

# Ion-Exchange Membranes Prepared by Blending Sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide) with Polybenzimidazole

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**ABSTRACT:** New ion-exchange acid/base-blend (SPPO/PBI) membranes were prepared by mixing *N,N*-dimethylacetamide (DMA) solutions of sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) in the ammonium form and of polybenzimidazole (PBI), casting the solution as a thin film, evaporating the solvent, and treating the membrane with aqueous hydrochloric acid. The resulting membranes were found insoluble in DMA. The preliminary tests of the membranes were carried out in an H<sub>2</sub>/O<sub>2</sub> fuel cell at room temperature. Their performance in the fuel cell increased with the increase in the concentration of SPPO sulfonic acid groups in the blend, but the membranes formed with the highly sulfonated SPPO alone or predominating, which swelled excessively in water, did not give reproducible results, and their performance was usually inferior to that of the membranes having an optimum ratio of both components. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1118–1127, 2002

**Key words:** poly(phenylene oxide); blends; polyelectrolytes; membranes

## INTRODUCTION

Proton exchange membrane fuel cell has attracted considerable attention as a nonpolluting power generator. The proton exchange membrane is a vital part of the cell. The membrane must not only be a good conductor for hydrogen ions, but also an electronic insulator; it must have low permeabilities to the reactant fuel and oxidant (hydrogen or methanol and oxygen); it must show mechanical strength; and it must be chemically and thermally stable under the cell operation conditions.

Proton exchange membranes suitable for application in fuel cells have been prepared from a variety of polymeric materials. First, membranes<sup>1</sup> were based on sulfonated phenol-formaldehyde resins (lacking hydrolytic stability) or on sulfonated copolymers of styrene with divinylbenzene (with poor oxidation stability). Current membrane materials used in fuel cells are perfluorinated polymers with sulfonic acid groups in side chains,<sup>2</sup> such as Nafion (Du Pont), which have excellent chemical stability. Such membranes are, however, expensive, which limits their use in large-scale applications. Therefore, there is a demand for new chemically and thermally stable polymer membranes combining the properties of perfluorinated membranes with lower cost and better processability.

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A solution to this problem could be the development of partially fluorinated membranes by the radiation grafting of vinyl monomers (styrene and a vinyl crosslinker) to fluorinated films such as poly(tetrafluoroethene),<sup>3</sup> poly(tetrafluoroethene-co-hexafluoropropene),<sup>4</sup> poly(ethene-*alt*-tetrafluoroethene),<sup>5</sup> or poly(vinylidene fluoride)<sup>6</sup> films and subsequent sulfonation. Partially fluorinated membranes may be also based on a perfluorinated film impregnated with sulfonated poly(1,1,2-difluoro-2-phenylethene).<sup>1,7</sup>

A solution, which avoids the fluorine chemistry, consists of the preparation of membranes from arylene main-chain polymers. These polymers exhibit, in many cases, very good thermal, hydrolytic, and general chemical resistance.<sup>8</sup> The polymers need to be chemically derivatized (e.g., sulfonated) to generate protonic conductivity. One example of these polymers is poly(ether sulfone).<sup>9</sup> Although membranes of a highly sulfonated poly(ether sulfone) had insufficient mechanical stability in the water-swollen state, covalently crosslinked membranes had excellent mechanical strength, but sulfonamide crosslinks were probably not sufficiently stable for hydrolysis. Crosslinked sulfonated poly(ether sulfone) ion-exchange membranes were also obtained by mixing sulfonated and sulfinated poly(ether sulfone)s.<sup>10</sup> Only sulfinate groups were covalently crosslinked; poly(ether sulfone) with sulfonate groups was entangled in the network. Blending of sulfonated poly(ether sulfone) with aminated poly(ether sulfone) resulted in acid-base blends,<sup>11</sup> which were densely ion-crosslinked by the formation of salts. Such densely crosslinked membranes had both good proton conductivity and low permeability to methanol, which makes them candidates for a direct methanol fuel cell. Other resistant aromatic polymers attracting attention were sulfonated poly(phosphazene),<sup>12</sup> sulfonated polyimides with rigid naphthalene moieties,<sup>13</sup> sulfonated poly(ether ether ketone),<sup>11,14-16</sup> and in particular, polybenzimidazole (PBI). PBI is a basic polymer that can be doped with a strong acid such as phosphoric or sulfuric acid. Phosphoric acid-doped PBI membranes<sup>17-20</sup> exhibit good proton conductivity, low gas permeability, excellent oxidative and thermal stability, and good mechanical flexibility at high temperatures (200°C); they were investigated for use in H<sub>2</sub>/O<sub>2</sub> and direct methanol fuel cells.<sup>21,22</sup> A thorough review on the development of the proton exchange membranes for fuel cells is presented by Savadogo.<sup>23</sup>

