Journal of Electroanalytical Chemistry 706 (2013) 117–126

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Adding free volume to PEG based anhydrous proton conducting electrolytes with bulky copolymers

Benjamin Yancey [1], Jason E. Ritchie *

Department of Chemistry and Biochemistry, The University of Mississippi, MS 38677, United States

ARTICLE INFO

Article history:
Received 29 May 2013
Received in revised form 2 August 2013
Accepted 7 August 2013
Available online 21 August 2013

Keywords:
Poly(ethylene glycol)
Proton conductivity
Hybrid inorganic/organic polymers
Free volume
Viscosity

ABSTRACT

We have synthesized several H^+ conducting siloxane copolymers with a methyl polyethylene glycol siloxane ($MePEG_nSiO_{1.5}$; $n = 3, 7, 12, 16$) and diphenyl siloxane, isobutyl siloxane, and 3,3,3-trifluoropropyl siloxane copolymers. These copolymers where prepared to test if copolymerization with bulky groups can add free volume to our $MePEG_n$ polymer, and thus affect ion transport properties. We also found that the fractional free volume (FFV) could be increased in short $MePEG_n$ copolymers with the diphenyl and isobutyl copolymers, while with longer $MePEG_n$ groups ($n = 12, 16$), the pure $(MePEG_n–SiO_3)_m$ polymer already has a large free volume and that the added copolymers only dilute that already maximized free volume. The increase in FFV did not correspond to an increase in ionic conductivity. Ionic conductivity appears to be more a function of the volume fraction of PEG ($V_{f,PEG}$) than FFV.

1. Introduction

The demand for more efficient and greener energy sources has led to an increased interest in fuel cells. Polymer electrolyte membrane fuel cells (PEMFC) are especially important for stationary and automotive applications. These fuel cells have a polymer electrolyte membrane that physically and electrically separates the anode from the cathode, and serves the critical role of conducting H^+ cations from the anode to the cathode. Effective polymer electrolytes need to have physical and chemical properties that support cation mobility and mechanical durability [1–4].

Nafion, a sulfonated fluoropolymer, is a widely used polymer electrolyte in PEMFC, because of its chemical stability, mechanical properties, and high conductivity when wet. Nafion's major disadvantages, however, are the cost, poor hydrophobicity, and an ionic conductivity that is dependent on hydration of the membrane. These disadvantages typically limit the operation temperature of a Nafion based PEMFC to less than 80 °C [5]. Nafion membranes have been modified by the incorporation of inorganic moieties, such as silica and titanium oxide, into the polymer matrix to produce hybrid materials with increased operating temperatures, but with decreased ionic conductivity at all temperatures and relative humidities. It is surmised that the incorporation of these moieties interrupts the hydrophilic channels present in Nafion [6–8]. One exception in these studies is that mesoporous silica with sulfonic acid functionalities shows increased conductivity at high temperature (95 °C) over a wide range of relative humidities (50–100%) [9].

Polyethylene glycol (PEG) polymers have been shown to conduct small cations in the absence of water, but do not, by themselves, have the mechanical stability needed for fuel cell applications. However, the attachment of PEG to a crystalline inorganic material gives a hybrid organic/inorganic material combining the mechanical properties and chemical stability of the inorganic material with the high conductivity of PEG [10–14].

Siloxanes are easy to functionalize, and are chemically and mechanically stable [15–19]. In addition, siloxanes can be coupled with PEG and polyethylene glycol monomethyl ether (MePEG) by hydrosilylation of an allyl-modified PEG to form the organic/inorganic hybrid [1,15,16,20–22]. The chemical and physical properties (structure, thermal and mechanical stability) of these organic/inorganic hybrid systems (including the PEG/POSS system) are fairly well understood [1,10,11,22], however, the properties of these materials related to ionic conductivity in polymers are less well understood (i.e., the relationship between free volume, viscosity, density, and ionic conductivity). In fact, Wunder and co-workers have studied lithium ion transport in hybrid systems of POSS functionalized with PEG and have found that their system can form a biphasic morphology with a conductive, ion-transporting phase, and a non-polar, non-conductive phase [23].

