# Novel Proton-Conducting Polyelectrolyte Composed of an Aromatic Polyether Containing Main-Chain Pyridine Units for Fuel Cell Applications

N. Gourdoupi, A. K. Andreopoulou, V. Deimede, and J. K. Kallitsis*

*Department of Chemistry, University of Patras, University Campus, GR-26500 Rio-Patras, Greece, and Foundation of Research and Technology Hellas, Institute of Chemical Engineering and High-Temperature Chemical Processes, P.O. Box 1414, GR-26500 Patras, Greece*

A new high-molecular-weight, soluble, wholly aromatic polyether bearing polar pyridine and phosphinoxide groups along the main chain is presented. This easily processable polyether presents excellent film-forming properties, high glass-transition temperature (up to 260 °C), and thermal stability up to 500 °C, all together combined with an ability to form ionically conductive materials after doping with phosphoric acid. The polar groups throughout the polymeric chains enable high acid uptake and subsequent high ionic conductivity for the doped membranes in the range of $10^{-2}$ S/cm. Characterization of all polymeric materials prepared was performed using NMR, size exclusion chromatography, thermal and mechanical analysis, and conductivity measurements. The oxidative stability of the materials was studied using hydrogen peroxide, and the treated membranes were further characterized using dynamic mechanical analysis and FT−Raman spectroscopy. The conductivity of the doped membranes was determined as a function of the doping level. The temperature dependence of the conductivity was also studied.

## Introduction

Fuel cells have attracted increasing attention in recent years as a clean, silent, and efficient power source.[1] Polymer electrolyte membrane fuel cells (PEM-FC) operating at about 90 °C are currently the best candidates for automobile applications.[1,2] However, up to now, the low temperature PEMFCs demand hydrogen of high purity and humidification of the feed gases, thus their operation cost increases sufficiently. In these cells high ionic conductivity is obtained at high levels of humidity where proton mobility is combined with a water flow through the membrane (electroosmotic drug effect). On the other hand, when methanol, which is considered an environmentally friendly fuel, is selected in direct methanol fuel cells (DMFCs), permeability through the membrane remains the key disadvantage of current materials in use.[3] By increasing the temperature at which FCs operate, advantages such as increased catalyst's activity, decreased susceptibility of the anode's catalyst to poisoning due to impurities in the fuel stream, easier thermal management than conventional PEM fuel cells, etc., can arise.[4−6] Particularly

poisoning of the anode's catalyst, a key parameter if a low-cost $H_2$ supply is to be used, can be overcome in FCs operating above 150 °C in which more than 1% CO content in the fuel stream does not disturb the operation efficiency.[7]

The basic prerequisites for a polymeric material to be used as a membrane for high-temperature PEMFCs are good mechanical, thermal, and chemical stability, high glass-transition temperature, and increased ionic conductivity after doping with a strong acid. Besides polybenzimidazole (PBI), which is a well-established high-temperature polymeric electrolyte,[4,5] there is a significant research effort nowadays toward the development of some novel polymeric materials which fulfill the above requirements.

Keeping these considerations in mind, polyelectrolytes composed of thermally and chemically stable aromatic main chain backbones are proper candidates. Such materials could either be new polymeric structures[8−13]

* To whom correspondence should be addressed. Phone: 3061-997-121. Fax: 3061-997-122. E-mail: J.Kallitsis@upatras.gr.
(1) Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345.
(2) Dresselhaus, M. S.; Thomas, F. L. *Nature* **2001**, *414*, 332.
(3) Kreuer, H. D. *Chem. Phys. Chem.* **2002**, *3*, 771.
(4) Wang, J.-T.; Savinell, R. F.; Wainright, J.-S.; Litt, M.; Yu, H. *Electrochim. Acta* **1996**, *41*, 193.
(5) Wainright, J.-S.; Wang, J.-T.; Weng, D.; Savinell, R. F.; Litt, M. *J. Electrochem. Soc.* **1995**, *142*, L121.
(6) Haile, S. M. *Mater. Today* **2003**, *3*, 24.

(7) Qingfeng, L.; Hjuler, H. A.; Hasiotis, C.; Kallitsis, J. K.; Kontoyannis, C. G.; Bjerrum, N. J. *Electrochim. Solid-State Lett.* **2002**, *5*, A125.
(8) Poppe, D.; Frey, H.; Kreuer, K. D.; Heinzel, A.; Muelhaupt, R. *Macromolecules* **2002**, *35*, 7936.
(9) Rulkens, R.; Wegner, G.; Thurm-Albrecht, T. *Langmuir* **1999**, *15*, 4022.
(10) Vanhee, S.; Rulkens, R.; Lehmann, V.; Rosenauer, C.; Koehler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136.
(11) Brodowski, G.; Horrath, A.; Ballauff, M.; Rehahn, M. *Macromolecules* **1996**, *29*, 6962.
(12) Wittemann, M.; Kelch, S.; Blaul, J.; Hicke, P.; Guilleaume, B.; Brodowski, G.; Horrath, A.; Ballauff, M.; Rehahn, M. *Macromol. Symp.* **1999**, *142*, 43.
(13) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411.

