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Influence of toluene on CO₂ and CH₄ gas transport properties in thermally rearranged (TR) polymers based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)

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Abstract

Separation of complex gas mixtures, such as natural gas using polymer membranes, often involves components with a wide range of condensabilities and propensity to interact with the polymer, potentially changing the transport properties of all components. There are few studies of such phenomena in the open literature. Here, the influence of toluene, a surrogate aromatic contaminant in natural gas, on pure and mixed CO₂ and CH₄ gas transport properties at 35 °C was investigated for a thermally rearranged (TR) polymer prepared from a polyimide precursor based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxy-phenyl) hexafluoropropane dianhydride (6FDA). As the polymer was exposed to CO₂, CH₄, and their equimolar mixture, at a toluene activity of about 0.3, CO₂ and CH₄ permeability coefficients decreased by more than 90% relative to their respective pre-exposure values due to antiplasticization and competitive sorption. CO₂/CH₄ selectivity went through a maximum as toluene activity increased, reflecting the interplay between competitive sorption, antiplasticization, and plasticization. The recovery of gas permeation properties was explored by measuring CO₂ and CH₄ permeabilities after removing toluene from the feed. These effects were largely reversed when toluene was removed from the feed gas mixture. Toluene vapor sorption was determined as a function of toluene activity, and the sorption data were used to help rationalize the changes in CO₂ and CH₄ gas permeability coefficients in the presence of toluene. A qualitative assessment of antiplasticization and competitive sorption effects was provided using the partial-immobilization dual mode model.

Keywords: Thermal rearrangement, Mixed gas, Toluene, Gas separation

1. INTRODUCTION

Contaminants and impurities, such as heavy aliphatic hydrocarbons, water, aromatics, and H_2S , are often present in natural gas streams. Raw natural gas, for example, can contain 5 to 15% C2-C6 aliphatic hydrocarbons [1, 2]. In addition, up to 1000 ppm of water and 500 ppm of BTEX aromatics (benzene, toluene, ethylbenzene, and xylene) can be present in such streams [1]. With typical natural gas operating conditions at 50 °C and 20-60 bar, these impurities can approach unit activity and even condense onto the membrane surface [1].

The presence of such contaminants may have deleterious effects on polymer gas transport properties [3]. Tanihara et al. [4] reported that after 1600-7600 ppm of toluene was introduced to an equimolar H_2/CH_4 feed gas mixture at 10 atm and 50 °C, a polyimide hollow fiber experienced a ~60% loss in H_2 permeance and an ~84% loss in H_2/CH_4 selectivity. Omole et al. [5] observed that as toluene concentration increased in a CO_2/CH_4 mixture feed stream, CO_2 permeance in a crosslinked polyimide hollow fiber decreased by as much as 80%, and CO_2/CH_4 selectivity initially increased from ~37 to ~39 at low toluene concentration (50 ppm) before decreasing to ~31 at higher toluene concentration (1000 ppm). Additionally, different contaminants may have different effects on light gas (e.g., H_2 , CO_2 and CH_4) permeation properties. For example, White et al. [6] studied the influence of various contaminants on mixed gas transport properties of a proprietary polyimide film. Naphthalene immediately decreased gas flux through the membrane (> 50% decrease) but had little effect on CO_2/CH_4 selectivity; toluene significantly decreased the CO_2/CH_4 selectivity (~ 34% decrease) but had little effect on CO_2 permeability; and *n*-hexane increased CO_2 permeability (~55% increase) and decreased CO_2/CH_4 selectivity (~42% decrease) [6]. Such different effects on permeation performance demonstrate the difficulty in generalizing/predicting trends in gas transport

properties in the presence of contaminants and highlight the necessity of studying specific polymer/contaminant combinations of interest.

The impact of contaminants on gas separation performance has been attributed generally to three factors: antiplasticization, plasticization and competitive sorption [7-13]. When certain low-molecular-weight compounds are incorporated into a polymer matrix, the compounds may increase polymer modulus and strength, while decreasing elongation at break and impact resistance, a phenomenon called antiplasticization [14-18]. In gas separation applications, the presence of such compounds, including toluene at low activity, may significantly decrease gas permeability [8, 9, 14-21]. For example, Maeda et al. studied the effects of low concentrations of various additives, such as tricresyl phosphate (TCP), N-phenyl-2-naphthylamine (PNA), and 4,4'-dichlorodiphenyl sulfone (DDS) on gas transport properties of polysulfone (PSF) and poly(phenylene oxide) (PPO) [14, 16-18]. After incorporating 30 wt% PNA into PSF, CO₂ permeability decreased from 5.82 Barrer to 0.22 Barrer [14]. Such permeability decreases were accompanied by either an increase or decrease in gas selectivity. For example, as the concentration of Kronitex 50, an aromatic additive, in PPO increased, CO₂/CH₄ selectivity initially increased from 15.6 to 16.8 at low additive concentrations and then decreased to 14.8 at higher additive concentrations [17]. Additionally, Maeda et al. concluded that the addition of these additives decreased gas solubility, but the major contribution to permeability reductions was a reduction in polymer free volume that led to a decrease in penetrant diffusion coefficients in the polymer matrix [18].

