# Side Chain Crosslinking of Aromatic Polyethers for High Temperature Polymer Electrolyte Membrane Fuel Cell Applications

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ABSTRACT: Novel aromatic polymers bearing polar pyridine units in the main chain and side chain crosslinkable hydroxyl and propargyl groups have been successfully synthesized. The polymers have been investigated in terms of their critical properties related to their application in high temperature polymer electrolyte membrane fuel cells, such as doping ability, mechanical properties, and thermal stability. Crosslinked membranes were prepared by direct crosslinking of hydroxyl side chain groups with decafluorobiphenyl used for the first time as a crosslinking agent. However, further functionalization of hydroxyl groups to the propargyl derivative has also led to

**INTRODUCTION** Fuel cells are a more environmentally friendly and efficient alternate power source compared with existing power sources. Polymer electrolyte membrane fuel cells (PEMFCs) have exceptional advantages hence they find appliance in stationary and mainly vehicular applications.<sup>1</sup> The proton exchange membrane (PEM) is the core of the fuel cell, which must fulfil several requirements, such as high ionic conductivity, high thermal, mechanical and chemical stability, as well as low fuel or gas permeability. Up to now, Nafion is the mostly well-known perfluorinated polymer used in PEMFCs operating up to 80  $^\circ\text{C}.^{2\text{--4}}$  Besides its several advantages, such as excellent chemical stability and high performance, a main drawback is the low proton conductivity at temperatures higher than 100 °C, since dehydration of the membrane occurs. Recently, research has been devoted in the development of PEMFCs operating at temperatures above 100 °C.<sup>5,6</sup> Operation at high temperatures offers the distinct advantages of high carbon monoxide tolerance, easier thermal management, and enhanced kinetics on both electrodes resulting in higher energy efficiency. Polybenzimidazole (PBI) doped with phosphoric acid is the most extensively studied polymer electrolyte used in high temperature PEMFCs due to its high ionic conductivity and excellent thermal stability.7-10 Alternate polymer electrolytes for high temperature PEMFCs

crosslinked polymers after thermal curing. Both types of crosslinked membranes exhibited higher glass transition temperatures as well as lower doping levels when doped in phosphoric acid compared with the non crosslinked analogs, confirming the formation of a successfully crosslinked network. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 207–216, 2012

**KEYWORDS**: aromatic polyethers; copolymerization; crosslinking; high temperature PEM fuel cells; membranes

based on aromatic polyethers bearing main chain and/or side chain pyridine units have been developed by our group.<sup>11–15</sup> These copolymers possesses good mechanical properties and excellent thermal, oxidative as well as chemical stability. Furthermore, the polar pyridine units interact with and/or retain phosphoric acid molecules, thus resulting in proton conductive materials.

However, the high temperature PEMs are mostly designed for residential application where durability up to 40.000 h is required. In addition, operation at higher temperatures and more specifically in the range of 200-220 °C will open new horizons because of the prospect to join the fuel cell with a methanol reformer in a combined single cell.<sup>16-18</sup> Hence, the development of new electrolytes with improved mechanical and thermal properties as well as adequate ionic conductivity still remains a challenge. An effective approach to improve PEM properties is the crosslinking method, which includes the ionic and covalent crosslinking. Ionic crosslinking is based on interaction forces between different types of ionomers, such as acid-base polymers.<sup>19-22</sup> However, ionic crosslinking is not effective at high temperatures because of membrane's mechanical integrity loss. Covalent crosslinking is more favorable because in this case membranes can

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**SCHEME 1** Synthesis of 1,4-bis(4-hydroxyphenyl)-2,5-dimethoxybenzene (4).

preserve their properties even at elevated temperatures. There are several possibilities for covalent crosslinking, e.g., the crosslinking of double bonds with benzoyl peroxide,<sup>23–26</sup> bisazides,<sup>27–32</sup> and photochemical crosslinking.<sup>33–35</sup> The crosslinking of triple bonds has been described as well, e.g., the thermal crosslinking of polymers containing endcapped ethynylphenyl<sup>36–41</sup> or phenylethynyl<sup>42</sup> moieties by trimerization of the alkynes to stable benzene systems. Another example for covalent crosslinking is the crosslinking of PBI with dihalides, such as *p*-xylene dichloride<sup>43</sup> and *p*-xylene dibromide.<sup>44</sup>

In this work, we report the synthesis, crosslinking and characterization of new aromatic polymers bearing pyridine units in the main chain and side cross-linkable hydroxyl and propargyl groups. The triple bonds were thermally crosslinked since this method leads to highly stable benzene systems. On the other hand, side hydroxyl groups offer various possibilities for functionalization and crosslinking, because of their ability to act after deprotonation by a base as nucleophiles in nucleophilic substitutions. Reaction of these nucleophilic species with di- or polyhalides leads to crosslinked systems. Decafluorobiphenyl, a compound that has been widely used in several polycondensation reactions as monomer<sup>37,39,42,45,46</sup> has been chosen in this report as crosslinking agent because of its high thermal, chemical, and oxidative stability. Furthermore, this compound was used to increase membrane's hydrophobicity, thus enabling the phase separation.4 The effect of the amount of the decafluorobiphenyl crosslinker on the thermal and mechanical properties as well as on acid doping ability of the crosslinked membranes was studied. In all cases, crosslinked membranes showed improved mechanical in terms of glass transition temperatures  $(T_{g}s)$  as well as thermal properties and lower doping levels when impregnated with phosphoric acid compared with the non crosslinked ones.

