European Polymer Journal 44 (2008) 4054–4062

Contents lists available at ScienceDirect

European Polymer Journal

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

Poly(arylene ether) ionomers containing sulfofluorenyl groups: Effect of electron-withdrawing groups on the properties

Takuya Shimura, Kenji Miyatake *, Masahiro Watanabe *

Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan

ARTICLE INFO

Article history:
Received 2 May 2008
Received in revised form 1 August 2008
Accepted 17 September 2008
Available online 25 September 2008

Keywords:
Ionomers
Fuel cells
Poly(arylene ether)s
Proton conduction
Electron-withdrawing groups

ABSTRACT

For polymer electrolyte membrane fuel cell (PEMFC) applications, the effect of electron-withdrawing groups on the properties of sulfonated poly(arylene ether) (SPE) ionomer membranes was investigated. A series of poly(arylene ether)s containing fluorenyl groups and electron-withdrawing groups (sulfone, nitrile, or fluorine) was synthesized, which were sulfonated with chlorosulfonic acid using a flow reactor to obtain the title ionomers. The ionomers had high molecular weight ($M_n > 77$ kDa, $M_w > 238$ kDa) and gave tough, ductile membranes by solution casting. The ion exchange capacity (IEC) of the membranes ranged from 1.6 to 3.5 mequiv/g as determined by titration. The electron-withdrawing groups did not appear to affect the thermal properties (decomposition temperature higher than 200 °C). The presence of nitrile groups, especially at positions *meta* to the ether linkages, improved the oxidative stability of the SPE membranes, while it led to a deterioration of the hydrolytic stability. The perfluorinated biphenylene groups were effective in providing high mechanical strength with reasonable dimensional change, probably due to a somewhat decreased water absorbability. The SPE membrane containing sulfone groups showed the highest proton conductivity (10^{-3}–10^{-1} S/cm) at 20–93% RH (relative humidity) and 80 °C. The nitrile-containing SPE membrane showed smaller apparent activation energies for oxygen and hydrogen permeability and is thus considered to be a possible candidate for applications in PEMFCs.

1. Introduction

Ionomer membranes are of interest for a variety of applications, such as sensors, actuators, batteries, and fuel cells [1]. In particular, recent progress in the area of polymer electrolyte membrane fuel cells (PEMFCs) has stimulated considerable interest in proton-conductive ionomer membranes. Perfluorinated ionomers [2,3], e.g., Nafion (DuPont), are the state-of-the-art in fuel cell membranes; however, there is a great demand for alternative, non-fluorinated ionomers, which are considered to be promising in terms of providing improved high temperature stability, decreased gas permeability, and greater environmental friendliness (or recyclability), as well as lowered production costs [4–13].

A reasonable approach for this purpose is the acid functionalization of hydrocarbon polymers [14]. For example, aromatic polymers are attractive candidates as base frameworks due to their excellent thermal and chemical stability and high susceptibility to electrophilic sulfonation reactions. A number of aromatic polymers such as poly(ether ether ketone)s [15], poly(arylene ether)s [16], polyimides [17–19], polyphosphazenes [20,21], polybenzimidazoles [22,23], polyphenylenes [15], and others have been sulfonated or doped with mineral acids. Some of the resulting ionomer membranes are claimed to show high proton conductivity at high temperature. We have recently reported that the sulfonated poly(arylene ether sulfone)s containing fluorenylidene biphenylene groups showed high performance in fuel cell operation and survived for as long as

---

* Corresponding authors. Tel./fax: +81 55 220 8707.
E-mail address: miyatake@yamanashi.ac.jp (K. Miyatake).

0014-3057/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2008.09.017

5000 h without significant degradation [24–26]. The properties of the polyether ionomer membranes have been improved by detailed molecular consideration (number and position of methyl group substitution and/or copolymerization) [27]. However, proton conductivity and durability are still issues and need to be further improved. There have been a number of recent research relevant to this topic [28–31].

As part of an overall program in which we are seeking to develop new, high-stability, high-conductivity fuel cell ionomers, we examine herein the effects of modifying the hydrophobic component on the properties of the sulfonated polyether membranes. We hypothesize that electron-withdrawing groups should effectively lower the electron density of the attaching aromatic rings, resulting in decreased susceptibility to oxidative attack by radical species. A series of poly(arylene ether)s containing sulfofluorenyl groups as the hydrophilic component and electron-withdrawing groups (sulfone, nitrile, or fluorine) on the hydrophobic main chain was synthesized, and the thermal, oxidative, hydrolytic, and mechanical stability, water uptake, proton conduction, and gas permeability were investigated. The substitution position of the nitrile groups was also examined.