or modified engineering polymers[14−23] like polysulfone and poly(etherketone). Polymeric blends have also been exploited as proton-exchange membranes for fuel cell applications.[19,24−28] More specifically the development of novel polyelectrolytes bearing polar side groups and rigid or semirigid polymeric main chains has been thoroughly investigated in respect to their miscellization behavior.[9,29−30] Sulfonated aromatic polyethers can also offer high stability and ionic conductivity after doping with water.[14−19] Blending of such sulfonated polyethers with PBI resulted in materials with high ionic conductivity and improved mechanical properties, which have been already successfully applied in fuel cells operating at temperatures above 150 °C.[24]

Following this approach we report on the synthesis of a new high-temperature polymeric electrolyte containing pyridine and phosphinoxide units along the main chain. The particular polymer and a structurally modified one were rationally designed taking into account the ability of the phosphinoxide group and pyridine ring to interact with phosphoric acid to ensure improved phosphoric acid uptake and consequently high ionic conductivity. This aromatic polyether showed exceptional thermal and oxidative stability, good mechanical and film forming properties, and high glass-transition temperature combined with high ionic conductivities after doping with phosphoric acid.

## Results and Discussion

In our attempt to synthesize polymeric materials stable at high temperatures, which could also be doped with strong acids such as phosphoric acid, we have initially designed and synthesized new monomeric diols containing a pyridine ring. Monomers were prepared using palladium-mediated cross coupling[31] of 2,5- or 2,6-dibromopyridine with a properly protected boronic acid. Scheme 1 presents reaction sequences employed for the preparation of diols **3** and **4**. More specifically, 2,5-dibromopyridine and 2,6-dibromopyridine were coupled under Suzuki coupling conditions with the THP-protected hydroxyphenylboronic acid, using Pd(PPh$_3$)$_4$ as catalyst. Both reactions proceeded smoothly and quantitively with no loss of the end group functionalities, thus producing the corresponding THP-end-protected monomers in gram-scale quantities. Removal of the THP moieties was performed under acidic conditions, in dilute HCl/H$_2$O and THF mixtures. Use of previously employed camphorosulfonic or *p*-toluenosulfonic acids was avoided because of their complexation with the pyridine moieties. On the other hand, deprotection with dilute HCl solutions (5%) allowed quick removal of the THP groups,[32] while subsequent stirring in aqueous Na$_2$CO$_3$ solutions for a few hours easily reversed any protonation of the pyridine groups. Characterization of both final monomeric diols, **3** and **4**, was performed using $^1$H and $^{13}$C NMR with assignment of all peaks proving the proposed structures and moreover the absence of any protonated pyridine moieties.

High-temperature polymerization of diols **3** and **4** with phosphinoxide difluoride[33,34] was employed for various reaction times. High-molecular-weight polymers were obtained in most cases, as can be seen in Table 1. Both polymers **I** and **II** showed solubility in common organic solvents such as CHCl$_3$, allowing for their GPC and NMR characterization. GPC measurements, using CHCl$_3$ as eluent versus PS standard calibration, revealed molecular weights ($M_n$) up to 77 000. It is known that calibration with PS standards overestimates the MW in the case of rigid polymers. In our case, however, the increased solubility due to the presence of the tetrahedral phenylphosphinoxide moieties in the main chain, as well as the film-forming ability, even for the lower-molecular-weight samples, show that the obtained MW values cannot significantly differ from the absolute ones.

A representative $^1$H NMR spectra for polymer **I$_e$** and that obtained for the initial diol **3** (inset) are presented in Figure 1. As can be easily observed in the polymer spectrum, no aromatic protons neighboring the hydroxy end groups can be detected at 6.88 ppm, further supporting that high-molecular-weight polymers were obtained.

The mechanical properties of polymers **I** were examined by means of dynamic mechanical analysis (DMA). Polymer **II**, due to its low MW and lower $T_g$, was not considered for further evaluation. For polymers **I**, even the lower MW ones ($M_n \approx 7000$) exhibited good film-forming properties, thus the influence of the MW on their glass-transition temperatures could be thoroughly investigated. As presented in Figure 2, glass-transition temperatures from 244 °C and up to 260 °C were obtained, supporting an increased rigidity when compared to those of hydroquinone analogues.[35]

(14) Lufrano, F.; Gatto, I.; Staiti, P.; Antonucci, V.; Passalacqua, E. *Solid-State Ionics* **2001**, *145*, 47.

(15) Lufrano, F.; Squadrito, G.; Patti, A.; Passalacqua, E. *J. Appl. Polym. Sci.* **2000**, *77*, 1250.

(16) Iwasaki, K.; Yamamoto, T.; Harada, H.; Tarahara, A.; Satoh, K. Eur. Pat. Appl. EP 932213, 1999.

(17) Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29.

(18) Kerres, J.; Velrich, A.; Haring, Th.; Baldaut, M.; Gebhardt, V.; Preidel, W. *J. New Mater. Electrochem. Syst.* **2000**, *3*, 229.

