



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Water and sodium transport and liquid crystalline alignment in a sulfonated aramid membrane

Jianwei Gao^{a,c}, Ying Wang^b, Ben Norder^c, Santiago J. Garcia^a, Stephen J. Picken^c, Louis A. Madsen^b, Theo J. Dingemans^{a,c,*}

^a Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands

^b Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

^c Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

ARTICLE INFO

Article history:

Received 3 February 2015

Received in revised form

15 March 2015

Accepted 20 March 2015

Available online 20 April 2015

Keywords:

Liquid crystal polymer

Anisotropy

Ionic crosslinking

Ion transport

NMR diffusion

ABSTRACT

Two sulfonated aramids, poly(2,2'-disulfonylbenzidine terephthalamide) (PBDT) and poly(2,2'-disulfonylbenzidine isophthalamide) (PBDI), were synthesized with the aim to explore their unique morphology for proton exchange membrane applications. Due to the different polymer structures, PBDT forms a nematic liquid crystal, whereas PBDI is isotropic. Both polymers show excellent thermal stabilities ($T_d^{5\%} > 400$ °C), high storage moduli ($E' = 3\text{--}15$ GPa) and crosslinked films are flexible and easy to handle. Pulsed-field-gradient NMR diffusometry reveals that the in-plane water diffusion in the nematic PBDT membrane is as high as 3.3×10^{-10} m²/s, whereas the diffusion in amorphous PBDI is only 2.5×10^{-10} m²/s. Whereas neat and crosslinked PBDI shows isotropic diffusion, neat PBDT shows a high diffusion anisotropy ($D_{\parallel}/D_{\perp} = 3.0$), which increases as a function of crosslink density ($D_{\parallel}/D_{\perp} = 4.6$ at 80% crosslinking). This diffusion anisotropy is substantially higher than that typically observed for low molecular weight liquid crystals and for oriented polymeric conductors such as Nafion[®] ($D_{\parallel}/D_{\perp} \sim 2.0$). The nematic order in the PBDT membrane also promotes directed ionic conductivity, *i.e.* Na⁺ conductivity in PBDT is 2.24×10^{-2} S/cm and 1.67×10^{-2} S/cm for PBDI, respectively. We propose that the rigid-rod PBDT chains form nano-scale hydrophilic channels, which act as pathways for transporting water molecules and ions.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are able to directly convert chemical fuels, *e.g.* hydrogen or methanol, into electricity. The advantages of fuel cells over other energy generating devices are significant. Fuel cells offer a high power density and are easy to install and operate. In addition, they are constructed from solid-state components and their operation has a low impact on the environment [1–4]. The performance of a fuel cell depends primarily on the membrane electrode assembly (MEA). The MEA comprises a proton exchange membrane and electrodes with embedded catalyst [5,6]. The proton exchange membrane (PEM) is one of the key components of a fuel cell and therefore much research has been devoted to the design and synthesis of suitable polymers for the PEM. Currently, perfluorosulfonic acid membranes (PFSA), such as Nafion[®], have been widely used as proton conducting membranes due to their high

* Corresponding author at: Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands.

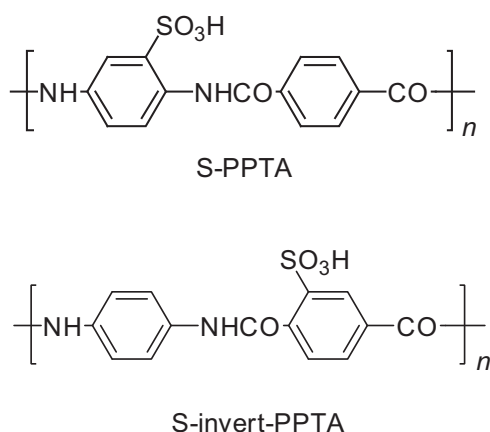
E-mail address: t.j.dingemans@tudelft.nl (T.J. Dingemans).

chemical and mechanical stability as well as high proton conductivity. But the drawbacks of Nafion[®] such as low durability, high methanol cross over and high cost, have limited large scale application of this material [7,8]. As a result, a large number of alternative sulfonated hydrocarbon polymers and their derivatives have been synthesized and tested in fuel cells over the past 30 years [9–13]. Over the years, the relationship between morphology and ion conductivity has been investigated and more attention was devoted to polymers with ordered structures [14–16]. Different block copolymers, mostly AB diblocks, have been designed to control the morphology of the polymer membranes in order to improve proton conductivity [17,18,20,21]. Most AB block copolymers for fuel cell applications contain a hydrophobic block and a hydrophilic block. The hydrophobic block forms a mechanically and chemically stable matrix whereas the hydrophilic block forms the conductive phase [28–30]. Block identity and block length control the micro-phase separation, which in turn controls the conductive phase dimension of the membrane.

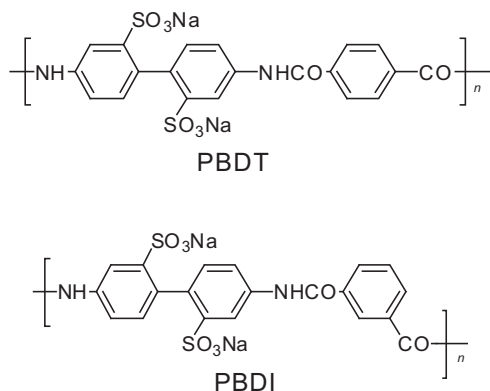
Recently, researchers reported that the sulfonated form of poly(*p*-phenylene terephthalamide) (PPTA) can be used as a PEM for fuel cells. Every and co-workers explored sulfonated aramid polyelectrolytes with liquid crystal (LC) morphologies. Two water-soluble

