



An all-aromatic polypyridine: Monomer and polymer synthesis; Film formation and crosslinking; A candidate fuel cell membrane



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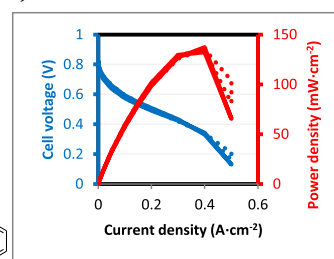
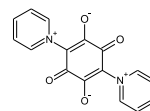
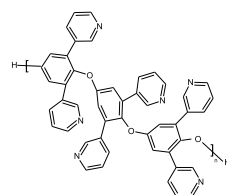
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HIGHLIGHTS

- New monomer polymerized to high molecular weight, at kg scale.
- High proton conductivity in fully aromatic membranes in the dry state.
- Membrane casting integrated with MEA assembling.
- Fuel cells built and tested with dry gases at 150 °C.

GRAPHICAL ABSTRACT

Poly[(2,6-di-3-pyridyl)-1,4-phenylene oxide] (“PYPO”)



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ABSTRACT

2,6-di (3-pyridyl)phenol and the title polymer are synthesized at 1 kg scale. Polymer is processed and crosslinked without the introduction of non-aromatic moieties after shaping into membranes. Attractive proton conduction, at high temperature (140–180 °C: 300 mS cm⁻¹) and at room temperature (60 mS cm⁻¹) are recorded *in the dry state* (higher numbers at modest humidity) and excellent retention of properties after challenge by humidity (in contrast with state-of-the-art PBI membranes). Functional fuel cells are made and tested.

In prolonged use the membrane is plasticized and this seems attributable to curing reversal at the hydrogen electrode. For high temperature fuel cell use, another curing scheme (again without the introduction of aliphatic character) must be found.

1. Introduction

Polymer membrane fuel cells hold the best promise for sustainable, electrical, mobility offering long range, rapid tank filling with hydrogen - (in the longer term) from electrolysis based on carbonless power. The state-of-the-art polymer-electrolyte-membrane fuel cells (PEMFCs) use perfluoropolymer sulfonic acid membranes, which require very high humidity to achieve useful proton conductivity, hence rather low operating temperatures and sophisticated water management, resulting in

complex systems [1]. The low temperatures require ultra-pure hydrogen fuel to avoid catalyst poisoning. Essentially the same constraints apply to aromatic hydrocarbon sulfonates (such as sulfonated PEEK) that have been proposed for fuel cell applications [1].

A type of PEMFC that received much attention in the past fifteen or so years operates at 150–225 °C with a membrane of polybenzimidazole (PBI) swollen with strong phosphoric acid [2]. These ALL-AROMATIC polymers can survive the severe OXIDATIVE stress at the fuel cell CATHODE (the oxygen reducing reaction – ORR – furnishes hydroxyl and

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hydroperoxy radical intermediates). Such systems can operate with impure hydrogen, cooling is much easier at the higher temperature, and water management now consists in *protecting* the membrane against moisture: the PBI polymers precipitate from polyphosphoric acid (used in the polymerization) by diluting with water (such as when isolation of the pure polymer is desired) and the acid-swollen membranes must be considered as partially dissolved – where the crystalline fraction provides the mechanical integrity and the dissolved fraction provides the proton conductivity [3,4]. When these membranes can absorb moisture (they are hygroscopic) the polymer precipitation progresses and the proton conductivity degrades while phosphoric acid is expelled from the (collapsing) system. This problem is harder to deal with in vehicle operation than in continuously-running stationary systems.

We have investigated the synthesis of an all-aromatic polypyridine that is soluble even in dilute acid and has a much lower T_g than the PBI polymers, that we succeeded in crosslinking after shaping into thin film with a crosslinker that does not introduce any aliphatic character into the system. Earlier efforts [5] directed at pyridine-functional PEMFC membranes, stemming from elaborate syntheses, showed much lower proton conductivities than observed in this work (*viz.*, 80 vs. 300 mS cm⁻¹).

Here we report our efforts at monomer- and polymer synthesis, the membrane shaping, crosslinking and acid-activation, the very attractive proton conductivities and moisture resistance observed, and PEMFC testing. Based on the high proton conductivities recorded in films made from lab-scale polymer synthesis, we needed larger amounts of materials to enable in-depth film formation studies and fuel cell evaluations – hence a kg scale polymer effort was undertaken.

2. Materials and procedures

All reagents, chemicals, materials and (AR quality) solvents were obtained from commercial sources, and were used as received: Biosolve, Merck and Cambridge Isotope Laboratories for deuterated solvents; and Aldrich, Acros, ABCR, Merck, Fluorochem and Fluka for chemicals, materials and reagents.

Supporting Information detailing analytical procedures and electrical measurements, syntheses for a kg scale effort, and spectra is provided separately in [Appendix A](#).

