



Synthesis and gas permeation properties of a novel thermally-rearranged polybenzoxazole made from an intrinsically microporous hydroxyl-functionalized triptycene-based polyimide precursor



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ABSTRACT

A hydroxyl-functionalized triptycene-based polyimide of intrinsic microporosity (TDA1-APAF) was converted to a polybenzoxazole (PBO) by heat treatment at 460 °C under nitrogen atmosphere. TDA1-APAF treated for 15 min (TR 460) resulted in a PBO conversion of 95% based on a theoretical weight loss of 11.7 wt% of the polyimide precursor. The BET surface area of the TR 460 (680 m² g⁻¹) was significantly higher than that of the TDA1-APAF polyimide (260 m² g⁻¹) as determined by nitrogen adsorption at -196 °C. Heating TDA1-APAF for 30 min (TRC 460) resulted in a weight loss of 13.5 wt%, indicating full conversion to PBO and partial main-chain degradation. The TR 460 membrane displayed excellent O₂ permeability of 311 Barrer coupled with an O₂/N₂ selectivity of 5.4 and CO₂ permeability of 1328 Barrer with a CO₂/CH₄ selectivity of 27. Interestingly, physical aging over 150 days resulted in enhanced O₂/N₂ selectivity of 6.3 with an O₂ permeability of 185 Barrer. The novel triptycene-based TR 460 PBO outperformed all previously reported APAF-polyimide-based PBOs with gas permeation performance close to recently reported polymers located on the 2015 O₂/N₂ upper bound. Based on this study, thermally-rearranged membranes from hydroxyl-functionalized triptycene-based polyimides are promising candidate membrane materials for air separation, specifically in applications where space and weight of membrane systems are of utmost importance such as nitrogen production for inert atmospheres in fuel lines and tanks on aircrafts and off-shore oil- or natural gas platforms. Mixed-gas permeation experiments also demonstrated good performance of the TR 460 membrane for natural gas sweetening with a CO₂ permeability of ~1000 Barrer and CO₂/CH₄ selectivity of 22 at a typical CO₂ wellhead partial pressure of 10 bar.

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1. Introduction

Membrane-based gas separation is a well-established industrial technology with great potential for a wide diversity of large-scale industrial applications, such as natural gas sweetening, hydrogen recovery, CO₂ separation from flue gas, and air separation [1–3]. It was estimated in 2002 that ~50% of the membrane-based gas separation market was based on onsite nitrogen production from

air [3]. The success of membranes in air separation can be attributed to the ubiquitous clean feed gas, a simple single-stage process design and the delivery of the nitrogen product gas at feed pressure. Commercial polymeric membrane materials, including tetrabromopolycarbonate, Matrimid[®] polyimide and polysulfone, are offering selectivities of ~6–7 that can produce 99% nitrogen but with low oxygen permeability of ~1–2 Barrer [3]. Currently, poly(phenylene oxide) is the most permeable polymer membrane used for commercial air separation with an oxygen permeability of 16 Barrer and O₂/N₂ selectivity of 4.9 [4]. It is interesting to note that these commercial air separation membrane materials fall far below the O₂/N₂ permeability/selectivity trade-off curve reported by Robeson in 1991 [5]. Hence, there is a strong incentive for development of advanced polymers that exhibit better performance for air

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separation. Specifically, in applications where space and membrane system weight limitations play a major role, such as nitrogen blanketing of fuel tanks on aircrafts and oil and natural gas offshore platforms, require polymer membranes with higher permeability without significant loss of O₂/N₂ selectivity compared to commercial air separation membranes.

Polymers of intrinsic microporosity (PIMs), first introduced by Budd and McKeown in 2004, are a rapidly expanding class of amorphous glassy ladder polymers [6,7]. PIMs have an inherent, interconnected porosity with micropores of less than 20 Å resulting from inefficient packing of polymer chains in the solid state [8,9]. PIM-1 (Fig. 1), the prototype of this materials class is a spirobisindane-based ladder polymer, which has a Brunauer-Teller-Emmett (BET) surface of ~860 m g⁻¹, excellent solution processability and thus good thin-film formation properties. Furthermore, PIM-1 and a related bis(phenazyl)-derived spirobisindane ladder polymer (PIM-7) demonstrated very high gas permeability and moderate selectivity for a variety of gas pairs, defining the 2008 upper bound for O₂/N₂ separation [10].

More recently, intrinsically microporous polyimides (PIM-PIs) were developed with performance close to the 2008 upper bounds for several important gas pairs [11–14]. Ghanem et al. [11,12] and Rogan et al. [15] reported the first series of PIM-PIs based on spirobisindane dianhydrides and various diamines, which displayed excellent gas permeability with moderate selectivity. Thereafter, PIM-PIs with enhanced selectivity were prepared with newly designed sterically hindered monomers based on spirobifluorene-, ethanoanthracene-, Tröger's base-, and triptycene-building blocks [12–20]. Recently, our group synthesized TDA1-APAF, a hydroxyl-functionalized triptycene-based PIM-PI (Fig. 1), which exhibited notable performance for O₂/N₂ and CO₂/CH₄ separation [21].

