



Synthesis and characterisation of a new sulphonated hydrocarbon polymer for application as a solid proton-conducting electrolyte



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ABSTRACT

Proton-conducting polymers were prepared by sulphonation of polyindene (PInd) with chlorosulphonic acid with various degrees of sulphonation (DSs) and characterised by ¹³C and ¹H NMR, FTIR spectroscopy, TGA, DSC, and IES. The NMR spectra of the sulphonated polyindene (SPInd) showed only the mono-ring-substituted product at the meta-position. The SPInds are hydrophilic, and their water uptake increased with increasing DS. The SPInds exhibited 10 to 17% bound water, and samples with DSs of 21 and 96% exhibited conductivities of 10⁻⁴ and 10⁻² S·cm⁻¹ at room temperature, respectively.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are one of the cleanest power sources for both stationary and portable applications. In the last decade, interest has increased in the development of hydrocarbon polymer electrolytes for proton exchange membranes (PEMs), because the PEM is one of the most important components in a fuel cell [1–4]. Electroactive polymers have been investigated with respect to the nature of their ionic groups, polymer backbones, methods of synthesis, and functionality, and they typically possess properties such as hydrophilicity and ionic conductivity [2,5–7]. The current interest in new polymer electrolytes has been spurred by the search for improved materials for alternative energy sources such as fuel cell membranes [3,7–9]. Currently, membranes of perfluorinated ionomers are used in PEMFCs, and those produced by DuPont Co. (trade named Nafion) exhibit a proton conductivity of 10⁻² S·cm⁻¹

at room temperature [10]. The proton conductivity of Nafion membranes drops below 10⁻⁶ S·cm⁻¹ when the water uptake decreases due to dehydration, which occurs if they are used at temperatures above 100 °C [11]. The development of membranes superior to Nafion has increased the interest in new polymer electrolytes that focus on durability and water uptake for energy production in PEMFCs at intermediate and high operating temperatures. These polymer electrolytes should have high chemical and thermal stability, and two main groups of polymers have been widely investigated for this purpose. One group is polymers containing inorganic elements, e.g. fluorine in fluorocarbon polymers [12–17], and the other group is composed of aromatic polymers with phenylene backbones obtained by polycondensation reactions, such as poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) [18–23], polysulphone [23–26], polyimide [27–29], polybenzimidazole [30,31], and their derivatives. Polymer electrolytes with rigid skeletons are particularly attractive for high-temperature applications, and various polymers have been reported in the literature, typically decorated with sulphonic (–SO₃H) [3,4,8,9,19,23,32–34] or phosphonic acid [35,36] moieties. The sulphonation of aromatic compounds, an electrophilic substitution reaction, is widely used in the production of arylsulphonic acids [18–27,32–34,37–40], and the sulphonation of rigid polymers has proven to be a versatile and effective method to obtain polymer electrolytes with a controlled degree of sulphonation. The aim of this work was to produce a new proton-conducting polymer from an amorphous hydrocarbon polymer with a polycyclic skeleton with phenylene side groups by sulphonating the aromatic ring with chlorosulphonic acid. This polymer, contrary to the

Abbreviations: PEMFCs, proton exchange membrane fuel cells; PEMs, proton exchange membranes; PInd, polyindene; SPInds, sulphonated PInds; DS, degree of sulphonation; DCE, 1,2-dichloroethane; IEC, ion exchange capacity; EIS, electrochemical impedance spectroscopy; TGA, thermogravimetry analysis; DSC, differential scanning calorimetry.

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aromatic hydrocarbon polymers obtained by polycondensation reactions, presents no heteroatom in the main chain. The pristine polymer, polyindene (PInd), was obtained by the cationic polymerisation of indene (Ind), and the main chain of the PInd is composed of cyclopentene rings with attached phenylene groups. This unique structure endows the molecule with stiffness and a glass transition temperature higher than 200 °C [41,42]. The sulphonated PInds (SPInds) were chemically characterised by NMR and FTIR spectroscopy, and the degree of sulphonation (DS) was also calculated. SPInd in its acid form exhibits high conductivities as a proton-conducting solid at room temperature and is currently being used in our group in the preparation of cationic-exchange membranes such as those already reported for blends of PVA and sulphonated low molecular weight indene-co-styrene resin [43].

2. Experimental

2.1. Materials

Indene (95%; b.p. 175–185 °C; 116.16 g·mol⁻¹), aluminium trichloride (AlCl₃, 99.99%), and chlorosulphonic acid (ClSO₃H; ≥98%; b.p. 151–152 °C; 116.52 g·mol⁻¹) were purchased from Aldrich. Ethanol (96%), 1,2-dichloroethane (DCE; 99%), and *n*-hexane (95%) were purchased from Quimex, and dimethylacetamide (DMAc; PA) was supplied by Synth. Before use, the AlCl₃ was soaked in dichloroethane and finely ground. All the other chemicals were used as received without any purification.

2.2. Polymerisation of indene

The indene polymerisation was performed in a 250 mL glass reactor at –20 °C under a N₂ atmosphere according to a previously reported procedure [41]. The polymerisation was carried out in DCE with an Ind/AlCl₃ molar ratio of 100/1 for 300 min. The obtained polymer was precipitated in ethanol and filtered. The samples were dried in an oven at 100 °C for 24 h and then stored in a desiccator in the dark. The number-average molecular weight and polydispersity of the PInd were 3.3 × 10⁴ g·mol⁻¹ and 2.1, respectively [41].