(19) Poppe, D.; Zerfass, T.; Muelhaupt, R.; Frey, H. Sulfonated and Carboxylated Copoly(arylenesulfone)s for Fuel Cell Applications. In *Functional Condensation Polymers*; Carraher, C. E., Swift, C. G., Eds.; Kluwer Academic: New York, 2002; p 83.

(20) Wiles, K. B.; Bhanu, V. A.; Wang, F.; McGrath, J. E. *Abstracts of Papers, 224th ACS National Meeting, Boston, MA, August 18−22, 2002*.

(21) Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J.; Zawodzinski, T. A.; McGrath, J. E. *Macromol. Symp.* **2001**, *175*, 387.

(22) Wang, F.; Kim, Y.; Hickner, M.; Zawodzinski, T. A.; McGrath, J. E. *Polym. Mater. Sci. Eng.* **2001**, *85*, 517.

(23) Wang, F.; Ji, Q.; Harrison, W.; Mecham, J.; McGrath, J. E.; Formato, R.; Kovar, R. *Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26−30, 2000*.

(24) Deimede, V.; Voyiatzis, G. A.; Kallitsis, J. K.; Qingfeng, L.; Bjerrum, N. J. *Macromolecules* **2000**, *33*, 7609.

(25) Hasiotis, C.; Qingfeng, L.; Deimede, V.; Kallitsis, J. K.; Kontoyannis, C. G.; Bjerrum, N. J. *J. Electrochem. Soc.* **2001**, *148*, A513.

(26) Kerres, J. A. *J. Membr. Sci.* **2001**, *185*, 3.

(27) Bashir, H.; Linares, A.; Acosta, J. L. *Solid State Ionics* **2001**, *139*, 189.

(28) Kerres, J. A.; Ullrich, A.; Meier, F.; Haring, T. *Solid State Ionics* **1999**, *125*, 243.

(29) Bockstaler, M.; Koehler, W.; Wegner, G.; Fytas, G. *Macromolecules* **2001**, *34*, 6353.

(30) Bockstaler, M.; Koehler, W.; Wegner, G.; Vlassopoulos, D.; Fytas, G. *Macromolecules* **2000**, *33*, 3951.

(31) Mijaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(32) Andreopoulou, A. K.; Kallitsis, J. K. *Macromolecules* **2002**, *35*, 5808.

(33) Smith, C. D.; Gungor, A.; Keister, K. M.; Marand, H. A.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 93.

(34) Hay, A. S. *Prog. Polym. Sci.* **1999**, *24*, 45.

(35) Ding, Y.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 519.

