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Plasticization-resistant hollow fiber membranes for CO_2/CH_4 separation based on a thermally crosslinkable polyimide

Chien-Chiang Chen[a], Wulin Qiu[a], Stephen J. Miller[b], William J. Koros[a,*]

[a] School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332-0100, United States
[b] Chevron Energy Technology Company, 100 Chevron Way, Richmond, CA 94802-0627, United States

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ABSTRACT

Decarboxylation-induced thermal crosslinking has been demonstrated to be effective for stabilizing membranes against plasticization in dense films. This study extends this promising crosslinking approach from dense films to industrially relevant asymmetric hollow fiber membranes. Crosslinkable asymmetric hollow fiber membranes were spun from a carboxylic acid containing polyimide, 6FDA-DAM:DABA. Dope and spinning conditions were optimized to obtain fibers with a defect-free selective skin layer. It is found that slightly defective fibers suffered severe selectivity loss after thermal crosslinking, suggesting that defect-free property is essential to the performance of the resulting crosslinked hollow fiber membranes. The crosslinked fibers were tested for CO_2/CH_4 separation. The excellent plasticization resistance under high pressure feeds (with highest CO_2 partial pressure of 400 psia) suggests that these robust membranes are promising for aggressive natural gas purification.

1. Introduction

Oil, natural gas and coal are by far the most important energy source, accounting for more than 80% of the energy consumption in U.S. Of these three fossil fuels, natural gas has the smallest CO_2 footprint, and natural gas is an abundant U.S. resource. About 90% of natural gas consumption in U.S. is met by domestic production [1], thereby providing a secure, reliable and relatively environmentally friendly energy resource.

Raw natural gas contains mostly CH_4, but also contains various amounts of impurities such as CO_2, N_2, H_2S, H_2O, and heavy hydrocarbons. Carbon dioxide is the most abundant impurity in many wells and must be reduced to meet pipeline specification. The removal of CO_2 alleviates the risk of pipeline corrosion, increases the heating value of the natural gas and reduces compression costs. Acid gas (CO_2 and H_2S) removal from natural gas is currently one of the largest industrial membrane gas separation applications. High energy efficiency, low capital, operating and maintenance costs make membranes an attractive approach for acid gas removal. Moreover, the compact and robust nature of hollow fiber membrane modules is desirable for offshore and remote applications. Polymer membranes are currently the most attractive option because of their cost and processability advantages over zeolite or ceramic membranes. The use of polymer membranes is limited by swelling-induced performance losses in aggressive feeds with high CO_2 content and heavy hydrocarbons; therefore, more robust membranes are needed.

This paper describes robust asymmetric hollow fiber membranes for CO_2 removal from natural gas, and in some cases CO_2 content of the natural gas stream can be higher than 70%. Membranes that exhibit plasticization resistance in CO_2 have been shown to have plasticization resistance to other contaminants such as aromatics [2–4]. Plasticization-resistant polyimide membranes may allow these polyimides to maintain attractive separation performance not only in natural gas but also in refinery and petrochemical industries, such as olefin/paraffin [5] and aromatic/aliphatic separation [6].

2. Background and theory

2.1. Membrane transport theory

Gas transport in nonporous polymer membrane is described by the solution-diffusion theory. A gas penetrant sorbs into the feed side of the membrane, then diffuses through the membrane, and finally desorbs into the permeate stream.

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* Corresponding author. Tel.: +1 404 385 2845; fax: +1 404 385 2683.
E-mail address: bill.koros@chbe.gatech.edu (W.J. Koros).

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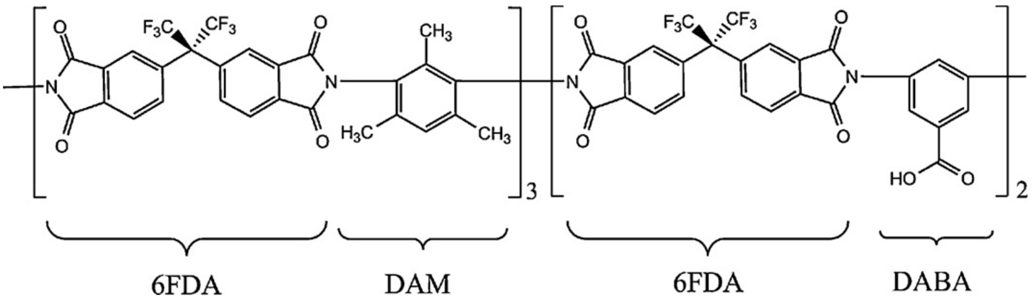

Fig. 1. Chemical structure of 6FDA-DAM:DABA (3:2).