As contaminant concentration sorbed in a polymer increases, it may induce swelling of the polymer matrix, which increases polymer inter-chain spacing and may increase polymer segmental mobility, thereby increasing penetrant diffusion coefficients, lowering the polymer's

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4 size-sieving ability and decreasing gas selectivity. This phenomenon is called plasticization
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6 [22-26]. For glassy polymers, even after plasticizers are removed, the dilated polymer matrix
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8 may not immediately relax to its pre-swollen state. Consequently, the polymer may retain
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10 additional free volume long after exposure to such contaminants, a phenomenon known as
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12 conditioning [27, 28].
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16 For glassy polymers, more condensable contaminants, such as toluene and higher
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18 hydrocarbons, typically have a higher affinity for Langmuir sites in the polymer matrix than less
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20 condensable penetrants, such as CO₂ and CH₄. Preferential sorption of more condensable
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22 components can decrease solubility of less condensable penetrants, leading, in some cases, to
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24 lower gas permeability and higher selectivity [29]. This phenomenon is called competitive
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26 sorption.
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31 This study explores the influence of toluene, a surrogate aromatic contaminant in natural
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33 gas, on CO₂ and CH₄ pure and mixed gas permeation properties of a thermally rearranged (TR)
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35 polymer prepared from a polyimide precursor based on 3,3'-dihydroxy-4,4'-diamino-biphenyl
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37 (HAB) and 2,2'-bis-(3,4-dicarboxy-phenyl) hexafluoropropane dianhydride (6FDA). TR
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39 polymers are a relatively recent class of materials that, due in part to high free volume and
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41 favorable free volume distribution, has interesting gas separation performance [30, 31]. TR
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43 polymers are generally prepared by thermally treating a polyimide precursor in an inert
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45 atmosphere to rearrange the polymer structure to a more open and highly chemically and
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47 thermally stable poly(benzoxazole)-type structure. Several studies have reported structure-
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49 property relationships [32-35] and free volume distribution [36-38] of these materials.
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51 However, most TR polymer gas transport studies are based on pure gas experiments. There are
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53 few reports of mixed gas permeation properties of TR polymers [31, 39, 40], and to the best of
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our knowledge, there are no reports of the influence of aromatic contaminants on mixed gas permeation properties of TR polymers.

Pure gas permeation, diffusion, and sorption properties of HAB-6FDA and its TR analogs have been reported elsewhere [30, 41]. Recently, we reported mixed gas CO₂/CH₄ transport properties of HAB-6FDA and its TR analogs [39]. At low CH₄ fugacity (< ~10 atm), mixed gas CH₄ permeability was depressed relative to pure gas transport properties due to competitive sorption, leading to an increase in CO₂/CH₄ selectivity. In this study, we seek to elucidate the influence of toluene on both pure and mixed gas CO₂/CH₄ permeation properties of a TR polymer prepared from HAB-6FDA. Toluene sorption and desorption was investigated, and the dual mode sorption model was used to interpret the sorption isotherms. Additionally, the partial-immobilization dual mode model was used to provide a qualitative assessment of antiplasticization and competitive sorption effects.

2 EXPERIMENTAL

2.1 Materials

A polyimide precursor based on 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) and 2,2'-bis-(3,4-dicarboxy-phenyl) hexafluoropropane dianhydride (6FDA) was synthesized via chemical imidization as described previously [30]. HAB was purchased from Chriskev (Lenexa, KS, USA), and 6FDA was purchased from Alfa Aesar (Ward Hill, MA, USA). Prior to synthesis, HAB was dehydrated by heating it at 50 °C under full vacuum for 12 h. To prevent possible photo-degradation of HAB, the monomer container and the vacuum oven window were covered with aluminum foil. 6FDA was heated at 200 °C under partial vacuum for 6 h and then maintained at 120 °C under full vacuum for 12 h to remove any water arising

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4 from closure of any hydrolyzed dianhydride rings. *N*-methyl-2-pyrrolidinone (NMP,
5 anhydrous), pyridine (purity ~ 99.9%), acetic anhydride (purity ~ 99.5%), and
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7 dimethylacetamide (DMAc, anhydrous) were purchased from Sigma Aldrich (St. Louis, MO,
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9 USA) and used as received.
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15 **2.2 Polymer synthesis and casting**

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18 HAB-6FDA polyimide was synthesized via condensation polymerization of diamine and
19 dianhydride followed by chemical imidization [30, 42]. A detailed synthesis procedure was
20 presented earlier [41], so only a brief summary is provided here. A poly(amic acid) was formed
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22 by reacting equimolar amounts of HAB and 6FDA in NMP at 0 °C for 24 h. Afterwards, the
23 polyimide was obtained via chemical imidization by adding excess acetic anhydride and pyridine
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25 (8 moles of acetic anhydride and 8 moles of pyridine per mole of HAB) to the mixture at 60 °C
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27 and stirring for 1 h. The resulting polymer was precipitated in about 2 L of pure methanol and
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29 heated under vacuum at 100 °C for 24 h, 150 °C for 24 h, and 200 °C for 48 h to remove solvent.
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38 The chemical structures of the monomers and polyimide are presented in Figure 1.
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Figure 1: Chemical structures of the monomers (HAB and 6FDA), HAB-6FDA polyimide precursor (HAB-6FDA PI), and the corresponding polybenzoxazole TR polymer (HAB-6FDA TR) after thermal rearrangement [30].

