Polymer 53 (2012) 3659–3668

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Controlling phosphonic acid substitution degree on proton conducting polyphosphazenes

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ARTICLE INFO

Article history:
Received 14 March 2012
Received in revised form
2 June 2012
Accepted 18 June 2012
Available online 27 June 2012

Keywords:
Phosphonic acid
PEM fuel cell
Polyphosphazene

ABSTRACT

This paper is to describe the development of a synthetic strategy for the preparation of phosphonic acid functionalized poly(aryloxyphosphazene) membranes with different substitution degree of phosphonic acid. Synthesized polymers have been characterized by standard spectroscopic techniques; FT-IR, ^{1}H, ^{31}P and ^{19}F NMR and element analysis. Proton conductivities of phosphonic acid substituted polymers have been investigated with impedance spectroscopy at different temperatures. Furthermore, the correlations of the proton conductivity and ion exchange capacity with the substitution degree of phosphonic acid have also been investigated. Thermal properties and water uptake properties of the polymers are also investigated. It is found that the proton conductivity and initial decomposition temperature of the polymers increases up to an appropriate amount of phosphonic acid substitution degree, which can be a useful PEM candidate for fuel cells.

1. Introduction

Proton exchange membranes (PEM), have received much attention, as a key material for operation of a proton exchange membrane fuel cell (PEMFC), because of their high-energy conversion efficiency and near-zero pollutant emission promising materials for clean power sources in portable and stationary electronic applications [1–4]. Currently, perfluorosulfonic acid (PFSA) membranes such as Nafion produced by DuPont are widely used as the PEM in PEMFC because of their high oxidative stability as well as high proton conductivity compared to most hydrocarbon based membranes. However, high costs, loss of proton conductivity at high temperature due to the loss of water and relatively high methanol diffusion can be considered as the main disadvantages of PFSA membranes for further applications [5,6]. Therefore, development of alternative PEM materials has been extensively investigated by many research groups to achieve high proton conductivity and application at conditions of high temperatures with lower fuel crossover [7–11]. Particularly, much attention has been focused on the synthesis, characterization, and proton conductivity of phosphonic acid-based membranes, with their application aimed in PEMFCs [9–11]. The structure and local proton mobility of poly(vinyl phosphonic acid) (PVPA) have been previously investigated using solid-state NMR under fast magic angle spinning [12]. It is found that the proton migration of PVPA is mediated by acidic protons through a hydrogen bonding network. The proton conductivity dependence of phosphonic acid concentration on PEM materials has been studied and high values can be achieved with sufficient phosphonic acid concentrations [13]. Furthermore, the relation between water uptake, self-condensation and proton conductivity of PVPA has been investigated by Kaltbeitzel *et al* [14] and as they reported the condensation limits the conductivity by reducing the phosphonic acid sites taking part in the proton transport [14].

Polyphosphazenes (PPs) are linear polymers containing an inorganic backbone formed by alternating phosphorus and nitrogen atoms and with two side groups linked to the phosphorus atoms. Considering their good film-forming ability, chemical stability and chemical structure tailoring property, poly(organophosphazene)s are promising membrane materials and therefore sulphonated and azol substituted PPs have been investigated as PEMFC membranes [15–19]. However, sulphonation of poly(aryloxyphosphazenes) require harsh reaction conditions and therefore phosphonic acid functionalized polyphosphazenes can be a viable alternative. The phosphate side groups are initially incorporated onto PPs through a phosphorus–oxygen–carbon linkage [20]. But, these polymers were

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http://dx.doi.org/10.1016/j.polymer.2012.06.033

susceptible to hydrolysis and thermal cleavage, and therefore could not be used for fuel cell applications [21]. More stable carbon–phosphorus linkage has been used as an alternative approach to incorporate the phosphonate groups onto the poly(aryloxyphosphazene)s [22,23] and it is found that phosphonic acid functionalized poly(aryloxyphosphazenes) have better proton conductivities than to the sulfonated polyphosphazene analogues and markedly lower methanol diffusion characteristics than Nafion [20–24]. However, due to the high reactivity nature of the reagents used in the reaction process to introduce phosphonate groups to the PPs, it was not possible to reach uncrosslinked soluble polymeric poly(aryloxyphosphazene)s with high phosphonation degree [23]. Therefore, the relevance of studying the synthesis and characterization of phosphonated PPs is not only based on the fundamental issues to be addressed but also on their potential applications in FCs.

In this preliminary study we have investigated the ease of controlling the concentration of arloxyphosphonic acid substitution degree on polyphosphazene by sequential treatment of poly(dichlorophosphazene) (PDCP) with (4-diethylphosphonate)phenol and 2,2,2-trifluoroethanol in the presence of NaH in THF. Novel phosphonated aryloxy-fluoroalkoxy random copolymers with a phosphonation ratio varying between %25 to %75 and a fully phosphonated aryloxyphosphazene polymer have been isolated. The phosphonate groups on the polymers have been converted to phosphonic acid by two step reaction process and yielded phosphonic acid substituted poly[(4-phosphonophenoxy)(2,2,2-trifluoroetoxy) phosphazene]s and poly[bis(4-phosphonophenoxy)phosphazene]. The thermal properties of all polymers were investigated with DSC&TGA and proton conductivity of phosphonic acid substituted polymers has been investigated by impedance spectroscopy at selected temperatures.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (trimer) (Otsuka Chemical Co. Ltd) was purified by fractional crystallization from n-hexane. The crystallized trimer ($N_3P_3Cl_6$) was further purified by vacuum sublimation before the ring opening polymerization and only 60% of the material was allowed to be sublimed. The deuterated solvents ($CDCl_3$, D_2O and DMSO-d_6) for NMR spectroscopy and the following chemicals were obtained from Merck: NaH (60% suspension in mineral oil), ethanol, HCl (37%), tetrahydrofuran (THF), 2,2,2-trifluoroethanol, bromotrimethylsilane, 4-bromophenol, $NiBr_2$, mesitylene, triethylphosphite. All other reagents and solvents were reagent grade quality and obtained from commercial suppliers.