Swager has shown that the free volume of a polymer can be increased by the copolymerization of a polymer with a bulky comonomer. Swager has modified the free volume of several

---

* Corresponding author. Tel.: +1 662 915 7294.
E-mail address: jritchie@olemiss.edu (J.E. Ritchie).

[1] Current address: Department of Chemistry, The University of Alabama at Birmingham, AL 35294-1240, United States.

1572-6657/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jelechem.2013.08.006

polymers by copolymerization with triptycene or t-butyl derivatives to alter the free volume [24]. By introducing bulky groups into the polymer backbone, they found that the overall free volume of the polymer was increased. This is important, because in free volume theory, all transport properties (η, σ, D, etc.) of a material are dependent on the free volume in the material [25,26]. The diffusion of a particle through a material is described as a translation across a void in the particles vicinity [27]. In this paper we describe how to increase the free volume of our organic/inorganic hybrid electrolytes in order to study the effect of free volume in the polymer electrolyte on the observed ionic transport properties in the polymer electrolyte. We accomplish this by adding bulky copolymers to our MePEG$_n$ polymer.

2. Materials and methods

2.1. Materials

Polyethylene glycol monomethyl ether ($CH_3(OCH_2CH_2)_n OH$ = MePEG$_n$OH, M_n = 164, 350, 550, 750, n = 3, 7.24, 12.0, 16.3; Aldrich) was dried at 60 °C under vacuum for approximately 24 h prior to use.

This paper will refer to tri(ethylene glycol) monomethyl ether MW = 164, as MePEG$_3$OH, the poly(ethylene glycol) monomethyl ether M_n = 350, as MePEG$_7$OH, M_n = 550 as MePEG$_{12}$OH, and M_n = 750 as MePEG$_{16}$OH. Triethoxysilane (Aldrich), allyl bromide (Acros), sodium sulfite (Fischer), diphenyl dimethoxysilane (Ph_2Si) (Aldrich), 3,3,3-trifluoropropyl trichlorosilane (TFPSi) (Aldrich), isopropyl trimethoxysilane (iBuSi) (Aldrich) were all used as received. Amberlite IRA-400(Cl) anion exchange resin (Aldrich) and Amberlite IR-120H cation exchange resin (Aldrich) were used as received. Phosphorus tribromide was diluted to a 1.98 M solution in dry diethyl ether before use. Solid sodium metal (Aldrich) and sodium hydride (Aldrich) were rinsed thoroughly with hexanes prior to use to remove the mineral oil that they were stored in. Dry tetrahydrofuran (THF) and diethyl ether (Et_2O) were obtained from a Distillation Dispensary System, under argon, immediately prior to use, and kept under an inert atmosphere.

2.2. Methods

The density and concentrations of the polymer samples were measured as previously described [22]. The concentrations of the MePEG$_7$SO$_3$H acid/MePEG$_n$ Copolymer mixtures were calculated by converting the mass of both the acid and the polymer to volume using their respective densities. Then the mass of acid was converted to moles by using the acid's molecular weight and was divided by the total volume of the acid plus polymer (this method specifically assumes that the volumes are additive).

The viscosity of the polymer samples was measured using a Brookfield DV-III Ultra Programmable Rheometer. A CPE-40 spindle was used and the viscosities measured under a flow of dry nitrogen at 3 different rotational speeds which were averaged. The rotational speeds were selected to keep the torque in a range of 10–100%. The samples were dried at 50 °C under vacuum prior to measurement.

Gel permeation chromatography (GPC) measurements were performed using a Polymer Laboratories ELS-2100 evaporative light scattering detector with two 30 cm PL Mixed-D analytical columns. Polystyrene molecular weight standards (PL-EasiCal PS-2, MW range 580–480,000) were used to calibrate the MW range prior to running unknown samples. THF was then allowed to elute through the column for 30 min to remove any remaining samples and to equilibrate the system. GPC samples were made by dissolving 2–3 mg of sample in 1 g THF.