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an attractive material for the preparation of membranes because it possesses excellent film- and membrane-forming properties as well as high thermal and chemical stability.<sup>24</sup> Its ionic derivative, sulfonated PPO (SPPO), has been tested as a membrane material for gas separation,<sup>25-27</sup> reverse osmosis,<sup>28-30</sup> and ultrafiltration.<sup>31</sup> Besides good permeation properties, SPPO has shown good thermal stability<sup>25,32</sup> and resistance against aqueous solutions of strong acids and bases and oxidation agents.<sup>33</sup>

In this study, acid-base blends of PBI and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were prepared. The aim was to prepare new thermally and chemically stable ion-exchange membranes with good electrochemical properties, which should be cheaper than perfluorinated membranes.

## EXPERIMENTAL

### Materials

1,2-Dichloroethane (Aldrich, anhydrous, 99.8%), chloroform (Fluka, puriss. p.a.), *N,N*-dimethylacetamide (DMA) (Fluka, purum, >98%), *N,N*-dimethylformamide (Fluka, purum, 99%), chlorosulfonic acid (Fluka, purum >98%), ferrous chloride tetrahydrate (Fluka, puriss. p.a.), hydrogen peroxide (Fluka, puriss. p.a.) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (Spolana Neratovice, Czech Republic,  $M_w = 208,000$ , by light scattering) were used as received. Polybenzimidazole (PBI), full chemical name poly(5,5'-bibenzimidazole-2,2'-diyl-1,3-phenylene), (Hoechst Celanese) was available as a 10% *N,N*-dimethylacetamide solution stabilized with lithium chloride (LiCl <2%). Nafion 117 membranes (DuPont, obtained from Aldrich) were pretreated by boiling in 3% H<sub>2</sub>O<sub>2</sub>, rinsing in boiling water, boiling in 0.5 M H<sub>2</sub>SO<sub>4</sub>, and finally rinsing in boiling water (each step 1 h).

### Low Degree of Sulfonation of PPO

PPO was dissolved in 1,2-dichloroethane (45°C) to a 3% solution. Chlorosulfonic acid in 1,2-dichloroethane (5% solution) was slowly added with stirring to the polymer solution at 45°C (molar ratio PPO monomer unit/ClSO<sub>3</sub>H 1 : 0.26). The precipitated sulfonated product was removed by filtra-

tion, washed thoroughly with distilled water, left to stand in an excess of aqueous ammonia overnight, filtered off, washed with distilled water, and dried. The S, N, and Cl contents (by elemental analysis) were 5.62, 2.45, and 0.11, respectively. Degree of sulfonation of the sample, calculated from the S content (Cl content was not considered), and assuming that one aromatic ring bears one sulfonic acid group maximally and that degree of sulfonation of 100%, means that each aromatic ring bears one sulfonic acid group, is 25.4%.

### High Degree of Sulfonation of PPO

PPO was dissolved in chloroform to a 3% solution. Chlorosulfonic acid in chloroform (5% solution) (molar ratio PPO monomer unit/ClSO<sub>3</sub>H 1 : 1.96) was slowly added while stirring to the polymer solution at 25°C until the sulfonated PPO precipitated. The precipitate was removed from the mixture, extracted with water, allowed to stay in aqueous ammonia overnight, washed with distilled water, and dried. The S, N, and Cl contents were 8.43, 3.64, and 0.15%, respectively, which corresponds to the degree of sulfonation of 42.4%.

### Spectroscopy

IR spectra of PPO and SPPO samples were recorded on a Perkin-Elmer Paragon 1000 PC spectrometer using a KBr pellet. <sup>1</sup>H (300.13 MHz)- and <sup>13</sup>C (75.5 MHz)-NMR spectra of SPPO samples in (CD<sub>3</sub>)<sub>2</sub>SO solution were recorded on a Bruker Advance DPX300 at 25°C. <sup>15</sup>N-NMR spectra (solid state) were recorded on a Bruker Advance DPX400, 4 kHz, at 25°C. The PBI/SPPO sample for the <sup>15</sup>N-NMR analysis was prepared by mixing of 15 g of 10% DMA solution of SPPO (degree of sulfonation 42.4%, sulfonic acid groups in H<sup>+</sup> form) with 5 g of the 10% PBI solution in DMA. The precipitated product was removed by filtration and washed thoroughly first with DMA and then with water and dried in a vacuum. The PBI powder was obtained by the precipitation of 10 mL of the PBI solution into 500 mL of water, the PBI · H<sub>2</sub>SO<sub>4</sub> powder by the precipitation into 500 mL of 1 M aqueous H<sub>2</sub>SO<sub>4</sub>.

