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Blends of Aromatic Polyethers Bearing Polar Pyridine Units and Their Evaluation as High Temperature Polymer Electrolytes

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Summary: Aromatic polyethers containing polar pyridine units in the main chain have been synthesized using different difluoride monomers. Copolymers of 2,5-(4′,4″dihydroxy biphenyl)-pyridine and 3,3′,5,5′-tetramethyl-[1,1′-biphenyl]-4,4′-diol with bis(4-fluorophenyl) sulfone or phenyl phosphine oxide difluoride or decafluorobiphenyl (PTMPySF, PTMPyPO, PTMPyDF) were synthesized. These polymeric structures despite their common structural characteristics, showed totally different behavior in terms of solubility and acid doping ability. Blends of these copolymers have been prepared in order to be evaluated in terms of fuel cell relevant parameters like acid doping ability and conductivity. In most cases flexible membranes were obtained by solution casting. The acid doping ability was controlled based on the blend constituents and composition. The doped membranes exhibited high conductivity values, in the range of 10^{-3} S/cm at room temperature which is increased at 2.5×10^{-2} S/cm at temperatures up to 180 °C.

Keywords: blends; compatibility; copolymerization; fuel cells; polyethers

Introduction

Polymers that can be used as polymeric electrolytes are of high priority mainly due to their potential application in fuel cells in the renewable energy sector.[1–4] In terms of structural consideration, these materials should combine hydrophobic segments with polar hydrophilic groups that are able to interact with molecules that promote the proton transport such as water or strong acids. The prerequisite for the appearance of high ionic conductivity in combination with the membrane quality and mechanical integrity, are the key properties for the application of these materials in fuel cells. Since the phase separation[5–8] of the hydrated or doped membranes is a critical issue, blending of polymers may offer an additional way to control phase separation at various levels and at the same time to combine different properties of the selected polymers to be blended. In cases where the operational temperature is higher than 100 °C, there are several advantages which result in the improvement of the overall performance and simplification of the system.[9–12] Polymers that are able to be doped with strong acids are the most preferable candidates in this case. Phosphoric acid doped polybenzimidazole[9–18] membranes have been used in fuel cell operating at temperatures up to 200 °C with low humidification and high CO tolerance.[11,13] Polymer blends have also been used as high temperature polymer electrolytes taking advantage of the possible

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interaction of different polymers in order to prepare materials that combine high ionic conductivity with good mechanical properties.[19–23]

Other type of homopolymers and copolymers bearing pyridine units into an aromatic polyether backbone[24–27] have been proposed by our group as alternative high temperature polymer electrolytes which combine high ionic conductivity, after doping with phosphoric acid, with excellent thermal and mechanical properties and high oxidative stability.

In this paper we report on the synthesis of some new fluorinated aromatic polyethers containing pyridine units in the main chain and their blends with analogous sulfone or phenyl phosphinoxide type aromatic polyethers.

Experimental Part

Materials

Syntheses of monomers and copolymes **I** (PTMPySF) and **II** (PTMPyPO) were made according to published procedures.[24,26] All chemicals and solvents were purchased from Aldrich or Merck and used as received without purification unless otherwise specified.

Synthesis of PTMPyDF Copolymers

To a degassed flask equipped with a Dean-Stark trap were added 2,5-(4′,4″dihydroxy biphenyl)-pyridine (3.6 mmol, 0.95 g), 3, 3′, 5,5′-tetramethyl-[1,1′-biphenyl]-4,4′-diol (8.4 mmol, 2.03 g), decafluorobiphenyl (12.0 mmol, 4,01 g), K_2CO_3 (13.92 mmol, 1.92 g), toluene (5 ml), and DMAc (15 ml) for copolymer **IIIa** as an example. The mixture was degassed and filled with argon and stirred at 120 °C for 48h, and then stirred at 160 °C for 6h. The obtained viscous solution was diluted in DMAc and precipitated in 20-fold excess mixture of 2.5/1 $MeOH/H_2O$, washed with H_2O and hexane, and dried at 80 °C under vacuum. The same procedure was followed to produce polymers with different pyridine molar percentages (e.g. copolymer **IIIb**), by varying the feed ratio of the pyridine diol to the tetramethyl diol monomers. The results for the different copolymers in terms of molecular weight characterization and copolymer composition for the different copolymers used are depicted in Table 1.