**Scheme 1**[a]
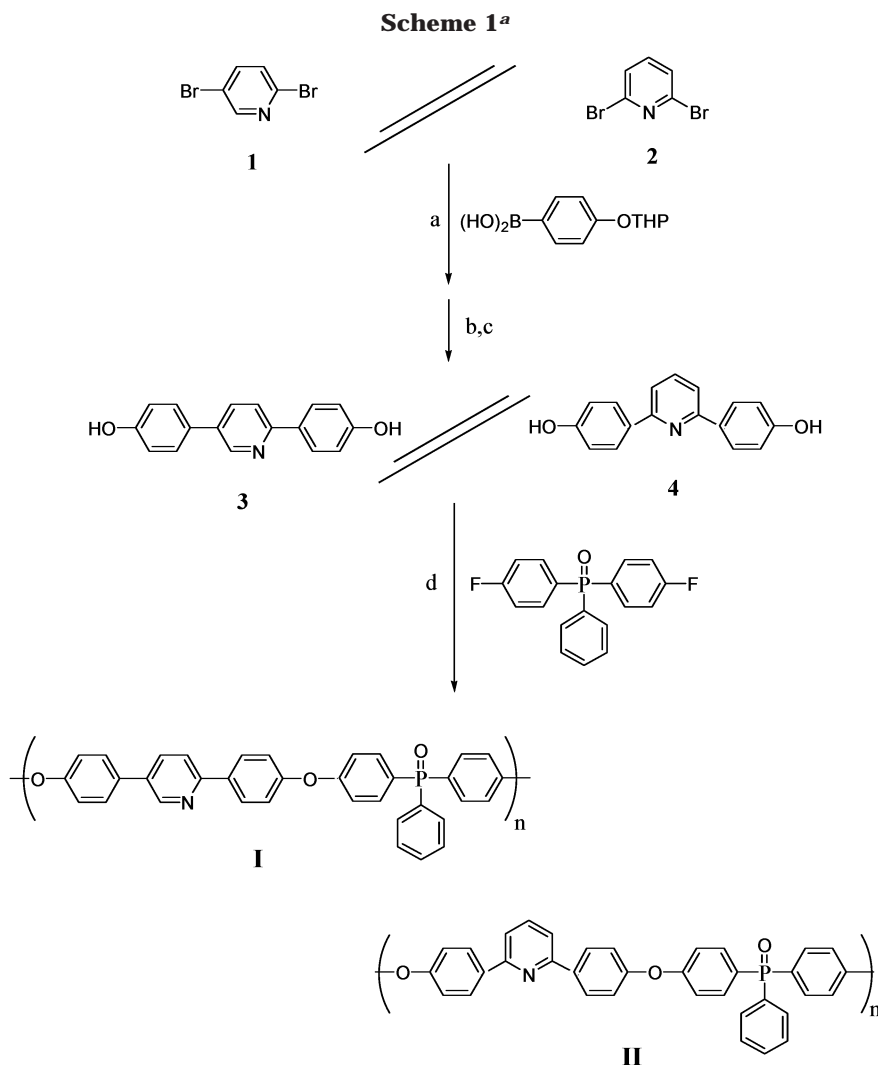


[a] (a) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ 2M, Tol, reflux 24 h, 83%. (b) HCl (37%), THF, MeOH, rt, 18 h, 90%. (c) THF, Na$_2$CO$_3$ 0.1 M, 93%. (d) DMF, Tol, K$_2$CO$_3$, 150 °C 48 h and 180 °C 6 h.

**Table 1. Gel Permeation Chromatography of the Synthesized Polymers**

| polymer | $M_n$ | $M_w$ | disp |
|---|---|---|---|
| **I$_a$** | 9600 | 26500 | 2.7 |
| **I$_b$** | 6700 | 16300 | 2.5 |
| **I$_c$** | 7300 | 22300 | 3.1 |
| **I$_d$** | 4900 | 13100 | 2.7 |
| **I$_e$** | 77000 | 240000 | 3.1 |
| **I$_f$** | 41900 | 84000 | 2.0 |
| **II** | 3400 | 5300 | 1.6 |

As expected, based on their wholly aromatic structure, these polymers also revealed exceptional thermal stability as proven by their thermogravimetric analysis (TGA) both in N$_2$ and air atmospheres (see Figure 3). The temperature for the 10% weight loss was observed at 540 and 560 °C in air and nitrogen atmospheres, respectively.

Besides an increased thermal stability and good mechanical properties, membranes applicable in fuel cells should also present good oxidative stability. Thus, preliminary accelerated tests have been performed on membranes by treatment with 3% H$_2$O$_2$ solutions in the presence of ferrous ions for 72 h at 80 °C.[36,37] It is known that when PBI membranes are treated with H$_2$O$_2$ their mechanical integrity is significantly decreased. How-

ever, when DMA measurements were performed on our membranes after treatment with hydrogen peroxide, no noticeable changes were detected, either to their integrity or to their mechanical properties compared to the ones before such a treatment, see Figure 4. To explore whether some structural changes have occurred during the hydrogen peroxide treatment of the membrane which could not be detected as a change in the mechanical properties of the films, spectroscopic characterization using FT−Raman and $^1$H NMR was performed. Comparing the FT−Raman spectra of the membranes before and after treatment with H$_2$O$_2$, no structural changes were observed, as shown in Figure 5. The absence of any change was further confirmed by $^1$H NMR spectroscopy.

The protonation of the membrane after its exposure to a strong acid for a long period of time could possibly affect its thermal stability, so we compared the thermogravimetric results before and after treatment with H$_3$PO$_4$ for 5 h and 1000 h (Figure 6). As can be clearly seen, the membrane is hydrolytically stable, as there are no changes of the thermal stability between the

(36) Hubner, G.; Roduner, E. *J. Mater. Chem.* **1999**, *9*, 409.
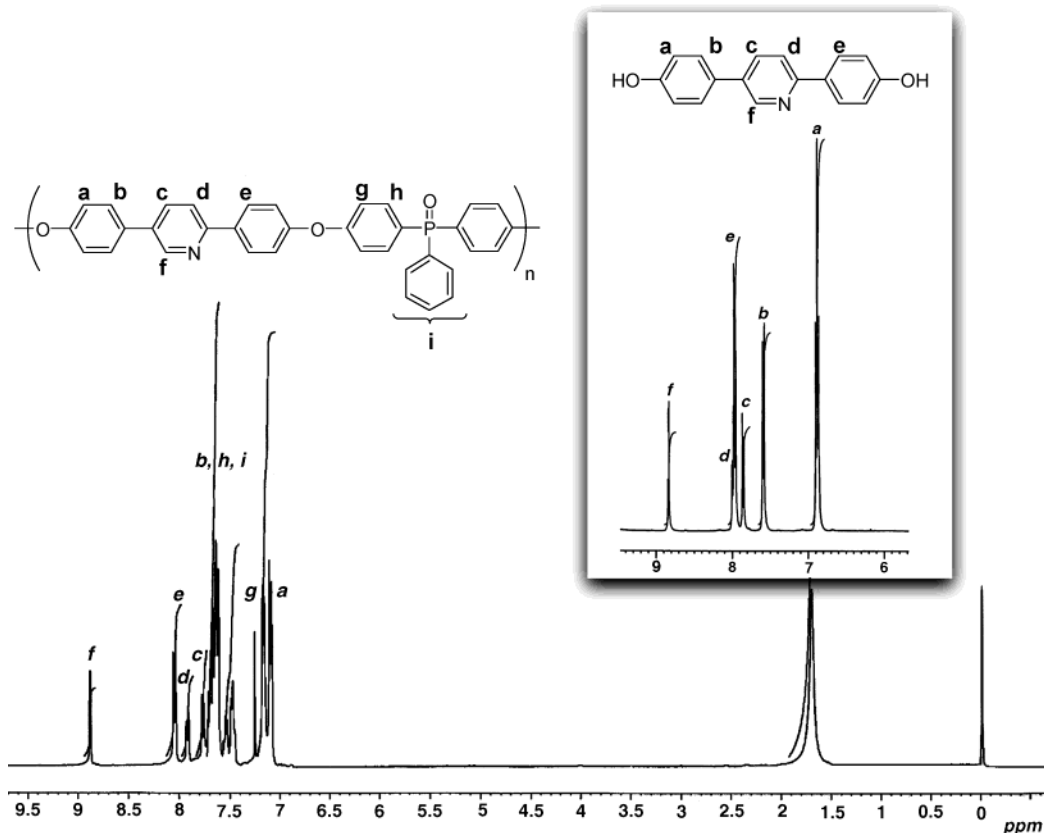(37) Kosmala, B.; Schauer, J. *J. Appl. Polym. Sci.* **2002**, *85*, 118.

