Chemically cross-linkable polyimide membranes for improved transport plasticization resistance for natural gas separation

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ABSTRACT

A series of cross-linkable membrane materials based on the 6FDA-DAM:DABA (3:2) polyimide with enhanced transport plasticization resistance were synthesized to separate CO_2 from CH_4. Glycidol was used as a cross-linking agent to modify 6FDA-DAM:DABA (3:2) efficiently and form a transesterification reaction-based cross-linking. The conversion was calculated by solution ^{1}H NMR. These materials were also characterized via density, glass transition temperature, permeation, and sorption measurements. Pure (CO_2, CH_4) and mixed gas (CO_2/CH_4) permeation was studied on dense films of these materials up to 700 psia (1000 psia) for pure CO_2 (50%:50% CO_2:CH_4 mixed gas) feed. Compared to the 6FDA-DAM:DABA (3:2) membrane, CO_2-induced plasticization resistance for cross-linked membranes was enhanced in aggressive feed streams. Under CO_2 feed conditions at 35 °C, plasticization for the 41% glycidol-modified cross-linked membrane was not observed up to approximately 450 psia. Glycidol-induced cross-linking offers an excellent balance of selectivity, permeability, and plasticization resistance. The glycidol-modified 6FDA-DAM:DABA (3:2) is competitive with the earlier reported 1,3-propanediol modified materials. Possible issues such as resistance to contaminants may be final determinants in choice of approach; however, this topic was beyond the scope of the current study.

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1. Introduction

Natural gas usage has increased rapidly because of the growing global population and industrial activity. Natural gas consumption is predicted to increase by 64% from 113 trillion cubic feet in 2010 to 189 trillion cubic feet in 2040. Because of its lower carbon intensity compared with coal and oil, natural gas is expected to be the preferred fuel for the electric power and industrial sectors to reduce greenhouse gas emissions [1]. Natural gas is mostly methane (CH_4), 75–90% of the total. Raw natural gas also contains CO_2, water, H_2S, hydrocarbons (C_{3+}), and other gases. CO_2, which contributes to corrosion of pipelines, is the most common contaminant and needs to be removed to meet pipeline specifications [2]. The removal of CO_2 from raw natural gas is an important step in natural gas processing.

Currently, aqueous amine absorption processes are the dominant purification technologies for CO_2 and H_2S and can significantly reduce CO_2 and H_2S (<2% CO_2, <4 ppm H_2S). However, these processes require large capital investment to construct absorption towers and incur high maintenance and operation costs. Operations must be carefully monitored and large amounts of absorbent materials are required. On the other hand, compared to conventional gas separation processes, polymeric membrane-based processes offer several benefits due to low capital investment, simple operation, low maintenance, and small footprint [2,3]. Membrane technologies also provide some options for the bulk removal of CO_2 and other impurities through hybrid absorption-membrane processes [3].

Currently, commercially available polymers for gas separation membranes are glassy polymers, such as polysulfones, cellulose acetates, and polyimides. Glassy polyimides are rigid and thermally stable polymers that can be synthesized from a wide variety of diamines and dianhydrides. In particular, the large array of 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)-based polyimides has been investigated because they offer high common solvent solubility, are amenable to hollow-fiber spin process applications, and have good mechanical properties. They also have excellent intrinsic CO_2/CH_4 separation properties, i.e., high productivity and selectivity [4–13]. The introduction of a $-C(CF_3)$ group tends to increase the fractional free volume (FFV) in the polymer matrix, thereby providing high productivity and

restricting the torsional motion of neighboring phenyl rings, which results in high selectivity of CO_2/CH_4 [13,14].

Despite these attractive features, polymeric membrane performance is limited and challenged by so-called "transport plasticization", or "plasticization" for short. In transport plasticization more subtle effects are involved than in traditional large scale mechanical property plasticization. For transport plasticization referred to here, only very localized regions around a given penetrant are affected by small degrees of swelling. When polymer membranes are exposed to high-pressure, the presence of more condensable gases, such as CO_2 and H_2S, leads to excess swelling of the polymer chains and increases the segmental mobility. The swelling results in a loss of size and shape discrimination, causing significant reduction of separation properties [15].