2.3. Sulphonation of polyindene

The polyindene sulphonation was carried out in a four-neck round-bottom flask under a N₂ atmosphere following procedures described in the literature [40,44]. PInd (10 g) and DCE (60 mL) were added into the flask, and the mixture was heated to and stirred at 40 °C for 30 min. The PInd solution was cooled to –2 °C, and specified amounts of ClSO₃H/10 mL DCE were then gradually added to the flask according to the desired degree of sulphonation. The reactive mixture was kept at –2 °C under 300 rpm for 2 h. The obtained sulphonated polyindenes were precipitated in ethanol and recovered by filtration and then washed with *n*-hexane until the filtrate reached a pH of approximately 7. The SPInds were purified by reprecipitation using DMA as a solvent and *n*-hexane as a precipitant. The SPInd samples in their acid form were dried in a vacuum oven at 60 °C until the solvent was fully removed. The SPInd samples were stored in a desiccator in the dark prior to use. Prior to the thermal analysis, electronic microscopy observations, and electrochemical impedance spectroscopy measurements, the samples were kept in a desiccator under a relative humidity of 30% at 25 °C for 24 h.

2.4. Characterisation of SPInd

The degree of sulphonation and the ion exchange capacity (IEC) of the SPInds were evaluated using an acid–base titration. An SPInd sample (in triplicate) was placed in a 1 M NaCl solution for 24 h to exchange the H⁺ ions for Na⁺ ions. The proton release was evaluated by titrating aliquots of the solution with 0.01 M NaOH at 25 °C using a pH meter as an

indicator. The DS, expressed in mol% per repeating unit, and the IEC, expressed in mequiv·g⁻¹, were calculated, respectively, with the following equations:

$$DS = (116 \times M_{\text{NaOH}} \times V_{\text{NaOH}}) / (W_{\text{sample}} - 0.081 \times M_{\text{NaOH}} \times V_{\text{NaOH}})$$

and

$$IEC = (V_{\text{NaOH}} \times M_{\text{NaOH}}) / W_d$$

where 116 is the molar mass (g·mol⁻¹) of the PInd repeating unit, M_{NaOH} is the molarity of the standard solution of NaOH (mol·L⁻¹), V_{NaOH} is the volume consumed of the NaOH solution to neutralise the SPInd solution (mL), 0.081 is the molar mass (g·mol⁻¹) of the SO₃H group divided by 100, and W_(sample) and W_d denote the weight (g) of the sample.

The SPInds were characterised by ¹³C NMR (LA-400 spectrometer, JEOL) in DMSO-*d*₆ at 100 MHz at room temperature, and PInd was comparatively analysed in DCE. SPInd was also characterised by ¹H NMR (LA-100, JEOL) in DMSO-*d*₆ at 100 MHz at room temperature. The pristine PInd and SPInds were evaluated by infrared spectroscopy (FTIR Spectrum 1000, PerkinElmer) using KBr pellets (ASTM E 168-06).

The viscosity of the SPInd samples with different DSs was evaluated in distillate water at 25 °C using an Ubblohde viscometer (mod.: 0b, diameter: 0.46 mm, K: 0.005 mm²/s).

The thermal stability of the SPInds (20 mg) was investigated using a thermogravimetric analyser (TGA 2050 thermobalance, TA Instruments) over the temperature range of 25–1000 °C at a heating rate of 20 °C·min⁻¹. During the experiment, the oven was purged with N₂ gas at a flow rate of 100 cm³·min⁻¹. The water content, apex peak temperature of degradation, mass loss percentage, and ash content were evaluated and compared to the parent PInd.

The thermal behaviour of the SPInds (5 mg) over the temperature range of 24–250 °C at a heating rate of 10 °C·min⁻¹ was investigated using a differential scanning calorimeter (DSC Q20, TA Instruments). During the analysis, the system was purged with N₂ gas at a flow rate of 80 cm³·min⁻¹. The temperature calibration was carried out using indium as a reference (T_m = 156.60 °C and heat flow = 28.5 J·g⁻¹), and the baseline was calibrated using empty pans. The samples (5 mg) were pre-heated under air from room temperature to 190 °C at 10 °C/min (1st run), cooled to 40 °C, and then re-heated from that temperature to 250 °C at 10 °C/min (2nd run). Both the first and second run endothermic curve profiles were taken for the comparative analysis due to the different water contents before and after heating the sample to 250 °C.

The chemical oxidation of the SPInd 50% was investigated using Fenton's reagent, which is one of the standard tests for oxidative evaluation of polymeric membranes and organic compounds. About 0.3 mg of SPInd 50% was dissolved in a 100 mL Fenton solution consisting of 3 wt.% H₂O₂ and 2 ppm Fe²⁺ (in form of FeSO₄·7H₂O). The Fenton solution with the sample (pH of 3) was contained in an Erlenmeyer and agitated at 80 °C for 30 min. After the oxidation process, the product was recovered by evaporating the water from the solution, and it was dried in an oven at 100 °C for at least 12 h. The oxidized SPInd 50% was analysed by FTIR and TGA as described above.

The surface texture of the SPInd particles was examined using a scanning electron microscope (JSM-5800, JEOL) with an electron acceleration voltage of 20 kV. Prior to the analysis, the specimens, obtained as thin flat discs (see item 2.5), were cryogenically fractured and gold coated to render them conductive.

2.5. Proton conductivity measurements

The electrochemical impedance spectroscopy (EIS) measurements were performed using an electrochemical analyser (PGSTAT 30/FRA 2, Autolab) over the frequency range from 10⁶ to 10⁻¹ Hz, and the

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