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## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

# In situ restoring of aged thermally rearranged gas separation membranes



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## ARTICLE INFO

## Article history:

Received 25 May 2016

Received in revised form

13 July 2016

Accepted 13 July 2016

Available online 15 July 2016

## Keywords:

Thermally rearranged polymer membrane

Aging

Restoring

## ABSTRACT

Physical aging in high free-volume polymer membranes is one of the main hurdles limiting their application in gas separation. The recovery of membrane separation properties without the need to disassemble the module, although challenging, would provide significant advantages for applications in various fields. In this work, an in situ restoring procedure for the recovery of mass transport in aged membrane modules made of thermally rearranged polymer membranes was developed in which the modules were exposed to methanol at 80 °C. The thermally rearranged hollow fiber membrane modules were subjected to long-time operation to investigate their aging: the CO<sub>2</sub> and N<sub>2</sub> permeances were monitored at different temperatures, pressures, and feed compositions over a total period of 727 days with two long-time runs of 185 and 263 days, interspersed by a stand-by period of 240 days, and with each run followed by a restoring. In both long-time runs, CO<sub>2</sub> and N<sub>2</sub> permeance dropped as a result of aging, whereas the selectivity remained nearly constant. The permeances were fully recovered after the proposed restoring procedure was applied, demonstrating its efficacy and repeatability for membrane aging recovery, even for an extremely aged membrane exposed to various conditions for nearly two years.

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## 1. Introduction

Membranes made from high free volume polymers, such as polymers with intrinsic microporosity (PIMs), thermally rearranged (TR) polymers, and Tröger's base polymers, are today considered as candidates of choice for low-energy gas separation owing to their high permeability and good selectivity coupled with easy processability and good mechanical properties. Contrary to most polymers, whose performance is limited by the Robeson trade-off, these polymers approach or in some cases exceed such upper bounds for several gas pairs, exceeding the limit within the region of high permeability and medium selectivity. However, their advantages are offset by their rapid performance drop during aging, namely their declines in separation performance, especially in terms of permeability. This phenomenon is mainly related to the fact that glassy polymers are not at a thermodynamic equilibrium and tend to relax over time, densifying the polymer chains and thus reducing the excess free volume [1–5]. In high free-volume

polymers, this phenomenon can be much more severe than in conventional low free-volume polymers. As clearly elucidated by Pinnau et al. [6], physical aging occurs in all PIMs owing to the high free volume brought about by their greater backbone rigidity, which serves as a driving force for more extensive and rapid physical aging of the bulk microstructure. A similar phenomenon can be expected for TR polymers due to their high excess free volume. TR polymers with microporous structures have attracted much interest for many industrial applications in gas separation. Membranes prepared with TR polymers show excellent separation performance owing to their complex microstructures, whose cavity size and distribution can be tuned by means of the choices of template molecules and thermal treatment protocols [7–12]. The ready control available over the average interchain spacing and the free volume distribution leads to targeted size-sieving effects that can promote specific separations [11]. Moreover, in the applications of these membranes for CO<sub>2</sub> separation [13,14], which is a much more condensable gas than the permanent gases present in mixtures (N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, etc.), CO<sub>2</sub> preferentially occupies Langmuir sorption sites, thereby reducing the sorption capacity for permanent gases in the surrounding region, and thus decreasing the permanent gases' solubility in the polymer [15]. Additionally, CO<sub>2</sub> sorbed onto Langmuir sites creates a blocking effect that slows

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the diffusion of light gases, thus decreasing the polymers' permeability for these gases [16].

In our previous work [17], we demonstrated the suitability of this type of polymer membrane for CO<sub>2</sub> separation from flue gas streams, specifically considering a ternary mixture of composition similar to that of flue gas in humidified conditions. Even under high relative humidity and temperature, the TR hollow fiber membranes still performed well in gas separation, confirming their good performance despite the presence of water vapor.

However, various studies have demonstrated substantial aging over time for TR membranes [18,19] and this performance decline has been found to be much faster for asymmetric membranes with thin selective layers. This is a fundamental aspect to be taken into account, because asymmetric membranes with thin selective layers, and those of hollow fiber geometry in particular, are preferred for industrial applications, in order to maximize the permeation flux and therefore to minimize the required footprint [20].

Various approaches have been proposed to suppress or, at least, to limit the extent of physical aging in polymer membranes, including the use of polymer blends [21,22], thermal cross-linking [23], UV cross-linking, [24] and the addition of nanoparticles [4,25,26]. The former three treatments may reduce the aging rate but tend to worsen the permeability or selectivity, whereas the latter can modify the microstructure of the membrane matrix, influencing the free volume distribution and hindering the densification of the polymer matrix.

An innovative approach to allow wider use of these membrane types, including large-scale implementation, is to develop membrane modules that can be reused extensively with periodic restoring of their separation properties. This would represent an important asset for prolonging the lifetime of TR hollow fiber membranes, an option that is particularly attractive from an application perspective.