## **RESULTS AND DISCUSSION**

Aromatic polyethers bearing main chain and/or side chain pyridine units,<sup>11–15</sup> are promising candidates for application in high temperature PEMFCs. However, to further improve the mechanical strength and the thermal properties, which are critical parameters of PEMs, and thus to increase the long-term durability at temperatures of 200 °C and above, novel aromatic polyethers bearing side cross-linkable groups have been synthesized. In this work, side dimethoxy-based polymers have been prepared and modified to the hydroxyl

analogs after ether cleavage. These polymers were used either directly for covalent crosslinking or by further functionalization to triple bonds that were crosslinked by thermal treatment.

Aromatic poly(ether sulfone)s have been synthesized via nucleophilic aromatic substitution ( $S_NAr$ ) of a bis(aryl fluoride) with phenolate-derivatives. Alternate routes for the synthesis of poly(ether sulfone)s and ketones using bis(aryl chloride)s instead of fluorides, bearing in mind the economical and ecological aspects, have been described.<sup>47–50</sup>

For the successful preparation of the aforementioned polymers via nucleophilic aromatic substitution, the corresponding diols **4** and **8** have been prepared in large quantities and good yields. The synthetic procedures followed for the synthesis of the two new aromatic diols **4** and **8** are outlined in Scheme 1 and 2. Both monomers were prepared by Suzuki coupling, while similar Suzuki couplings with dialkoxy diboronic acids have already been reported.<sup>51,52</sup> In the case of diol **4** the 2,5-dimethoxy-1,4-phenylene diboronic acid (**1**) reacted with the THP-protected 4-bromophenol (**2**) resulted in the precursor of the diol **3** (Scheme 1). Coupling of 4-methoxyphenylboronic acid (**6**) with THP-protected 2,5-dibromohydroquinone (**5**) led to compound **7** (Scheme 2). Following deprotection of the alcohols under acidic conditions in both cases resulted in diol **4** and **8**, respectively.

Novel dimethoxy-based polymers (I, II, V) have been synthesized via nucleophilic aromatic substitution of the new diols 4 or 8, 2,5-bis(4-hydroxyphenyl)pyridine and 3,3',5,5'-tetramethyl[1,1'-biphenyl]-4,4'-diol with bis(4-fluorophenyl)sulfone, as shown in Schemes 3 and 4. The chemical structures of the new dimethoxy-based polymers were verified by <sup>1</sup>H NMR spectroscopy. High molecular weights were obtained in all cases as proven by gel permeation chromatography (GPC), which are shown in Table 1. The high molar percentage (50-60 mol %) of 2,5-bis(4-hydroxyphenyl)pyridine monomer used in all synthesized polymers (I, II, V) should guarantee the sufficient doping ability. On the other hand, different molar ratios of hydroxyl groups were used in the case of terpolymers V to study the effect of the amount of hydroxyl groups on the crosslinking since high molar percentage of hydroxyl groups can lead to efficient crosslinking. All dimethoxy bearing polymers were soluble in solvents, such as CHCl<sub>3</sub>, dimethylacetamide (DMAc), dimethylformamide (DMF), and N-Methylpyrrolidon (NMP) and showed excellent film forming properties.



**SCHEME 2** Synthesis of 1,4-bis(4-methoxyphenyl)-2,5-dihydroxybenzene (8).



SCHEME 3 Synthesis of dimethoxy-based copolymers (I, II) and dihydroxy-based analogs (III).

The aforementioned polymers were all modified to the side hydroxy-based analogs by ether cleavage with boron tribromide. However, in Table 1 only the dihydroxy-based polymers (III, VI) that were used for crosslinking are listed. The successful ether cleavage was confirmed by <sup>1</sup>H NMR spectroscopy. A representative example for the ether cleavage of dimethoxy bearing copolymers is as follows: the dimethoxybased precursor II exhibited a characteristic peak located at 3.81 ppm attributed to the methyl protons (not shown here). After ether cleavage this peak is disappeared and a new characteristic peak rose at 9.07 ppm which is attributed to the hydroxyl groups (Fig. 1).