### Determination of Ion Exchange Capacity (IEC)

#### IEC by Titration

The membrane (0.1 g) was cut into small pieces and suspended under stirring in 10 mL of satu-

rated aqueous solution of NaCl for 4 days and titrated with 0.1 M NaOH. Solution pH was measured with a glass pH-electrode and a pH meter (Corning 340).

#### IEC Based on Sulfonic Acid Groups Content

IEC was calculated from the sulfur content determined by elemental analysis using the relationships  $IEC = 1200.SD/(120 + 80.SD)$  and  $SD = 120.S/(32 - 80.S)$ , where SD and S are degree of sulfonation and sulfur content in the polymer, respectively.

### Film Casting

DMA solutions (5%) of SPPO (in the NH<sub>4</sub><sup>+</sup> form) and of PBI were mixed in different ratios. The mixture was cast onto a glass plate and the solvent was slowly evaporated at 80°C. The film was removed from the glass plate by immersion into a water bath. The resulting membrane was washed in water for several days, then immersed into 1 M aqueous HCl for 24 h and then again washed in water. The membranes used in fuel cell experiments were 80 ± 9 μm thick (measured with a mechanical thickness gauge).

The membranes of SPPO alone (in the NH<sub>4</sub><sup>+</sup> form) were cast from 15% DMF solutions. The subsequent treatment (including the conversion into the H<sup>+</sup> form) and the thickness of the membranes were the same as in the case of SPPO/PBI membranes.

The PBI membrane was cast from the 10% DMA solution (Hoechst Celanese). The subsequent treatment (including the treatment with 1 M HCl) and the thickness of the membranes were the same as in the case of SPPO/PBI membranes.

### Membrane Swelling

Membrane strips were immersed into DMA or water at 25°C. After 24 h the strips were removed from the liquid, wiped with tissue paper, weighed, dried in vacuum, and again weighed. The degree of swelling in water (DS) and the weight loss in DMA (extractable polymer) (EXT) were determined using the relations  $DS = (W_S - W_{02})/W_{02}$  and  $EXT = (W_{01} - W_{02})/W_{02}$ , respectively, where  $W_S$  is the weight of a swollen strip,  $W_{01}$  is the weight of a dry strip before swelling and  $W_{02}$  is the weight of a dry strip after swelling.

### Thermal Stability

The thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Thermal Analysis

Controller TAC 7/DX from 30 to 700°C at a heating rate of 10°C/min in air atmosphere. The samples were dried in vacuum at a room temperature for 14 days; nevertheless, prior to analysis, they were in contact with atmospheric humidity for several hours.

### Oxidative Stability

Membrane samples 8 × 3 cm were immersed into 3% H<sub>2</sub>O<sub>2</sub> aqueous solution containing 4 ppm FeCl<sub>2</sub> · 4 H<sub>2</sub>O at 80°C for 72 h. The weights of dried samples before and after the experiment were compared.

### Ionic Conductivities

The resistance was determined in 0.1 M KCl at 25°C. The measuring cell consisted of a cylindrical container in the bases of which cylindrical electrode holders were fixed juxtaposed to each other. Each electrode holder was equipped with a thread and bore a ring with internal thread that could be moved by rotation on the electrode holder. The internal diameter of the rings was nearly equal to that of circular platinum electrodes firmly pasted on the holders. The leads to the electrodes were centered through the holders. By rotation, the rings moved and joined tightly one to the other. So, a cylindrical chamber was formed 2.87 cm in diameter and 0.36 cm thick. The two bases of the chamber were consequently formed by slightly platinized platinum foils—electrodes; the wall was the internal part of the rings. For measurement, the container with separated rings was filled with 0.1 M KCl, a membrane strip 3.5 × 5 cm was inserted between the rings and the rings were tightened together. So, the measuring chamber was insulated from the electrolyte in the rest of the container. From the whole membrane strip, a circle 2.87 cm in diameter was exposed to the electric current and the electrolyte layers between electrodes and the membrane were only 0.18 cm thick. The whole cell was inserted in an incubator at 25°C, joined with the Wayne Kerr bridge by means of four leads ended with Kelvin clamps and, after 2 h, the measurement could start. The whole impedance spectrum between 300 kHz and 20 Hz, namely both resistance and capacitance, was recorded. Capacitance (after recalculation) represents then the imaginary part, resistance the real part of the impedance. Instead of capacitance, loss angle can be measured, for

example, to determine the resonance conditions and the suitable region of frequency. It was found that at 100 kHz the dependence of resistance on frequency is not significant. After several measurements, the membrane was taken out of the cell, the rings were again tightened together, and the electrolyte without the membrane was measured. Resistance was then calculated as

$$R_m = R_{m+s} - R_s \left( \frac{d-x}{d} \right),$$

where  $R_m$  is membrane resistance,  $R_{m+s}$  is resistance of the membrane with the solution,  $R_s$  resistance of the solution,  $d$  distance between electrodes and  $x$  thickness of the membrane. Resistance of the solution has been corrected for membrane thickness, as the distance between electrodes was fixed and small.

