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Crosslinked wholly aromatic polyether membranes based on quinoline derivatives and their application in high temperature polymer electrolyte membrane fuel cells

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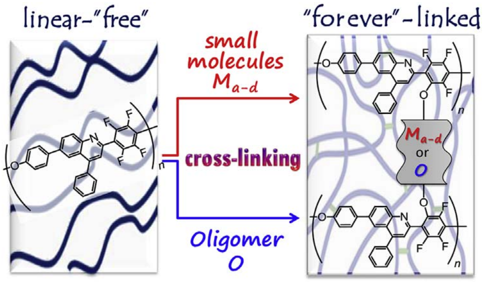
HIGHLIGHTS

- fully aromatic polyether quinolines are prepared from a difunctional AB monomer.
- crosslinking via stable aromatic ether bonds afforded high acid dopable membranes.
- the doped crosslinked membranes have dimensional stability, high ionic conductivity.
- single cell tests showed ability of the membranes to operate up to 200 °C.
- stable fuel cell operation at 200 °C for more than 200 h was demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

An AB type difunctional quinoline based monomer bearing a pentafluorophenyl unit combined with a phenol functionality is being synthesized and homopolymerized to create linear aromatic polyethers as polymer electrolytes for HT-PEM FCs applications. Several conditions are tested for the optimized synthesis of the monomer and homopolymer. Additionally, covalent crosslinking through aromatic polyether bond formation enables the creation of wholly aromatic crosslinked polymeric electrolyte membranes. More specifically, the perfluorophenyl units are crosslinked with other hydroxyl end functionalized moieties, providing membranes with enhanced chemical and mechanical properties that are moreover easily doped with phosphoric acid even at ambient temperatures. All membranes are evaluated for their structural and thermal characteristics and their doping ability with phosphoric acid. Selected crosslinked membranes are further tested in terms of their single cell performance at the temperature range 160 °C–200 °C showing promising performance and high conductivity values even up to 0.2 S cm^{-1} in some cases.

1. Introduction

High Temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEM FCs) offer the possibility for electricity generation using either low purity hydrogen or liquid fuels like methanol due to their ability to operate at temperatures above 160 °C and up to 220 °C where the catalyst can tolerate large amounts of carbon monoxide [1–10]. High temperature operation enables also the direct combination of a

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methanol reformer and a HT-PEM FC in a compact mode [11–14]. From the membrane point of view and in order to assure stable operation at such high temperatures over time, high thermal and mechanical stability is required. Simultaneously and in order to retain the phosphoric acid bound to the membrane, a large amount of interacting sites with the phosphoric acid groups are necessary. For the chemical stabilization and mechanical durability, covalent crosslinking of the membranes is widely recognised as the most efficient methodology. Early attempts for crosslinking were applied to PBI membranes by using the reaction of the NH groups of the imidazole ring with compounds bearing chloromethyl groups [15]. Since then, a lot of efforts have been published targeting to optimize this methodology [16–23]. However, engaging the NH group in the crosslinking reaction normally resulted on reduction of the doping ability and subsequent conductivity decrease. Thus, further attempts using other reaction sites engaged in Friedel-Craft reactions [24] or benzoxazine units formation [25] or Diels-Adler reactions [26] or even dual crosslinking using covalent end-group binding combined with ionic crosslinking [20] where used to overcome this problem.

Another approach for creating polymer electrolyte membranes able to be doped with phosphoric acid is the aromatic polyethers containing pyridine units either as main chain or both main chain and side chain functionalities [27–29]. A large number of copolymers have been evaluated and used as membranes for Fuel Cells operating up to 180 °C, leading to the commercialization of this technology [30]. Also for this type of membranes, crosslinking was attempted by using derivatives of these copolymers bearing side crosslinkable groups [31–34].

In all the cases of crosslinked PBI and in most cases of the crosslinked aromatic polyethers bearing pyridine units, aliphatic moieties were introduced to enable the crosslinking bond formation or created during the crosslinking reaction. However, these aliphatic parts can eventually become instability sites when a membrane operates under a harsh oxidative environment in elevated temperatures even above 200 °C. In a few cases, the crosslinking reactions led to robust chemical units formation like oxadiazole bridges but in those cases evolution of gases during the crosslinking procedure led in some cases to pinholes formation along the crosslinked membranes which restricted their practical application and scale up preparation of membranes [32].

Based on the above observations, we have made further attempts to overcome bottlenecks of the previously developed crosslinking procedures, namely the insertion of aliphatic units and the doping ability decrease. Thus, a new generation of polymer electrolyte membranes were carefully designed and prepared [35]. These membranes are based on the polymerization of an AB type difunctional monomer having a pentafluorophenyl unit combined with a phenol functionality, namely the 6-(4-hydroxylphenyl)-(2-perfluorophenyl)-4-phenyl-quinoline [36]. This monomer can be easily homopolymerized without the high purity restrictions of typical high temperature polycondensations between aromatic diols and aromatic dihalides. These linear homopolymers show a very high phosphoric acid uptake due to the ability of the quinoline units to interact with phosphoric acid molecules. More importantly, crosslinking of this homopolymer can be performed using crosslinkers with phosphoric acid dopable units like the 2,6-bis(4-hydroxyphenyl) pyridine [37] or its aromatic polysulfone oligomers [38] or with aromatic non-dopable diols.