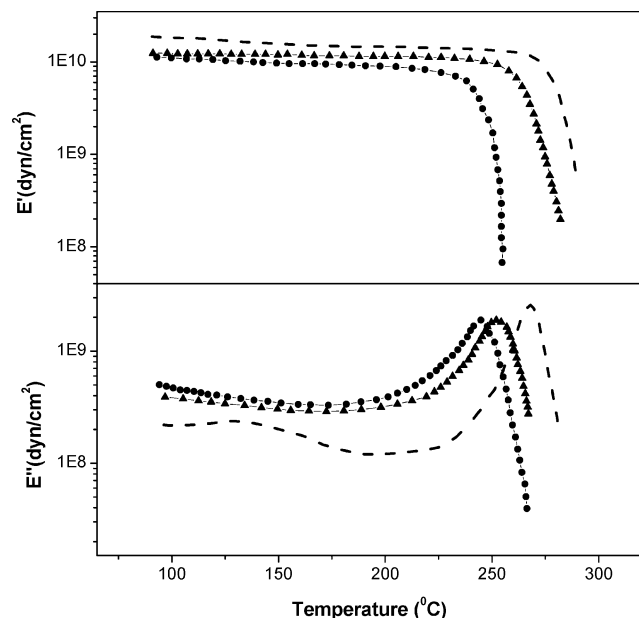**Figure 1.** $^1$H NMR spectra of polymer $I_e$ and the initial monomer/diol **3** (inset).



**Figure 2.** Temperature dependence of the storage (E′) and loss (E″) modulus for polymers $I_c$ (-●-), $I_a$ (-▲-), and $I_e$ (−−).



**Figure 3.** TGA thermograms in nitrogen (-▲-) and air (-■-) atmosphere of polymer $I_e$.

protonated membrane doped with $H_3PO_4$ for 5 h and the one kept for 1000 h at 80 °C. The FT−Raman spectroscopic characterization of the doped membranes was used to evaluate the effect of the phosphoric acid treatment on the membranes. FT−Raman spectra of polymer $I_e$ before and after doping with $H_3PO_4$ are presented in Figure 7, where the region around 1600 cm$^{-1}$ is also given as an inset. Upon doping with phosphoric acid, a new peak appears at 1630 cm$^{-1}$ which
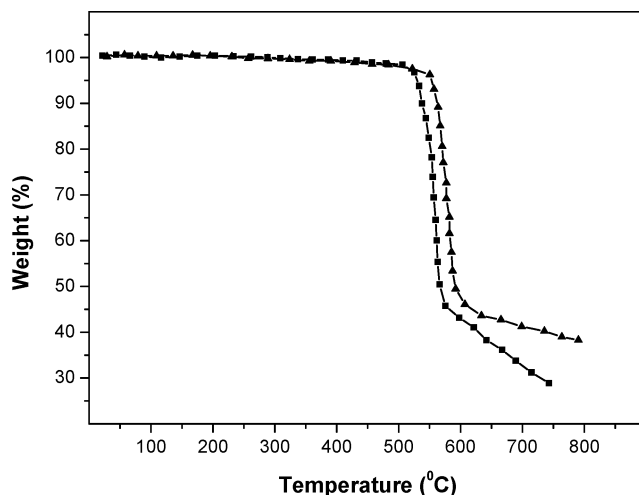
is attributed to the (C=N) vibration of the protonated pyridine ring[39] of the polymer. A further spectroscopic study of the doped polymer is in progress.

