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Propylene/propane plasticization in polyimide membranes

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ABSTRACT

Polyimides have been considered as attractive polymers to be used in membrane based separation processes to separate propylene/propane mixtures. However, propane and propylene tend to plasticize polyimide membranes. In this study, we used molecular simulation techniques to gain insight on the relationship between molecular structure and plasticization of polyimides due to the sorption of propane and propylene molecules. Three fluorinated polyimides with different backbone rigidities were considered for this purpose: 6FDA–ODA, 6FDA–DPX and 6FDA–DAM (6FDA: 4,4-hexafluoroisopropylidene-diphthalic anhydride; DAM: 2,4,6-trimethyl-m-phenylene diamine; ODA: and 4,4-oxydianiline; DPX: 2,5-dimethyl-p-phenylenediamine). A combination of molecular dynamics and Monte Carlo methods was used to estimate sorption induced changes in the polymer matrices. Structural analyses such as radial distribution function, free volume, and local dynamics analyses were carried out to better understand the plasticization mechanism. Results showed that propane and propylene sorption capacities also depend on the polymer-penetrant interactions in addition to the fractional free volume of the polymer which has been shown as the dominant factor for CO_2 sorption on the same polyimides in our previous work. The polymer-penetrant interactions are more dominant for propylene than propane due to high polarizability of propylene resulting from π-electron complexation. The analysis of preferential sorption sites in both single and binary gas adsorption reveals that site preferences are altered in binary gas adsorption due to the competition between propane and propylene molecules. The dianhydride structure contain the most preferential sorption site and hence is plasticized in the single gas adsorption case, whereas, the most preferential sorption site moves to the diamine structure in case of binary sorption, especially in more flexible polyimides such as 6FDA–ODA.

1. Introduction

Among various polymeric membrane materials in gas separation area, aromatic polyimides (PIs) are an important group of polymers with outstanding thermal and chemical stability, and good mechanical properties [1]. They are synthesized by the reaction of dianhydride and diamine monomers, which govern selectivity towards separation of commercially important gas pairs such as O_2/N_2, CO_2/CH_4, H_2/CH_4, H_2/N_2 and propylene/propane. Hence, for a specific application selection of an appropriate monomer pair is crucial for the preparation of membranes with high selectivity and permeability. Numerous extensive experimental studies have been reported in the literature about PIs synthesized using different dianhydride/diamine combinations [2–6]. Hence, due to the interdependence of chemical structures and gas transport properties [7], selection of an appropriate monomer pair is crucial for the preparation of membranes with high selectivity for a specific application. For example, polyimides with large substituents such as 4,4-hexafluoroisopropylidene-diphthalic anhydrides (6FDA) containing two bulky CF_3 groups; 2,4,6-trimethyl-m-phenylene diamine (DAM) and 1,2,4,5-tetramethylbenzene (TeMPD) diamine containing three and four CH_3 groups, respectively; 4,4′-hexafluoroisopro-pylidene dianiline (6FpDA) diamine containing two bulky CF_3 groups, have been considered due to the increase of the polymer's fractional free volume (FFV) giving rise in permeation rates for olefin/paraffin separations [8–16].

In membrane based gas separation processes, sorption induced volume swelling and plasticization appear to be a serious concern, limiting the use of PIs as membrane material for gas separation involving CO_2, H_2S and condensable hydrocarbons such as propylene (C_3H_6) and propane (C_3H_8). Plasticization is a pressure dependent phenomena and occurs when the concentration of these gases in glassy polymers, such as PIs, is high enough to cause swelling in the polymer, i.e. reduce chain alignment and increase inter-segmental mobility and FFV [8–12]. The upturn pressure obtained in the plasticization in the permeability versus pressure

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plot is known as the plasticization pressure. At this point due to the loss in size discrimination ability, there would be a significantly high selectivity decrease, therefore it is important to test membranes with mixed gas compositions. In the case of C_3H_6/C_3H_8 separation, the sorption-induced swelling phenomena allow C_3H_8 to diffuse at an increased rate relative to that in unplasticized polymer, which decreases the membrane selectivity. Staudt-Bickel and Koros [8] observed plasticization of the membrane with pure propylene by the upturn in permeability values around a propylene upstream pressure of 3 bars. They further tried to define plasticization effect with a 50:50 mixed gas propylene/propane permeation test. The mixed gas selectivity decreases from an ideal selectivity of 13–7. Propylene and propane, both being condensable, tend to plasticize polymeric membranes, even at partial pressures as low as 2 bar [12].

Plasticization has to be minimized by proper molecular design to overcome the permselectivity reduction, which requires a fundamental understanding of penetrant induced plasticization. Only a few experimental studies investigating plasticization effect of propane and propylene in polyimides have been reported in the literature [8–12,17–22]. While most polymers have very low selectivity (1–2) for propylene/propane separations, Das and Koros summed up all transport properties of polyimides and showed that polyimides have higher selectivity (10–30) than other polymers investigated [12]. In most of these studies, 4,4-hexafluoroisopropylidene-diphthalic anhydride (6FDA)-based polyimides were preferred for propane and propylene separation due to their superior performances. Mainly the observed plasticization pressure among these studies was between 2 and 5 atm. In order to suppress plasticization, cross-linking and thermal treatment were used. Visser and Wessling [20] and Das and Koros [12] investigated binary mixtures of propylene and propane and concluded that when both components of show autoplasticization, facilitated plasticization can be observed if process parameters or material properties cause high degree of swelling.

