Proton-conducting properties of the membranes based on poly(vinyl phosphonic acid) grafted poly(glycidyl methacrylate)

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ABSTRACT

Proton-conducting properties of the graft copolymer electrolytes were examined throughout this work. The homopolymers poly(glycidyl methacrylate), PGMA and poly(vinyl phosphonic acid), PVPA were synthesized by free-radical polymerizations of the monomers glycidyl methacrylate, GMA, and vinyl phosphonic acid, VPA, respectively. The graft copolymers were produced by grafting of PVPA onto PGMA via ring opening of ethylene oxide groups. To examine the influence of the concentration of VPA on the proton conductivity, several graft copolymers were produced at various stoichiometric ratios with respect to monomer repeat units. The materials were characterized by FT-IR and ^{1}H NMR spectroscopy and the thermal properties were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). The TGA results demonstrated that the samples are thermally stable up to at least 150 °C. The proton conductivities of humidified and dry samples were studied via impedance spectroscopy. In the anhydrous state, the proton conductivity of P(GMA)-graft-P(VPA)$_{10}$ was 5×10^{-5} S/cm at 150 °C. The proton conductivity of the same material increased with the humidity content and reached to 0.03 S/cm at 80 °C under 50% of RH, which approached to that of Nafion® at the same humidification level.

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1. Introduction

The research activities in the solid proton conductive polymer electrolytes dramatically increased due to their potential application in industrial chemical energy convention devices such as proton exchange membrane fuel cells (PEMFC). Especially research trend has been focused on the development of anhydrous or low humidity polymer electrolytes to maintain adequate proton conductivity at higher temperatures. Since, the operation of fuel cells at higher temperatures, i.e., in excess of 100 °C, provides additional advantages such as, improvement of CO tolerance of platinum catalyst, improve mass transportation, increase reaction kinetics and simplify the water management and gas humidification [1,2]. Humidified perfluorosulfonic acid membranes such as Nafion® have been widely investigated in fuel cell applications due to its high proton conductivity below 100 °C. Despite their high thermal and chemical stability, these membrane materials have some disadvantages including complex external humidification, high material cost and high methanol crossover where these have slowed down their widespread industrial application [3,4].

In order to overcome those limitations, a number of studies have been performed to produce novel polymer-based materials that can transport protons under anhydrous conditions. In this context, phosphoric acid based systems are widely studied for that purpose since pure H_3PO_4 itself is a good proton conductor because of its extensive self-ionization and low pK_a. Structure diffusion was proposed as the proton transport mechanism in fused phosphoric acid, where the transference number of proton is close to unity [5]. Although several homogeneous polymer electrolytes were reported in earlier studies [6–9], phosphoric acid doped polybenzimidazole (PBI), showed better physicochemical properties and promising fuel cell performance [10–13].

PVPA is a simple polymeric acid which can be produced by free-radical polymerization of vinyl phosphonic acid, VPA [14]. In the earlier studies, the blends and copolymers of PVPA with several heterocyclic molecules were studied and the former materials showed higher proton conductivity results in the anhydrous state [15–19]. Yazawa et al. prepared polyvinyl phosphonic acid, PVPA and 3-glycidoxypropyltrimethoxysilane graft membranes [20]. They reported a maximum proton conductivity of 3.7×10^{-2} S/cm at 80 °C under 90% of relative humidity. Recently, we immobilized several heterocyclic proton solvents into poly(glycidyl methacrylate), PGMA by ring opening of the epoxide ring and obtained high proton conductive membranes after doping with phosphoric acid [21,22].

Previously, the structure and the local proton mobility of the homopolymer, PVPA were studied by solid-state NMR under fast magic angle spinning [23]. The study concluded that the proton migration of

PVPA is mediated by acidic protons through a hydrogen bonding network and condensation of acidic units blocked the proton transport resulting in a significant decrease in the proton conductivity.

Also the relation between water uptake, self-condensation and proton conductivity of PVPA was investigated by Kaltbeitzel et al. [24]. They suggested that even after annealing and drying the material, water takes part in the conductivity mechanism. The condensation limits the conductivity, as it reduces the phosphonic acid sites taking part in the proton transport. Thus, maximum proton conductivity of 10^{-3} S/cm was reached under 1 bar H_2O atmosphere. Modification of VPA based membranes via copolymerization, blending or grafting is considered to improve the mechanical strength and stability and reduces the condensation of phosphoric acid units [19].

In this context, grafting of the PVPA over organic polymers such as poly(glycidyl methacrylate) would be interesting where the final material can have high proton conductivity.

In this work, PGMA was produced by free-radical polymerization and then grafted with PVPA over epoxide units at several stoichiometric ratios (Fig. 1). The films were characterized by FT-IR, TG and DSC. Proton conductivities of both anhydrous and humidified samples were measured by AC impedance spectroscopy and discussed according to polymer compositions.

2. Experimental

2.1. Materials

Glycidyl methacrylate (>97% Aldrich), vinyl phosphonic acid (>95% Fluka), Toluene (>99% Merck), DMF (>99% Fluka), α-α'-Azodiisobutyramidin Dihydrochlorid (AIBHC, >%98 Fluka), Methanol (>99% Merck) were used as received. α-α'-Azobisisobutyronitrile (AIBN; Merck) was recrystallized from THF prior to use.