Considering that the main scope of this work is the exploitation of these polymers as polyelectrolytes for high-temperature fuel cell applications, an important prerequisite, besides good thermal stability, is their ability to dope with a strong acid thus resulting in high ionically conductive materials. The doping behavior of polymer $I_e$ with phosphoric acid 85% is depicted in Figure 8. Various conditions were exploited in order to

(38) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(39) Drelinkiewicz, A.; Hasik, M.; Quillard, S.; Paluszkiewicz, C. *J. Mol. Struct.* **1999**, *511*, 205.
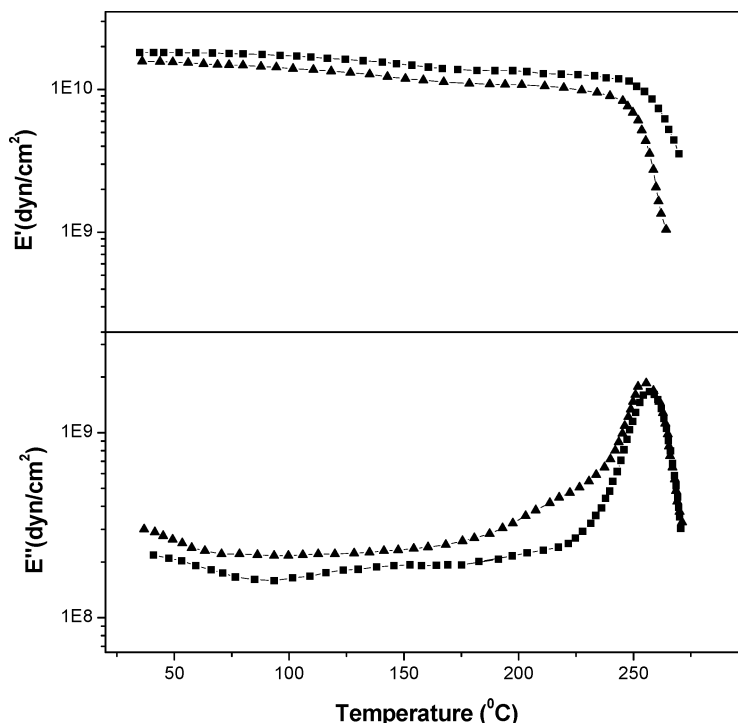
**Figure 4.** Temperature dependence of the storage (E′) and loss (E″) modulus of polymer $I_f$ before (-▲-) and after (-■-) treatment with $H_2O_2$.



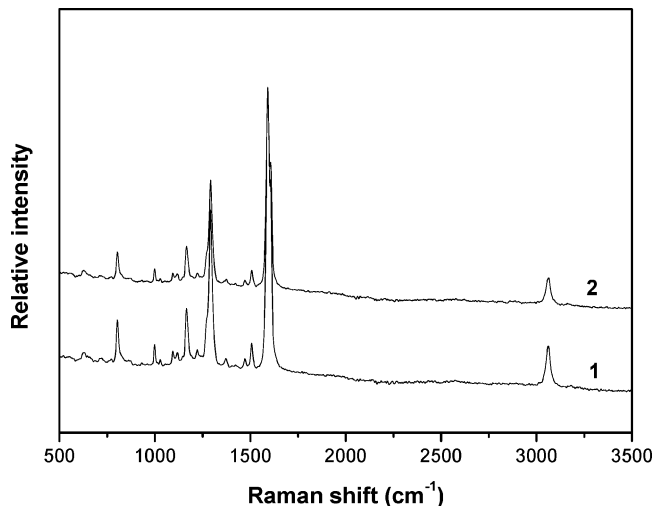**Figure 5.** FT−Raman spectra of polymer $I_f$ before (**1**) and after (**2**) treatment with $H_2O_2$.



**Figure 6.** TGA thermograms of polymer $I_e$ before (-●-) and after doping with $H_3PO_4$ for 5 h (−−) and 1000 h (-▲-).

increase the doping level. At room temperature, polymer $I_e$ hardly absorbs any phosphoric acid. When, however, the doping temperature was raised to 50 °C, a plateau was reached after 5 h, whereas a higher doping level and a plateau at 300 wt % were obtained at a doping temperature of 90 °C. This behavior can be attributed to the presence of the pyridine units which are protonated, as was supported by FT−Raman. These protonated rings act as sites where interactions with phosphoric acid molecule can occur, thus increasing the acid uptake. The protonation of the pyridine ring and the subsequent polar interactions with the phosphoric acid anion can be seen as a way to create sites on the polymeric chain in which free phosphoric acid molecules can interact and immobilize.

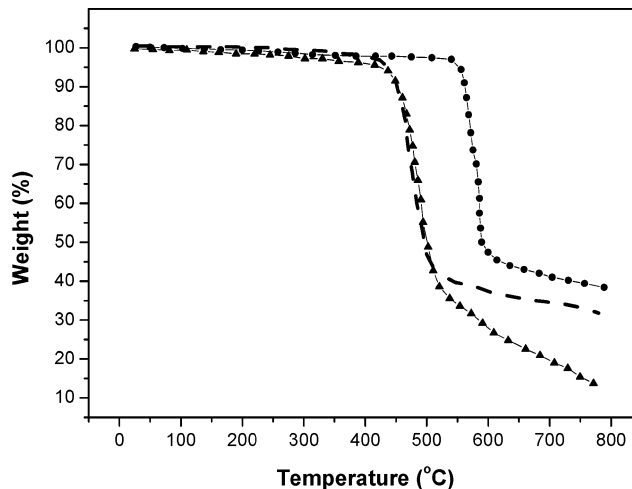Although it is difficult to express in a quantitative way because of the absorbed phosphoric acid, the doped films show good mechanical integrity even for the highest attended doping levels. Stretching of the doped membrane resulted in elongation higher than 100%, supporting the good mechanical behavior of these materials.

