



Synthesis and characterization of new fluorinated copolymers based on azole groups for fuel cell membranes

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ABSTRACT

Two new fluorinated copolymers synthesized by grafting ω -hydroxyl pyrazolic (Trip) and triazolic (Trit) tripods onto poly(chlorotrifluoroethylene-*alt*-2-iodoethyl vinyl ether) copolymer (poly(CTFE-*alt*-IEVE)) are reported. These copolymers were prepared in two steps: the ω -hydroxy nitrogenous heterocycles reacted with iodine atoms of poly(CTFE-*alt*-IEVE) copolymer followed by the deprotection of the benzyl group. The chemical structures of tripod monomers and resulting copolymers were characterized by nuclear magnetic resonance and infrared spectroscopies, elemental analysis, and mass spectrometry. The first analysis allowed one to determine the degree of grafting that reached 80 and 19% for copolymers bearing pyrazole and triazole, respectively. Membranes were processed in pellet form by compressing these copolymers. Thermal properties of the membranes, examined by thermogravimetric analysis and differential scanning calorimetry, showed that such copolymers were thermally stable up to 200 °C under air, and exhibited glass transition temperatures ranging between 31 and 47 °C. The temperature dependence of conductivity led to a simple Arrhenius behavior for both copolymers. Poly(CTFE-*alt*-IEVE)-*dep*-Trit_{19%} and poly(CTFE-*alt*-IEVE)-*dep*-Trip_{80%} copolymers had a maximum proton conductivity of $1.3 \cdot 10^{-3}$ and $5.91 \cdot 10^{-5}$ mS/cm respectively at 180 °C under quasi-anhydrous conditions. Cyclic Voltammetry (CV) study illustrated that the electrochemical stability domain for poly(CTFE-*alt*-IEVE)-*dep*-Trip_{80%} and poly(CTFE-*alt*-IEVE)-*dep*-triazole_{28%} copolymers extended 2.0 V.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising alternative energy conversion devices for transportation and stationary applications due to their high energy conversion efficiency and environmental benefits [1–6]. For their proper operation, the proton exchange membrane, which is considered as the key component, should present various properties such as (i) an efficient proton transfer of from the anode to the cathode, (ii) an impermeability to gases (hydrogen and oxygen) to prevent their mixing, and (iii) chemical and mechanical stability. For the last decade, fluorinated proton conducting copolymers [7–9] known by their remarkable thermal, chemical, electrochemical and mechanical properties, have widely been used as polymer electrolytes for proton exchange membranes for fuel cells (PEMFCs).

Nowadays, the most comprehensively used polymer electrolyte membranes are Nafion®, Aquavion®, 3M membrane®, Flemion®, and Fumion® materials that display high proton conductivities and chemical stabilities [8,10]. However, the low operating temperature of these

membranes, their price, and methanol crossover are the main drawbacks that led to the development of other classes of proton conducting polymer electrolytes, with the substitution of water by amphoteric nitrogenous heterocycles such as imidazole [11–13], tetrazole [14,15], benzimidazole [16–19], and 1,2,4-triazole [20–23].

Recently, we have reported the synthesis of new fluorinated copolymers bearing pyrazolic groups to develop membranes for PEMFCs [24]. Although endowed with high thermal and electrochemical stabilities, they exhibited poor proton conductivities. This arises from the position of nitrogen atoms in the pyrazole ring, which prevents from formation of a linear hydrogen bonded network [25]. An efficient solution would be to extend the spacer length between the heterocycle and the polymer chain, which can lead to an improvement in the proton conductivity while keeping good thermal and electrochemical properties.

Hence, the present article reports the synthesis of two new protected pyrazolic and triazolic tripodal reactants and their grafting onto an alternating fluorinated copolymer followed by cleavage of the protecting group. Then, the thermal and electrochemical properties of such

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resulting grafted fluorinated copolymers were studied and compared.

2. Experimental

The synthesis of all the organic intermediates and copolymers are described in the Supplementary material.

2.1. Materials

Tert-butyl peroxyphthalate (TBPPi, Trigonox 25- C75, 75 wt% solution in isododecane) was provided by Akzo Nobel (Compiègne, France). Chlorotrifluoroethylene (CTFE) was kindly supplied by Honeywell S.A (Morristown, N.J., USA). 1,1,1,3,3-Pentafluorobutane (C₄F₅H₅) (97%) was a gift from Solvay S.A. (Brussels, Belgium). All other chemicals and solvents were reagent grade purchased from Aldrich Chemical Co. and were used as received, except for 1,1,1,3,3-pentafluorobutane and acetone, which were distilled prior to use. The following intermediates: **1b**, **2b** and **3b** were prepared according to the procedure described in our recent study [24].