PPTA derivatives (Scheme 1) were synthesized with proton conductivities comparable to that of Nafion[®] [19,22]. Only limited data was presented on the proton conductivity because the polymers dissolved in water, and the low molecular weight of sulfonated PPTA limits the ability to prepare flexible membranes. Another recent study by Si et al., showed that a highly sulfonated and crosslinked *para*-phenylene-based polymer could form flexible and conductive films that performed well in fuel cell tests, but these materials require processing from polyphosphoric acid [31]. In addition to enabling ion conduction applications, sulfonation of high-performance aramid polymers such as Kevlar[®] and Twaron[®] shows promise for providing alternate routes to solution (e.g., water) processing of these structural materials, and avoid the current need for harsh processing solvents. In these studies and the present study, sulfonated aromatic polymers show promise for use as materials with low cost, high chemical and thermal stability, high conductivity, and tunable alignment properties.

In this study, we present water and sodium transport properties of two all-aromatic aramids, i.e. poly(2,2'-disulfonylbenzidine terephthalamide) (PBDT) and poly(2,2'-disulfonylbenzidine isophthalamide) (PBDI) [23,32–34]. As shown in Scheme 2, PBDT has a rigid polymer backbone, and forms a nematic liquid crystal phase in water, whereas PBDI has a kinked backbone structure and forms an isotropic solution in water. Both polymers can be obtained in high molecular weight (up to 18,000 g/mol) and both polymers can conveniently be crosslinked to yield insoluble, flexible membranes using barium ions.



Scheme 1. Chemical structures of sulfonated PPTA. In S-PPTA the sulfonic acid is located at the diamine moiety whereas in S-invert-PPTA the sulfonic acid is on the diacid moiety.



Scheme 2. Chemical structures of PBDT and PBDI. PBDT forms films with nematic ordering whereas PBDI forms only isotropic films.

We have previously reported detailed solution properties of PBDT, including molecular ordering, chain configurations, and sodium transport [32]. PBDT polymer becomes a nematic liquid crystal at very low concentrations (> 1.5 wt%) in water, with orientational order parameter $\langle P_2 \rangle = 0.76$ for the polymer chains, showing that the polymer chains are extremely rigid rods in solution. Using a lattice model along with SAXS and ²H NMR measurements, we investigated the dynamic coupling of water to the sulfonate groups and the rod-rod distance in a range of solution concentrations. The membranes described in the present paper follow behaviors as expected from our observations in water solutions.

Herein we present the thermo-mechanical properties and morphology of Ba²⁺-crosslinked liquid crystal PBDT and isotropic PBDI membranes. We further use pulsed-field-gradient (PFG) NMR diffusometry and ion (Na⁺) conductivity experiments to probe the water and ion transport. We demonstrate that ionic polymers with liquid crystal organization represent versatile candidates for tunable water and ion transport applications.

2. Experimental

2.1. Materials

2,2'-Benzidinedisulfonic acid (BDSA) (with 30 wt% water, Alfa-Aesar) was recrystallized using the following procedure: 5.0 g (~0.01 mol) of BDSA and 0.8 g (0.02 mol) of NaOH were dissolved in 15 mL of deionized water. Ethanol (50 mL) was added to the clear dark-red solution to precipitate the sodium form of BDSA (BDSA-Na). BDSA-Na was collected by filtration and then again dissolved in 25 mL of deionized water. Concentrated HCl (37%, 2 mL) was added to the solution to acidify BDSA-Na after which BDSA crystals precipitated from solution. This procedure was repeated 4 times and resulted in white needle-shaped crystals with a yield of 95%. Terephthaloyl chloride (TPC, 99%, Sigma-Aldrich) and isophthaloyl chloride (IPC, 99%, Sigma-Aldrich) were purified by vacuum sublimation prior to use. Polyethylene glycol with a molecular weight of 300 g/mol (PEG 300, Sigma-Aldrich), chloroform (98%, VWR), dichloromethane (98%, VWR) and sodium carbonate (99%, Sigma-Aldrich) were used without further purification.

2.2. Synthesis of linear and thermoset PBDT and PBDI

As shown in Scheme 3, PBDT and PBDI were synthesized by an interfacial polycondensation method reported by Sarkar et al. [23] PBDT was obtained as a white fibrous polymer in 60% yield and PBDI was obtained in 50% yield, respectively. PBDT FT-IR (cm⁻¹): 3369 (N–H stretching band), 1643 (C=O), 1585, 1518, 1498, 1468, 1381, 1305 (asymmetric stretch vibration sodium sulfonate), 1176, 1099 (symmetric stretch vibration sodium sulfonate), 1082, 1041, 1027, 993, 831. PBDI FT-IR (cm⁻¹): 3382 (N–H stretching band), 1637 (C=O), 1577, 1518, 1467, 1380, 1305 (asymmetric stretch vibration sodium sulfonate), 1176, 1096 (symmetric stretch vibration sodium sulfonate), 1084, 1041, 1027, 995, 832. Solution viscosities of the sulfonated polyamides, PBDT and PBDI, were measured using an Ubbelohde capillary viscometer at 25 °C and a polymer concentration of 0.5 g/dL in deionized water. The reduced viscosity of PBDT was 30.2 dL/g and that of PBDI was 4.3 dL/g. The molecular weight and molecular weight distribution of the samples were determined by size exclusion chromatography (SEC) using PPTA (Twaron 1010) as a reference sample. Both PBDT and PBDI were dissolved in 100% sulfuric acid (1 mg/ml) and analyzed. For PBDT, The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersity index

Download English Version:

<https://daneshyari.com/en/article/632904>

Download Persian Version:

<https://daneshyari.com/article/632904>

[Daneshyari.com](https://daneshyari.com)