Polyimide films, about 6-8 μm thick, were prepared via solution casting. A solution containing 4 g polymer per 100 mL of solvent was prepared by dissolving HAB-6FDA in DMAc. After vigorous stirring, the solution was first filtered through a 5.0 μm Millex-LS PTFE filter (Part# SLLS025NS, Millipore, Billerica, MA, USA) to remove any dust or particles and then cast onto a clean, flat, and level glass plate. The casting solution was heated at 80 °C and -25 cmHg for 24 h, 100 °C and -25 cmHg for 24 h, and then under full vacuum at 100 °C for another 12 h. Afterwards, films were immersed in deionized water, peeled off the glass plate, and dried further at 200 °C under full vacuum for 24 h to completely remove solvent, which was verified by thermogravimetric analysis.

2.3 Thermal rearrangement

Thermal rearrangement was achieved by heating polyimide films inside a Carbolite three-zone hinged tube furnace (Model HZS 12/-/600, Watertown, WI, USA). The tube furnace was purged with N₂ (UHP grade, Airgas, Austin, TX, USA) at 900 mL/min. A polyimide sample was initially heated to 300 °C at 5 °C/min and held at 300 °C for 1 h to ensure complete imidization [30]. Afterwards, the sample was heated to 450 °C at 5 °C/min and held at 450 °C for 30 min for thermal rearrangement. Finally, the sample was cooled to room temperature at 10 °C/min. In this study, the TR polymer derived from HAB-6FDA will be referred to as HAB-6FDA TR450. The chemical structures of HAB-6FDA and its corresponding TR analog are presented in Figure 1. Although the polybenzoxazole (PBO) is shown as a linear polymer, thermal rearrangement between neighboring polymer chains may occur, resulting in a crosslinked structure [30, 31]. The percent TR conversion is defined as 100 times the ratio of the actual mass loss of the sample during thermal rearrangement to the theoretical mass loss [30]:

$$\% TR Conversion = \frac{Actual Mass Loss}{Theoretical Mass Loss} \times 100 \quad (1)$$

This calculation assumes that any polyimide undergoing thermal rearrangement was converted to its corresponding PBO structure. A detailed analysis of the implications of this approach was reported by Sanders et al. [34]. The actual mass loss of the sample was calculated as the difference between the sample mass immediately before and after the TR process. Table 1 compares the physical properties of HAB-6FDA TR450 from this study with those reported previously [30, 39, 41]. A 6-8 µm thick HAB-6FDA film typically underwent about 84% TR conversion upon thermal treatment at 450 °C for 30 min. Previous studies used thicker films, since all penetrants considered in those studies were small gas molecules. In this study, thinner

films were required to give reasonable experiment durations, given the large contaminant molecule (toluene) and its slow desorption. However, if the film thickness is less than 2-3 μm , significant physical aging may result in TR polymers [43]. For example, Wang et al. reported that thin HAB-6FDA TR polymer films (1.8 μm thick) exhibited an 80% decrease in pure gas CH_4 permeability after about 1000 h of aging [43]. Therefore, thicknesses of 6-8 μm were chosen to provide a reasonable compromise between experiment duration and physical aging.

Table 1. Physical properties of HAB-6FDA TR450 from this study and literature.

Polymer	Thickness (μm)	TR conversion (%)	Density ¹ (g/mL)	Fractional free volume ²	Reference
HAB-6FDA TR450	6 – 8	84	1.28	0.233	This study
	30-50	76	1.34	0.196	[30, 41]
	~40	79	--	--	[39]

¹Density was determined based on Archimedes' principle using a Mettler-Toledo balance (Mettler-Toledo GmbH, P706039) equipped with a density kit. *N*-heptane was used as the buoyant liquid [30].

²Fractional free volume was calculated using Bondi's method [44], as described in detail elsewhere [30].

2.4 Pure gas permeation

Pure gas CH_4 and CO_2 permeability coefficients in HAB-6FDA TR450 were determined at 35 °C using a constant volume-variable pressure apparatus built in-house [45]. Gases were UHP grade (Airgas, Austin, TX, USA) and were used as received. The permeability coefficient of gas A, P_A , was determined as follows:

$$P_A = \frac{Vl}{fRTA} \left[\left(\frac{dp}{dt} \right)_{ss} - \left(\frac{dp}{dt} \right)_{leak} \right] \quad (2)$$

