The Effect of Structural Variations on Aromatic Polyethers for High-Temperature PEM Fuel Cells

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ABSTRACT: Three series of new aromatic polyether sulfones bearing phenyl, *p*-tolyl or carboxyl side groups, respectively, and polar pyridine main chain groups were developed. Most of the polymeric materials presented high molecular weights and excellent solubility in common organic solvents. More importantly, they formed stable, self-standing membranes that were thoroughly characterized in respect to their thermal, mechanical and oxidative stability, their phosphoric acid doping ability and ionic conductivity. Particularly, the copolymers bearing side *p*-tolyl or carboxyl groups fulfill all necessary requirements for application as proton electrolyte membranes in high temperature fuel cells, which are glass transition temperatures

INTRODUCTION More than 160 years have passed since the demonstration of the conversion of chemical energy into electrical energy using a primitive fuel cell.¹ However, in the last decades, there has been a significant increase in research, development, and investment in this technology due to the benefits that it offers such as high efficiency, no existence of the mobile parts, and no emissions of environmental polluting gases.² Specifically, the proton exchange membrane fuel cell (PEMFC) has received particular attention as it allows increased operating times and functionality not only for stable but also for portable electronic devices.^{3,4} DuPont's Nafion, combining a robust tetafluoroethylene backbone with perfluorosulfonic acid side chains, is the state-of-the-art polymer electrolyte for low-temperature PEMFCs up to 100 °C.5-7 However, operation of PEMFCs at high temperatures provides a number of technological benefits, including acceleration of the electrode reactions, improved tolerance to impurities in the fuel gas, and simplified water and thermal management. A remarkable example of these polymeric materials is polybenzimidazole (PBI) that creates acid-base interactions when doped with strong protic acid.⁸⁻¹² In this line, considerable efforts have been made to increase proton conductivity while maintaining high thermal. mechanical, and chemical stabilities either based on PBIs¹³⁻¹⁵ or different polymeric structure, such as poly(phenylene sulfone)s,¹⁶ poly(ether sulfone)s,¹⁷ polyimides,¹⁸ and so forth.

higher than 220 °C, thermal stability up to 400 °C, oxidative stability, high doping levels (DLs) and proton conductivities of about 0.02 S/cm. Initial single fuel cell results at high temperatures, 160 °C or 180 °C, using a copolymer bearing *p*-tolyl side groups with a relatively low DLs around 200 wt % and dry H₂/ Air feed gases, revealed efficient power generation with a current density of 0.5 A/cm² at 500 mV. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4325–4334, 2011

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One promising class of polymers for high-temperature PEMFCs are fully aromatic polyethers or copolyethers-bearing pyridine polar groups along the main backbone.^{19–21} These polar pyridine groups are responsible for acid-base interactions with phosphoric acid. Thus, such polyethers present increased phosphoric acid doping levels (DLs) and high ionic conductivities in the range of 10^{-2} S/cm. More importantly, they present excellent thermal and oxidative stabilities, and they have been effectively used in polymer electrolyte fuel cells operating at temperatures even up to 200 °C.^{22–27}

The versatility of the polymerization reaction and the large number of possible comonomers allows the creation of numerous polyelectrolytes. Combining the polar pyridine units with apolar or polar ones either as side or as main chain groups, all these at various ratios, can lead to a vast library of polymeric materials whose properties greatly depend on the precise chemical and topological architecture of the backbone and the pendant groups.

Following this concept, we decided to investigate new series of aromatic polyethers synthesized from the pyridine diol and bisfluorophenyl sulfone along with diols bearing either two phenyl or *p*-tolyl side groups, or one carboxyl side group. The phenyl and the tolyl side groups were chosen

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SCHEME 1 Synthesis of copolymers I, II, and III.

because their size is expected to increase the free volume inbetween neighboring polymeric chains in the bulk thus increasing the doping ability of the copolymers. The carboxyl side groups could interact with the phosphoric acid molecules, also increasing the doping ability of the copolymers. Indeed, all three series of copolymers prepared herein showed high DLs. Moreover, we had the opportunity to investigate the influence of the different side chains on the mechanical, thermal, and conducting properties of the final copolyethers. A membrane electrode assembly (MEA) was prepared from one of the copolymers with *p*-tolyl side groups and was tested in a single fuel cell operating at high temperatures, showing efficient power generation.