2.2. Equipment and methods

Elemental analysis was carried out using a Thermo Finnigan Flash 1112 instrument. FT-IR spectra were recorded on a Bruker Alpha-P in ATR in the range of 4000 cm^{-1}–400 cm^{-1}. Gelpermeation chromatography was performed with an Agilent 1100 series GPC system equipped with Chemstation software with the aid of "GPC Add On" software to calculate the average molecular weights (Mw and Mn) against polystyrene standards. ^1H and ^{31}P NMR spectra were recorded in $CDCl_3$, DMSO-d_6 and D_2O solutions on a Varian 500 MHz spectrometer. Thermal properties of the compounds were investigated on Mettler Toledo TGA/SDTA 851 thermogravimetric analysis (TGA) and differential scanning calorimeter DSC 821^e (DSC) equipped with Mettler Toledo Star^e software at a heating rate of 10 °C min^{-1} under nitrogen flow (50 mL min^{-1}) between 25 and 700 °C for TGA and -40–100 °C for DSC, respectively. Considering the anhydride formation and water absorption of the polymers freshly dried samples were quickly transferred into a vacuum chamber and let to cool to room temperature and spectro grade argon filled in to chamber before removing the sample from vacuum. Then the sample used for DSC analysis and the second heating DSC results were used to calculate glass transition temperatures. The ion exchange capacities (IEC) of samples were determined by volumetric titration [25]. A known amount of freshly dried sample was immersed and stirred in 30 mL of 0.10 N NaOH/1.0 M NaCl mixed aqueous solution (1/4 by volume) for 12 h at room temperature and 15 mL of 0.10 N HCl solutions was added. Then the excess amount of HCl was back titrated with 0.025 N NaOH aqueous solutions in the presence of phenolphthalein indicator. The IEC value (mmol/g) of the sample is calculated using the Eq. (1);

$$\mathrm{IEC} = 0.025(\mathbf{V}_{\mathrm{NaOH}} - \mathbf{V}_B)/\mathbf{W}_{\mathrm{dry}} \tag{1}$$

where $\mathbf{V}_{\mathrm{NaOH}}$ is volume of 0.025 N NaOH aqueous solutions for the volumetric titration, $\mathbf{V}_{\mathrm{B}}$ is volume of the NaOH aqueous solution for blank titration, and $\mathbf{W}_{\mathrm{dry}}$ is dry weight of the sample. The proton conductivity studies of new polymers were performed using a Novocontrol Alpha-N high resolution dielectric-impedance analyser. After drying in vacuum oven polymer membranes were sandwiched between platinum blocking electrodes and the conductivities were measured in the frequency range from 0.1 Hz to 3 MHz at various temperatures with continuous nitrogen flow in a closed cell. The temperature was controlled with a Novocontrol cryosystem, which is applicable between −100–250 °C. To determine the humidity effect the membranes were weighed in dry state and then immersed in water and waited 2 h for swelling and then excess water on the surface is dried with paper. The amount of absorbed water is calculated and with no time interval the proton conductivity is carried out in the same system.

3. Synthesis

Poly(dichlorophosphazene) (PDCP) was prepared by ring opening polymerization of hexachlorocyclotriphosphazatriene at 250 °C in a sealed tube [26]. 4-diethylphosphorylphenol (DEPP) was synthesized according to literature procedure [27].

3.1. General procedure for synthesis of polymers 1-4

The specific reaction conditions used for these syntheses are listed in Table 1. The general experimental procedure described for polymer **1** below and a similar synthetic procedure followed for the synthesis of polymers **2**-**4** by using a constant amount of PDCP (2.0 g, 17.2 mmol) in ~110 mL of dry THF and changing the stoichiometric amount of the sequentially added DEPP and TFE reagents respectively (Table 1). DEPP (1.98 g, 8.6 mmol, 0.5 eq) was dissolved in 30 mL of THF and added drop wise to a suspension of NaH (0.38 g, 9.5 mmol) in 20 mL THF and let to stir over 2 h. 2,2,2-trifluoroethanol (TFE)(2.92 g, 29.2 mmol, 1.7eq) was dissolved in 30 mL of THF and added drop wise to a suspension of NaH (1.31 g, 32.7 mmol, 1.9eq) in 20 mL THF and let to stir over 1 h. The sodium 4-diethoxyphosphorylphenolate was added drop wise to a stirring solution of PDCP (2 g, 17.2 mmol/monomer, 1 eq) in 110 mL of THF and stirred in glove box under argon atmosphere for 2 h. The sodium salt of TFE was then added drop wise to reaction mixture and stirred for 24 h. The reaction mixture was then refluxed for a further 5 days to complete the substitution. The reaction mixture was cooled to room temperature and THF was removed under