where f is the fugacity of the gas feed, R is the gas constant, V is the downstream volume, l is film thickness, T is absolute temperature, A is sample area, $\left(\frac{dp}{dt}\right)_{leak}$ is the system leak rate, and $\left(\frac{dp}{dt}\right)_{ss}$ is the rate of pressure rise in the downstream volume when gas permeation is at steady state. The leak rate was determined by isolating the downstream and upstream sections of the permeation apparatus and monitoring changes in the downstream pressure for about 1 h. Fugacity was used to account for non-idealities [39] and was calculated using the second virial coefficient equation of state [46]. Film thickness was measured with a precision micrometer (Mitutoyo, Aurora, IL, USA). Permeability coefficients are expressed in units of Barrer, where $1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3 (\text{STP}) \text{ cm}}{\text{cm}^2 \text{ s cmHg}}$ [45]. Ideal selectivity, $\alpha_{A/B}$, is the ratio of permeability of the more permeable penetrant to that of the less permeable penetrant [45].

2.5 Gas/vapor permeation system

Gas permeation of gas mixtures was determined at 35 °C using a gas/vapor permeation apparatus built in-house. A schematic of the system is shown in Figure 2, and the design is similar to that reported by Lee et al. [47]. The feed gas flow rate was regulated by a Brooks mass flow controller (labeled ‘MFC’ in Figure 2, Model SLA5850, Brooks Instruments, Hatfield, PA, USA) with a maximum gas flow rate of 50 cm³(STP)/min. The upstream pressure was monitored using a 1500 psig (104 bar) pressure transducer (‘PT1’, Model STJE, Honeywell Sensotec, Columbus, OH, USA) and was regulated using a 500 psig (35 bar) backpressure regulator (‘PR’, Swagelok, Austin, TX, USA). The downstream pressure was monitored using a 10 Torr (0.013 bar) Baratron pressure transducer (‘PT2’, Part# 626A11TBE, MKS, Methuen, MA, USA). Gas flow rate was measured using a digital universal gas flowmeter (‘FM’, Model

ADM1000, Agilent Technologies, Santa Clara, CA, USA). Gas concentrations in either the retentate or permeate streams were analyzed using a gas chromatograph ('GC', Model 7890A, Agilent Technologies, Santa Clara, CA, USA) equipped with a thermal conductivity detector (TCD) and Heysep Q packed column (0.318 cm O.D.).

Figure 2: Schematic of the mixed gas/vapor permeation apparatus. The nomenclature used is as follows: mass flow controller (MFC), pressure regulator (PR), gas chromatograph (GC), pressure transducer (PT), flow meter (FM), and needle valves (V1, V2, etc.).

Toluene vapor was introduced to the feed gas using a syringe pump (Model 100DM, Teledyne Isco, Lincoln, NE, USA) that can operate at pressures up to 695 bar and precisely meter flow rates as low as 1×10^{-5} mL/min, with an accuracy of $\pm 0.5\%$ of the set point. To ensure introduction of a steady, continuous stream of toluene to the feed gas (rather than an irregular drop by drop amount of toluene), a poly(ether ether ketone) capillary tube (50 μ m I.D. and 360 μ m O.D. (Part# PM-2602-F, IDEX, Oak Harbor, WA, USA)) was used to feed liquid

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4 toluene from the syringe pump into the feed gas. The mixture of feed gas and toluene passed
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6 through a 1 L stainless steel ballast cylinder filled with Pro-pak[®] distillation packing (Z210536,
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8 Sigma-Aldrich, St. Louis, MO, USA). As indicated in Figure 2, the ballast tank and associated
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10 tubing were submerged in a water bath held at 55 ± 1 °C. This temperature was chosen to
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12 increase the toluene vaporization rate. Additionally, the large ballast volume and packing
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14 allowed sufficient mixture residence time for toluene vaporization and mixing with the feed gas.
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16 Afterwards, the mixture passed through a four-way valve (Part# SS-43YFS2, Swagelok, Austin,
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18 TX, USA), which could direct the mixture either to the GC for concentration analysis or to the
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20 permeation cell for permeation measurements. Coils of tubing between the four-way valve and
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22 the membrane sample holder allow the feed gas temperature to equilibrate with the water bath
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24 temperature (35 °C).
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31 Prior to beginning a permeation experiment, a polymer sample was degassed in the
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33 membrane sample holder for at least 12 h by keeping valves V1-5, V8, and V10 open and the
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35 other valves closed. Before feed gas was introduced to the membrane, a leak test was
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37 conducted by monitoring the downstream pressure for 1 h with V2, V4, V5, and V8 closed.
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39 Next, a gas/vapor mixture feed was introduced to the film by closing V5, V6, and V9 and
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41 opening V8. Depending on the permeation rate, V10 could be opened to provide additional
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43 downstream volume. The feed flow rate was set to have a stage cut (i.e., the ratio of feed flow
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45 rate to permeate flow rate) of less than 1% to prevent concentration polarization [45]. The
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47 retentate stream, after sweeping the film surface, was either purged by closing V7 and opening
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49 V6 or sent to the GC for analysis by closing V6 and opening V7.
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56 A desired toluene activity in the feed was achieved by setting an appropriate toluene flow
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58 rate using the syringe pump and checking the toluene concentration in the feed using the GC.
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Multiple GC analyses were performed over a span of several hours after toluene was introduced to the feed to ensure that the toluene activity was consistent. To guarantee attainment of pseudo-steady state conditions, permeation measurements began at least six times after the time lag of the slowest permeating species in the feed gas mixture. The permeability of gas A, P_A , was determined according to Equation (3):