The dependence of the conductivity on the doping level was also examined. The conductivity values obtained for films with doping levels ranging from 60 to 260 wt % are depicted in Figure 9 (inset). Conductivities in the range of $10^{-2}$ S/cm were obtained for doping levels higher than 200 wt %. A sample of polymer $I_e$ doped with 240 wt % phosphoric acid was also selected in order to evaluate the temperature dependence of the conductivity at a related humidity of 60%. An increase of the conductivity with temperature was obtained, showing a more or less linear dependence, as depicted in Figure 9.
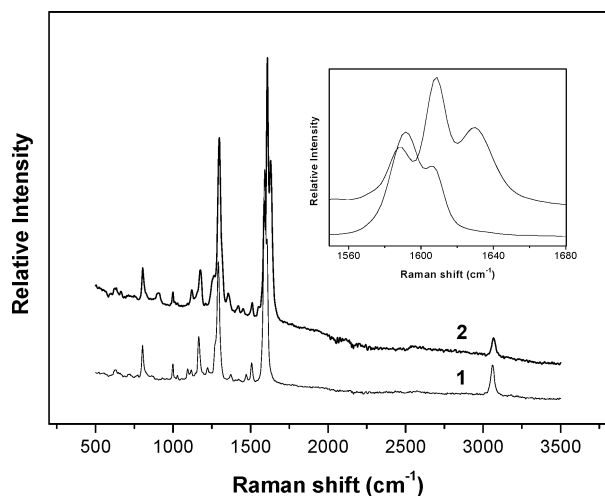
**Figure 7.** FT-Raman spectra of polymer $I_e$ before (**1**) and after (**2**) doping with $H_3PO_4$. Inset: 1550–1680 cm$^{-1}$ region.
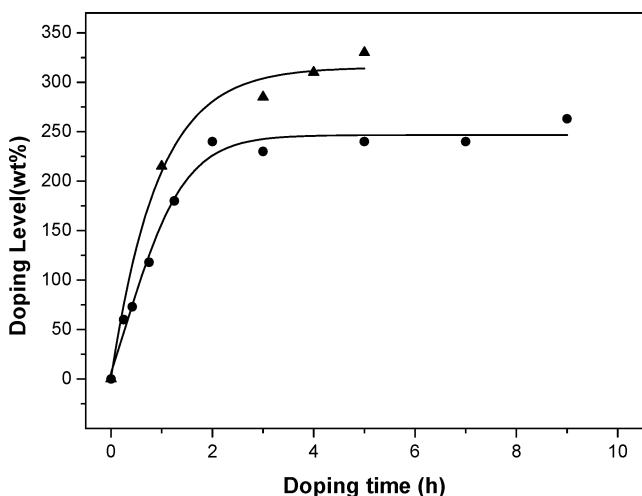


**Figure 8.** Time dependence of doping level (wt %) of polymer $I_e$ at 50 °C (-●-) and 90 °C (-▲-).
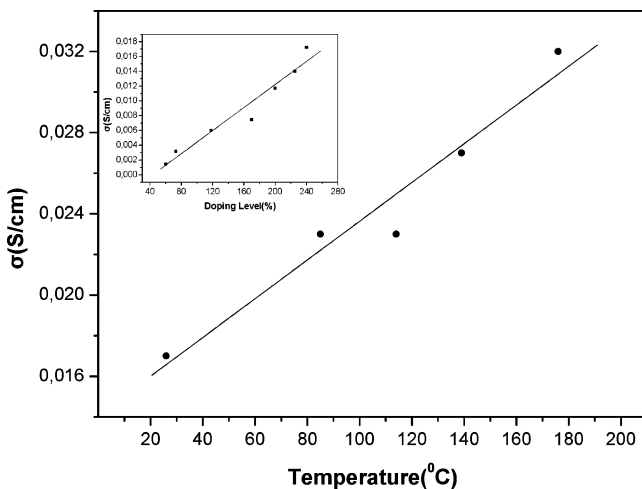


**Figure 9.** Temperature dependence of ionic conductivity of acid doped polymer $I_e$, with a doping level of 240 wt % $H_3PO_4$. The relative humidity was 60%. Inset: Ionic conductivity of polymer $I_e$, as a function of doping level (wt %).

In conclusion, flexible membranes based on aromatic polyethers bearing polar pyridine units in the main chain were synthesized and studied with respect to their mechanical and electrochemical behavior. These mem-

branes combine excellent thermal and oxidative stability with the ability to give ionically conductive materials after doping with phosphoric acid.