### Fuel Cell Experiments

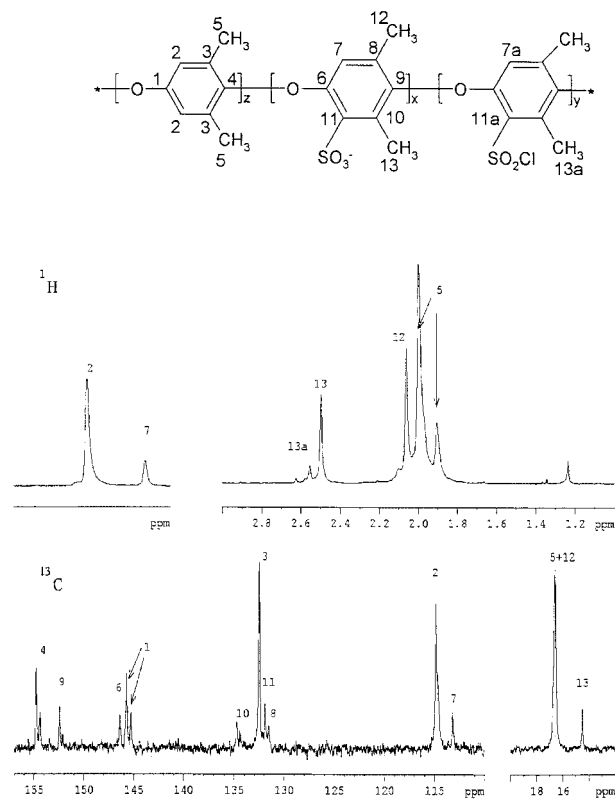
A commercial fuel cell (PEMFC-Kit, H-TEC, Lubeck, Germany) with detachable platinized electrodes having an active area of 16 cm<sup>2</sup> was used for membrane testing. No special treatment was used for the membrane–electrode assembly. The fuel cell was operated on pure hydrogen (passed to the cell through a water bath) and pure oxygen at atmospheric pressure at 25°C. Typical time of testing of a membrane in the cell was 80 h.

## RESULTS AND DISCUSSION

### Sulfonation of PPO

PPO was sulfonated with chlorosulfonic acid either in a chloroform solution, which is a common technique of the PPO sulfonation<sup>25–30</sup> or in a 1,2-dichloroethane one. In both cases, the sulfonated product precipitates after the addition of a certain amount of chlorosulfonic acid to the reaction mixture and can be easily isolated. The amount of chlorosulfonic acid needed for the precipitation of SPPO from the 1,2-dichloroethane solution is, however, smaller and, therefore, the degree of sulfonation of the obtained SPPO is lower (25.4 vs. 42.4% for the sample sulfonated in chloroform).

The relevant parts of the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of SPPO together with the formula of SPPO are shown in Figure 1. A small peak at 2.55 ppm in <sup>1</sup>H-NMR spectrum indicates the presence



**Figure 1** Relevant parts of the 300.13 MHz  $^1\text{H}$ - and 75.5 MHz  $^{13}\text{C}$ -NMR spectra of SPPO with a degree of sulfonation 25.4%.

of sulfonyl chloride groups attached to aromatic rings in small concentration as also very small amounts of chlorine were found in SPPO samples by elemental analysis. The sulfonyl chloride groups attached to aromatic rings can be quite stable in pure water for many days.<sup>34</sup> Disubstituted aromatic rings were not found in either SPPO.

Infrared spectra of unsulfonated PPO and SPPO are shown in Figure 2. In the SPPO spectrum, new peaks appear at  $1063\text{ cm}^{-1}$  ( $\nu_s$  S=O) and  $1397\text{ cm}^{-1}$  ( $\delta$  N—H in the  $\text{NH}_4^+$  group) and, on the other hand, the intensity of the peak at  $3044\text{ cm}^{-1}$  ( $\delta$  C—H in aromatic rings) is decreased.

### Film Casting

DMA is a good solvent for the PBI base as well as for SPPO, both in the acid and ammonium forms. If DMA solutions of the PBI base and SPPO in the acid form are mixed, a precipitate is immediately formed and no homogeneous film can be prepared.

Homogeneous membranes can be prepared by mixing DMA solutions of the PBI base and SPPO in the ammonium form, casting films and evaporating the solvent. The membrane is then treated with aqueous HCl to remove the ammonium ions.

