



Cardo-type random co-polyimide membranes for high pressure pure and mixed sour gas feed separations

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ABSTRACT

A series of aromatic random co-polyimide membranes based on 6FDA-Durene/CARDO backbone with varying content of CARDO moiety (3:1; 1:1 and 1:3) were synthesized for enhanced acid gas separation performance. Gas transport properties of pure and mixed gas streams consisting of H₂S, CO₂, He, CH₄, N₂ and C₂H₆ through the dense films of the co-polyimide were studied. Mixed sweet gas tests were done with feeds containing no H₂S up to 55 bar, while mixed sour gas measurements were conducted with feeds containing H₂S up to 34 bar for 10% H₂S and 20% H₂S. The membranes exhibit very attractive pure gas transport properties, as CO₂ permeability and CO₂/CH₄ selectivity are up to 323 barrer and 35 respectively. Furthermore, the transport properties of sour gas mixture consisting of five gases were also found attractive, as the CO₂/CH₄ and H₂S/CH₄ ideal selectivities are in the range of 18–23 and 19–21 respectively; while CO₂ and H₂S permeabilities are in the range of 38–51 and 40–47 barrers respectively for 20% H₂S in the gas mixture. These values and separation performance exhibited by the co-polyimide are comparable and very competitive even, as compared to the values obtained in some of the high performance polymeric membranes that have been reported in the literature. The stability of the random co-polyimide 6FDA-Durene/CARDO membrane under these aggressive environments is quite remarkable.

1. Introduction

For many decades, natural gas (NG) has been a popular energy source and its demand as an efficient fuel is continuously increasing worldwide [1]. Most of the gas reserves around the world are of low-quality with high contents of impurities, which include acid gas (carbon dioxide (CO₂) and hydrogen sulfide (H₂S)), water, heavy hydrocarbons (C₃+) and other contaminants such as helium, nitrogen, mercaptans etc. For NG to meet the sales gas specification, these contaminants especially acid gas that constitute the largest amount in many existing NG reserves have to be removed. One of the major requirement for NG sweetening process involve the separation of acid gases from NG and this treatment is very important in order to prevent corrosion of transportation pipeline, reduce atmospheric pollution, and avoid other detrimental effects [2].

The removal of acid gases from NG streams require very efficient separation technologies, and NG sweetening process currently constitutes a major industrial gas separation processes. Membrane-based NG separations and membrane-absorption hybrid processes have emerged as among the fastest growing technologies, due to their lower

capital cost, higher energy savings, smaller size, environmental friendly and more economically viable as compared to conventional technologies such as stand-alone pressure swing adsorption (PSA) and stand-alone absorption process [3,6,7]. However, the inadequate performance of the current existing polymeric membranes impedes the full utilization of the application opportunities on the industrial scale [8–10]. Some of the challenges include inability to achieve both high permeability and selectivity, selectivity-permeability trade-off, membrane plasticization and physical aging. These certainly inhibit long-term gas separation performance and membrane stability. Thus, polymeric membrane materials with high permeation properties (i.e., both high permeability and selectivity) are indispensable to the viability of membrane-based NG separations and membrane-absorption hybrid processes.

While many membranes have been developed for the separation of CO₂/CH₄ over the past several decades, only few studies have considered the development of membranes for simultaneous separation of CO₂ and H₂S at moderate to high concentration of H₂S and feed pressure [3–5,11]. Such studies include the development of 6FDA-DAM: DABA (3:2) for simultaneous removal of CO₂ and H₂S from sour natural

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Nomenclature

J_i	volumetric flux of component i expressed as ($\text{cm}^3(\text{STP})/\text{cm}^2 \text{ s}$)		penetrant gas/ cm^3 of polymer per pressure)
l	membrane thickness (cm)	P_o	permeability coefficient pre-exponential factor (Barrer)
p_{i0}	partial pressure of component i on the feed side (cm Hg)	S_o	solubility coefficient pre-exponential factor ($\text{cm}^3(\text{STP})/\text{cm}^3 \text{ cmHg}$)
p_{i1}	partial pressure of component i on the permeate side (cm Hg)	D_o	diffusion coefficient pre-exponential factor (cm^2/s)
D_i	diffusion coefficient of component i (cm^2/s)	R	universal gas constant ($0.278 \text{ cm}^3 \text{ cm Hg}/(\text{cm}^3(\text{STP}) \text{ K})$),
S_i	solubility coefficient of component i ($\text{cm}^3(\text{STP})$ of	T	absolute temperature (K)
		E_p	activation energy of permeation (kJ/mol)
		ΔH_s	enthalpy of sorption or heat of solution (kJ/mol)
		E_D	activation energy of diffusion (kJ/mol)