RESULTS AND DISCUSSION

In this project, our main goal is by all means, the development of novel polymer electrolytes gathering all necessary properties for application in high temperature PEMFCs, at or above 180 °C. Nevertheless, we also focus on understanding how structural variations may alter and most importantly improve the final polymeric properties. For that reason, we synthesized and studied new aromatic polyethersulfones-bearing pyridine polar main chain groups and phenyl, *p*-tolyl or carboxyl side groups, which are directly comparable to previous copolyethers that have proved efficient polyelectrolytes for PEMFCs.^{19–27}

Monomer 2,5-di(methyl phenyl)benzene-1,4-diacetate was synthesized via the Suzuki coupling²⁸ of *p*-toluene boronic acid²⁹ and 2,5-dibromo-1,4-phenylene diacetate. 2,5-Diphenylbenzene-1,4-diacetate³⁰ was prepared according to literature while 3,5-dihydroxy benzoic acid was commercially available. These diols were copolymerized at different ratios with 2,5-bis(4-hydroxy-phenyl)pyridine¹⁹ and bis(4-fluorophenyl)sulfone under K₂CO₃/KOH or K₂CO₃ mediated direct nucleophilic substitution polycondensation at elevated tem-

peratures in DMF/toluene or N-methylpyrrolidone (NMP)/ toluene mixtures.³¹ It is well established that in S_NAr reactions, bis(aryl fluoride)s are generally more reactive than other aryl halides (chlorides, bromides, and iodides, etc.) and in combination with the sulfone activating group lead to high molecular weight polymers. Moreover, extensive studies have been performed for the correlation of the aryl halide, the bisphenolate, the solvent and the temperature used, to the molecular weight and possible chain termination reactions occurring during such S_NAr polymerizations.³²⁻³⁶ Another interesting approach toward aromatic polyethers has also been previously reported, using the Scholl reaction at which oxidative polymerization of monomers with non-nucleophilic aromatic groups can be accomplished.³⁷ The synthetic route for the copolymers is given in Scheme 1, where x denotes the feed of the pyridine bearing diol in the copolymerization reaction. Copolymers I and II were soluble in common organic solvents such as N,N-dimethylacetamide (DMAc), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or chloroform (CHCl₃). As a result, they were characterized by means of ¹H NMR in respect to their structural perfection and monomers' ratio, as presented in Figure 1(a,b), and via gel permeation chromatography (GPC) for their molecular characteristics (Tables 1 and 2, respectively). On the other hand, copolymers **III** were insoluble in chloroform; thus, their ¹H NMR characterization was performed in DMSO- d_6 [Fig. 1(c)] while they could not be directly characterized via GPC. However, when copolymers III were refluxed in thionyl chloride for 24 h and then precipitated in methanol, they were transformed or at least partially transformed in their methyl ester form that was soluble in chloroform and could be subsequently characterized via GPC (Table 3, entries IIIe, f, I, j).

For copolymers I, the comonomers composition calculation was based on the proton near the pyridine nitrogen (a) at



FIGURE 1 ¹H NMR spectra of copolymers (a) **Ia** and (b) **IIh** in CDCl₃ at r.t., and (c) **IIIe** in DMSO- d_6 at 50 °C.

8.9 ppm and the aromatic protons (*j*) of the diphenyl sulfone unit of the second block. For copolymers **II** their composition calculation was based on the methyl protons (*m*) of the *p*-tolyl side groups at 2.3 ppm and the proton (*a*) next to the nitrogen of the pyridine ring at 8.9 ppm. Copolymers' **III** composition estimation by means of ¹H NMR proved more complicated due to the two blocks solubility difference in DMSO-*d*₆. Specifically, the pyridine bearing block was less soluble in DMSO-*d*₆ at room temperature in contrast to the second block carrying the carboxyl side groups. It was found that only spectra recorded at 50 $^{\circ}$ C or higher temperatures afforded adequately resolved signals of the pyridine block's protons, whereas for the various temperatures used, the peak integrations also varied. Thus, the copolymers **III** comonomers' ratios by means of ¹H NMR given in Table 3 are mostly indicative.