Propargyl-based copolymer **IV** has been synthesized by nucleophilic substitution reaction of propargyl bromide with dihydroxy copolymer **III** (Scheme 5). It should be noticed that the preparation of propargyl-based copolymers was only possible by using dihydroxy-based copolymer **III**, since deprotonation of dihydroxy-based copolymer **I** at elevated

temperatures led to insoluble gelatine like material; a surprising result in view of the fact that copolymer I and III have very similar chemical structures. Becuase of this solubility problem, crosslinking of copolymer I with decafluorobiphenyl was not feasible as well. <sup>1</sup>H NMR spectrum of IV showed the disappearance of the peak located at 9.07 ppm attributed to hydroxyl protons and the formation of two new peaks at 4.74 ppm and 3.50 ppm. These peaks are assigned to the methylene protons and the terminal alkyne proton, respectively, confirming the successful substitution of the hydroxyl groups with propargyl moiety (Fig. 2). Further evidence for a successful substitution is given by IR spectroscopy, where a weak band at 3290 cm<sup>-1</sup> could be observed, characteristic for terminal alkynes.

As already mentioned, covalent crosslinking results in membranes with high chemical and thermal stabilities.<sup>53–59</sup> Side chain triple bonds can be crosslinked through the formation of a network of stable benzene systems. Thermal curing of



SCHEME 4 Synthesis of dimethoxy-based terpolymers (V) and dihydroxy-based analogs (VI).

Materials

TABLE 1 Characteristi	s of Synthesized Polymers
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Polymer	x/y/z (mol %)	M <sub>n</sub>	M <sub>w</sub>	Ι		
Copolymers	Copolymers PPy(x)MeO(y)coPSF					
la	60/40/0	42,750	65,980	1.5		
l <sub>b</sub>	60/40/0	39,140	64,600	1.7		
Copolymers PPy(x)MeOPh(y)coPSF						
lla	60/40/0	42,000	76,440	1.8		
ll <sub>b</sub>	60/40/0	45,850	65,220	1.4		
Copolymers	Copolymers PPy(x)OHPh(y)coPSF					
III	60/40/0	-	_	-		
Copolymers PPy(x)Prop(y)coPSF						
IV	60/40/0	-	_	_		
Terpolymers PPy(x)MeOPh(y)TM(z)coPSF						
Va	55/34/11	70,340	111,180	1.6		
V <sub>b</sub>	56/33/11	53,880	89,080	1.7		
V <sub>c</sub>	50/28/22	102,680	161,420	1.6		
V <sub>d</sub>	52/12/36	39,750	65,380	1.7		
Terpolymers PPy(x)OHPh(y)TM(z)coPSF						
VI	52/12/36	-	-	-		

copolymer **IV** led to a covalent crosslinked network which could be confirmed, i.a. by the results of dynamic mechanical analysis (DMA) (Fig. 3).

Since thermal crosslinking can be induced even by drying the membranes under vacuum at 160 °C or during the DMA experiments, comparison of the glass transition temperatures of the propargyl copolymer **IV** with the crosslinked one **IV**<sup>CL</sup> is not reliable. The methoxy-based copolymer **II** can be used as an alternate for comparison of the mechanical properties, since it contains no cross-linkable groups. As it is shown in Figure 3, the crosslinked copolymer **IV**<sup>CL</sup> exhibited higher glass transition temperature ( $T_g$ ) compared with copolymer **II**, as it was expected. The improvement of the  $T_gs$  is contributed to the decreased flexibility of the polymer chains by the formation of a crosslinked network structure through the thermal curing. The glass transition temperature of the crosslinked copolymer **IV**<sup>CL</sup> is 325 °C, which is considerably higher than the  $T_{\rm g}$  of copolymer **II** by 90 °C. Furthermore, the storage modulus after crosslinking was not decreased above 370 °C, but it reached a plateau and this behavior is characteristic for crosslinked networks. The  $T_{\rm g}$  of copolymer **IV**<sup>CL</sup> is among the highest reported values for crosslinked copolymers containing triple bonds: crosslinking of ethynylphenyl terminated copolymers leads to a maximum  $T_{\rm g}$  of 258 °C,<sup>36</sup> while in the case of side chain ethynyl bearing copolymers there is an increase of the glass transitions temperature up to 312 °C.<sup>37</sup>

An indirect method to confirm a successful crosslinking is to compare the weight percentage of the soluble fraction of non crosslinked and crosslinked membranes. The non crosslinked membranes II and III were completely soluble in DMAc after heating at 60 °C for 16 h, whereas the crosslinked membrane  $IV^{CL}$  was almost insoluble (only 11 wt % was soluble under the same conditions), denoting the effective crosslinking.