2.2. Characterization

¹H, ¹⁹F and ¹³C NMR spectra were recorded at on a Bruker AC 400 or 250 instrument. Spin resonances are reported as chemical shifts (δ) in parts per million (ppm) and referenced to the residual peak as an internal standard of the deuterated solvent employed (deuterated chloroform (CDCl₃), dimethyl sulfoxide (DMSO) or *N,N*-dimethylformamide (DMF)). Spin multiplicity is shown by *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet. Mass spectra were recorded on a Platform II Micromass instrument (ESI⁺, CH₃CN/H₂O: 50/50). Melting Point uncorrected was determined in capillary on IA9100 (Electrothermal) apparatus. Elemental analysis was carried out with a Perkin Elmer 240C Elemental Analyzer. Cyclic voltammograms (CV) were obtained with Voltalab PGZ 100, and carried out in 0.1 M tetraethylammonium tetrafluoroborate (TEATFB)/Acetonitrile. Size exclusion chromatography (SEC) was achieved by means of a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer, and a set of four columns connected in series: Styragel (Waters) HR4 5 μm, HR3 analyses 5 μm, PL and Gel (Polymer Laboratories) 5 μm and 100 Å. Monodispersed poly(methyl methacrylate) (PMMA) standards were used for calibration. Aliquots were sampled from the reaction medium, diluted with dimethylformamide (DMF) up to a known concentration (C_p, t) ~2% wt%, filtered through a 20 μm out PTFE Chromafil membrane, and finally analyzed by GPC at 30 °C, at a flow rate of 0.8 mL/min. Thermogravimetric analysis (TGA) were carried out on 10 to 15 mg samples, in air, using a Q50 apparatus from TA Instruments. The heating rate was 10 °C·min⁻¹ from room temperature up to 800 °C. Differential scanning calorimetry (DSC) measurements were performed on 10 mg of copolymer from -100 to +200 °C using a heating rate and cooling rate of 20 °C·min⁻¹, cooling from 20 °C to -50 °C at 20 °C/min, isotherm plateau at -50 °C for 5 min, first heating from -50 to 200 °C at 20 °C/min, cooling from 200 to -50 °C at 20 °C/min, isotherm plateau at -50 °C for 3 min, second heating from -50 °C to 200 °C at 20 °C/min and last cooling from 200 °C to 20 °C, the sample was heated again and the T_g was measured by the inflection point in the heat capacity pump.

Ion exchange capacities (IECs) were measured following the method reported by Campagne et al. [16]: Dry copolymer membrane (W = 1 g) in its protonated form was immersed 24 h in an aqueous solution of sodium chloride (3 mol·L⁻¹). The quantity of protons exchanged was titrated with potassium hydroxide (C_b = 0.01 mol·L⁻¹), using phenolphthalein as an indicator. IEC was calculated by the following equation:

$$IEC = (C_b \times V_e)/W$$

where V_e stand for the volume of the NaOH solution at the equivalence.

2.3. Elaboration of pellet membranes

The copolymers were first dried in a vacuum oven at 80 °C to eliminate traces of solvent. Then, such copolymers were ground and compressed in pellets form (compressed at 1.27 10³ MPa). The prepared pellets (thickness = 0.43 mm; area = 0.78 cm²) were dried again at 80 °C before assessing the conductivity measurements.

2.4. Conductivity measurements

The proton conductivity of the membranes was determined as reported in our previous work [24] in the frequency range from 10⁰ to 10⁷ Hz for each temperature and under a flow of dry nitrogen (0% RH). The following equation was used to calculate the conductivity (σ):

$$\sigma_{AC} = I \cdot L/U \cdot S = 1 \cdot L/R \cdot S$$

where L, S, R, I and U are the sample thickness, the cross-sectional area between pellet and electrode, the resistance, the current and the electrical voltage (fixed at 0.5 V), respectively. All measurements were achieved in triplicate to ensure the reproducibility of results.

3. Results and discussion

The synthesis of such anhydrous membranes consists in the preparation of fluorinated copolymers bearing heterocyclic azoles, which can ensure a proton conductivity through the membrane by a hydrogen bonded network. One of the most used methods deals with the grafting a functionalized azole onto a solid substrate [12, 24]. However, the labile hydrogen atom born by the nitrogen atom in these azole derivatives is quite reactive, especially in basic medium, and may induce undesirable side reactions. To avoid them, these azole functions were first protected, and after chemical modification, further deprotected. As previously reported [24], the benzyl group has been chosen since it fulfills these criteria.

3.1. Synthesis of protected azole tripodal ligands

The chemical reaction for the synthesis of these tridental structures is displayed in Scheme 1.

The first step was the benzylation of the triazolic (**1a**) and pyrazolic (**1b**) esters in α position using benzyl bromide in 56 and 80% yields, respectively. Structures of these compounds were confirmed by NMR and IR spectroscopy, mass spectrometry, and elemental analysis. However, it should be noted that the benzylation in β position may also occur (Scheme 2) due the prototropy phenomenon and led to triazolic (**2'a**) and pyrazolic (**2'b**) esters, respectively.

As reported in a previous study [24], the ¹³C NMR spectroscopy enables to determine the benzylation position of pyrazole. Similarly, it was demonstrated [26] that, from the ¹³C NMR spectrum of the resulting compound after benzylation of triazole, the chemical shifts of the C5 and C3 carbon atoms are centered at about 143.2 and 151.8 ppm, respectively (Fig. 1).

In the case of triazole, the ¹³C NMR spectrum that exhibits a chemical shift centered at 145.2 ppm (Fig. S2) evidences that the benzylation was performed in the α position. Then, **2a** and **2b** esters were transformed to the corresponding **3a** and **3b** alcohols using lithium aluminum hydride. The addition of thionyl chloride onto these compounds led to **4a** and **4b** chlorinated derivatives. Finally, **5a** and **5b** tripods were obtained by the condensation of one equivalent of 3-aminopropan-1-ol with two equivalents of **4a** and **4b** chlorinated compounds, respectively, using an excess of anhydrous sodium carbonate and acetonitrile as the solvent as reported in the literature [27, 28]. These structures were confirmed by spectroscopic methods (¹H and ¹³C NMR) and mass spectrometry. For **5b** tripod, the thin layer chromatography (TLC) showed also the presence of monoalkylation structure **5'b** (Fig. 2) evidenced by ¹H NMR (Fig. S13) and mass

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