Already in the past in-situ regeneration methods were developed specifically for carbon membranes also in hollow fiber module configuration by Koros [27,28] and Hägg [29] et al. Thermal and chemical treatments, N<sub>2</sub>-purge, propene purge are among these methods. Moreover, prior literature has demonstrated that methanol soaking of some polymer membranes reversed the effect of physical aging for highly permeable glassy polymers, effectively resetting their history [30–32].

In this work we proposed an in situ restoring procedure for TR hollow fiber membrane module using methanol. Previously described restoring approaches have included disassembly of hollow fibers and soaking in a methanol bath; contrastingly, in the present approach we directly injected methanol into aged membrane modules without any disassembly. To the best of our knowledge, no such in situ restoring technique has been explored in previous literature. To address the viability and repeatability of this procedure, the CO<sub>2</sub> and N<sub>2</sub> permeances of the TR membrane module were monitored over a period of 727 days, split into two runs of 185 days and 263 days under continuous exposure to feed gas. The two runs were interrupted by a stand-by period of 240 days and two restoring steps after the first and the second runs. The membrane aging behavior was analyzed using single gases and gas mixtures (both dried and humidified), and the impact of water clustering on aging was also evaluated. The restoring procedure was thoroughly assessed and optimized, and the optimized procedure fully recovered the pristine separation properties of the TR hollow fiber membrane modules. It should be noted that this work is solely focused on restoring membrane performance by means of a simple in situ treatment; we do not presently attempt to explain the chemical/physical action of methanol upon the membrane matrix.

## 2. Materials and methods

### 2.1. Membrane preparation

The precursor used for TR polymeric hollow fiber membrane preparation was a hydroxypolyimide (HPI, synthesized in-house) with the chemical structure shown in Fig. 1. Precursor HPI hollow fiber membranes were fabricated and then subjected to thermal treatment to convert the HPI into thermally rearranged polybenzoxazole (TR-PBO, Fig. 1). The fabrication protocols used are described in detail elsewhere [12,33–35]; the fibers thus obtained had selective layers ca. 0.5–1 μm thick.

### 2.2. Evaluation of mass transport properties

The mass transport properties of the TR polymeric hollow fiber membrane module were measured for a prolonged period, alternating the supply of single gases and gas mixtures containing CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>, with temperatures ranging from 25 to 75 °C and pressures between 2 and 6 bar. The feed gas was also passed through a humidifier to manipulate the humidity. The experimental apparatus is schematically illustrated in Fig. 2.

The hollow fiber membrane module, which had an active membrane area of ca. 70 cm<sup>2</sup>, was placed in a low-temperature furnace to keep it at a constant temperature. To maintain the desired feed flow rate, gas streams (both single-gas and mixed-gas) were fed through an in-line mass flow controller upstream of the hollow fiber module. A back pressure regulator and a pressure gauge on the retentate line were used to maintain the desired transmembrane pressure difference in the module. The retentate and permeate flow rates were measured by two soap film bubble flow meters, one for each line. To provide humid gases, the feed stream was fed into a humidifier upstream of the module, held at the same temperature and pressure as the membrane, to assure stream saturation. Three humidity sensors on the feed, retentate, and permeate lines were used to measure the relative humidity of each stream during the long-time measurements.

The hollow fiber membrane module was exposed to a gas stream at all times (except during the stand-by period); nitrogen was pumped into the module to maintain a transmembrane pressure difference of 1 bar when no experiment was being performed. Prior to any change in the feed gas type, the module was opportunely “washed” by feeding the gas of interest for 30 min before measurement was resumed. The membrane separation performance was evaluated in terms of the selectivity (Eq. (1)) and permeance (Eq. (2)) under the permeation driving force expressed by Eq. (3).

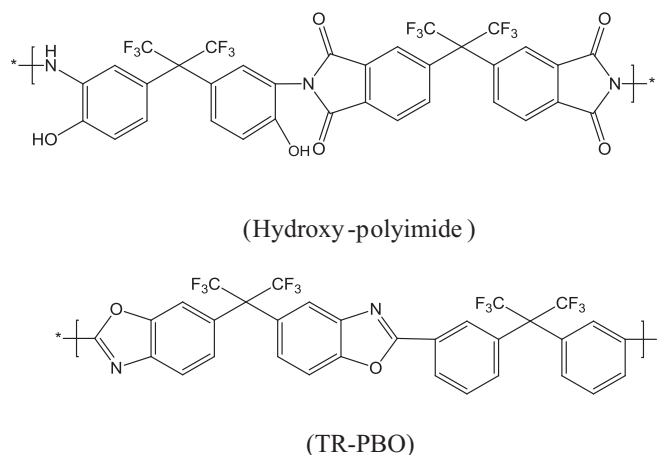


Fig. 1. Chemical structures of the HPI precursor and TR-PBO polymer.

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