Another critical parameter that was evaluated is the acid doping ability of the crosslinked membranes. The doping ability of the crosslinked membrane  $IV^{CL}$  impregnated in phosphoric acid at 80 and 100 °C is shown in Figure 4. For comparison reasons, the doping ability of the membrane of copolymer II is presented as well. In general, it is known that since crosslinking leads to the formation of more compact chemical structures, the acid doping level as well as the proton conductivity is decreased. As expected, crosslinked membrane  $IV^{CL}$  showed lower doping levels compared with the one of copolymer II at 80 °C and 100 °C. More specifically, the crosslinked membrane  $IV^{CL}$  had a doping level of around 160 wt %, while the non crosslinked one had a doping level of around 290 wt % after 24 h at 100 °C.

At higher temperatures ( $120 \,^{\circ}$ C), the crosslinked membrane partially started to dissolve. This behavior could be explained by the presence of the alkyl ether groups, which are sensitive for protonation by the acid resulting in the formation of an ionic species that can increase the solubility of the membrane in phosphoric acid at elevated temperatures.



FIGURE 1 <sup>1</sup>H NMR of copolymer III in deuterated dimethylsulfoxide with the assignment of the peaks.



SCHEME 5 Synthesis of propargyl-based copolymer (IV).

Another very promising crosslinking method for the formation of covalent networks is the nucleophilic substitution of dihalides or polyhalides, e.g., the crosslinking of PBI with pxylene dichloride<sup>43</sup> and dibromide,<sup>44</sup> respectively. In this study, decafluorobiphenyl was used as a crosslinker because of its high thermal, chemical, oxidative stability as well as its increased hydrophobicity. crosslinking with the decafluorobiphenyl compound can lead to more stable aryl ether bonds compared with alkyl ethers, which would be created in the case of crosslinking with xylene dihalides. As shown before in the case of copolymer  $IV^{CL}$ , alkyl ether groups could be the reason for membrane's dissolution processes in phosphoric acid at elevated temperatures due to its protonation. Furthermore, the method with a crosslinker enables the control of the crosslinking density by varying the molar ratio of hydroxyl groups as well as the weight percentage of the decafluorobiphenyl used as crosslinker.

Dihydroxy-based polymers (III, VI) reacted with decafluorobiphenyl resulted in the formation of a covalently bonding network. To control the degree of crosslinking, two different parameters, the weight percentage of the crosslinker as well as the molar percentage of hydroxyl groups involved in the



**FIGURE 2** <sup>1</sup>H NMR of copolymer **IV** in deuterated dimethylsulfoxide with the assignment of the peaks.

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FIGURE 3 DMA curves of crosslinked copolymer IV<sup>CL</sup> compared with dimethoxy-based copolymer II.

crosslinking, have been evaluated. Crosslinked membranes with different weight percentages of decafluorobiphenyl used as crosslinker have been prepared, as it is shown in Table 2. As the weight percentage of the crosslinker increases, the mechanical integrity of the crosslinked membranes as well as the acid doping ability is decreased. More specifically, crosslinked membrane III<sup>5CL</sup> prepared from copolymer III with composition 60/40 with 5 wt % crosslinker exhibited good mechanical properties, while crosslinked membrane  $\mathrm{III}^{\mathbf{10CL}}$  with 10 wt % crosslinker became more fragile. Preparation of free standing crosslinked membranes with 20 wt % crosslinker was not possible. Crosslinked membrane VI<sup>6CL</sup> prepared from dihydroxy terpolymer VI with composition 52/12/36 and 6 wt % crosslinker showed very good mechanical integrity. Crosslinked samples prepared from terpolymer with composition 56/33/11 with 6 and 7 wt % crosslinker have been prepared as well (not listed in Table 2). As expected, the doping level of the crosslinked membrane with the higher weight percentage of decafluorobiphenyl (7 wt %) was lower. As mentioned before, the effect of the different



**FIGURE 4** Time dependence of doping level (wt %) of **II** and  $IV^{CL}$  at 80 °C and 100 °C in 85 % H<sub>3</sub>PO<sub>4</sub>.

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ABLE 2 Characteristics o	f Crosslinked an	d Non Crosslinked	Membranes
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Polymer	x/y/z (mol %)	Crosslinker (wt %)	T <sub>g</sub> (°C)	Film Quality	Soluble Fraction (wt %) <sup>a</sup>	Doping Level (wt %) <sup>b</sup>
III	60/40/0	0	250	+++	100	200
III <sup>5CL</sup>	60/40/0	5	320	++	8	180
III <sup>10CL</sup>	60/40/0	10	-	+	6	150
VI	52/12/36	0	284	+++	100	180
VI <sup>6CL</sup>	52/12/36	6	301	++	11	150

<sup>a</sup> Soluble fraction in DMAc after heating at 60 °C for 16 h.

<sup>b</sup> 24 h at 100 °C.

+++ Very good.

++ Good.