### SPPO/PBI Interactions

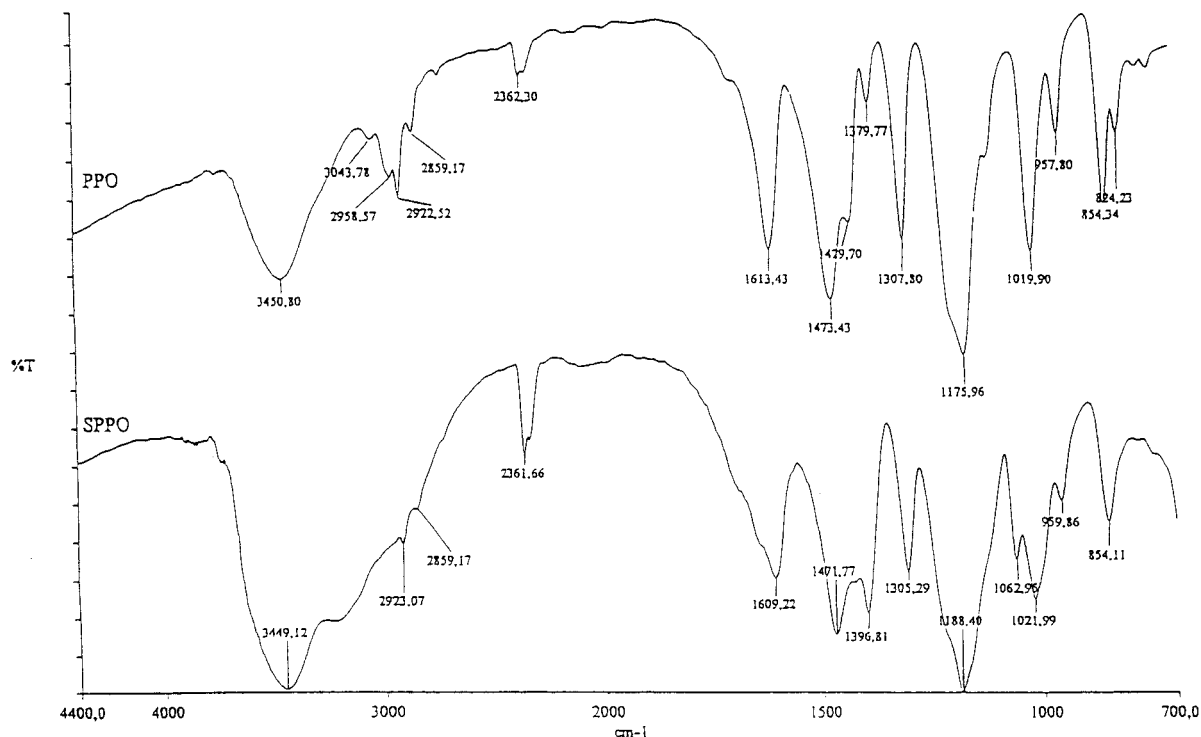
It is known<sup>11,35,36</sup> that upon mixing of an acidic polymer with a basic one, the interactions between the polymers occur by formation of hydrogen bonds and by proton transfer from the acidic to the basic groups. The proton transfer between the two polymers can be proven by comparing infrared spectra of the basic polymer in a pure state and in the mixture.<sup>35</sup> PBI is a basic polymer ( $\text{p}K_a = 5.5$ ),<sup>37</sup> which can be readily complexed by a strong acid by the protonation of the imino nitrogen site.<sup>18,19,37</sup> In the case of SPPO/PBI blends, strong absorption bands of SPPO, however, mask the bands of protonated PBI ( $3000\text{--}2500\text{ cm}^{-1}$  broad band and four bands between  $1630$  and  $1309\text{ cm}^{-1}$ ; ref. 18), and it is not possible to get reliable evidence of the proton transfer from the IR spectra.

Proton transfer from SPPO to PBI is clearly seen in the  $^{15}\text{N}$ -NMR spectrum (Fig. 3) of the PBI/SPPO blend: the amine peak is shifted from  $140\text{ ppm}$  in pure PBI to about  $150\text{ ppm}$  in the blend. The similar shift can be observed with pure PBI, which is protonated with  $\text{H}_2\text{SO}_4$ .

The interactions between PBI and SPPO should lead to a crosslinked blend that is insoluble in contrast to the both polymers alone. The results of solubility tests of the prepared membranes are given in Table I. The tests were carried out in DMA, in which both polymers before blending are soluble. It can be seen that when the concentration of PBI in the blend was high enough, the membranes were in DMA completely insoluble. If the concentration of PBI in the blend was small, a part of a membrane material could be extracted with DMA, and this part was considerably greater in the case of SPPO with a lower degree of sulfonation.