$$P_A = \frac{Vly_A}{f_A RTA} \left[\left(\frac{dp}{dt} \right)_{ss} - \left(\frac{dp}{dt} \right)_{leak} \right] \quad (3)$$

where f_A is the fugacity of gas A, R is the gas constant, V is downstream volume, l is film thickness, T is absolute temperature, A is sample area, y_A is mole fraction of A in the permeate stream, and $\left(\frac{dp}{dt} \right)_{leak}$ and $\left(\frac{dp}{dt} \right)_{ss}$ are the rates of pressure rise in the downstream volume during the leak test and when the gas permeation was at pseudo-steady state, respectively. Table 2 presents the gas compositions and nomenclature of different gas feed streams considered in this study.

Table 2. Gas compositions and nomenclature of the different feed streams considered in this study.

Gas	Composition (mol%)			Nomenclature
	CO ₂	CH ₄	Toluene	
CO ₂	100	0	0	Pure gas
CH ₄	0	100	0	
CO ₂ /CH ₄	50	50	0	Binary mixed gas
CO ₂ /Toluene	Balance	0	1700, 0* ppm	Gas/vapor mixed gas
CH ₄ /Toluene	0	Balance	1700, 0* ppm	
CO ₂ /CH ₄ /Toluene	49.8-50.0	49.8-50.0	0* – 4400 ppm	Ternary mixed gas

*After toluene was removed from the gas feed, the experiment nomenclature was not changed both for clarity and because some toluene may still remain in the polymer sample, at least during the early stages of the desorption phase of the experiment.

2.6 Gravimetric sorption of toluene

The pure toluene vapor sorption isotherm in HAB-6FDA TR450 was determined using a McBain spring balance apparatus [48]. About 10 mg of polymer sample was hung on a highly sensitive helical, non-rotating quartz spring purchased from Ruska Industries (Houston, TX, USA). The spring, alongside a reference rod, was suspended inside a water-jacketed glass chamber, whose temperature was maintained at 35 ± 0.1 °C using a thermostatic bath equipped with a recirculation pump (Haake K20, Thermo Fisher Scientific, Waltham, MA, USA). The spring constant was 0.38 mg/mm, which was obtained by calibrating the spring extension with copper wires of different known masses. The glass chamber was connected to a vacuum pump (Model 1402N, Ideal Vacuum Products, Albuquerque, NM, USA) for sample degassing and toluene vapor removal.

Liquid toluene, stored in a glass reservoir, was degassed and purified by five freeze-thaw cycles [49]. Prior to introducing toluene vapor to the system, the polymer sample was degassed for at least 24 h. Then, toluene vapor was slowly fed to the glass chamber until a desired toluene activity was reached. Toluene activity was defined as f/f_{sat} , and the saturation fugacity (f_{sat}) of toluene was determined by first calculating the toluene vapor pressure using Antoine's equation [50], and then calculating the corresponding fugacity using the second virial coefficient equation of state [46]. The resulting value for f_{sat} at 35 °C was 0.0624 bar. As the sample sorbed toluene, its mass increased, and the spring extended. The spring position relative to the reference rod was monitored using a monochrome industrial camera (Model DMK 23U274, The Imaging Source, Charlotte, NC, USA), and ImageJ software was used to analyze these kinetic sorption data [51]. This automated recording continued until the spring position remained constant for several hours. After that, additional toluene vapor was introduced to the system for

subsequent sorption steps. Toluene uptake by the polymer was determined stepwise up to a toluene activity of 0.7. Afterwards, toluene vapor was slowly removed by carefully pulling vacuum, and the desorption behavior was recorded.

Sorption of gases and vapors in glassy polymers is commonly described using the dual mode sorption model [2, 22, 52]:

$$C_A = k_{D_A} f_A + C'_{H_A} \frac{b_A f_A}{1 + b_A f_A} \quad (4)$$

where f_A is fugacity of A, k_{D_A} is the Henry's law solubility constant, C'_{H_A} is the Langmuir sorption capacity, and b_A is the Langmuir affinity parameter.