+ Bad.

molar percentage of the hydroxyl groups on crosslinking has been studied as well. Comparing polymers with composition 40 mol % (III<sup>5CL</sup>) and 12 mol % (VI<sup>6CL</sup>) of hydroxyl containing units, respectively, while keeping almost the same amount of decafluorobiphenyl, it is shown that crosslinking was more effective in the case of III<sup>5CL</sup>. This observation is supported by the DMA data, since in the case of terpolymer with 12 mol % hydroxyl containing units (VI), the difference in  $T_g$  values of the crosslinked and the non crosslinked membrane was only 16 °C, while in the case of copolymer with 40 mol % hydroxyl containing units (III) was 70 °C (Table 2). Measurements of the weight percentage of the soluble fraction of the crosslinked membranes were also conducted as it can be seen in Table 2. The crosslinked membranes (III $^{\rm 5CL},$  III $^{\rm 10CL},$  VI $^{\rm 6CL}$ ) were almost insoluble, only 6-11 wt % was soluble in DMAc after heating at 60 °C for 16 h, while the non crosslinked membranes were completely soluble, indicating the successful crosslinking.

The mechanical properties of the crosslinked membrane in comparison with the non crosslinked one were studied by DMA (Table 2). The crosslinked membrane III<sup>5CL</sup> with 5 wt % crosslinker exhibited higher glass transition temperature compared with the non crosslinked one III. The  $T_{\rm g}$  of the crosslinked membrane III<sup>5CL</sup> was 320 °C, by 70 °C higher compared with the non crosslinked one III ( $T_{\rm g}$  around 250 °C).

The thermal stability of the crosslinked polymers was evaluated by thermogravimetric analysis (TGA). The decomposition behavior for two different crosslinked ( $III^{CL5}$  and  $VI^{6CL}$ ) and one non crosslinked membrane III has been compared

**TABLE 3** TGA Data of Crosslinked Polymers III<sup>5CL</sup>, VI<sup>6CL</sup>, and the Non Crosslinked One III

Polymer	<i>T</i> <sub>d(5%)</sub> (°C)	Weight Loss (wt %) at 500 °C	Weight Loss (wt %) at 800 °C
ш	440	15	51
III <sup>5CL</sup>	490	5	27
VI <sup>6CL</sup>	340	20	42

(Table 3). In all cases, the crosslinked membranes exhibited higher thermal stability compared with the corresponding non crosslinked ones. The crosslinked membranes were thermally stable up to 410 °C, while for the noncrosslinked ones, a small weight loss has been observed at this temperature. At temperatures above 550 °C, the improved thermal stability of the crosslinked membranes is evident, since crosslinking enhances the thermal stability of the polymer main chain. In details, the crosslinked III<sup>5CL</sup> showed a  $T_{d(5\%)}$  at 340 °C. The higher thermal stability of crosslinked III<sup>5CL</sup> compared with VI<sup>6CL</sup> confirmed the more effective crosslinking as it was also supported by the previous data obtained by DMA analysis.

The doping ability of the crosslinked membranes as well as the non crosslinked ones in phosphoric acid at  $100^{\circ}$  C is given in Figure 5. As expected, crosslinked membranes exhibited lower doping level compared with the non crosslinked ones. As already mentioned, since crosslinking was more effective in the case of III<sup>5CL</sup>, should result in lower



**FIGURE 5** Comparison of the doping ability of the crosslinked membranes III<sup>5CL</sup> and VI<sup>6CL</sup> with the corresponding non cross-linked ones III and VI with 85%  $H_3PO_4$  at 100 °C.



FIGURE 6 Temperature dependence of doping ability of III<sup>5CL</sup> with 85%  $H_3PO_4$ .

doping levels compared with the crosslinked membrane  $\rm VI^{6CL}$ . In contrary, the crosslinked membrane  $\rm III^{5CL}$  showed higher doping levels (180 wt %) compared with the cross-linked membrane  $\rm VI^{6CL}$  (150 wt %). A possible explanation for this finding is the higher molar percentage of hydroxyl containing units (40 mol % for  $\rm III^{5CL}$ ) that can interact with phosphoric acid, thus resulting in higher doping levels. The same observation can be made with the non crosslinked membranes where membrane  $\rm III$  with 40 mol % of hydroxyl containing units had a doping level of 200 wt %, while the corresponding VI with 12 mol % had 180 wt %.

Although the obtained doping levels of the crosslinked membranes are lower compared with the non cross linked ones, they are still acceptable for membrane's use as polymer electrolytes for high temperature PEMFCs. To further enhance the doping ability and thus the ionic conductivity of the crosslinked membranes, the doping ability has been evaluated at higher temperatures (120 and 140 °C) as well. As it is shown in Figure 6, the doping ability of crosslinked  $III^{5CL}$  was improved with increasing temperature. In details,  $III^{5CL}$  showed a maximum doping level of 230 wt % at 140 °C after 24 h, while the doping level at 100 °C was 180 wt %.