## Experimental Section

**Materials and Instrumentation.** 2-Tetrahydropyranyl-oxy-4-phenyl boronic acid,[32] bis(4-fluorophenyl) phenylphosphine oxide,[33] and catalyst Pd(PPh$_3$)$_4$[38] were prepared according to literature procedures. Tetrahydrofuran (THF) was distilled from sodium in the presence of benzophenone prior to use. All chemicals and solvents were purchased from Aldrich or Merck and were used without further purification unless otherwise noted. $^1$H and $^{13}$C NMR spectra were obtained on a Bruker Advance DPX 400 and 100 MHz, spectrometer, respectively, with deuturated CHCl$_3$ or DMSO. Gel permeation chromatography (GPC) measurements were carried out using a Polymer Lab chromatographer equipped with two Ultra Styragel columns (10$^4$, 500 Å) and a UV detector (254 nm), and using CHCl$_3$ as eluent. DMA measurements were performed using a solid-state analyzer RSA II, Rheometrics Scientific Ltd., at 10 Hz. Conductivity measurements were carried out by the current interruption method using a potentiostat/galvanostat (EG and G model 273) and an oscillator (Hitachi model V-650F). Thermogravimetric analysis (TGA) was performed at a DuPont 990 thermal analyzer coupled to a DuPont 951 TGA accessory.

**Monomer Syntheses.** *(a) Syntheses of 2,5-Bis(4-hydroxyphenyl)pyridine.* To a degassed mixture of 2,5-dibromopyridine (6 mmol, 1.42 g), 2-tetrahydropyranyl-oxy-4-phenyl boronic acid (15 mmol, 3.33 g), and Pd(PPh$_3$)$_4$ (0.3 mmol, 0.35 g) were added toluene (42 mL) and 2 M Na$_2$CO$_3$ (12 mmol, 6 mL) under a continuous stream of argon. The solution was vigorously stirred at reflux for 24 h under argon. The organic layer was afterward separated and the organic solvent was removed under reduced pressure. The residue was treated with MeOH, filtered, and dried under vacuum. Thus, the THP-protected diol was obtained in 83% yield, 2.15 g.

To a solution of the THP-protected diol (5 mmol, 2.15 g) in THF (50 mL) and MeOH (12 mL) was added HCl 37% (10 mmol, 0.82 mL), and the mixture was then stirred at room temperature for 18 h. The precipitated product was filtered and then deprotonation was performed using a suspension of the protonated diol in THF, which was treated with Na$_2$CO$_3$ 0.1 M at room temperature for 30 min. Filtration, washing with water and cold hexane, and drying under vacuum gave diol **3** in 84% yield, 1.1 g.

$^1$H NMR($d_6$-dmso): 6.88 (*t*, 4H), 7.59 (*d*, 2H), 7.86 (*d*, 1H), 7.98 (two *d*, 3H), 8.83 (*d*, 1H).

$^{13}$C NMR($d_6$-dmso): 116.39, 116.82, 119.69, 128.55, 130.18 133.84, 134.82, 147.44, 154.86, 158.46, 159.32.

*(b) Syntheses of 2,6-Bis(4-hydroxyphenyl)pyridine.* Monomer **4** was prepared in a procedure analogous to that for the syntheses of diol/monomer **3** starting from 2,6-dibromopyridine (6 mmol, 1.42 g) and obtained in 68% yield, 1.07 g.

$^1$H NMR($d_6$-dmso): 6.88 (*d*, 4H), 7.69 (*d*, 2H), 7.81 (*t*,1H), 8.03 (*d*, 4H).

$^{13}$C NMR($d_6$-dmso): 116.35, 117.36, 128.81, 130.71, 138.70, 156.31, 159.37.

**Syntheses of poly(Bis(4-phenyl enoxide)-2,5-pyridine) Phenyl Phosphinoxide (PPyPO).** To a degassed flask equipped with a Dean–Stark trap were added diol **3** (4 mmol, 1.05 g), bis(4-fluorophenyl)phenylphosphine oxide (4 mmol, 1.26 g), K$_2$CO$_3$ (4.64 mmol, 0.64 g), toluene (8 mL), and DMF (12.6 mL). The mixture was degassed under Ar and stirred at 150 °C for 48 h, and then stirred at 180 °C for 6 h. The obtained viscous product was diluted in CHCl$_3$ and precipitated in a 10-fold excess mixture of 2:1 MeOH/H$_2$O, washed with H$_2$O, and dried at 80 °C under vacuum.

*Gourdoupi et al.*

$^1$H NMR(CDCl$_3$): 7.1 (*d*, 4H), 7.16 (*d*, 4H), 7.47−7.71 (three *m*, 11H), 7.77 (*d*,1H), 7.92 (*d*, 1H), 8.05 (*d*, 2H), 8.88 (*s*, 1H).

$^{13}$C NMR(CDCl$_3$): 118.347, 118.477, 120.420, 120.552, 120.944, 128.987, 132.370, 132.468, 134, 135.5, 134.62, 134.58, 135.312, 148.295, 155.661, 156.242, 156.953, 161.083.

The molecular weight results for the different preparations are summarized in Table 1.

CM0347382