An alternative method to introduce microporosity into glassy polymers is based on the formation of polybenzoxazoles (PBO) by a high-temperature (>400 °C) decarboxylation and rearrangement reaction of polyimide precursors bearing hydroxyl-functional groups in ortho-position to the imide linkages [22]. In 2007, Park et al. reported gas permeation properties of a family of thermally-rearranged (TR) PBO polymers, which exhibited: (i) exceptional CO₂ permeability and good CO₂/CH₄ selectivity, (ii) resistance to plasticization, and (iii) excellent chemical stability [22–24]. Using soluble hydroxyl-functionalized polyimide precursors allows fabrication of hollow fibers using conventional technology and subsequent conversion of the polyimides to PBOs by thermal treatment with desirable transport properties [25,26]. Most TR-derived PBO polymers are based on low-free-volume polyimide precursors made from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6-FDA) and 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF) or 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) [23,24,27–32]. So far, only a few reports described the use of hydroxyl-functionalized intrinsically microporous polyimides (PIM-PIs) as precursors for the formation of PBOs, including spirobisindane- and spirobifluorene-based building blocks [33–36].

Recently, a PBO derived from a low-free-volume triptycene dianhydride/APAF-based polyimide (TPHI) showed commendable gas separation performance. The PBO made by heat treatment of TPHI at 400 °C for 2 h (PBO conversion of 87% based on theoretical weight loss of 9.7 wt% for full conversion) showed CO₂, N₂, and CH₄ permeabilities of 320, 16 and 8.3 Barrer, respectively, combined with CO₂/N₂ and CO₂/CH₄ selectivities of 20 and 39 [32]. Unfortunately, O₂ permeability data were not reported in this work.

Here, we report the synthesis (Scheme 1) and gas transport properties of a TR membrane prepared from a recently reported intrinsically microporous triptycene-based hydroxyl-functionalized PIM-PI [21]. The pristine polyimide was prepared by a one-step polycondensation reaction between a commercial hydroxyl-containing diamine monomer (APAF) and 9,10-dimethyl-2,3,6,7-triptycene tetracarboxylic dianhydride (TDA1) monomer, as previously reported by our group [21,37]. The TR membranes were characterized by FTIR, BET, XRD and TGA measurements. Additionally, pure and mixed-gas permeation properties of pristine TDA1-APAF and TDA1-APAF-derived TR membranes (fresh and physically aged) were performed to demonstrate their potential as highly permeable and selective membranes for air and natural gas separation applications.

2. Experimental

2.1. Materials

The compounds 1,2-dimethoxybenzene, 2-aminobenzoic acid, trifluoromethanesulfonic anhydride, acetic anhydride, 1,1'-bis(diphenylphosphino)ferrocene, tris(dibenzylideneacetone) dipalladium(0), boron tribromide (BBr₃), zinc cyanide, potassium hydroxide, and isoquinoline were obtained from Aldrich and used as received. 9,10-Dimethyl-2,3,6,7-triptycene tetracarboxylic dianhydride (TDA1) monomer was synthesized as previously described [37]. The monomer 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF) was purchased from Aldrich and purified by vacuum sublimation at 220 °C. *m*-Cresol was distilled under reduced pressure and stored under nitrogen in the dark over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used as received [21].

2.2. Polymer characterization of pristine and thermally rearranged TDA1-APAF membranes

Fourier transform infrared (FTIR) measurements were carried out using a Varian 670-IR spectrometer. Thermogravimetric analysis (TGA) was performed with a TG 209 F1 (Netzsch) coupled with a NETZSCH QMS 403 C Aëolos[®] mass spectrometer (MS) under nitrogen atmosphere with a heating rate of 5 °C/min up to 800 °C. The BET surface areas of the pristine TDA1-APAF and TR 460 were determined by N₂ sorption at –196 °C using a Micromeritics ASAP-2020. Powder samples were degassed under high vacuum at 120 °C

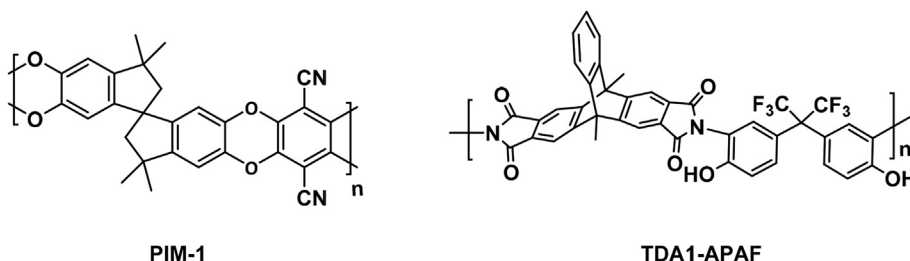


Fig. 1. Structures of PIM-1 and OH-functionalized PIM-PI (TDA1-APAF).

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