Characterization

^{1}H NMR spectra were obtained on a Brucker Advance DPX 400 MHz spectrometer. The samples were dissolved in deuterated chloroform ($CDCl_3$) using TMS as internal standard.

Gel permeation chromatography (GPC) measurements were carried out using a Polymer lab chromatographer equipped with two Ultra Styragel columns (10^4, 500Å), UV detector (254 nm), and $CHCl_3$ as eluent, at 25 °C with a flow rate of 1 ml/min.

DMA measurements for the estimation of glass transition temperature (Tg, see Table 1) were conducted using a solid-state analyzer RSA II, Rheometrics Scientific Ltd., at 10 Hz.

Table 1.
Results for the different copolymers used in this study, in terms of molecular weight characterization and copolymer composition for the synthesized copolymers.

A/a	copolymers	x (mol %)	GPC results			Tg (°C)	Sol. Prop
			Mn	Mw	Disp		
I.	PTMPySF	60	72200	104300	1.5	280	√
IIa.	PTMPyPO	60	20900	39400	1.9	260	√
IIb.	PTMPyPO	80	6500	10600	1.6	275	√
IIIa.	PTMPyDF	30	15500	48700	3.1		√
IIIb.	PTMPyDF	20	55100	82300	1.5		√

√: Excellent solubility +: good solubility −: insoluble

Membrane Preparation of Polymer Blends (PTMPySF/PTMPyPO) and (PTMPyPO/PTMPyDF)

Blends were prepared by dissolving the copolymers PTMPySF and PTMPyPO or PTMPyPO and PTMPyDF in DMAc at different weight ratios. The solution mixtures were stirred for 3 h at room temperature and were then poured onto glass plates and placed in an oven at 85 °C for 20h. Membranes with good mechanical properties were obtained. To remove any excess of remained solvent, the membranes were dried under vacuum at 150 °C for 3 days. All studied blends are given in Table 2.

Determination of Acid Uptake

Membranes were immersed in 85 wt% H_3PO_4 solution at various temperatures and doping times. Surface-attached phosphoric acid was quickly removed by wiping with tissue paper and the weight of the dry membranes was determined. The acid uptake content can be calculated as follows:

$$\text{Acid Uptake content}(\%) = [(w_{wet} - w_{dry})/w_{dry}] \times 100\%$$

where w_{wet} and w_{dry} are the masses of wet and dried samples, respectively.

Proton Conductivity Measurements

All measurements were performed at a conductivity four probe cell at room temperature or at elevated temperatures in a closed vessel with controlled humidity conditions. 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).

Results and Discussion

The main objective of this work was to compare the different copolymers that have been prepared previously (like PTMPySF and PTMPyPO) with the newly synthesized fluorinated copolymers PTMPyDF as well as to extent their application by simply blending copolymers of complimentary properties and structural characteristics. Thus the first part of this study is devoted to the comparison of the solubility properties and the acid doping ability of the three copolymer structures as shown in Scheme 1 and their blends composed of these copolymers.

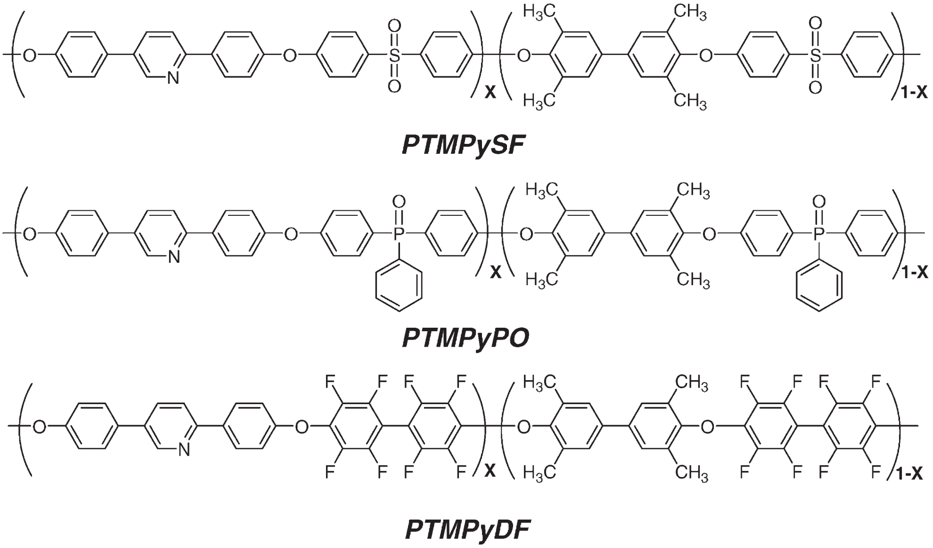
Further on, the possible application of these blends in high temperature polymer electrolyte fuel cells (HT-PEM FC) is investigated by means of proton conductivity measurements.