3. RESULTS AND DISCUSSION

3.1. Pure and mixed gas permeation properties without toluene

Table 3 presents pure and binary mixed gas CO₂ and CH₄ permeability coefficients in HAB-6FDA TR450 at 35 °C. An equimolar (50/50 mol%) CO₂/CH₄ mixture was used for the binary mixed gas experiments. For both pure and mixed gas feeds, CO₂ and CH₄ permeability coefficients decrease as fugacity increases, which is consistent with typical dual mode trend [53]. At similar feed fugacities, the difference between pure and binary mixed gas CH₄ permeability coefficients is greater than that for CO₂ permeability coefficients. For example, at around 4.8 atm, pure gas CO₂ permeability (600 Barrer) is 6% higher than binary mixed gas CO₂ permeability (565 Barrer), but pure gas CH₄ permeability (28.4 Barrer) is 18% higher than binary mixed gas CH₄ permeability (24.1 Barrer). As a result, binary mixed gas CO₂/CH₄ selectivity (23.4) is about 11% higher than pure gas CO₂/CH₄ selectivity (21.1). These trends are

consistent with those reported by Gleason et al. [39]. The depression of CH₄ permeability in the presence of CO₂ is attributed primarily to competitive sorption effects [39]. Because CO₂ is more condensable than CH₄ [54], CO₂ absorption in the Langmuir domains, i.e., in the non-equilibrium excess volume of this glassy polymer, is favored relative to that of methane, and this phenomenon would reduce CH₄ solubility and, in turn, CH₄ permeability more than that of CO₂.

Table 3. Pure and binary mixed gas permeability coefficients of CO₂ and CH₄ and CO₂/CH₄ selectivity values of HAB-6FDA TR450 at 35 °C.

Feed Gas Type	CO ₂		CH ₄		CO ₂ /CH ₄ Selectivity
	Fugacity (atm)	Permeability (Barrer)	Fugacity (atm)	Permeability (Barrer)	
Pure gas	4.8	600	4.8	28.4	21.1
	9.4	510	9.7	26.3	19.4
Binary mixed gas (50/50 mol%) CO ₂ /CH ₄	4.7	565	4.9	24.1	23.4
	8.9	490	9.4	22.9	21.4

Pure and binary mixed gas permeabilities in HAB-6FDA TR450 from this study are generally higher than those reported previously [30, 39]. For example, at 35 °C and an upstream fugacity of about 9-10 atm, pure and binary mixed gas CO₂ permeabilities of HAB-6FDA TR450 from this study are roughly 20-30% higher than those reported earlier [30, 39]. The film thickness in this study (~6-8 µm) is less than that in previous studies (~40 µm) (cf., Table 1). As a result, at fixed thermal treatment conditions, HAB-6FDA from this study undergoes more extensive TR conversion than that reported in thicker films, leading to higher fractional free volume and higher gas permeability. The higher permeability coefficients in thinner TR polymers is consistent with results reported by Wang et al., who demonstrated that the extent of thermal rearrangement and gas transport properties depend on film thickness [43, 55]. For example, Wang et al. reported that upon thermal treatment at 390 °C for 30 min, a 15

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4 μm polyimide precursor underwent 48.9% TR conversion, whereas a 1 μm sample underwent
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6 74.9% TR conversion [43]. Wang et al. attributed such thickness dependence to the enhanced
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8 polymer segmental mobility in thin films, which might shift the balance of intra/intermolecular
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10 reactions that favors more polymer crosslinking, thereby increasing TR conversion [55].
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12 Consequently, the initial pure gas CH_4 permeability (before significant aging) of a thick TR
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14 sample ($\sim 21 \mu\text{m}$) was about 50% lower than that of a thin TR film ($\sim 2 \mu\text{m}$) [43]. The results
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16 reported in this study are consistent with trends from the literature.
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23 **3.2 Influence of toluene on gas/vapor mixed gas transport properties**

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26 Figure 3 presents the influence of toluene, at an activity of 0.28 (i.e., 1700 ppm), on
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28 relative CO_2 permeability at 9.4 atm CO_2 fugacity and 35 $^\circ\text{C}$. To clarify the presentation and
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30 explanation of the results, the actual CO_2 permeability was normalized to its value in a fresh film
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32 at the same feed fugacity before exposure to toluene (510 Barrer, cf., Table 3). First, pure gas
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34 CO_2 permeability in a toluene-free feed was monitored over time to serve as a control for the
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36 experiment. Any change in CO_2 permeability with time in this toluene-free feed would be due
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38 to factors, such as physical aging, that are unrelated to toluene exposure. Next, a fresh HAB-
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40 6FDA TR450 sample was loaded into the gas/vapor permeation apparatus, and toluene was
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42 introduced into the CO_2 feed. Gas/vapor mixed gas CO_2 permeability was monitored for three
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44 days to ensure that pseudo steady-state conditions were reached. Then, after three days, toluene
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46 was removed from the feed, and CO_2 permeability was monitored over time to investigate the
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48 recovery behavior. As shown in Figure 3, after toluene was initially introduced to the feed,
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50 CO_2 permeability decreased to about 7% of its initial value within 12 h and remained stable over
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52 the next three days. After toluene was removed, CO_2 permeability initially increased to about
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135 % of the pre-exposure value within 24 h, and then gradually decreased at a rate similar to that of the toluene-free control.

Figure 3: Influence of toluene (activity = 0.28, 1700 ppm) on pure and gas/vapor mixed gas CO₂ relative permeability (▲) of HAB-6FDA TR450 at 9.4 atm CO₂ fugacity and 35 °C. Toluene-free pure gas CO₂ permeability (●) was monitored over time as a control. Absolute CO₂ permeability coefficients are presented in the Supplementary Information.