Thus, in this paper we report on the preparation of linear aromatic polyethers containing main chain quinoline units and their crosslinking using dihydroxyl aromatic crosslinkers resulting in wholly aromatic crosslinked polymer electrolyte membranes. The membranes were structurally characterized while their ability to absorb phosphoric acid was examined in detail proving their ability to absorb large amounts of phosphoric acid even at low temperatures. Preliminary examination of the fuel cell performance of the crosslinked membranes using hydrogen/oxygen or hydrogen/air feed gases showed reasonable fuel cell performance and extremely high conductivity values above 0.2 S cm^{-1}. Current research effort is being devoted to further optimize the application of these polymer electrolytes in membrane electrode assemblies (MEAs) for high temperature fuel cell applications.

2. Results and discussion

2.1. Perfluorophenyl-quinoline homopolymers

The AB type monomer 6-(4-hydroxylphenyl)-(2-perfluorophenyl)-4-phenyl-quinoline (**OHPh5FQ**) employed in this study was recently developed and used for the modification of carbon nanostructures, carbon nanotubes and fullerenes, using the perfluorophenyl functionality as the reactive site [36]. Herein, further optimization of the monomer's synthetic procedure was performed leading to its scale up production in multigram quantities. The synthetic methodology used is shown in Scheme S1 using the previously developed 6-bromo-(2-perfluorophenyl)-4-phenyl-quinoline [39]. Suzuki cross coupling [40] of the **Br-5FQ** precursor with the THP-protected phenyl boronic acid [41] and subsequent deprotection of the phenol group under acidic conditions afford the desired AB type monomer **OHPh5FQ**. In a parallel approach aiming at substantially reducing the cost production of this AB-difunctional monomer **OHPh5FQ**, the chlorine bearing perfluorophenyl quinoline precursor was developed as shown in Scheme S2, for which cheaper starting materials are employed. Fig. S1a – c provides the ^{1}H NMR spectra with assignment of all peaks, for the precursor THP-protected monomer and for the final monomer, **OHPh5FQ**. The THP protons which appear at 5.5, 3.9, 3.65 and 2–1.4 ppm (Fig. S1a), are clearly absent in the deprotected hydroxyl bearing monomer (Fig. S1b and S1c). Fig. S1b presents the intermediate protonated **OHPh5FQ** monomer prior to its deprotonation with aqueous Na_2CO_3. The sharp peak at 9,7 ppm corresponds to the proton bound to the quinoline's nitrogen atom. Fig. S1c shows the spectrum of the final deprotonated monomer prior to polymerization.

The polymerization of the **OHPh5FQ** monomer was performed under high temperature polycondensation conditions using potassium carbonate (K_2CO_3) as base and a high boiling point, polar aprotic organic solvent such as *N*-methyl-2-pyrrolidinone (NMP) or dimethylsulfoxide (DMSO), as shown in Fig. 1. The ability of the perfluorinated ring to undergo nucleophilic aromatic substitution at the "para" position is assured by the presence of the additional fluorine atoms [42,43]. The homopolymers characterization via ^{1}H NMR spectroscopy is given in Fig. 1. Casting of these linear soluble polymers from different polar solvents like DMA, NMP or cyclopentanone resulted in high quality films, as shown by the membrane image of Fig. 1.

Different polymerization conditions were tested (Table 1) trying to increase the molecular weight of the final linear homopolymer. At the same time maintaining the solubility and thus the processability of the homopolymer in common organic solvents, was a critical aspect of the performed trials since side reactions due to the presence of the additional fluorine atoms should be minimized in order to avoid the formation of an insoluble product. The most decisive factors were the polymerization temperature and duration. On the other hand, and contrary to typical high temperature polycondensations involving two or more comonomers, the herein employed AB-type difunctional monomer excluded limitations due to stoichiometry mismatches. Kinetic studies and characterization of molecular weights (Fig. 2 and Table 1) of the linear polymers were performed via Size Exclusion Chromatography (SEC). High molecular weight polymers are obtained in most cases even within just a few hours depending on the polymerization temperature. However, when the molecular weight exceeded 70 kDa the polymer became partially insoluble in common organic solvents, which as above mentioned is attributed to the reaction proceeding also with the additional fluorine atoms of the perfluorinated ring. Therefore, temperature was maintained at around 110 °C–120 °C for 3 h or up to 12 h in order to ensure solubility to the final homopolymer. It was found that these conditions were optimum in obtaining sufficient MWs around 20 kDa and soluble homopolymers.