### Ion Exchange Capacity

The interactions between acidic and basic groups can be also confirmed by comparing the ion exchange capacity (IEC) based on sulfonic acid groups content: in the membrane calculated from the sulfur content, and the IEC determined by



**Figure 2** IR spectra of PPO (upper curve) and SPPO with a degree of sulfonation 25.4% (lower curve).

acid-base titration. It can be seen in Figure 4 that the IEC based on the sulfur content and the IEC based on the acid-base titration reasonably agree for the membranes prepared from SPPO alone. In the case of the blend membranes, the IEC based on the acid-base titration is lower than that based on sulfonic groups content, and the difference increases with the increase in the PBI concentration in the blend. It is evident that sulfonic acid groups bound to the PBI basic groups cannot release protons to the solution to be titrated in contrast to the free sulfonic acid groups. The difference between IEC calculated from the sulfur content and IEC found by titration should correspond to the amount of sulfonic acid groups complexed in the blend.

#### Membrane Swelling in Water

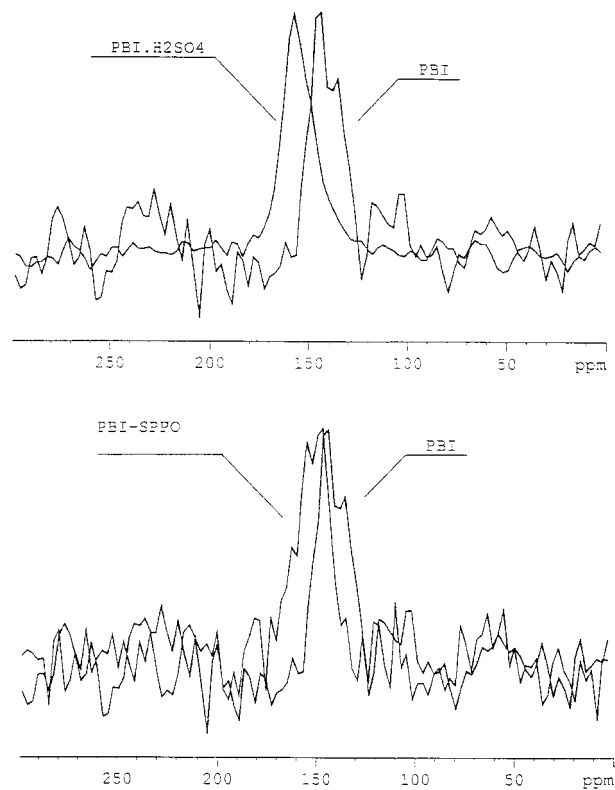
Although PBI is a moderately hydrophilic polymer, SPPO is a highly hydrophilic one. The membranes of PBI alone swell in water only slightly; with increasing concentration of SPPO in the blend, the degree of swelling in water increases (Fig. 5). The membranes prepared from pure

SPPO with a degree of sulfonation of 42.4% or from blends with concentrations of this SPPO above than ca. 80 wt % swell in water excessively, which impairs their mechanical strength.

#### Membrane Stability

Thermal stabilities of the prepared membranes were studied by thermogravimetry. TGA thermograms for membranes from PBI alone, from SPPO with a degree of sulfonation of 42.6%, and from a PBI/SPPO blend (weight ratio of components 1 : 1 w/w) are shown in Figure 6. The weight loss of all the membranes at about 100°C can be attributed to the loss of moisture absorbed from air (before TGA analysis the films were exposed to air). The PBI membrane is perfectly stable up to about 620°C; the membrane of SPPO alone up to about 230°C, and the blend membrane up to about 300°C. All the values should be sufficient for any application as ion-exchange membranes; it should be born in mind, however, that they refer only to the short-term stabilities.

Preliminary tests of oxidative stability were carried out by immersing membrane samples into



**Figure 3**  $^{15}\text{N}$ -NMR spectra of PBI,  $\text{PBI} \cdot \text{H}_2\text{SO}_4$  and PBI/SPPO blend.

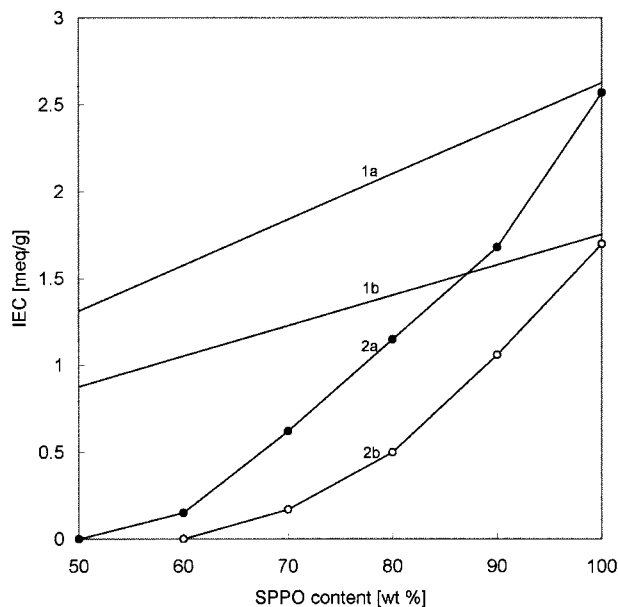
3%  $\text{H}_2\text{O}_2$  aqueous solution containing ferrous ions for 72 h at  $80^\circ\text{C}$ . No change of weight of samples before and after the experiment was observed with the membranes formed by SPPO (degree of sulfonation 25.4%) alone or in mixtures with PBI and with the membranes formed by SPPO (degree