Crosslinked membranes obtained according to the here presented methodology are currently optimized to be applied in membrane electrode assembly construction and single cell testing.

#### EXPERIMENTAL SECTION

#### Materials

2,5-Bis(4-hydroxyphenyl)pyridine,<sup>11</sup> 2,2'-((2,5-dibromo-1,4phenylene)bis(oxy))bis-(tetrahydropyran),<sup>14</sup> 2,5-dimethoxy-1,4-phenylene diboronic acid,<sup>40</sup> 4-methoxyphenylboronic acid<sup>60</sup> and 1-bromo-(4-tetrahydropyran-2-yloxy)benzene<sup>61,62</sup> were prepared according to literature. All other chemicals and solvents were purchased from Aldrich without any further purification.

# Materials

# Instrumentation

<sup>1</sup>H NMR spectra were obtained on a Bruker Advance DPX 400 MHz spectrometer. The samples were dissolved either in deuterated chloroform or dimethylsulfoxide with TMS used as internal standard. GPC measurements were performed on a Polymer Lab chromatograph equipped with two Plgel 5  $\mu$ m mixed columns and a UV detector (254 nm), using CHCl<sub>3</sub> as eluent with a flow rate of 1 mL/min at 25 °C and polystyrene standards. DMA were carried out using a solid-state analyzer RSA II (Rheometrics Scientific Ltd.) at 10 Hz. TGA was performed on a Labsys  $T_{\rm g}$  of Setaram under nitrogen with a heating rate of 10 °C /min. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer.

## Monomer Synthesis

#### Synthesis of Monomer 4

Synthesis of 1,4-bis(4-(tetrahydropyran-2-yloxyphenyl))-2,5-dimethoxybenzene (3). 2,5-Dimethoxy-1,4-phenylene diboronic acid (1) (2.00 g, 8.86 mmol), aqueous solution of 2 M Na<sub>2</sub>CO<sub>3</sub> (35.4 mL) and DMF (65 mL) were degassed under vacuum. 1-Bromo-(4-tetrahydropyran-2-yloxy)benzene (2) (9.11 g, 35.43 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.373 g, 0.53 mmol) were added and the reaction mixture was heated at 155 °C for 5 d. After cooling to room temperature, the mixture was added to ice/water, stirred for 0.5 h, filtered, and washed with water and hexane. The solid was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> and filtered to remove the catalyst. The solvent was removed, MeOH was added and stirred overnight. The white product was filtered, washed with MeOH and dried under vacuum at 60 °C. 1.62 g (37 % yield) was received from compound **3**.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.61–1.75 (m, 6 H), 1.87–1.93 (m, 4 H), 2.00–2.08 (m, 2 H), 3.61–3.66 (m, 2 H), 3.78 (s, 6 H), 3.94–3.98 (t, 2 H), 5.48 (s, 2 H), 6.95 (s, 2 H), 7.11–7.13 (dd, 4 H), 7.51–7.53 (dd, 4 H).

**Synthesis of 1,4-bis(4-hydroxyphenyl)-2,5-dimethoxybenzene (4).** To a solution of **3** (1.62 g, 3.30 mmol) in tetrahydrofuran (50 mL) was added 37 % HCl (0.8 mL) and then the mixture was stirred overnight at room temperature. The solvent was reduced under pressure and the mixture was added to ice/water. The solid was filtered, washed with water and hexane and dried under vacuum at 60 °C. 1.04 g (98 % yield) was received from the desired monomer **4**.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 3.74 (s, 6 H), 6.79–6.82 (dd, 4 H), 6.92 (s, 2 H), 7.36–7.38 (dd, 4 H), 9.45 (s, 2 H).

#### Synthesis of Monomer 8

Synthesis of 1,4-bis(4-methoxyphenyl)-2,5-(tetrahydropyran-2-yloxy) benzene (7). To a degassed mixture of 4methoxyphenylboronic acid (6) (4.90 g, 32.24 mmol), aqueous 2 M Na<sub>2</sub>CO<sub>3</sub> (27 mL) and DMF (50 mL) were added 2,2'-((2,5-dibromo-1,4-phenylene)bis(oxy))bis(tetrahydropyran) (5) (4.69 g, 10.75 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.75 g, 0.65 mmol). The reaction mixture was heated at 125 °C for 3 d. After cooling to room temperature, the mixture was added to ice/water, stirred for 0.5 h, filtered and washed with water and hexane. The solid was dissolved in  $CH_2Cl_2$  and filtered to remove the catalyst. The solvent was removed and a small amount of MeOH added to the residue and stirred overnight. The product was filtered, washed with MeOH and dried under vacuum at 50 °C. The crude product 7 was used as received in the next step.