gas streams. Under mixed gas feed conditions with 20% H_2S , 20% CO_2 and 60% CH_4 at 35 °C and up to 62 bar, $\text{H}_2\text{S}/\text{CH}_4$ and CO_2/CH_4 selectivities of above 22 and 27 respectively; and H_2S and CO_2 permeabilities of about 40 and 60 respectively were observed [3,4]. Yi *et al.* also investigated the sour gas permeation properties of hydroxyl-functionalized polymer of intrinsic microporosity with $\text{H}_2\text{S}/\text{CH}_4$ and CO_2/CH_4 selectivities of about 30 and 25 respectively; and H_2S and CO_2 permeabilities of about 60 and 50 respectively for a mixed gas feed conditions of 15% H_2S , 15% CO_2 and 70% CH_4 at 35 °C and up to 48 bar [5]. Furthermore, Achoundong *et al.* studied the acid gas permeation behavior of modified cellulose acetate membranes with $\text{H}_2\text{S}/\text{CH}_4$ and CO_2/CH_4 selectivities of about 27.5 and 20 respectively and; H_2S and CO_2 permeabilities of about 190 and 136 respectively for a mixed gas feed conditions of 20% H_2S , 20% CO_2 and 60% CH_4 at 35 °C and up to 48 bar [11]. Aside from the these few studies that have focused on moderate to high concentration of H_2S and feed pressure, most other previous studies have generally focused on low concentrations of H_2S and low feed pressure due to hazardous nature of H_2S [8–10]. Even though, these studies, which are mainly focused on rubbery membranes, have shown good membrane performance, however, since rubbery membranes separate based on solubility selectivity, the CO_2/CH_4 separation capability of the polymeric membranes decline sharply and much lower than those of other state-of-the-art glassy polymers such as polyimides and cellulose acetate (CA) [3,6,7]. In addition, the mechanical stability of rubbery polymers tends to fall significantly below that of glassy polymeric membranes. Moreover, since many gas reservoir wells can reach pressures well above 70 bars and H_2S concentration of more than 20%, more aggressive feeds need to be considered, and this is a focus of our study. This study has therefore focused on very high H_2S composition (up to 20%) in the gas mixture and up to 55 bar for mixed sweet gas permeation properties studies and 34 bar for mixed sour gas transport properties studies.

Amongst the polymeric membrane materials that have been investigated for acid gas separations from NG over the last few decades, glassy aromatic polyimides have emerged as major state of the art membranes that have attracted a lot of attention [3–7,12–45]. Some of these polymers exhibit very good permeation properties for various gas pairs (e.g., CO_2/CH_4 ; He/CH_4 ; N_2/CH_4 ; $\text{H}_2\text{S}/\text{CH}_4$; etc., [3–5,22,23]); chemical resistance, high mechanical strength and thermal stability. Since NG is usually treated at high pressures (up to 70 bar) and typically saturated with heavy hydrocarbons (C_3+) and water vapor, membranes fabricated from polyimides can easily be used for treating NG because of its excellent properties previously described. Polyimide membranes have shown remarkable permeation properties, especially high selectivities for CO_2/CH_4 separation [3–5,24–29]. In light of the presence of CF₃ groups in Hexafluorodianhydride (6FDA)-based polyimides that result in chain stiffness and hindrance to chain packing, which thus enhances permeability and selectivity, several studies have been carried out on these type of polyimides as gas separation membranes [3–5,22–28,33–35].

Furthermore, the permeation properties of 6FDA-based co-polyimides containing three homo-polyimides (i.e., 6FDA, mPDA and durene moieties) have also been investigated as gas separation membranes in the last few years [22,23,30–34]. Co-polymerization of

certain type of homo-polyimides result in membranes with very attractive and improved gas separation performance than what is usually obtainable with homo-polyimides. These polymers can be simply prepared from existing, commercially available materials. Even though the 6FDA-based co-polyimides (i.e., containing 6FDA, mPDA and durene moieties) show high pure gas CO_2/CH_4 selectivity of up to 61 and attractive mixed sour gas $\text{H}_2\text{S}/\text{CH}_4$ and CO_2/CH_4 selectivities of about 23 and 27 respectively, however, the pure and mixed gas permeabilities are very low (i.e., pure gas CO_2 permeability of 40 barrer and mixed sour gas CO_2 and H_2S permeabilities of 13 and 11 barrers respectively) [22,23]. Other types of 6FDA-based co-polyimide previously reported [3–5] showed very attractive pure and mixed gas permeabilities and very good $\text{H}_2\text{S}/\text{CH}_4$ and CO_2/CH_4 selectivities. However, in order to enhance the separation performance of the polymeric membranes even further and optimize these materials for better gas separation, chemical modifications that include substitution of other pertinent moieties or monomers and bulky functional groups in the co-polyimides backbone is necessary. This can be achieved by substituting bulky CARDO moiety with mPDA in the existing copolymers. This CARDO functionality, which is sometime called hinge or loop in Latin [35] and polymers containing this loop or hinge shaped functionalities in the polymer backbone are referred to as CARDO polymers [35]. These polymers exhibit high solubility and high thermal stability and because of its stiffness and bulky nature, CARDO moiety hinders the packing and restrict the rotational mobility of the polymer backbones. In view of these exceptional properties, CARDO-based polyimides are expected to have potential for enhancing gas separation performance. Several studies have reported attractive CO_2 separation properties of some CARDO-based polymers [35–45], and it is pertinent to believe that substituting CARDO moiety with mPDA in the existing copolymers could significantly improve the gas permeation performance of the co-polyimides. One of such studies involved the development of CARDO-copolybenzoxazole by thermal induced structural rearrangement, which resulted to an increment of 3 times in CO_2 permeability as compared to the CO_2 permeability in the non-cardo counterparts [43,44]. In addition, commercially available polyphenylene oxide (PPO) and CARDO-type polyimide membranes have also been investigated for gas separation, and it was observed that PPO exhibited high selectivity and moderate permeance, while the CARDO-type polyimide membrane showed moderate selectivity and high permeability for CO_2/CH_4 and CO_2/N_2 separations [39,41,42].

In light of this, the preparation of series of aromatic CARDO-type random co-polyimides containing three homo-polyimides (i.e., 6FDA, mPDA and CARDO moieties) was investigated in this work. The effects of CARDO substitution and varying segmental length of the moiety in the polymer backbone on the physical and gas transport properties were investigated via pertinent pure and gas mixture permeation measurements. Detailed studies that include preparation, pure and sour gas mixture transport properties have been conducted on the co-polyimide (6FDA–mPDA/durene) - containing no CARDO in our previous work [22,23]. The aim of this study is to achieve enhancement in the gas separation performance and transport properties and thus, in this work, gas transport properties of the CARDO type random co-polyimides were

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