**Table I** The Weight Loss of SPPO/PBI Membranes After Extraction with DMA

Content of SPPO in the Blend with PBI (wt %)	EXT <sup>a</sup> (wt %)	EXT <sup>b</sup> (wt %)
50	0	0
60	4	0
70	28	0
80	36	2
90	69	12
100	100	100

<sup>a</sup> Polymer extractable from the SPPO (degree of sulfonation 25.4%)/PBI membrane.

<sup>b</sup> Polymer extractable from the SPPO (degree of sulfonation 42.4%)/PBI membrane.

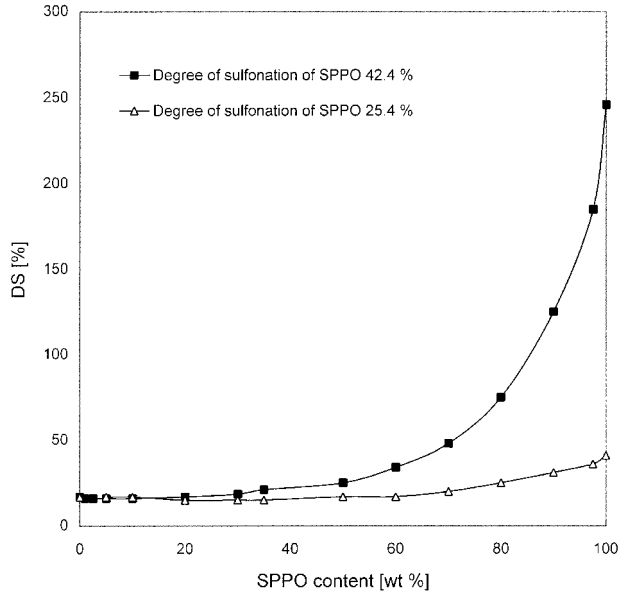


**Figure 4** Dependence of ion exchange capacity (IEC) calculated from the sulfur content in the blend (1a, 1b) and determined by acid-base titration (2a, 2b) on the SPPO content in the blend: (a) SPPO with a degree of sulfonation 42.4%; (b) SPPO with a degree of sulfonation 25.4%.

of sulfonation 42.4%) in mixtures containing at least 20 wt % of PBI. The membranes formed by SPPO (degree of sulfonation 42.4%) alone or containing 90 wt % of this SPPO and 10 wt % of PBI lost <1% of their weight.

#### Ionic Conductivities

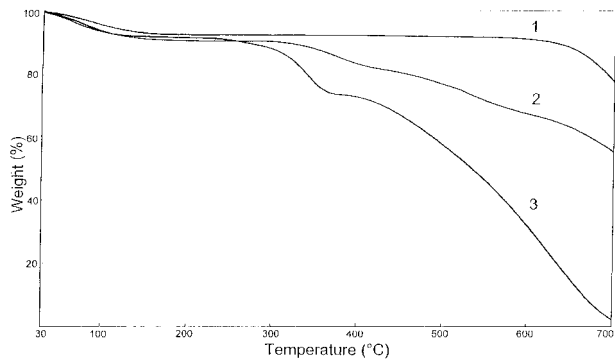
Ionic conductivities of prepared membranes in a KCl solution are shown in Figure 7. The membranes are conductive if the concentration of sulfonated PPO in the blend is higher than a percolation threshold. It is plausible that the blend membranes with the conductivities under the threshold have the vast majority of sulfonic acid groups of SPPO bound to the PBI basic groups, and these sulfonic acid groups cannot contribute to the overall proton conductivity. The conductivities of membranes above percolation threshold increase with the increasing concentration of sulfonic acid groups in the membrane. Membranes containing more than 80 wt % of highly sulfonated SPPO had very high conductivities (comparable to that of 0.1 M KCl solution); therefore, their exact value could not be determined by the used method.