Synthesis of 1,4-bis(4-methoxyphenyl)-2,5-dihydroxybenzene (8). To a solution of 7 (3.75 g, 7.65 mmol) in tetrahydrofuran (80 mL) was added 37 % HCl (10 mL), and then the mixture was stirred overnight at room temperature. The solution was extracted with ethyl acetate, the organic layer was washed three times with water, dried over MgSO<sub>4</sub> and evaporated. The residue was purified by recrystallization in toluene and 1.72 g (70 % yield) of the desired monomer **8** was received.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm): 3.78 (s, 6 H), 6.81 (s, 2 H), 6.96– 6.98 (dd, 4 H), 7.48–7.50 (dd, 4 H), 8.82 (s, 2 H).

#### **Polymer Synthesis**

# Synthesis of Dimethoxy-Based Polymers

Synthesis of PPy(x)MeO(y)coPSF copolymers (I). A typical polymerization is as follows. To a degassed flask equipped with a Dean Stark trap was added a mixture of 2,5-bis(4-hydroxyphenyl)pyridine (0.6126 g, 2.33 mmol), 1,4bis(4-hydroxyphenyl)-2,5-dimethoxybenzene (4) (0.5000 g, 1.55 mmol), bis(4-fluorophenyl)sulfone (0.9859 g, 3.88 mmol), K<sub>2</sub>CO<sub>3</sub> (0.622 g, 4.50 mmol), toluene (7 mL) and DMF (20 mL). The reaction mixture was stirred at 150 °C for 16 h under argon. After removal of the azeotropic mixture of the formed water with toluene, the temperature was raised gradually at 180 °C. The reaction mixture was stirred at this temperature for 20 h. The obtained viscous solution was poured into MeOH, where a white solid was precipitated. The solid was washed with MeOH, filtered, stirred in water at 60 °C and drying at 80 °C under vacuum for 1 d. Copolymers characteristics are given in Table 1.

Synthesis of PPy(x)MeOPh(y)coPSF copolymers (II). The same procedure as described for copolymer I was followed for the synthesis of copolymer II using monomer 8 instead of 4. A mixture of 2,5-bis(4-hydroxyphenyl)pyridine (0.3676 g, 1.40 mmol), bis(4-fluorophenyl)sulfone (0.5916 g, 2.33 mmol), 1,4-bis(4-methoxyphenyl)-2,5-dihydroxybenzene (8) (0.3000 g, 0.93 mmol), K<sub>2</sub>CO<sub>3</sub> (0.373 g, 2.70 mmol), toluene (4.5 mL) and dimethylacetamide (DMAc) (13 mL) was stirred at 150 °C for 16 h and at 180 °C for 22 h. The viscous solution was precipitated in MeOH. The solid was stirred in water at 60 °C and dried under vacuum at 100 °C for 1 d. Copolymers characteristics are given in Table 1.

**Synthesis of PPy(x)MeOPh(y)TM(z)coPSF terpolymers (V).** The same procedure was followed for the synthesis of terpolymers **V** by using three diols, the 1,4-bis(4-methoxyphenyl)-2,5-dihydroxybenzene **(8)**, 2,5-bis(4-hydroxyphenyl)pyridine and 3,3',5,5'-tetramethyl[1,1'-biphenyl]-4,4'-diol. A mixture of 2,5-bis(4-hydroxyphenyl)pyridine (0.8000 g, 3.04 mmol), bis(4-fluorophenyl)sulfone (1.2876 g, 5.07 mmol), 1,4-bis(4-methoxyphenyl)-2,5-dihydroxybenzene **(8)** (0.1631 g, 0.51 mmol), 3,3',5,5'-tetramethyl[1,1'-biphenyl]-4,4'-diol (0.3684g, 1.52 mmol),  $K_2CO_3$  (0.8116 g, 5.880 mmol), toluene (4.5 mL) and DMF (9 mL) was stirred at 150–160 °C for 17 h and at 180 °C for 3 h. The viscous solution was precipitated in MeOH/H<sub>2</sub>O 2/1, stirred in water at 60 °C and dried under vacuum at 160 °C for 1 d. The results are summarized in Table 1.

# Synthesis of Dihydroxy-Based Polymers Synthesis of PPy(x)OHPh(y)coPSF copolymers (III)

A representative example for the preparation of copolymers **III** is as follows. Boron tribromide (0.35 mL, 3.59 mmol) was added slowly via a septum to a solution of copolymer **II** (1.00 g, 2.00 mmol) in dry  $CH_2Cl_2$  whereat immediately a solid was formed. The reaction mixture was stirred overnight and added to a saturated NaHCO<sub>3</sub> solution. Because voluminous agglomerates were formed, after filtration and washing with water and hexane, for further purification the product was dissolved in hot DMAc and poured into water to give a white solid of **III** in a yield of 95 % (0.93 g, 1.90 mmol) after drying under vacuum at 100 °C for 1 d. The same procedure was followed for the preparation of terpolymers **VI**.