Advances in molecular modeling provide an excellent opportunity to quantitatively investigate penetrant induced plasticization and understand the mechanisms behind it. However, there is no molecular simulation study that focus on propane and propylene-induced plasticization in polyimides, while a significant amount of research has been done on polymers such as polystyrene, poly[1-(trimethyl silyl)-1-propyne] (PTMSP) and poly(vinyl alcohol) (PVA) [23–25]. Although all these polymers were rubbery and easy to simulate compared to rigid glassy polymers such as polyimides, computer simulation studies overestimated the solubility coefficients nearly by one order of magnitude in all these studies.

In this study, molecular simulation techniques were used to estimate the degree of plasticization of 6FDA-based PI membranes induced by sorption of propane and propylene molecules. The 6FDA-based PIs exhibit high gas permeabilities and low chain packing densities as a result of the blockage of the rotation of phenyl rings by $-C(CF_3)_2-$ linkage [26] and membranes with commercially attractive selectivities may be obtained by changing the diamine structure. PIs such as 6FDA–DAM, 6FDA–DPX and 6FDA–ODA (Fig. 1) have a strong potential for O_2/N_2, CO_2/CH_4 and C_3H_6/C_3H_8 separation applications [27]. In our previous study on CO_2-sorption induced plasticization of these three PIs [28]; the structural properties, such as glass transition temperature (T_g), FFV and its distribution, d-spacing, radius of gyration, and cohesive energy density, along with sorption isotherms were investigated from simulations to understand the dynamics of polymer chains and penetrants and the comparison was made with the experimental data available in the literature to provide an insight to structure-plasticization relationship. In this study, we extend our methodology to examine the plasticization phenomena in propylene/propane separation.

2. Theory and background

Gas transport through dense polymeric membranes is typically described by the solution-diffusion mechanism [29] where the driving forces of pressure, temperature, concentration, and electromotive force are interrelated and that the overall driving force producing movement of a permeant is the gradient in its chemical potential. The solution-diffusion model assumes that the chemical potential of the feed and permeate fluids are in equilibrium with

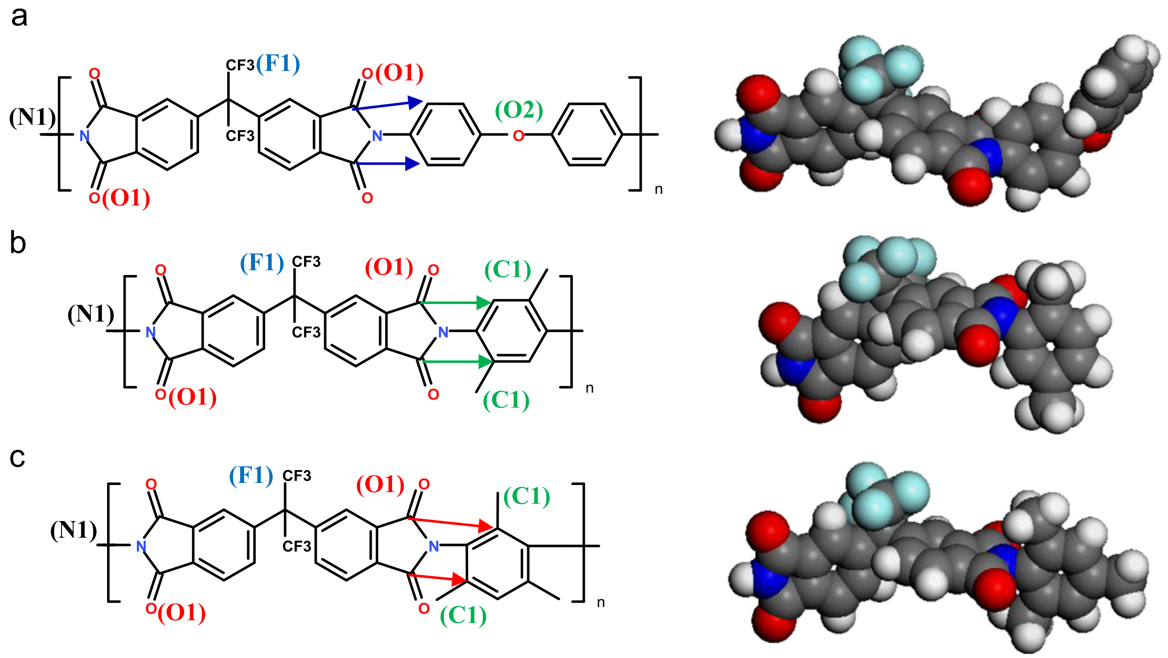

Fig. 1. Structures of constructed repeat units for (a) 6FDA–ODA, (b) 6FDA–DPX and (c) 6FDA–DAM. Vectors connect the carbon atoms neighboring the dianhydride–diamine linkage. Typical sorption sites are shown in parenthesis.