



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Gas sorption, diffusion, and permeation in thermally rearranged poly(benzoxazole-co-imide) membranes

Seungju Kim^{a,b}, Kyung Taek Woo^a, Jong Myeong Lee^a, Jeffrey R. Quay^c, M. Keith Murphy^d,
Young Moo Lee^{a,b,*}

^a WCU Department of Energy Engineering, Hanyang University, Seoul 133-791, Republic of Korea

^b School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea

^c Air Products and Chemicals, Inc., Allentown, PA, USA

^d Air Products and Chemicals, Inc., St. Louis, MO, USA

ARTICLE INFO

Article history:

Received 18 September 2013

Received in revised form

16 November 2013

Accepted 19 November 2013

Available online 28 November 2013

Keywords:

Thermally rearranged polymers

Gas sorption

Solubility coefficient

Solution diffusion model

Polybenzoxazole-co-imide

ABSTRACT

Thermally rearranged polymer membranes exhibit extraordinary gas permeability based on a rigid polymer structure with a high free volume element. In this study, TR poly(benzoxazole-co-imide) membranes from 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA), 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB), 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (bisAPAF), and 2,4,6-trimethyl-m-phenylenediamine (DAM) were prepared to improve their gas separation properties. Copolymer membranes of polyimides and TR polybenzoxazoles may be desirable to generate efficient gas transport properties as well as to process polymers into fiber or film forms. Gas permeability, diffusivity, and solubility of the precursor polyimide and TR poly(benzoxazole-co-imide) membranes were investigated to characterize gas transport properties for small gas molecules including H₂, O₂, N₂, CH₄, and CO₂. Thermal rearrangement process resulted in an increase in polymer free volume, which improved the diffusion and sorption coefficients.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Membrane gas separations have played an important role in the gas production industry as an alternative technology of traditional gas separation processes such as cryogenic distillation and absorption [1]. Membrane processes allow for a small footprint and low energy consumption that are advantageous compared to other separation processes [2,3]. Membrane materials for gas separation applications have been investigated to overcome the current material performance limits, the “upper-bound” established by Robeson in 1991 and revisited in 2008 [4,5]. Among various membrane materials, including metallic and inorganic materials, polymeric membranes have been commercialized with high gas flux based on the asymmetric structure. However, only a few commercial polymers, such as cellulose acetate (CA), polyimides (PI), and poly(phenylene oxide) (PPO), have been used [1,6]. Various studies have been conducted to improve the membrane performance in aspects of gas permeability and selectivity. As a result, a number of microporous polymer membranes have exhibited improved gas transport performance [7–11].

* Corresponding author at: School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea. Tel.: +82 2220 0525.

E-mail addresses: ymlee@hanyang.ac.kr, jms@hanyang.ac.kr (Y.M. Lee).

Fundamental studies on the gas transport mechanism of polymer membranes are required to improve membrane performance and to overcome the upper bound. For polymeric membranes in gas separation, the solution–diffusion model is considered as a well-defined gas transport mechanism [10].

Gas permeability through polymeric membranes is usually determined as a product of gas diffusivity and solubility in the solution–diffusion model [10]. Gas solubility is a thermodynamic parameter that provides the amount of penetrants sorbed in the polymer matrix in equilibrium states. Gas diffusivity is a kinetic parameter related to the rate at which penetrants move in the polymer matrix [1]. Polymer membranes have been investigated to improve gas permeability in a way of enhancing the gas diffusivity and/or gas solubility of materials. Rubbery polymer membranes typically exhibit high gas solubility for condensable gases and sorption-selective gas separation properties [12]. The membranes demonstrate a high CO₂ solubility coefficient, resulting in high CO₂ permeability. Rubbery polymer membranes, such as poly(ethylene oxide) (PEO) and polyvinylamine (PVAm), have demonstrated high CO₂ separation performance with sorption-based CO₂ permeation [13–16]. Glassy polymer membranes demonstrate diffusivity-based gas permeability that is governed by chain rigidity and free volume elements. Moreover, free volume in the polymer acts as a gas transport pathway through the membrane matrix [17–19]. Microporous organic polymers,

including amorphous fluoropolymers (AF polymer), polymers of intrinsic microporosity (PIMs), and thermally rearranged polymers (TR polymers), exhibit very high gas permeability due to their rigid polymer structure with high free volume elements [3,20–24]. Various polymeric membrane materials, including polydimethylsiloxane (PDMS), poly(1-trimethylsilyl-1-propyne) (PTMST), polycarbonate (PC), PIMs, and TR polymers, have been characterized for their sorption properties in order to understand the gas transport properties [8,11,25–31].

Recently developed TR polymers are a type of microporous organic polymer that possess extraordinary gas permeability with relevant gas selectivity [21]. TR polymers are prepared from a precursor polyimide with functional groups at the *ortho*-positions to the imide bond by a thermal conversion reaction, resulting in so-called a thermal rearrangement. The intramolecular chemical reaction of the thermal rearrangement between the *ortho*-positioned functional groups and imide-carbonyl groups form benzoxazole rings that are chemically and thermally stable due to their rigid structures. Moreover, thermal conversion in the solid state results in a dramatic increase in the free volume elements and improves gas transport properties. Gas transport properties of TR polymer membranes depend on the chemical structure of the polymer backbone [32]. The fractional free volume is considered an important factor to improve the gas permeability. However, polymer rigidity has recently received much attention as a key factor to improve membrane performances [17–19]. Precursor polyimides are prepared by a polycondensation reaction of diamine and dianhydride monomers. The choice of monomers considering the chemical structure and structural rigidity can determine membrane performance. Introduction of bulky and rigid monomers, such as 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA), 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (bisAPAF), and 3,3'-dihydroxy-4-4'-diamino-biphenyl (HAB) as dianhydride and diamine, was shown to improve the gas permeation properties of TR polymer membranes [32–35].