Based on our previous work concerning the solubility behaviour, copolymer **I** was synthesized at a 60/40 pyridine/tetramethyl diol ratio, since higher pyridine contents lead to low molecular weight partially

Table 2.
Results for the studied blends **I-II** and **II-III**, in terms of blend composition and film forming properties.

Copolymer Blends			% w.t ratio	Solvent Casting	Film Properties
Cop.I PTMPySF	Cop.II PTMPyPO	Copy.II PTMPyDF			
I	IIa	–	90/10	DMAc	√
I	IIa	–	75/25	DMAc	√
I	IIa	–	6040	DMAc	√
I	IIa	–	50/50	DMAc	√
I	IIa	–	20/80	DMAc	√
I	IIb	–	50/50	DMAc	√
I	IIb	–	20/80	DMAc	√
–	IIa	IIIa	70/30	DMAc/$CHCl_3$	+/−
–	IIa	IIIa	80/20	DMAc/$CHCl_3$	+/−
–	IIa	IIIb	70/30	DMAc/$CHCl_3$	+/−
–	IIa	IIIb	80/20	DMAc/$CHCl_3$	+/−
–	IIa	IIIb	50/50	DMAc	+

√: Excellent film +: good film −: brittle film



Scheme 1.
Chemical structure of copolymers **I** (PTMPySF), **II** (PTMPyPO) and **III** (PTMPyDF).

soluble polymers with moderate mechanical properties.[24] In the second case of copolymer **II** (PTMPyPO) the 60/40 composition was selected simply for comparison reasons but also higher pyridine content (80/20) was used since the presence of the phenyl phosphine oxide group and the kink that this group introduce to the main chain,[27,28] enabled solubility allowing thus the introduction of the rigid bis(phenyl) pyridine units in higher amounts. In the case of the decafluoro derivative copolymers **III** (TMPyDF), the solubility was limited due to the rigidity of all respective co-monomers used. Specifically, it was immediately noticed that the solubilization effect that the tetramethyl biphenyl diol brings due to the presence of the side methyl groups, in cases of copolymers **I** and **II**, is not enough to enable solubility in the case of copolymer **III**, in combination with the presence of the rigid bis(phenylene)pyridine groups. Thus copolymers of high contents of the tetramethyl biphenyl diol were selected, giving high molecular weight, film forming soluble polymers like those of 30/70 (**IIIa**) and 20/80 **(IIIb)** pyridine/tetramethyl diol monomers. The results for all copolymers used are summarized in Table 1, where x denotes the molar content of the pyridine unit.

The ^{1}H NMR of PTMPyDF is depicted in Figure 1, where the copolymer composition can be estimated, based on the aromatic proton (a) near the nitrogen of the pyridine ring at 8.9 ppm and the aromatic protons (i) of the tetramethyl biphenyl moiety at 6.9 ppm.

Despite the low solubility of the fluorinated copolymers, the high hydrophobicity that these fluoroderivatives introduce is a key advantage that structures like PTMPyDF are persisting. Thus the blending of copolymers with different acid doping ability but also with completely different hydrophobicity could result in materials with a controlled phase separation but still able to be doped with phosphoric acid.

As it was mentioned in the introduction the doping ability of such materials with strong acids is a necessary condition of their further possible application as polymer electrolytes for high temperature fuel cells. The fluorocopolymers, though having some pyridine content, show no phosphoric acid uptake in contrast to the other two

