



# Ethylene/ethane permeation, diffusion and gas sorption properties of carbon molecular sieve membranes derived from the prototype ladder polymer of intrinsic microporosity (PIM-1)



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## ABSTRACT

Fine-tuning the microporosity of PIM-1 by heat treatment was applied to develop a suitable carbon molecular sieve membrane for ethylene/ethane separation. Pristine PIM-1 films were heated from 400 to 800 °C under inert N<sub>2</sub> atmosphere (< 2 ppm O<sub>2</sub>). At 400 °C, PIM-1 self-cross-linked and developed polar carbonyl and hydroxyl groups due to partial dioxane splitting in the polymer backbone. Significant degradation occurred at 600 °C due to carbonization of PIM-1 and resulted in 30% increase in cumulative surface area compared to its cross-linked predecessor. In addition, PIM-1-based CMS developed smaller ultramicropores with increasing pyrolysis temperature, which enhanced their molecular sieving capability by restricted diffusion of ethylene and ethane through the matrix due to microstructural carbon densification. Consequently, the pure-gas ethylene permeability (measured at 35 °C and 2 bar) decreased from 1600 Barrer for the pristine PIM-1 to 1.3 Barrer for the amorphous carbon generated at 800 °C, whereas the ethylene/ethane pure-gas selectivity increased significantly from 1.8 to 13.

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## 1. Introduction

Ethylene/ethane separation is accomplished through equilibrium-based energy-intensive distillation processes [1]. Alternatively, membrane technology could offer substantial savings to this application because membranes do not require a phase change for the separation of the feed components [2]. In recent years, gas separation with membranes has successfully found large-scale commercial use for natural gas upgrading and nitrogen production from air [3,4]. To date, however, polymer membranes have not reached the minimum requirements for viable ethylene/ethane separation due to: (i) insufficient selectivity (e.g. ~3–6 under ideal pure-gas permeation conditions) and low permeability [5–10] and (ii) potential penetrant-induced plasticization leading to reduced mixed-gas selectivity [9]. The former issue can be addressed by rational design of the pore size and pore distribution (PSD) of the membrane material, while the latter demands materials that can withstand the high activities of the ethylene/ethane feed under realistic industrial conditions.

Intrinsically microporous polymers (PIMs) represent the state-of-the-art among known solution-processable organic membrane

materials for gas separation [11–16]. PIMs often define the permeability/selectivity performance upper bounds of gas transport through polymers [17] as defined by Robeson [18,19] by virtue of their contorted and rigid polymer backbones that allow them to capitalize on interconnected pore sizes of less than 2 nm [20,21]. The prototype of the ladder-type PIM-family, PIM-1, was synthesized by polycondensation reaction of 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane and tetrafluoroterephthalonitrile. The polymer structure is shown in Fig. 1. The tetrahedral-spirobisindane moiety in its backbone promotes inefficient packing of its chains in the solid state [12,20,22]. Although the gas separation performance of PIM-1 has been placed on the upper bounds for several gas pairs, such as O<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/CH<sub>4</sub>, it is an inadequate material for ethylene/ethane separation with a high ethylene permeability of 573 Barrer but very low ethylene/ethane selectivity of 1.4 (measured at 25 °C and 1 atm) [23].

To achieve higher selectivity, the PSD in PIM-1 can be tailored by chemical and/or thermal means to potentially improve its gas separation properties. One possibility simply requires post-synthesis addition of functionalities to the polymer matrix to increase inter- and intra-chain interactions [24], which leads to enhanced densification of the polymer micropore structure. For example, the nitrile groups in PIM-1 can be substituted with polar moieties, such as carboxyl, amidoxime, thioamide or tetrazole, to enhance its permselectivity [24–27]. Another relevant approach to

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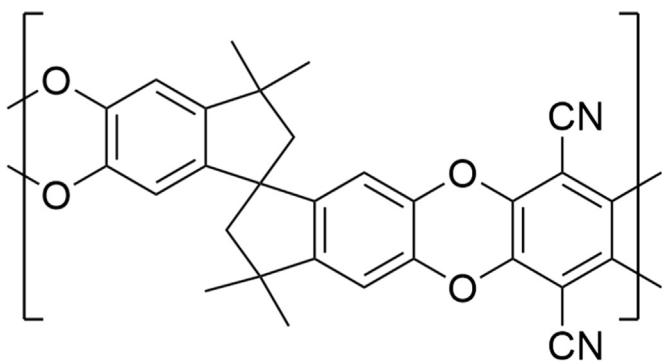


Fig. 1. Chemical structure of PIM-1.

densify the PSD of PIM-1 is via thermal annealing [28–32] or by further heat treatment so that specific chain degradation reactions are triggered. For example, PIM-1 self-cross-linked under vacuum at 300 °C showed a 400% increase in CO<sub>2</sub>/CH<sub>4</sub> pure-gas selectivity, reportedly via triazine formation [33]. A different mechanism was proposed in a subsequent study [34], where it was reported that O<sub>2</sub> was responsible of covalently bridging the PIM-1 chains starting at heat treatment around 300 °C. Fine-tuning of the microporosity in PIM-1 was performed by varying the O<sub>2</sub> content in the heating atmosphere (< 200 ppm) available prior to the onset of the polymer backbone decomposition (i.e. < 450 °C).