2. Experimental

2.1. Measurements

^{1}H (400 MHz) NMR experiments were performed on a Bruker AVANCE 400S spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) or deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal standard. Molecular weight measurements were performed via gel permeation chromatography (Jasco 880-PU) on an instrument equipped with two Shodex KF-805 columns and a Jasco 875 UV detector set at 300 nm. *N*,*N*-Dimethylformamide containing 0.01 M LiBr was used as the solvent at a flow rate of 1.0 mL/min. M_w and M_n were calibrated with standard polystyrene samples. TG/DTA was carried out with a Mac Science TG/DTA 2000, equipped with a Bruker MS 9600 mass spectrometer, at a heating rate of 5 °C/min under dry argon atmosphere.

2.2. Materials

2,6-Difluorobenzonitrile (2,6-DFB) (97%, TCI Co., Inc.), 3,5-difluorobenzonitrile (3,5-DFB) (99%, TCI Co., Inc.), decafluorobiphenyl (DFBP) (98% TCI Co., Inc.), 9,9-bis(4-hydroxyphenyl)fluorene (BHF) (98%, TCI Co., Inc.), potassium carbonate (99.5%, Kanto Chemical Co., Inc.), toluene (99.5%, Kanto Chemical Co., Inc.), chlorosulfonic acid (99%, Kanto Chemical Co., Inc.), and dichloromethane (99.5%, dehydrated, Kanto Chemical Co., Inc.) were used as received. 4-Fluorophenyl sulfone (FPS) (99%, Acros Organics) was purified by crystallization from ethanol. *N*,*N*-Dimethyl acetamide (DMAc) (99%, Kanto Chemical Co., Inc.) was dried over 3 A molecular sieves prior to use. Other chemicals were of commercially available grade and used as received.

2.3. Synthesis of homopolymers (PE-1a, -1b, -1c, and -1e)

The polymerization procedure for PE-1a has been reported in the literature [25]. The other homopolymers were synthesized in the same manner. A typical procedure is as follows. A 200-mL three-neck round-bottomed flask equipped with a magnetic stirring bar, an N_2 inlet, and an addition funnel was charged with BHF (5.0 mmol, 1.75 g), 2,6-DFB (5.0 mmol, 0.70 g), potassium carbonate (12.5 mmol, 1.73 g), toluene (3.0 mL), and DMAc (10 mL). The mixture was stirred at room temperature for a few minutes and heated at 140 °C for 3 h and at 165 °C for 3 h under N_2 atmosphere. Then, 60 mL of DMAc was added to the mixture to lower the viscosity. The mixture was poured dropwise into 1 L of deionized water to precipitate a white, flaky product. The crude product was washed with hot deionized water and methanol several times and purified by reprecipitation from chloroform/acetone. The resulting fibrous product was dried under vacuum at 60 °C for 15 h to give PE-1b in 65% yield. Using 3,5-DFB or DFBP instead of 2,6-DFB gave PE-1c in 70% yield or PE-1e in 40% yield, respectively.

2.4. Synthesis of copolymers (PE-1d)

Polymerization conditions for the copolymer were similar to those for the homopolymers. The molar ratio of 2,6-DFB to 3,5-DFB was set at 1:1. A white, flaky copolymer PE-1d was obtained in 65% yield.

2.5. Sulfonation

The sulfonation of fluorenyl-containing poly(arylene ether)s (PE-1) using a flow reactor was previously reported [32]. In order to achieve efficient mixing of polymer and chlorosulfonic acid solutions, a flow reactor was used in which both solutions were supplied through a narrow passage (1 mm) in the reactor via a microfeeder at a constant rate, so that the sulfonation reaction occurred rapidly before the sulfonated product precipitated out of the mixture. A typical procedure is as follows: a 200-mL syringe was charged with 100 mL of 0.01 M PE solution in dichloromethane, and a 100-mL syringe was charged with 30 mL of 0.1 M chlorosulfonic acid in dichloromethane. Both syringes were connected to the reactor via a Teflon tube. Each solution was supplied to the reactor simultaneously using the microfeeder. The flow rates of the polymer solution and the chlorosulfonic acid solution were set at 10 and 2–6 mL/min, respectively. The reaction was done at room temperature. The mixture obtained was poured dropwise into 500 mL of hexane. The resulting product was washed with hexane and water several times and dried under vacuum at 60 °C for 15 h to obtain a yellow powder of the sulfonated polymers (SPE-1).

2.6. Membrane preparation

SPE (0.35 g) solution in 10 mL of DMAc were cast onto a clean flat glass plate (9 cm × 6 cm). Drying the solution at 60 °C under atmospheric pressure for 15 h gave colorless and transparent membranes (50 μm thick). The mem-