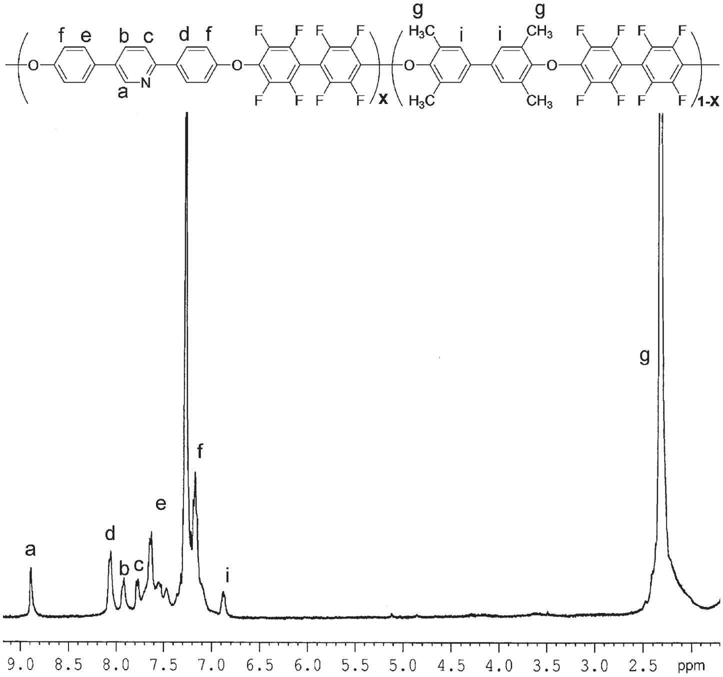


Figure 1.
^{1}H NMR spectrum of copolymer PTMPyDF with the assignment of the peaks.

copolymers, mainly due to the hydrophobic character of the dominant decafluorobiphenyl unit. A straightforward comparison of time dependent acid doping ability of all respective copolymers presented in this study is shown in Figure 2.

By comparing the chemical structure of these three copolymers, it is easily noticeable that despite the fact that the two diphenol comonomers are the same in all cases, the differences observed to the solubility properties as well as to the phosphoric acid doping behavior are obvious, supporting the extremely significant importance of the detailed polymeric structure on the key material properties. Thus having polymeric structures with common structural characteristics but behave in a completely different way in terms of solubility and acid doping ability we proceed with the preparation of blends (Table 2). More specifically, in order to increase the acid doping ability of copolymer **I**, we prepared blends of copolymers **I** and **II**, whereas by blending copolymers **II** and **III** we tried to resemble the acid doping ability with that of copolymer **I**.

In the last case the interesting point is to examine the influence of the polymer matrix, copolymer versus blend, on the

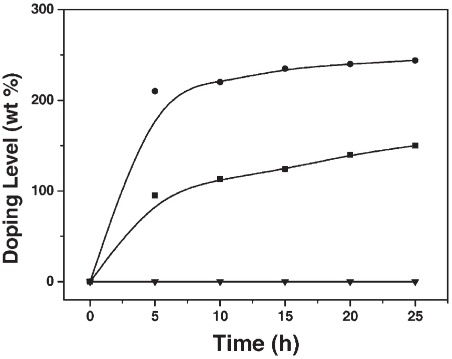


Figure 2.
Time dependence of doping level (wt %) of the copolymers PTMPyDF (▼), PTMPySF (■), and PTMPyPO (●) at 80 °C.

conductivity behavior. The blend compositions depicted in Table 2 were studied in respect to their acid doping ability and the polymer matrix on the conductivity at standard doping level.

Since the doping ability is drastically dependent on the doping conditions, in this presentation we selected doping with phosphoric acid at 80 °C for comparison reasons. It should be clear that higher doping values can be obtained by increasing the doping temperature as for example the PTMPySF copolymer where doping values up to 220 wt% can be obtained at 100 °C.[24]

As can be observed in Figure 3 the blends of copolymers **I** and **II**, at various weight ratios, resulted to membranes of intermediate doping behavior. An increase of the doping ability by increasing the ratio of copolymer **II** is clearly evident. Concerning the blends of copolymers **II** and **III**, a comparable doping behavior is observed (Figure 4), since PTMPyPO rich blends were selected and thus the doping character of copolymer **II** is prevailing.

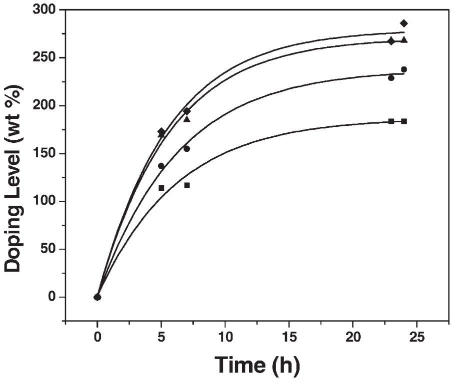


Figure 4.
Time dependence of doping level (wt%) of copolymer blends **IIa-IIIa** at ratios 70/30 (●), 80/20 (◆) and **IIa-IIIb** in ratio 70/30 (■), 80/20 (▲) at 80 °C.