As depicted in Table 1 for copolymers I, Table 2 for copolymers II, and Table 3 for copolymers III, respectively, molecular weights in the range from 8,000 to 45,000 were obtained depending on the copolymerization conditions, such as reaction time and temperature. The optimum conditions were found to be 24 h at 160 $^\circ\text{C}$ and 16 h at 180 $^\circ\text{C}$ affording higher molecular weight polymeric materials as obvious also from the integrity of the respective membranes. However, it must be kept in mind that the pyridine moieties along the polymeric backbones interact with the stationary phase of the GPC underestimating the true molecular weight. On the other hand, the rigid nature of these copolymers tends to overestimate their molecular weight. Thus, the obtained molecular characteristics differ from the true ones. Intrinsic viscosity measurements of copolymers IIh and IIIf are depicted in Figure 2 at 30 °C using N-methylpyrrolidone as solvent. The [n] values obtained were for IIh = 0.69 dL/g and for IIIf = 0.765 dL/g. For comparison reasons a well documented and optimized copolymer ($M_n = 27,000, M_w =$ 58,000 via GPC) of the pyridine diol at x = 60 and tetramethyl-biphenyl diol with bis(phenyl sulfone) is also given in Figure 2 presenting a [n] = 0.93 dL/g. It is obvious that the viscosity of this type of copolyethers is governed not only by molecular weight but also by the rigidity and the polarity of the main and side chains.

One of the main prerequisites to use a polymeric membrane in a fuel cell as an electrolyte is high proton conductivity. As a result, the ability of the membrane to absorb a strong protic acid such as phosphoric acid is required. As far as pyridine-based system is concerned, the increase of the phosphoric acid absorption is proportional to the increase of the pyridine groups' content. However, a very high level of acid absorption could cause the degradation of the membrane or leaching of the phosphoric acid during fuel cell operation. To have a straightforward comparison of the

Copolymers	$x - (1 - x)^{a}$	<i>M</i> _n ^b	<i>M</i> _w ^b	$M_{\rm w}/M_{\rm n}^{\rm b}$	Film Integrity
la	(60–40) 54–46	15,000	33,000	2.2	\checkmark
lb	(70–30) 56–44	8,000	14,000	1.8	Brittle
lc	(60–40) 54–46	46,000	70,000	1.5	\checkmark
ld	(70–30) 63–37	18,500	30,000	1.6	\checkmark
le	(60–40) 58–42	17,000	26,000	1.5	\checkmark
lf	(60-40) 53-47	15,000	23,000	1.6	\checkmark
lg	(60–40) 51–49	16,000	25,000	1.6	\checkmark

TABLE 1 Molecular Characteristics for Copolymers I and Integrity of the Membranes from Solution Casting

^a Polymerizations feed ratios in brackets and as calculated from ¹H NMR.

^b Polymerizations feed ratios in brackets and as calculated from GPC.



Copolymers	$x - (1 - x)^{a}$	<i>M</i> _n ^b	$M_{\rm w}{}^{\rm b}$	$M_{\rm w}/M_{\rm n}^{\rm b}$	<i>T</i> g (°C)	Film Integrity
lla	(60-40) 60-40	35,000	53,000	1.5		\checkmark
llb	(70–30) 67–33	30,000	48,000	1.6	238	<i>JJJ</i>
llc	(80–20) 72–28	16,500	28,000	1.7		1
lld	(60-40) 59-41	43,000	72,000	1.7		<i>JJJ</i>
lle	(80–20) 53–47	13,000	20,000	1.5		✓
llf	(60-40) 50-50	41,000	63,700	1.5		<i> </i>
llg	(70–30) 67–33	30,000	48,000	1.6	240	<i>JJJ</i>
llh	(60–40) 57–43	30,000	50,000	1.7	235	<i>\\\</i>
lli	(75–25) 64–36	25,000	36,000	1.5		<i>s</i>
llj	(60-40) 55-45	40,000	60,000	1.5	235	<i> J J J J J J J J J</i>
llk	(70–30) 58–42	45,000	72,000	1.6	238	<i>JJJ</i>
III	(70–30) 61–39	30,000	44,000	1.5	230	<i>」」」</i>
llm	(75–25) 65–35	20,000	28,000	1.5		<i>√√</i>
lln	(60–40) 61–39	34,000	83,000	1.9	225	<i>JJJ</i>