Various structural modifications have also been performed to investigate TR polymer membranes using various monomers in a precursor preparation [32–38]. Copolymerization of TR polymers with other glassy polymers was also investigated to improve their physical properties such as gas separation properties and processability [31,39–42]. A rigid and ladder-type polymer, polypyrrolone (PPL), was introduced to control the physical properties of poly(benzoxazole-co-pyrrolone) membranes. The more rigid PPL structure provided a selective site due to its well-packed structure. The poly(benzoxazole-co-pyrrolone) membrane exhibited relatively high selectivity with an improved molecular sieving effect [39]. Copolymerization with polyimide was also introduced. Gas permeability and selectivity were easily controlled by different ratios of imide portion during copolymerization. The imide portion in the poly(benzoxazole-co-imide) (PBO-PI) membranes controlled the cavity size and distributions, resulting in controlled gas separation performances [40]. Moreover, the fractional free volume and gas permeability of TR copolymer were controlled by using suitable anhydride and diamine [31]. Copolymerization with polyimide is a simple and useful method to improve membrane performance because polyimide is known as an excellent material with thermal and chemical stability and good mechanical properties [43,44].

In this study, copolymer membranes of hydroxyl-containing polyimide and polyimide (HPI-PI) were prepared and thermally rearranged into TR poly(benzoxazole-co-imide) (TR-PBO-PI). HPI-PI copolymers were prepared using 6FDA as the dianhydride, a hydroxyl-containing diamine, either bisAPAF or HAB, and 2,4,6-trimethyl-*m*-phenylenediamine (DAM) as the non-hydroxyl-containing diamine. The rigid structure of polyimide from DAM was introduced to improve membrane performance. The effects of the chemical structure of the TR copolymer membranes and their

precursor polymers on sorption properties were investigated. The gas permeability, diffusivity, and solubility of TR copolymer membranes were characterized to understand the gas transport phenomena of small gas molecules.

2. Experimental

2.1. Polymer preparation

2,2'-Bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (bisAPAF) and 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA) were purchased from Central Glass Co. Ltd. (Tokyo, Japan) and Daikin Industries, Ltd. (Osaka, Japan), respectively. 2,4,6-Trimethyl-*m*-phenylenediamine (DAM) and 3,3'-dihydroxy-4-4'-diamino-biphenyl (HAB) were purchased from Sigma Aldrich Co. (Milwaukee, WI, USA). The monomers, except DAM, were dried at 120 °C under vacuum for 12 h before use. DAM was dried at 40 °C under vacuum for 12 h considering its melting point of 89–91 °C. The reagents *N*-methyl-2-pyrrolidinone (NMP), *o*-xylene, and pyridine, used as solvent and catalysts, were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). All reagents were used as received without further purification.

Precursor copolymers of hydroxyl poly(amic acid) were prepared by polycondensation reactions of dianhydride and diamine, then converted into hydroxyl polyimide by chemical and azeotropic imidization methods using the experimental schemes developed in our previous report [33]. 6FDA as a dianhydride and two kinds of diamines, i.e., hydroxyl diamines (bisAPAF or HAB) and diamines (DAM), were used for copolymerization. Therefore, the precursor polyimide contained hydroxyl groups (or acetate groups by the chemical imidization method) from the hydroxyl diamine moiety. Synthesized copolymer precursors were precipitated in a 3:1 water:methanol solution for more than 12 h to wash residual solvents, and dried at 150 °C under vacuum. The precursors prepared from the chemical and azeotropic imidization methods were named cAcPI-PI and aHPI-PI, respectively.

Precursors were dissolved in NMP and formed into flat sheet membranes by the conventional solvent evaporation method on a clean glass plate and subsequently thermally rearranged into TR copolymer (PBO-PI) membranes. The polyimide precursor membranes were placed in a tubular furnace under an argon atmosphere and heated to 300 °C at a rate of 5 °C/min, held for 1 h to eliminate residual solvents and to complete imidization, then heated to 400 °C at a rate of 5 °C/min and held for 2 h to induce thermal rearrangement. The thermal treatment conditions were determined by TGA analysis in our previous report [41] and confirmed a thermal conversion of over 95% into the TR-PBO-PI structure by 400 °C treatment for 2 h. BisAPAF and HAB were used as hydroxyl diamines to investigate the effect of the diamine structure in terms of bulkiness and rigidity. DAM was used as a diamine with rigid benzene rings and bulky side methyl groups. TR copolymers prepared from cAcPI-PI and aHPI-PI were named cPBO-PI and aPBO-PI, respectively. Precursor polymers and TR polymers prepared from 6FDA, bisAPAF, and DAM combinations were named AD-polymers, i.e., AD-aHPI-PI, AD-cPBO-PI, etc. Precursor polymers and TR polymers prepared from 6FDA, HAB, and DAM were named HD-polymers, i.e., HD-cAcPI-PI, HD-aPBO-PI, etc. The polymer composition, preparation methods, and physical properties of polymers are listed in Table 1, and the general synthesis scheme and polymer structure are described in Fig. 1.

2.2. Gas permeation measurements

The gas permeability and selectivity of TR-PBO-PI membranes and their precursor membranes were determined using a constant

Download English Version:

<https://daneshyari.com/en/article/633813>

Download Persian Version:

<https://daneshyari.com/article/633813>

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