Permeability and selectivity are the two key intrinsic properties commonly used to evaluate the membrane performance. Permeability is a measure of membrane productivity and is defined as the flux (N_A) thorough the membrane normalized by fugacity driving force (Δf_A) and the thickness (l) of the membrane:

$$P_A = \frac{N_A \cdot l}{\Delta f_A} \tag{1}$$

The fugacity coefficients of CO_2 and CH_4 in the binary mixtures were estimated from the virial equation of state truncated after the second coefficient [7]. The most common unit for permeability is "Barrer", which is defined as

$$1 \quad \text{Barrer} = 1 \times 10^{-10} \frac{\text{cm}^3(\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}} \tag{2}$$

In the case of asymmetric membranes, where the thickness of the selective layer is not well defined, the membrane productivity is characterized by permeance, which is the fugacity driving force normalized flux:

$$\left(\frac{P}{l}\right)_A = \frac{N_A}{\Delta f_A} \tag{3}$$

Permeance is typically expressed in "Gas Permeation Unit" (GPU), which is defined as

$$1 \quad \text{GPU} = 1 \times 10^{-6} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}} \tag{4}$$

Membrane efficiency is evaluated by selectivity, which is defined as the ratio of the gas permeabilities or permeances:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \tag{5}$$

2.2. Plasticization and stabilization strategy

One of the major problems with polymer membranes in natural gas separation is plasticization, which is usually caused by high pressure CO_2 and heavy hydrocarbons. Plasticization occurs when these plasticizing components swell and dilate the polymer matrix, increasing the mobility of polymer chain segments, thereby increasing the diffusion coefficients of all penetrants in the membrane. The phenomenon on the macro scale reflects a softening and a depression of the glass transition temperature of the material, while on the chain segmental scale it reflects an increase in mobility and permeability but a reduction in selectivity [8]. Plasticization behavior of membranes is commonly characterized by a permeation isotherm (permeability or permeance versus pressure plot) [9–13]. An upswing in permeability is a typical indication of swelling and plasticization. The plasticization pressure is defined as the pressure at which the permeability starts to increase with increasing pressure [8,13]. Testing membranes with mixed gas feeds at relevant high pressure is important when penetrants (such as CO_2) can act as plasticizers. Unfortunately, most CO_2/CH_4 selectivities reported in the literature are obtained from pure gas permeation ("ideal" selectivity), or mixed gas permeation conducted at low feed pressure (less than 200 psia). Moreover, most plasticization studies are carried out using thick dense films (typically ~50 μm). On the other hand, most commercial gas separation membranes have an asymmetric morphology that contains a thin selective layer (typically less than 1 μm). Thin films have been shown to have different and more severe plasticization behaviors as compared to thick dense films of the same materials [12,14,15]. In thin films, plasticization usually occurs immediately without the initial drop in the permeability versus pressure plot, especially for the very thin polymer layers such as those found in asymmetric hollow fibers [16–19]. Since plasticization effects are significantly pronounced in thin membrane structures, the suppression of plasticization is especially important for asymmetric membranes.

Several approaches such as thermal treatment [11,20,21], polymer blending [22], semi-interpenetrating polymer networks [23] and crosslinking [16–18,24–27] have been applied to suppress plasticization. In this study, a recently discovered crosslinking approach [28] is implemented to address the issue of plasticization-induced selectivity losses. The crosslinkable polyimide used in this work is shown in Fig. 1 and the

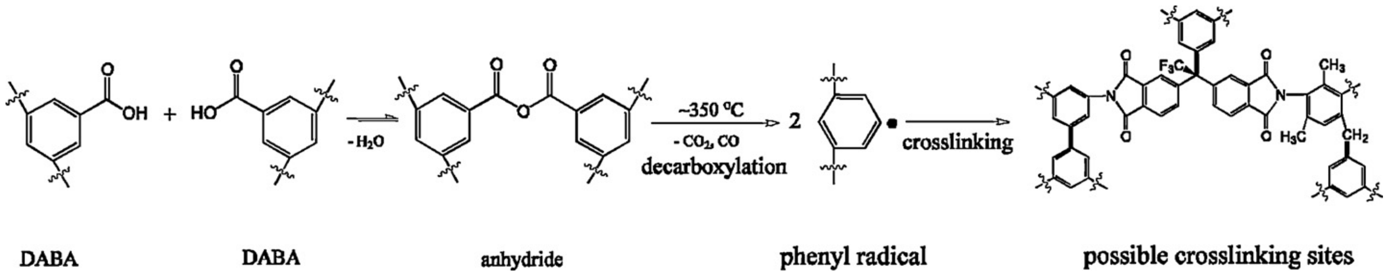

Fig. 2. Decarboxylation-induced thermal crosslinking mechanism. Bold lines are crosslinking bonds.