TABLE 2 Molecular Characteristics for Copolymers II and Integrity of Membranes from Solution Casting

^a Polymerizations feed ratios in brackets and as calculated from ¹H NMR.

^b Polymerizations feed ratios in brackets and as calculated from GPC.

copolymers doping behavior and the possible influence of the side groups, all membranes were prepared by casting of DMAc solutions having identical concentrations. Thus, the produced membranes were all of similar dimensions and their thickness was in the range of 100 μ m. The doping behavior of these membranes was studied after their immersion in 85% phosphoric acid at 100 °C for various time intervals.

For copolymers **I**, the DL values are depicted in Figure 3(a). It is obvious that the higher the ratio of pyridine groups, the higher is the phosphoric acid uptake of the membranes. However, despite their very high DLs, membranes of copolymer **I** were not further characterized, due to their low-film integrity. Figure 3(b) presents the acid absorption for copolymers **II** having different pyridine content. As it was expected, the acquired DL increases with *x* which is the percentage of the polar pyridine groups. Thus, the DL of copolymer **II**c

having x = 72 was the highest one, namely 460 wt % while for the copolymer **IIj** with the lowest x = 55 the maximum DL was 190 wt %. The doping ability of copolymers **III** with H₃PO₄ 85% at 100 °C is presented in Figure 3(c). Also in this case, high DLs up to 450 wt % were obtained; however, it must be noted that copolymers doping ability seems to correlate better with the theoretical *x* values, meaning the pyridine content in the copolymer and not with the experimentally estimated ones. This fact is in accordance with our previous statement that the calculated comonomers' ratios from ¹H NMR for copolymers **III** differ from the true ones. Moreover, the presence of the carboxylic acid side groups did not decrease the doping ability of copolymers **III** as has been observed for other copolymers having pyridine main chain groups and phosphonic acid side ones.³⁸

The mechanical properties of copolymers **II** were examined by means of dynamic mechanical analysis (DMA). In Figure 4(a),

Copolymers	$x - (1 - x)^{a}$	<i>M</i> _n ^b	<i>M</i> _w ^b	$M_{\rm w}/M_{\rm n}^{\rm b}$	<i>T</i> _g (°C)	Film Integrity
Illa	(60-40) 60-40					<i>JJJ</i>
IIIb	(60–40) 53–47					\checkmark
Illc	(75–25) 71–29				245	<i>JJJ</i>
llld	(60–40) 55–45					<i>JJJ</i>
llle	(60–40) 57–43	18,000	31,500	1.8	255	<i>JJJ</i>
IIIf	(60-40) 51-49	30,000	42,000	1.4	210	$\int \int \int$
lllg	(75–25) 74–26				211	<i>JJJ</i>
IIIh	(80–20) 70–30				207	<i>JJJ</i>
Illi	(60–40) 45–55	20,000	28,600	1.5	250	<i>JJJ</i>
IIIj	(60–40) 65–35	44,000	48,000	1.1	266	$\int \int \int$

TABLE 3 Molecular Characteristics for Copolymers III and Integrity of Membranes from Solution Casting

^a Polymerizations feed ratios in brackets and as calculated from ¹H NMR.

^b Polymerizations feed ratios in brackets and as calculated from GPC of copolymers III in their methylester form.