2.2. Sample preparation

Poly(glycidyl methacrylate), PGMA was produced by free-radical polymerization of glycidyl methacrylate monomer according to the literature [21]. Toluene and AIBN (1 mol%) were used as solvent and initiator, respectively. Poly(vinyl phosphonic acid) was produced by free-radical polymerization of vinyl phosphonic acid as discussed in an earlier study [14]. PGMA and PVPA were dissolved in DMF and methanol/water, respectively. A stoichiometric amount of PGMA and PVPA solutions was mixed to synthesize P(GMA)-graft-P(VPA)$_x$;
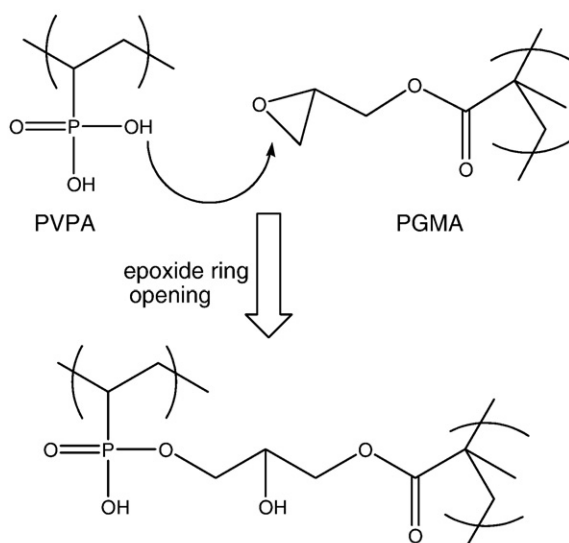

Fig. 1. The expected reaction scheme of P(GMA) and P(VPA).

$x = 3$, $x = 5$, $x = 10$ and $x = 20$. For example, to produce P(GMA)-graft-P(VPA)$_{10}$, 0.5 g PGMA in 10 ml DMF and 3.80 g PVPA in 20 methanol/water (5/1) were mixed and stirred for 24 h at 65 °C. The grafted samples, P(GMA)-graft-P(VPA)$_x$ were precipitated in acetone and purified by washing with methanol to remove unreacted PVPA. The absence of PVPA in methanol indicated the complete reaction. The graft copolymers are soluble in water and the aqueous solutions of the samples were cast in polished poly(tetrafluoroethylene), PTFE plates. The solvent was evaporated in vacuum oven at 50 °C. Transparent, hygroscopic and free-standing films were obtained and they were stored in the glove box for characterizations. In order to measure the proton conductivity of humidified samples, the dry films of the graft copolymers were weighed and 25% to 100% (water g/sample g) of water was absorbed in the films. The humidification process was made just before the measurement to prevent humidity loss.

2.3. Characterizations

^{1}H NMR measurement was performed with Bruker Avance 400 MHz in D_2O.

For FT-IR measurements, thin films of the samples were deposited on a silicon wafer, dried under vacuum and stored in glove box. The IR spectra (4000–400 cm^{-1}, resolution 4 cm^{-1}) were recorded with a Perkin Elmer FT-IR spectrum BX.

Thermal stabilities of the polymer electrolytes were examined by TG analyses with a Mettler-Toledo TG-50. The samples (~10 mg) were heated from room temperature to 700 °C under N_2 atmosphere at a scanning rate of 10 °C/min.

DSC measurements were carried out on a Mettler-Toledo DSC 30 under nitrogen atmosphere and heating–cooling curves were recorded at a rate of 10 °C/min.

The real (ε') and imaginary (ε'') parts of complex dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) were measured with a Novocontrol dielectric-impedance analyzer. The films were sandwiched between platinum blocking electrodes and the conductivities were measured in the frequency range of 0.1 Hz to 3 MHz at 10 °C intervals. The temperature was controlled with a Novocool Cryosystem, which is applicable between -100 °C and 250 °C. The dielectric data (ε', ε'') were collected during heating as a function of frequency. For conductivity data analysis, the real part of conductivity (σ') was calculated from the complex permittivity using the following relation, $\sigma' = \sigma_{ac} = \varepsilon_o \omega \varepsilon''$ where ε_o is the permittivity of the free space and $\omega (= 2\pi f)$ is the angular frequency.

3. Results and discussion

The graft copolymers were fabricated through reaction of PVPA over ethylene oxide units of PGMA. After precipitation, the materials were washed several times in methanol and the complete reaction of PVPA was confirmed by gravimetric methods as well as ^{1}H NMR spectroscopy. All the samples are water soluble and the solutions can be cast to produce free-standing films. The polymer P(GMA)-graft-P(VPA)$_{10}$ is the optimum composition in terms of mechanical strength and stability. Fig. 2 shows the pictures of P(GMA)-graft-P(VPA)$_{10}$ where the flexibility of this membrane was illustrated by wrapping it around a Teflon rod.

3.1. ^{1}H NMR spectrum

Fig. 3 shows ^{1}H NMR spectrum of P(GMA)-graft-P(VPA)$_{20}$. The spectrum exhibits resonances at 3.0–4.0 ppm, 1.0–2.5 ppm and 2.6 ppm. The signal at 2.6 ppm is assigned to the CH–P protons of VPA unit [14]. The signals between 3.0 and 4.0 ppm belong to CH_2–O and CH–O groups of GMA unit. The rest of the signals originates from the protons in the backbone of VPA and GMA units. The ratio of the