3. Results and discussion

3.1. Access to monomer

A relatively straightforward Suzuki-Miyaura synthesis [6–8] of 2,6-di (3-pyridyl)phenol from 2,6-dibromophenol [9] (protected as its benzyl ether) and 3-pyridineboronic acid [10] was employed for laboratory- and 1-kg-scale synthesis, to support membrane explorations. An important improvement relative to results when using the popular *N,N*-dimethylformamide as the solvent for the coupling reaction was achieved by substituting DMF by *N,N*-dimethylacetamide, thereby suppressing the (reductive) dehalogenation of the bromide substrate. DMF seems to act as a somewhat effective formic acid equivalent - reducing agent - in the presence of palladium catalysts. Another improvement was seen when eliminating phosphorus species by extraction (sulfuric acid solution of the product/toluene) prior to hydrogenative removal of the benzylic ether protection needed for the Suzuki-Miyaura coupling. See the [Supporting Information](#) for the optimized protocol.

With a view to larger scales, coupling [11] a pyridine Grignard with 2,6-dichlorobenzaldimine made from the agrochemical 2,6-dichlorobenzaldehyde, followed by Baeyer-Villiger oxidation of the aldehyde, succeeded at lab scale. See the [Supporting Information](#).

On the other hand, several approaches using protocols reported successful with homocyclic arenes, such as employing 3-aminated pyridine [12], or starting with acetophenone [13], failed for our target.

With a view to still larger scales, a three-step procedure (involving

nine chemical transformations) was worked out at up to 10 g final product scale – starting with 4-*t*-butylphenol and thermolytically generated cyclopentadiene (dicyclopentadiene heated in high boiling solvent at 270 °C), isolating the 2,6-bis Friedel-Crafts (methane sulfonic acid catalyst, room temperature) adduct as its crystalline carbamate with phenyl isocyanate. The tetra-aldehyde from ozonation in acetic acid at room temperature was cyclized in situ with hydroxylamine (room temperature) to the bipyridyl compound and isolated as 4-*t*-butyl-2,6-di (3-pyridyl)phenol by hydrolysis of the crude reaction mixture. Finally the *t*-butyl group was removed by hot acid treatment and the monomer isolated by neutralization of the mixture. This approach could not (yet) be used for kg-scale work. See [Supporting Information](#).

3.2. Polymerization

The well-known oxidative polycondensation [14] procedure of 2,6-dimethylphenol into the poly (2,6-dimethyl-1,4-phenyleneoxide) product known as PPO or PPE is performed in (chlorinated) hydrocarbon solvent, unsuitable for this case. We had to find a solvent system able to dissolve our high-melting, polar and self-associating monomer, such a solvent also being compatible with the oxidative polymerization. From a large series of solvents, tested on the polymerization of commercially available 2,6-diphenylphenol rather than the limited supply of dipyridylphenol, 3-chloropyridine [15] was selected as the best candidate. After a promising first trial, for a long time only oligomers with M_w 1000–8000 Da were isolated. Mass spectrometry on such oligomers coupled with viscosimetry enabled an estimate for Mark-Houwink parameters as $K = 0.448 \times 10^{-3}$, $a = 0.6$ (dl g⁻¹; measured at 0.2 g dl⁻¹ in 95% sulfuric acid, 20 °C), useful for comparing and optimizing our polymerization results. A dependable high-MW polymer (~100 kDa) yielding protocol was found, a streamlined isolation, with elimination of catalyst and almost all diphenoquinone side product immediately following polymerization by simple filtration of the reaction mixture before coagulation in *n*-heptane, and a second purification step (dissolve in THF and reprecipitate in *n*-heptane) to remove final traces of diphenoquinone. It is not clear whether the polishing step brings benefit downstream, but it was performed as a precaution in the fuel cell directed explorations discussed here. The polymerization must be carried out at about 60 °C higher temperature than is usual for 2,6-diphenylphenol and requires more catalyst. We speculate that this reflects shielding of catalyst in the very “pyridine-rich” environment and deactivation by coprecipitation of copper with diphenoquinone side product. Unsurprisingly, this reaction proceeds without peralkylated ethylenediamine or its oligomers that are required in traditional polyphenyleneoxide preparations that are performed in (chlorinated) hydrocarbon solvents.

Coagulation runs smoothly by stirring into excess heptane; redissolution in THF followed by renewed precipitation in heptane provides the purified polymer.

M_w 98 ... 125 kDa products were used in most of the investigations on free-standing films and PEMFCs. Early work involved M_w ~ 45 kDa polymer and Taron paper reinforcement.

The polymer, which is isolated in the amorphous state, T_g 225 °C, is soluble in a wide variety of organic solvents (but not in hydrocarbons) and in (even dilute) acids. It resists reduction up to – 2.15 V vs. SHE in acetonitrile, THF and DMF. After doping with phosphoric acid, the cationically charged polymer resists oxidation better than the uncharged fully-aromatic species. Also note that the polymer is *prepared* by catalysed oxidation at > 100 °C.

3.3. FILM formation, CURING, washing, ACIDIFYING

PYPO [16] shows a T_g of 225 °C (compare PBI: 430 °C, increases with hot annealing [17]) and is, in practice, essentially amorphous. Onset of (TGA) thermal degradation is 420 °C. The polymer is quite

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