FIGURE 2 Concentration dependence of reduced viscosity (n_{sp}/C) for copolymers **IIh** (-**O**-) and **IIIf** (-**A**-) in NMP at 30 °C. For comparison, the curve of a copolymer of the pyridine diol (x = 60) and of tetramethyl-biphenyl diol with diphenyl sulfone²¹ is also depicted (-**I**-).

is depicted the temperature dependence of storage (E') and loss (E'') modulus for copolymers **IIb** and **III**. The glass transition temperatures (T_g) were over 225 °C for most of these copolymers as can be seen in Table 2. Also, it is noticed that increased rigid pyridine diol content resulted in increased T_g values. Analogs results, that is, high T_g and E' values, were also obtained for most of the copolymers **III** (Table 3, Fig. 5). However, and even though, high T_g and good mechanical integrity are required for PEMFC applications, the membranes must withstand the strong oxidative environment of a fuel cell.

Fenton test is a reliable ex situ method to confirm the oxidative stability of the copolymers by exposing them in an aggressive environment as that of an operating fuel cell. The ferrous ions, in the presence of H_2O_2 , provide hydroxyl and peroxide radicals (HO \bullet and HO₂ \bullet , respectively) that can attack the polymeric backbone and destroy the membranes integrity. Thus, membranes of copolymers IIb, III were treated with 3 wt-% H_2O_2 solution in the presence of ferrous ions (4 ppm of FeCl₂) for 3 days at 80 °C.^{39,40} Despite this aggressive environment, the treated membranes presented excellent oxidative stability as can be seen by comparing the DMA diagrams before and after the treatment, Figure 4(a,b), respectively. In a step further, we tested our membranes under prolonged Fenton's test conditions. Even exposure for as long as 3 weeks in such an oxidizing environment did not deteriorate the membranes as shown in Figure 5 for copolymer IIIf. More proof for the membranes' oxidative stability comes from the thermogravimetric analyses of the samples before and after the Fenton test which is presented in Figure 6. The thermogravimetric analysis (TGA) curves of the treated samples showed small deviations from the initial membranes, both for the 3 days' [Fig. 6(a)] or the 3 weeks' [Fig. 6(b)] exposure in the Fenton's solution. In all cases, a high thermal stability is maintained, which is required for

polymer electrolytes applicable in high-temperature fuel cells. FTIR investigation of copolymer **IIIf** before and after 3 weeks treatment under the Fenton test conditions (Fig. 7) also did not reveal any structural changes, which has been additionally confirmed by ¹H NMR spectroscopy. It should be pointed out here that during the TGA experiments of copolymers **III**, several small weight losses were observed before the polymeric thermal decomposition process at around



FIGURE 3 Time dependence of doping level (wt %) at 100 °C of (a) copolymers **I**: **Ic** (-**▲**-), **Ie** (-**▲**-), **Ia** (-**▼**-); (b) copolymers **II**: IIm (-**■**-), III (-**●**-), IIj (-**▲**-), IIi (-**▼**-), IIh (-**♦**-), IIk (-**◀**-), IIb (-**▶**-), IIc (-*****-); and (c) copolymers **III**: IIIe (-**■**-), IIIh (-**●**-), IIIg (-**▲**-).



FIGURE 4 Temperature dependence of the storage (E') and loss (E'') modulus for the copolymers (a) before Fenton test **IIb** (-**II**-) and **III** (-**O**-), and (b) after Fenton for 3 days: **IIb** (-**II**-) and **III** (-**O**-).

400 °C [Fig. 6(b)]. These are attributed to the formation of anhydrite groups among the carboxyl acid moieties with simultaneous water loss.



FIGURE 5 Temperature dependence of the storage (E') and loss (E'') modulus for the copolymer **IIIf** before (- \bullet -) and after the Fenton test for 3 weeks (- \bigcirc -).