AC-impedance measurements were performed using a PAR 283 potentiostat equipped with a Perkin-Elmer 5210 lock-in amplifier [22]. Conductivity is determined from a Nyquist plot by the diameter of the high frequency semicircle [28]. NMR measurements were made with either a Bruker AC-300 or a Bruker DRX-500 instrument.

Strong acid ion exchange columns were prepared by placing 50 mL (95 meq) of Amberlite IR-120H ion exchange resin (1.9 meq/mL) in a chromatography column with a porous frit. Hydrochloric acid (1 M, 300 mL, 300 meq) was allowed to flow through the column to exchange all of the cation sites to H^+. Deionized water was then allowed to flow through the column until the pH of the column was near neutral pH (~6.0–8.0). Strong base exchange column were similarly prepared with 50 mL (70 meq) of Amberlite IRA-400 (Cl) ion exchange resin (1.4 meq/mL), followed by charging with Sodium hydroxide (1 M, 225 mL, 225 meq), and rinsing with deionized water to a near neutral pH.

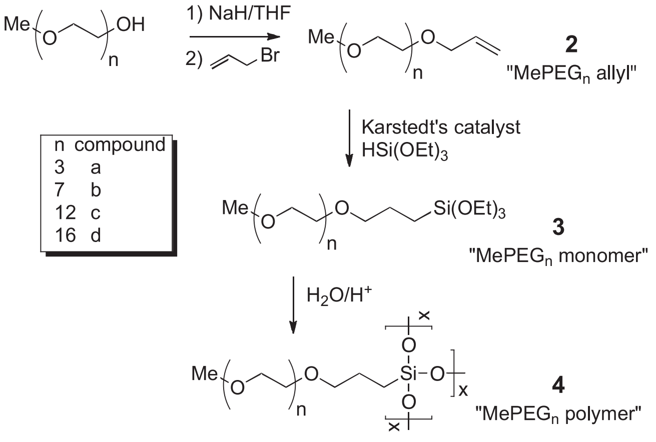
2.3. Synthesis

Scheme 1 describes the synthesis of MePEG polymers (**4a**–**d**) from MePEG$_n$OH (**1a**–**d**). Table S1 summarizes preparation of the sol–gel copolymers. Scheme 2 describes the preparation of bulky copolymers (**5a**–**d**, **6a**–**d**, **7a**–**d**) by copolymerization of the MePEG polymers (**4a**–**d**) with diphenyl dimethoxysilane, trifluoropropyl trichlorosilane, and isobutyl trimethoxysilane. All copolymers were made so that there was 10% w/w of the bulky group. **MePEG$_n$ allyl**: **(MePEG$_3$OCH$_2$CHCH$_2$) (2a)** and **(MePEG$_7$OCH$_2$CHCH$_2$) (2b)** were prepared as previously described [1,22,29]. **MePEG$_7$SO$_3$H acid** was prepared as previously described [22,29–31].

The details of the synthesis of the compounds shown in Schemes 1 and 2 are provided in the Supplementary Materials section.

2.4. End group analysis

End group analysis was performed on all of the prepared copolymers to test for uncondensed Si–OH from the sol–gel condensation to form the polymers. The uncondensed –OH groups were reacted with chlorotrimethylsilane, $(CH_3)_3Si–Cl$ (Scheme 3) to label each residual OH group with a trimethylsilyl group that can be integrated in the NMR spectra. In one experiment, MePEG$_7$ polymer (0.035 g, 0.079 mmol) was dissolved in 20 mL toluene in an argon purged flask. Then, a large excess of chlorotrimethylsilane (0.5 mL, 4 mmol) was added. The reaction mixture was stirred for 6 h. After which, 2.0 g K_2CO_3 was added to quench any unreacted



Scheme 1. Synthesis of MePEG$_n$ polymers.