The observed CO₂ permeability decrease in the presence of toluene is consistent with antiplasticization and competitive sorption. Toluene is a known antiplasticizer when incorporated into glassy polymers at low concentrations [5, 8, 56]. At such conditions, toluene can occupy free volume in a polymer matrix and could hinder chain motion, both of which could reduce penetrant diffusivity [22]. Additionally, toluene ($T_c = 591.8$ K [50]) is a highly condensable molecule that should compete very effectively with CO₂ ($T_c = 304.2$ K [50]) for sorption in the Langmuir sites, which would decrease CO₂ solubility in the presence of toluene

[41]. Consequently, these potential reductions in diffusivity and solubility likely contribute substantially to the observed 93% reduction in gas/vapor mixed gas CO₂ permeability. A qualitative assessment of antiplasticization and competitive sorption effects is provided below.

In addition, toluene, perhaps in conjunction with CO₂, could potentially swell the polymer and plasticize it. When toluene was present, any plasticization effect on CO₂ permeability was apparently overwhelmed by antiplasticization and competitive sorption. However, after toluene was removed from the feed, conditioning (i.e., swelling) of the polymer due to penetrant sorption was apparent based on CO₂ permeability increasing to values beyond those expected based on the initial toluene-free pure gas permeation results.

Figure 4 presents the influence of toluene, at an activity of 0.28 (i.e., 1700 ppm), on gas/vapor mixed gas CH₄ relative permeability at 9.7 atm CH₄ fugacity and 35 °C. The CH₄ permeability values in Figure 4 were normalized by the CH₄ permeability values in a fresh film at 9.7 atm CH₄ fugacity (26.3 Barrer, cf., Table 3). First, pure gas CH₄ permeability in a toluene-free feed was monitored over time to serve as a control for the experiment. Interestingly, over a fixed period of time with no toluene exposure, pure gas CH₄ permeability decreased less than pure gas CO₂ permeability (cf., Figure 3). For example, after seven days of constant exposure to CO₂ or CH₄, the sample experienced a ~16% decrease in pure gas CO₂ permeability and only a ~4% decrease in pure gas CH₄ permeability. If physical aging alone were responsible for the permeability decrease, then the reduction in permeability of a larger molecule, i.e., CH₄, should be more than that of a smaller molecule, i.e., CO₂ [57]. However, more condensable penetrants, i.e., CO₂, may plasticize the polymer to a certain extent, leading to an increase in polymer free volume and a decrease in T_g, which could accelerate physical aging [58-60]. Such an interplay between CO₂-induced plasticization and physical aging was

observed by Horn et al., who investigated the influence of CO₂ on physical aging of thin Matrimid polyimide films [60].

Figure 4: Influence of toluene (activity = 0.28, 1700 ppm) on pure and gas/vapor mixed gas CH₄ relative permeability (■) of HAB-6FDA TR450 at 9.7 atm CH₄ fugacity and 35 °C. Toluene-free pure gas CH₄ permeability (◆) was monitored over time and served as the control. Absolute CH₄ permeability coefficients are presented in the Supplementary Information.

The toluene effect on gas/vapor mixed gas CH₄ permeability was similar to that observed for CO₂. After toluene was introduced to the feed, CH₄ permeability decreased to about 3.6% of its initial value within 24 h and remained stable at this value for 3 days. Then, after 3 days, the toluene was removed from the feed, and CH₄ permeability initially recovered to about 80% of its pre-exposure value within three days, and gradually increased to about 90% of its pre-exposure value over the next five days. The main differences between the gas/vapor mixed gas CO₂ and CH₄ permeation behavior were the extents of permeability decrease upon toluene

exposure and permeability recovery after toluene removal. As already mentioned, CH₄ has a larger kinetic diameter (3.8 Å) than CO₂ (3.3 Å) [22], so CH₄ permeability should be more sensitive than CO₂ to any free volume changes due to antiplasticization [5]. Moreover, competitive sorption in the CH₄/toluene mixture should decrease the sorption of CH₄ more than that of CO₂, since CH₄ is less condensable ($T_c = 190.6$ K [50]) than either CO₂ ($T_c = 304.2$ K [50]) or toluene ($T_c = 591.8$ K [50]) [20, 61]. Therefore, it is reasonable that CH₄ permeability decreased more than that of CO₂ when toluene was present.

After toluene was removed, gas/vapor mixed gas CH₄ permeability recovered more gradually than CO₂ permeability. In addition, within the time frame of the experiment and in contrast to CO₂, CH₄ permeability did not return to a level higher than expected based on the control experiment. Because CO₂ is more condensable than CH₄ and, thus, more soluble in HAB-6FDA TR450 [41], the combination of toluene and CO₂ appears to have conditioned (i.e., swelled) the polymer matrix more than the combination of toluene and CH₄. As a result, after toluene was removed from the feed, gas/vapor mixed gas CO₂ permeability recovered more rapidly and to a greater extent than CH₄ did.