The four-probe current interruption technique was used for the investigation of the conductivity dependence on the acid DL for copolymers II and III (Fig. 8). Copolymers IIh and IIIe were chosen that reach maximum DLs around 250 wt % to be directly comparable to other bibliographic copolymers.^{26,27} The ionic conductivity increased with the DL and more specifically copolymer IIh possessed values in the range of 2 \times 10⁻² S/cm for a DL = 220 wt %. Higher conductivities were observed for copolymer IIIe reaching 2.5×10^{-2} S/cm at DL = 200 wt %. When compared with a copolymer having the same amount of pyridine polar groups (x = 60) along the polymeric backbone and methyl side groups²¹ (Fig. 8, red triangles), at a DL of 220 wt %, it is obvious that the presence of the larger side groups in the *p*-tolyl case or the more polar groups in the case of the carboxyl ones, facilitates not only higher DLs at lower doping temperatures but also higher conductivities at the same DLs. These facts clearly demonstrate that not only the main chain pyridine polar units interacting with the phosphoric acid dopant but also the accompanying comonomers size and chemical structure play a significant role in the overall doping ability and proton conductivity of the polyelectrolyte.

To further provide evidence of these copolymers suitability as polyelectrolytes in PEMFCs, initial single cell tests took place showing promising results. For copolymer **IIn** having a DL ~ 200 wt %, at a cell voltage of 500 mV, a current density of 0.5 A/cm² was obtained with H₂/Air feed gases at 180 °C without external humidification (Fig. 9). Optimization of different parameters involving the MEAs construction and the single cell operation conditions are in progress along



FIGURE 6 TGA thermographs under nitrogen of (a) copolymers **II**: after Fenton Test for 3 days and inset before Fenton Test **IIb** (black line), **III** (dash-dot-dot line) and **IIh** (dotted line); (b) copolymer **IIIf** before (black line) and after Fenton test for 3 weeks (dash-dot-dot line).

with the incorporation of copolymers **III** for MEAs fabrication. Long-term stability of these membranes under continuous fuel cell operation conditions will be also examined.



FIGURE 7 FTIR spectra of copolymer **IIIf** before Fenton (black line) and after Fenton test for 3 weeks (dash dot line).



FIGURE 8 Acid doping level dependence of proton conductivity for copolymers **IIh** with x = 57 (-**I**-), **IIIe** with x = 57 (-**O**-) at room temperature. For comparison, the curve of a copolymer of the pyridine diol (x = 60) and of tetramethyl-biphenyl diol with diphenyl sulfone²¹ is also depicted (- ∇ -).

EXPERIMENTAL

Materials

2,5-Bis(4-hydroxyphenyl)pyridine,¹⁹ 2,5-diphenylhydroquinone diacetate,³⁰ *p*-tolylboronic acid,²⁹ and palladium (II) tetrakis triphenyl phosphine $[Pd(PPh_3)_4]^{41}$ were prepared according to literature procedures. Phenyl boronic acid, bis(4-fluorophenyl)-sulfone, and 3,5-dihydroxybenzoic acid were purchased from Aldrich and used as received. All other chemicals and solvents were purchased from Aldrich or Merck and used without further purification.

Instrumentation

¹H NMR spectra were obtained on a Brucker Advance DPX 400 MHz spectrometer. The samples were dissolved either in deuterated chloroform (CDCl₃) or deuterated dimethyl sulfoxide (d_6 -DMSO) with TMS as internal standard.

GPC measurements were carried out using a Polymer Lab chromatographer equipped with two Plgel $5-\mu m$ mixed



FIGURE 9 *LV* curves for copolymer **IIn** with a doping level of 196 wt % at 160 °C (- ∇ -) and 180 °C (-**I**-). Thickness 80–95 μ m, 1.6 mg Pt/cm². Feed gas H₂/Air.

columns and a UV detector (254 nm), using $CHCl_3$ as eluent with a flow rate of 1 mL/min at 25 $\,^\circ C$ and polystyrene standards.

Viscosity measurements of the polymers were performed in N-methylpyrollidone solutions at 30 °C with an Ubbelohde-type viscometer in a Scott Gerate AVS 310.

FTIR spectra were recorded on a PerkinElmer 16PC FTIR spectrometer.

DMA measurements were conducted using a solid-state analyzer RSA II, Rheometrics Scientific, at 10 Hz.

TGAs were carried out on 10 mg of samples contained in alumina crucibles in a LabsysTM TG apparatus of Setaram under nitrogen and at a heating rate of 10 °C/min.

Proton conductivity measurements were conducted at a conductivity four-probe cell at room temperature. 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).