To enhance plasticization resistance, thermally and chemically cross-linked polymeric membranes have been developed for the separation of CO_2/CH_4 [16–19]. Recently, our group has investigated sub-T_g thermally annealed 6FDA-2,4,6-trimethyl-1,3-diaminobenzene (DAM):3,5-diaminobenzoic acid (DABA) (3:2) membranes. The chemical structure of 6FDA-DAM:DABA (3:2) is shown in Fig. 1. Thermal annealing at 350 °C leads to decarboxylation-induced cross-linking, which can stabilize membranes against swelling and plasticization in aggressive feed streams [16]. We have also developed ester cross-linked 6FDA-DAM:DABA (3:2) membranes by using 1,3-propanediol (PDMC, monoester cross-linking) as a chemical cross-linking agent. These membranes show an excellent balance of selectivity, permeability, mechanical properties, and anti-plasticization [18]. The chemical structure of PDMC polyimide is also shown in Fig. 1. Moreover, high performance asymmetric hollow-fiber membranes using PDMC polyimide have been developed. Asymmetric hollow fibers are industrially preferred in gas separation technology due to the high surface area to volume ratio [20,21].

The current paper explores an alternative cross-linking approach to the previously reported PDMC polyimide membranes [18,20,21].

The PDMC polyimide synthesis is performed via monoesterification. This reaction proceeds by adding a cross-linking agent to a polyimide solution. However, because of low reactivity, an excess amount of PDMC (40–70 times stoichiometric amount) is required to achieve high conversions [18,20]. To achieve the economics of scale required to synthesize these materials in a cost-effective manner, a simpler reactive modification process is preferable.
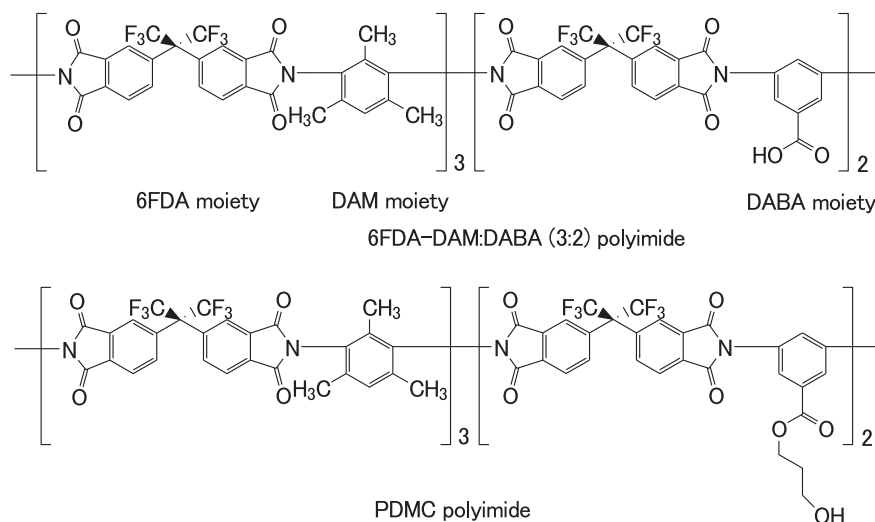

Fig. 2. Chemical structure of glycidol.

Therefore, a series of cross-linkable membrane materials based on 6FDA-DAM:DABA (3:2) polyimides were synthesized. Glycidol (Fig. 2) was chosen as a cross-linking agent to modify the 6FDA-DAM:DABA (3:2) efficiently. It can be predicted that the epoxy group of glycidol would react with the carboxyl group of the DABA moiety in 6FDA-DAM:DABA (3:2) (Fig. 4) and the glycidol-modified 6FDA-DAM:DABA (3:2) would form transesterification-based cross-linking via thermal treatment at high temperatures. The cross-linked polymer membranes were also expected to improve plasticization resistance by reducing the segmental mobility of polymer chains.

The chemical structures of the cross-linkable polymer materials were characterized by ^1H NMR. The membranes were also characterized via solubility, glass transition temperature (T_g), density, permeation, and sorption measurements. Pure gas (CO_2, CH_4) and mixed gas (CO_2/CH_4) permeation tests were performed on the dense films of these materials up to 700 psia for pure CO_2 and 1000 psia for 50%:50% CO_2:CH_4 gas feeds to enable comparison with previously reported PDMC materials [18].

2. Background and theory

Polymeric membrane performance is characterized by permeability and selectivity. Permeability is a measure of the membrane's intrinsic productivity, and selectivity is a measure of the separation efficiency. The permeability (P_i) of component i through a dense polymeric membrane is defined as the flux (n_i) normalized by the difference in partial pressure (Δp_i) and the thickness of the membrane (l), as described in Eq (1).

$$\mathbf{P}_i = \frac{(n_i \cdot l)}{\Delta p_i}. \tag{1}$$

Under a high-pressure gas stream containing highly non-ideal gases, such as CO_2 and H_2S, the fugacity driving force must be substituted for the partial pressure difference due to the behavior of non-ideal gases. For dense film membranes, the permeability (P_i) is defined as the flux (n_i) normalized by the fugacity driving force (Δf_i) and the thickness of the membrane (l), as shown in Eq (2).

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