In the second part of this study, we tried to examine if such blends could be applied in HT-PEM fuel cells. Since they have mechanical stability and membrane integrity even after doping with a strong acid at high levels, the last prerequisite of proton conductivity needed to be satisfied. In order to investigate this, we performed conductivity measurements using the four probe current interruption technique. It should be noticed that the results obtained by the four probe technique, should be considered as preliminary and true comparison can be realized using *in situ* single cell measurements. Figure 5 shows the conductivity values versus doping level for the copolymer blend **I-IIa** at a 90/10 weight ratio as an example. Conductivity values in the range of 10^{-2} S/cm are obtained for doping levels higher than 150 wt% and there is a weak increase for higher doping level values.

A blend of **I-IIa** with 75/25 weight ratio and at a doping level of 200 wt%, which can be directly compared to PTMPySF[24]

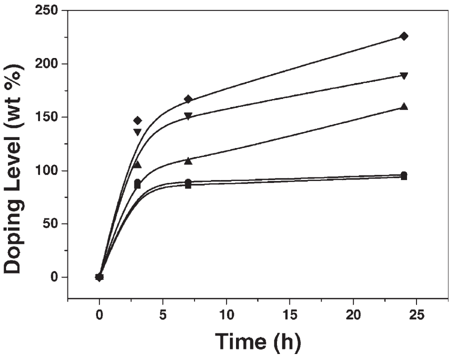


Figure 3.
Time dependence of doping level (wt%) of copolymer blends **I-IIa** at ratios 90/10 (■),75/25 (●),60/40 (▲), 50/50 (▼) and 20/80 (◆) at 80 °C.

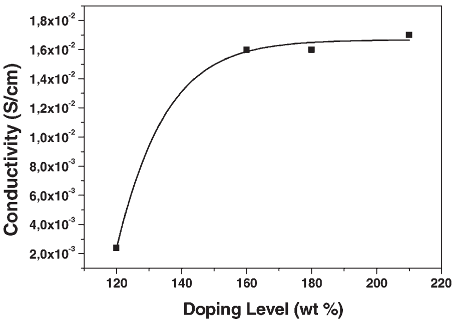


Figure 5.
Doping level dependence of ionic conductivity of the blend **I-IIa** 90/10, at room temperature.

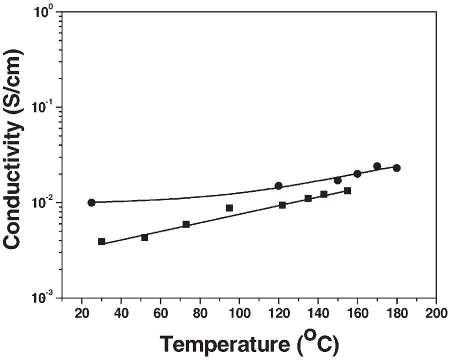


Figure 6.
Logarithmic plot of ionic conductivity versus temperature of the copolymer blend **I-IIa** 75/25 (-●) at doping level of 200 wt% H_3PO_4 compared to **I** (-■-) at doping level 190 wt% and 70% relative humidity.

was selected for a study of the conductivity versus temperature as shown in Figure 6. As observed, the conductivity values for this blend are in the range of 10^{-2} S/cm at the working temperature of an HT-PEM fuel cell (150–180 °C). By comparing these values with those of copolymer **I**, this material can be considered as applicable in the HT-PEM fuel cell technological area.

Conclusion

Aromatic polyethers bearing polar pyridine units in the main chain have been synthesized using different difluoride monomers in order to compare their solubility and acid doping ability properties. Despite the fact that these copolymers show comparable structural characteristics, their behavior concerning the aforementioned properties is totally different. Blends of these copolymers have also been prepared and studied regarding their controlled acid doping ability and conductivity behavior. Most of the obtained blend membranes exhibited good mechanical properties. The acid doping ability was depended on the blend composition and the blend constituent. Conductivity values, in the range of 10^{-2} S/cm were obtained at elevated temperatures.

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