pK_a = 5.37 for the benzimidazole unsubstituted (B) and pK_a = 4.54 for the *N*-sulfophenylbenzimidazole were then calculated. The pK_a obtained for B is the same as the value generally admitted for a benzimidazole (p$K_a \approx 5$). On the other hand, the lower value of the estimated pK_a for model A corroborates the assumption that the weakness of the acid−base interaction between the SO_3H group and the *N*-sulfophenylbenzimidazole does not prevent proton transport through the membrane.

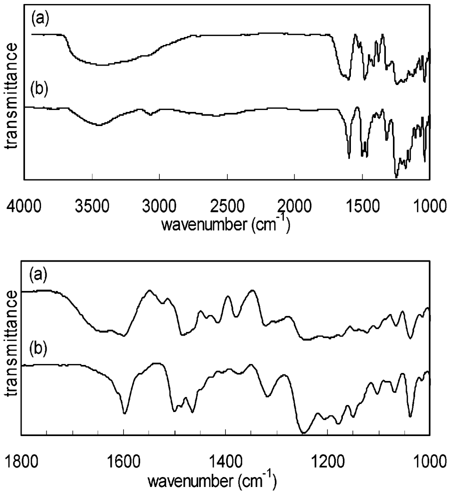


Figure 8. Infrared spectra in the regions 3000−1000 and 1800−1000 cm^{-1} of sPBI100 after soaking in NaOH aqueous solution (a) and sPBI100 (b).

However, the lower basicity of *N*-sulfophenylated PBI still seems to have an effect on the properties of the membranes. Indeed, the conductivity remains quite low even for the completely sulfonated PBI (sPBI100) in comparison with other kind of sulfonated polymers with the same IEC.

Second, this sPBI100 membrane becomes brittle on drying, which could be related to the highest rigidity of this PBI which could be related to the ionic SO_3H−benzimidazole interactions.[41] Fortunately, the water behaves as a plasticizer conferring flexibility to the membrane.

This acid−base complex can be prevented when the membrane is soaked in a NaOH aqueous solution. The spectra of a membrane were recorded before and after this treatment and are represented in Figure 8. A first evidence of the presence of this interaction on the nontreated membrane is the broad band observed in spectrum (b) near 2500 cm^{-1} which disappears on spectrum (a). Foglizzo et al.[50] attributed this band to the stretching vibration HN^+. In the case of sPBI100, this group comes from the protonation of the imino nitrogen atom by the sulfonic acid group. Another signal also disappears for the basic form of the membrane, at 1499 cm^{-1}, confirming that the benzimidazole is no longer protonated. Moreover, the peaks observed at 1560 and 1465 cm^{-1} are more intense in spectrum (b). These two peaks result from strong coupling between δ(NH) and ν(CN)[34] and thus are characteristic of the modification of the electronic structure and electron delocalization that occurs when the benzimidazole ring interacts with a sulfonic acid group.

The influence of the architecture of the polymer is also critical for the conductivity. For each composition, we observed a conductivity for sequenced copolymers higher than for random ones. On the other hand, for copolymers with the IEC = 1.6 mequiv/g, a slightly better conductivity was obtained for the 10 sulfonated repeat unit than the 5 sulfonated repeat unit. In any case, the best proton transport properties were obtained for the polymer blend. The conductivity of the membranes were up to 10 times higher than for the random copolymers and could be related to larger connected ionic domains. This observation is another evidence of the effect of polymer architecture on the membrane morphology and as a consequence on the conduction properties of the membrane. In this sense, starting from sulfonated monomers to synthesized sulfonated polymers allows to have a large number of combinations to design particular architectures.

Conclusions

An extensive experimental investigation has been carried out in order to synthesize ion-conducting polybenzimidazole from a new sulfonated tetraamine monomer. We showed that using functionalized monomer it is possible to obtain different sulfonated PBI architectures. Eaton reagent as polymerization solvent was proved to be useful for obtaining PBI with good molecular weights.

Concerning ionic conductivity of membranes, the specific acid−base interactions between benzimidazole rings and sulfonic acid groups affect strongly the proton transport. This phenomenon can be considered as less for the *N*-sulfophenyl-substituted PBI. These weak conductivities are also a consequence of the low water uptake of the membranes varying between 5 and 8 molecules of water per sulfonic acid group.

On the basis of a preliminary investigation on the chemical and thermal stability of this type of membrane not reported here and the fact that this conductivity can be improved by increasing the IEC, these sPBI can be considered as an interesting polymer for high-temperature PEMFC.

Acknowledgment. The authors thank the CNRS (Centre Nationale pour la Recherche Scientifique), CEA (Commissariat à l'Energie Atomique) and GDR PACEM for financial support. The authors are also indebted to F. Schietz for thermal analysis and A. Waton and C. Monnet for NMR technical support.

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MA0614139