Pyrolysis of a polymer beyond its initial decomposition temperature under essentially inert conditions produces carbon molecular sieve (CMS) membranes, which can display outstanding gas separation performance [35]. CMS have strongly size-sieving PSDs by virtue of their large array of ultramicropores (i.e. < 0.7 nm) [36], which are instrumental in distinguishing permeants based on the small differences of their molecular dimensions [37]. Furthermore, CMS membranes may be stable under harsh hydrocarbon saturated atmospheres, as demonstrated in previous studies [38,39]. However, in spite of their promising properties, only a few studies of CMS membranes have been reported for ethylene/ethane separation [38,40–45].

The CMS separation performance is controlled by a wide variety of parameters involved in the pyrolysis process. For example, the heating protocol [46–48] and the atmospheric composition [43,49–51] may lead to distinctly different microstructures in the CMS. Furthermore, the gas permeation properties of CMS membranes are also influenced by several polymer-precursor-determined properties: (i) pendant groups [52,53], (ii) glass transition temperature [54], and (iii) free volume [53,55,56]. PIM-1 represents an extreme case in all of these categories as it possesses polar cyanide groups, undetectable glass transition temperature and, at the same time, it is one of the most permeable glassy polymers known to date due to its high free volume [57]. To the best of our knowledge, there is no rigorous assessment available for the gas transport properties of CMS membranes generated from the spirobisindane-ladder prototype PIM-1. Here, ethylene and ethane sorption, diffusion and permeation data are reported for the first time in partially and fully carbonized membranes derived via thermal treatment from pristine PIM-1 films.

## 2. Experimental

### 2.1. Materials and characterization

Pristine PIM-1 was synthesized according to a previously reported procedure by Du et al. [58]. The molecular weight of PIM-1 was determined by gel permeation chromatography (Malvern HT-

350). The  $M_n$  was  $6.9 \times 10^4$  g/mol with a PDI of 2.42. A thermogravimetric analyzer (TGA, TA Instruments) was used to measure sample weight loss as a function of pyrolysis temperature. Evolved gases were identified with a quadrupole mass spectrometer (Hiden Analytical) coupled to the TGA with N<sub>2</sub> as the carrier gas. Fourier transform infrared (FTIR) spectra were acquired using a Thermo Nicolet iS10 infrared micro-spectrometer. X-ray diffraction (XRD) scattering was conducted on a Bruker D8 Advance diffractometer. Raman spectra of the carbonized films were obtained with a Horiba LabRam HR visible microscope. The internal structure of the samples was studied by CO<sub>2</sub> sorption at 0 °C using a Micromeritics 2020. The pore size distribution was calculated using the nonlocal density functional theory (NLDFT) model assuming a carbon-slit pore geometry using the software version 4.02 provided by Micromeritics.

### 2.2. Dense PIM-1 films fabrication and thermal annealing at 250 °C

Dense PIM-1 films were made by slowly evaporating 3% w/v polymer/THF solutions from a covered glass Petri dish under ambient conditions. The resulting  $100 \pm 10$  μm films (as measured with a digital micrometer) were then air dried for 12 h, methanol soaked for 12 h, and finally thermally annealed at 250 °C for 24 h under vacuum. The densities of the films of known thickness were determined gravimetrically by measuring the weight of the samples using a microbalance (Mettler Toledo) as well as their area with a scanner.

### 2.3. Cross-linking and carbonization of PIM-1 films

Round 25 mm diameter films of thermally annealed PIM-1 films were placed inside a Carbolite three-zone tube furnace in a quartz tube supplied with 1000 cm<sup>3</sup>(STP)/min of N<sub>2</sub> from a mass flow controller. The temperature was measured with a thermocouple adjacent to the sample. The concentration of oxygen exiting the furnace was measured with a Cambridge Sensotec Rapidox 3100 and confirmed to be less than 2 ppm at all times. The furnace temperature was ramped at 3 °C/min and then held isothermally for 30 min for each thermal stage, leading to: (i) cross-linking at 400 °C and (ii) CMS formation at 600 and 800 °C, respectively. After the isothermal soak, the furnace was allowed to cool down to room temperature. The gas permeation properties of the films were immediately tested after removal from the furnace. These measures were used to ensure data reproducibility.

### 2.4. Gravimetric sorption

Ethylene and ethane sorption isotherms in the pressure range from 1 to 15 bar were determined at 35 °C with a Hiden IGA apparatus. Gas sorption in organic glassy polymers can be described by the dual-mode sorption model [59]:

$$C = K_D p + \frac{C_H b p}{1 + b p}$$

where  $C$  is the total gas concentration in the glassy polymer,  $K_D$  is the Henry's law coefficient,  $C_H$  is the Langmuir hole capacity,  $b$  is the interaction parameter, and  $p$  is the gas pressure. Gas isotherms of carbon materials are typically expressed by the Langmuir model [60]:

$$C = \frac{C_H b p}{1 + b p}$$

The average gas solubility can be calculated for a fixed thermodynamic state as:

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