Monomer and Polymer Synthesis

2,5-Di(methyl phenyl)benzene-1,4-diacetate

2,5-Dibromohydroquinone diacetate was synthesized by bromination of the hydroquinone diacetate with 2 equiv of Br_2 in chloroform. To a degassed mixture of 2,5-dibromo-1,4phenylene diacetate (10 g, 28.4 mmol), *p*-tolylboronic acid (9.6 g, 71 mmol), and Pd(PPh₃)₄ (0.26 g, 0.227 mmol), 200 mL of toluene and aqueous Na₂CO₃ 2M (85 mL) were added under a continuous stream of argon. The solution was vigorously stirred at reflux for 24 h under argon. The organic layer was extracted with toluene, washed with 3 N HCl and water, and dried over MgSO₄. The organic solvent was removed under reduced pressure, and the residue was triturated with methanol, filtered out, and dried in vacuum. Recrystallization from toluene gave 8 g (80%) of the desired product.

¹H (NMR) (CDCl₃, δ ppm): 7.35 (d, 4H), 7.22 (d, 4H), 7.16 (s, 2H), 2.39 (s, 6H), 2.11 (s, 2H).

General Procedure for Copolymers I, II, and III

In a round-bottom flask equipped with a Dean Stark trap were added the required monomers, K_2CO_3 , KOH, DMF/toluene, or K_2CO_3 , NMP/toluene. The polymerization mixtures were heated at 150–170 °C and then at 180 °C. After the end of polymerization, they were precipitated in MeOH/H₂O mixtures, filtrated, stirred in H₂O at 60 °C, filtered, washed with H₂O, and dried under high vacuum at 100 °C for 2 days. Representative examples for each case are given below.

Copolymer Ia. 2,5-Bis(4-hydroxyphenyl)pyridine (0.34 g, 1.30 mmol), 2,5-diphenylhydroquinone diacetate (0.30 g, 0.86 mmol), bis(4-fluorophenyl)-sulfone (0.55 g, 2.16 mmol), K_2CO_3 (0.35 g, 2.54 mmol), KOH (0.12 g, 2.16 mmol), DMF (10 mL), and toluene (3 mL) were added in a degassed round-bottom flask. The reaction mixture was heated for 24 h at 160 °C and for another 12 h at 180 °C under argon atmosphere. The resulting viscous product was diluted in DMF and precipitated in a 10-fold excess mixture of 2/1 MeOH/H₂O. The obtained

copolymer was washed with H_20 and *n*-hexane, and dried at 80 °C under reduced pressure for 1 day.

Copolymer IIh. To a degassed round bottom flask 2,5-bis(4-hydroxy-phenyl) pyridine (0.49 g, 1.87 mmol), 2,5-di(methyl phenyl)benzene-1,4-diacetate (0.47 g, 1.25 mmol), bis(4-fluorophenyl)-sulfone (0.80 g, 3.13 mmol), K₂CO₃ (0.50 g, 53.63 mmol), KOH (0.175 g, 3.13 mmol), DMF (10 mL), and toluene (3 mL) were added and successively heated at 170 °C for 18 h and at 180 °C for 16 h under inert argon atmosphere. Then to the viscous product, 5 mL of DMF were added to dilute it, and this solution was precipitated in a 20-fold excess of MeOH/H₂O 5/1 mixture. The polymer was filtered, stirred in H₂O at 60 °C for 2 h, filtered and washed with water and hexane, and dried under high vacuum for 2 days at 100 °C.

Copolymer IIIa. A degassed round-bottom flask was charged with 2,5-bis(4-hydroxy-phenyl) pyridine (0.62 g, 2.36 mmol), 3,5-dihydroxybenzoic acid (0.24 g, 1.57 mmol), bis(4-fluorphenyl)sulphone (1.00 g, 3.93 mmol), K_2CO_3 (1.08 g, 7.86 mmol). NMP (20 mL) and toluene (9 mL) were then introduced and successively heated at 160 °C for 24 h and at 180 °C for 16 h under inert argon atmosphere to carry out dehydration and the controlled removal of the toluene from the reaction mixture. When the viscosity of the polymerization reaction was observed to increase the solution was cooled to room temperature and diluted with DMAc. The product was isolated by coagulation in HCl (0.01 M) solution. The precipitated copolymer was filtered to remove most of the salts washed several times with water and methanol and dried under high vacuum at 160 °C for 2 days.