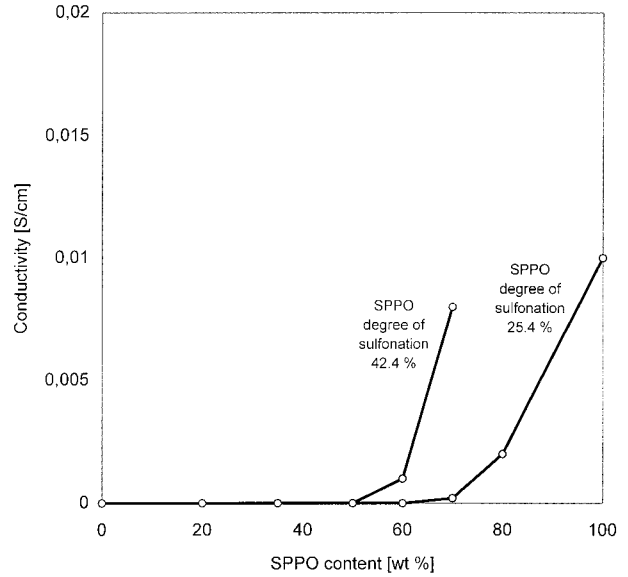
**Figure 5** Dependence of the degree of swelling (DS) of SPPO-PBI membranes in water on the SPPO content.

**Fuel Cell Experiments**

The membranes were tested in a simple hydrogen/oxygen fuel cell at room temperature and atmospheric pressure. The polarization curves show (Figs. 8 and 9) that the performance of membranes increases with the increase in the concentration of sulfonic acid groups in the membrane material. It can be controlled either by the SPPO concentration in the blend or by the sulfonation degree of SPPO. This dependence on the concentration of sulfonic acid groups has, however, two limitations: 1. The membranes with low concen-

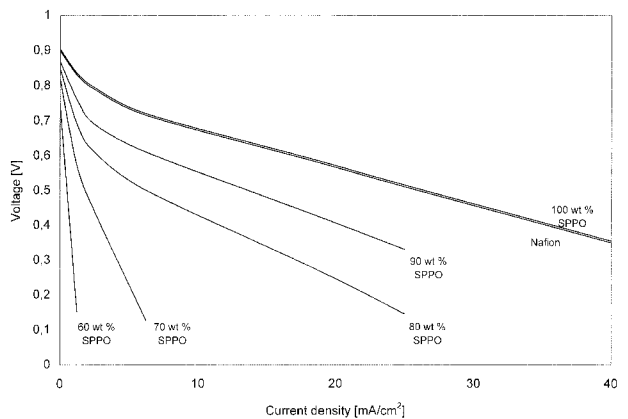


**Figure 6** TGA curves of membranes made of: (1) PBI; (2) 1 : 1 w/w SPPO (degree of sulfonation 42.4%)/PBI blend; (3) SPPO (degree of sulfonation 42.4%).



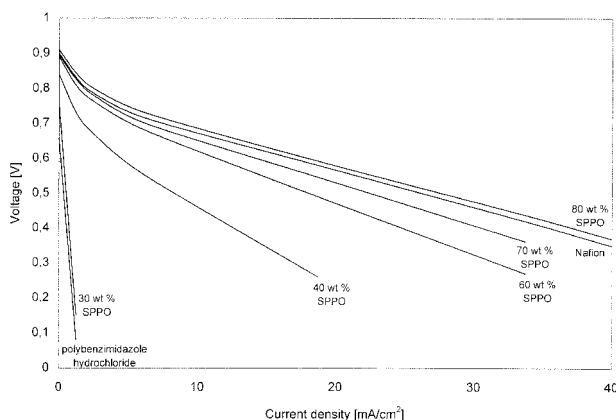
**Figure 7** Dependence of conductivities of SPPO-PBI membranes on the SPPO content.

trations of sulfonic acid groups (less than about 70 wt % of SPPO with a degree of sulfonation 25.4% or less than about 40 wt % of SPPO with a degree of sulfonation 42.4%) show negligible performance in the fuel cell regardless of their composition. A certain percolation threshold can be observed here, but, in contrast to that observed in the conductivity measurements (Fig. 7), it is not as sharp, and lies at lower SPPO concentrations in the blend. It is to be noted that the transport of H<sup>+</sup> ions across the membrane occurs in the fuel cell while in our conductivity measurements,



**Figure 8** Polarization curves of SPPO-PBI membranes with various contents of SPPO (degree of sulfonation 25.4%).





**Figure 9** Polarization curves of SPPO–PBI membranes with various contents of SPPO (degree of sulfonation 42.4%).

transport of  $K^+$  and  $Cl^-$  ions was involved. 2. The membranes with extreme water swellings (containing more than 80 wt % of SPPO with a degree of sulfonation 42.4%; Fig. 9) did not give quite reproducible results (therefore, their current–voltage curves are not given in the diagram). Nevertheless, their performance was usually somewhat inferior to the Nafion membrane, and to the best membranes tested here. This inferior performance is probably brought about by the gas leakage through the highly swollen membranes (Fig. 5).

## CONCLUSIONS

It is possible to prepare ion-exchange membranes by blending sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) with polybenzimidazole. The membranes are conductive for ions if the concentration of sulfonated PPO in the blend is higher than a percolation threshold. The ionic conductivities of membranes above percolation threshold increase with the increase in the concentration of sulfonic acid groups in the membrane.

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