# Synthesis of Propargyl-Based Copolymers Synthesis of PPy(x)Prop(y)coPSF Copolymers (IV)

 $\rm K_2CO_3$  (0.127 g, 0.92 mmol) was added to a solution of copolymer III (0.150 g, 0.31 mmol) in dry DMF (9 mL). After stirring for 1.5 h at 55 °C, the reaction mixture was cooled to room temperature (the flask was wrapped with foil to avoid light because of the light sensitivity of propargyl bromide) and 80 % propargyl bromide in toluene (0.04 mL, 0.37 mmol) was added. After 4 d stirring at room temperature, the mixture was dropped in an ice/water mixture, stirred for 1 h, filtered, washed with water and hexane and dried under vacuum at 30 °C for 1 d.

#### **Membrane Preparation**

Membranes were prepared by solution-casting method. The dried polymers were dissolved in DMAc at a concentration 3 wt %, filtered and poured onto a glass plate at 80  $^{\circ}$ C, where the solvent evaporated slowly. To remove any traces of the solvent, membranes were dried at 160  $^{\circ}$ C under vacuum for 3 d.

# **Crosslinking Procedures**

#### Crosslinking of Copolymer IV by Thermal Treatment

Copolymer **IV** (0.129 g, 0.25 mmol) was dissolved in DMAc and casted at 80 °C overnight. The membrane was heated gradually from 50 to 200 °C on a hotplate for 1 h, and then for 2 h more at 250 °C to complete the crosslinking reaction.<sup>37</sup> To remove any solvent residues, the membrane was dried under vacuum for 3 d at 160 °C.

# Crosslinking of Copolymer III with Decafluorobiphenyl Used as Crosslinker

A representative example of crosslinking with decafluorobiphenyl is the following. Copolymer **III** (0.146 g, 0.30 mmol) was dissolved in DMAc (3 mL),  $K_2CO_3$  (0.048 g, 0.34 mmol) was added and the reaction mixture was stirred at 55–60 °C for 1.5 h. Decafluorobiphenyl (0.0073 g, 0.02 mmol) dissolved in DMAc (0.5 mL) was added to the solution, which was filtered and then poured onto a glass substrate.

Crosslinked membranes were obtained following two-step procedure: first the glass plate was covered in an oven for 16 h at 80 °C, then the cover was removed and the membrane was obtained by casting at 120 °C. To remove any excess of the solvent, the membranes were dried for 3 d under vacuum at 160 °C.

# Crosslinking of Terpolymer VI with Decafluorobiphenyl Used as Crosslinker

Terpolymer **VI** (0.2829 g, 0.60 mmol) was dissolved in DMAc (15 mL) after heating at 70 °C for 17 h.  $K_2CO_3$  (0.094 g, 0.68 mmol) was added and the reaction mixture was stirred at 60 °C for 1.5 h. Decafluorobiphenyl (0.0169 g, 0.05 mmol) dissolved in DMAc (0.5 mL) was added to the solution, which was filtered and then poured onto a glass substrate. The mixture was left covered for 16 h at 80 °C in the oven. After removing the cover, the membrane was obtained by casting at 120 °C. The membranes were dried for 3 d under vacuum at 160 °C.

# **Doping Procedure**

Membranes were immersed in 85% phosphoric acid at different temperatures for different doping times, to study the doping behavior. After each immersion, the samples were wiped with paper and the weight gain was calculated from the sample's weight before and after the immersion. The doping level is defined as the weight percent of the acid (85%  $H_3PO_4$ ) per gram of each polymer.

#### CONCLUSIONS

Aromatic polyethers bearing polar pyridine units in the main chain and side chain cross-linkable hydroxyl and propargyl groups have been successfully prepared. The synthesized polymers showed high molecular weights, high  $T_{\rm g}$  values and thermal stability, as well as high doping levels when doped in phosphoric acid. Crosslinked membranes could be obtained either by direct crosslinking of hydroxyl groups with crosslinker or by further functionalization of hydroxyl groups to the propargyl analog. Crosslinking of propargylbased copolymers by thermal treatment leads to the formation of a stable network. The obtained crosslinked membranes showed very high glass transition temperatures up to 325 °C. The other method followed for covalent crosslinking is the nucleophilic substitution of polyhalides, such as decafluorobiphenyl with hydroxyl groups. In all cases, crosslinked membranes showed improved mechanical in terms of glass transition temperatures  $(T_{gs})$  and thermal properties as well as lower doping levels compared with the non crosslinked ones. The obtained phosphoric acid doping levels although lower compared with the non crosslinked ones are still in the range where useful high temperature electrolytes can be provided.

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