Membrane Preparation. The copolymers were dissolved in dimethylacetamide at room temperature. The solution was then purred in a glass Petri disk, and the solvent was slowly evaporated at 80 °C. The membranes were dried under vacuum at 160 °C for 3 days so as to remove the excess of solvent.

Doping Procedure. The produced membranes were immersed into 85 wt % phosphoric acid solution at 100 °C for various time periods to obtain maximum DL. The wet membranes were wiped, dried, and quickly weighted on analytical balance until a constant acid uptake was obtained. This membrane acid uptake is reported as a percentage and is determined as follows:

Acid uptake =
$$(W_{wet} - W_{dry}) \times 100/W_{dry}$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively.

Oxidative Stability-Fenton test. The oxidative stability (changes in structure, thermal, and mechanical properties) of the membranes was examined with dynamic mechanical analysis, TGA, ¹H NMR, and FTIR after immersion of undoped membrane samples into $3\%H_2O_2$ aqueous solution containing 4 ppm FeCl₂ at 80 °C for 72 h or for 3 weeks.

Conductivity Measurements. The initial electrochemical characterization of the acid-doped membranes was carried

out using the four-probe current interruption method. The dependence of the ionic conductivity versus DL was examined.

Membrane, electrodes preparation, MEA fabrication and testing. The phosphoric acid content in the membrane (196 wt %) was controlled by immersing a dry membrane in H₃PO₄ 85 wt % for 2 days at 140 °C. The phosphoric acidimpregnated membrane was sandwiched between two Pt electrodes where a certain amount of phosphoric acid was sprayed onto the catalytic layer. In this work, the cathode side and the anode side use the same electrodes with a catalyst loading 1.68 mg/cm^2 and the hot pressing takes place at 150 °C for 5 min. The hand-made electrodes were prepared from ink by mixing the catalyst powder (30 wt % Pt/C, E-Tek BASF Fuel Cell Division), the desired amount of polymeric binder and dimethylacetamide (DMA) as solvent, on a gas diffusion layer (GDL). GDL was homemade using carbon cloth from E-Tek BASF Fuel Cell Division on which was sprayed a slurry made of SAB carbon and PTFE dispersion, followed by sintering at 300 °C under static air for 40 min. Finally, the electrodes were heat treated under temperature and vacuum to remove the organic solvent. Pure and dry hydrogen and air gases were supplied to the anode and cathode compartments, respectively, for the operation of the cell at 160–180 $^\circ\text{C}$ and at ambient pressure. The effective dimensions of electrodes were 5×5 cm², and the electrochemical evaluation was carried out in a single cell with serpentine flow channels (Fuel Cell Technologies). The measurements were made in two-electrode arrangement. Polarization curves were recorded at different temperatures using the potentiostat/galvanostat PGSTAT30 with the steady state current recorded for 30 s after each potential was set. The electrochemical impedance spectra (EIS) were recorded at 0.2 A/cm² in the frequency range of 10 mHz to 20 kHz with an amplitude of sinusoidal signal of 100 mA, using the same equipment.

CONCLUSIONS

New aromatic polyether copolymers bearing polar pyridine main chain groups combined with either non polar or polar side chain ones, were synthesized. Optimization of the copolymers composition and their preparation conditions enabled the synthesis of soluble materials forming high quality films. Membranes prepared out of these materials were tested in respect to their thermal and oxidative stability. Even after prolonged treatment under strong oxidative conditions, Fenton's test, the membranes showed exceptional stability. The study of their phosphoric acid uptake and of their proton conductivity revealed that polymer electrolyte membranes with conductivities well above 10^{-2} S/cm were obtained. Finally, MEAs based on the p-tolyl bearing copolymer were also fabricated and tested in a single fuel cell at temperatures up to 180 $^\circ\text{C}$ showing promising performance, although the system is not yet optimized.

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