3.3 Influence of toluene on ternary mixed gas transport properties

Figures 5A and 5B present the influence of toluene, at an activity of 0.29 (i.e., 940 ppm), on ternary mixed gas CO₂ and CH₄ relative permeabilities. As presented in Figure 5A, the initial feed gas, prior to introduction of toluene, was a CO₂/CH₄ (50/50 mol%) mixture at 35 °C and 8.9 atm CO₂ fugacity (19.4 atm total feed pressure). CO₂ and CH₄ permeability coefficients were normalized to their respective binary mixed gas values (i.e., 490 Barrer for CO₂ and 22.9 Barrer for CH₄, cf., Table 3) before exposure to toluene. First, binary mixed gas CO₂ and CH₄ permeabilities in a toluene-free feed were monitored over time as a control. After about ten

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4 days of constant exposure to the feed mixture, there was little change in binary mixed gas CH₄
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6 permeability and a small decrease in binary mixed gas CO₂ permeability. Such changes in
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8 binary mixed gas permeability coefficients were less than those observed in the pure gas cases
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10 (cf., Figures 3 and 4), even though penetrant fugacity values were similar in both cases. One
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12 possibility is that at these permeation conditions, CH₄ may antiplasticize the polymer to a certain
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14 extent, occupying the polymer free volume and reducing the aging rate. Such antiplasticization
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16 effects may act against CO₂-induced plasticization and accelerated aging effects, resulting in
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18 smaller changes in gas permeability coefficients. Most previous physical aging studies using
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20 CH₄ were at lower feed fugacities (~2 atm) where CH₄ might act more as an inert probe
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22 penetrant [57]. At the higher fugacities used in this study, CH₄ may no longer be a perfectly
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24 inert probe molecule but may interact modestly with (i.e., antiplasticize) the polymer matrix.
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26 This effect may also partially explain why CH₄ pure gas permeabilities decreased less with time
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28 than pure gas CO₂ permeabilities (cf., Figures 3 and 4). However, this hypothesis deserves
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30 further experimental validation, and, in particular, additional studies are needed to separate these
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32 various effects.
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Figure 5: Influence of toluene (activity = 0.29, 940 ppm) on ternary mixed gas CO₂ and CH₄ relative permeabilities of HAB-6FDA TR450. The toluene-free feed gas in (A) was a CO₂/CH₄ (50/50 mol%) mixture at 8.9 atm CO₂ fugacity (19.4 atm total feed pressure) and 35 °C. Toluene-free binary mixed gas CO₂ and CH₄ relative permeability coefficients were monitored over time as a control. Absolute gas permeability coefficients are presented in the Supplementary Information.

Next, the influence of toluene on ternary mixed gas permeabilities was investigated using a fresh sample. As shown in Figure 5B, after toluene was introduced into the feed, both CO₂ and CH₄ permeabilities decreased to about 6% of their initial values within 24 h and remained stable at this value for 3 days. On Day 4, toluene was removed from the feed, and the ternary mixed gas CO₂ and CH₄ permeabilities increased to roughly 110 % and 120 % of their respective pre-exposure values. Because larger molecules, i.e., CH₄, should be more sensitive to increases in polymer free volume arising from penetrant-induced conditioning effects than smaller molecules [5, 22], i.e., CO₂, it is reasonable that ternary mixed gas CH₄ permeability recovered somewhat more than CO₂ after toluene was removed. Apparently, the presence of all three penetrants led to sufficient conditioning to result in ternary mixed gas CH₄ permeability

coefficients increasing to levels beyond their pre-exposure values, something not observed in the absence of CO₂ (cf., Figure 4).

Figure 6 compares the influence of toluene on gas/vapor and ternary mixed gas CO₂ and CH₄ relative permeabilities (Figure 6A) and selectivities (Figure 6B) at 35 °C. The CO₂ and CH₄ data in this figure are from Figures 3, 4, and 5B. As shown in Figure 6A, after toluene was removed from the film, ternary mixed gas CH₄ permeability recovered more (~120% of pre-exposure permeability) than gas/vapor mixed gas CH₄ permeability (~90% of pre-exposure permeability) over the time scale of this experiment. On the other hand, ternary mixed gas CO₂ permeability recovered less (~110% of pre-exposure permeability) than gas/vapor mixed gas CO₂ permeability (~135% of pre-exposure permeability). These differences in permeability recovery behavior support the earlier hypothesis that the combination of toluene and CO₂ potentially induces greater conditioning effects than the combination of toluene and CH₄. As a result, after toluene was removed, CO₂ experienced the largest increase in gas/vapor mixed gas relative permeability, and CH₄ experienced the largest increase in ternary mixed gas relative permeability.

Figure 6: Influence of toluene, at an activity of 0.28-0.29, on gas/vapor (filled symbols) and ternary (open symbols) mixed gas CO₂ and CH₄ (A) relative permeability and (B) selectivity at 35 °C. The CO₂ and CH₄ data in this figure are from Figures 3, 4, and 5B. In (A), the squares represent CH₄ relative permeability values, and the triangles represent CO₂ permeability values.

As shown in Figure 6B, after toluene was introduced to the feed, gas/vapor and ternary mixed gas CO₂/CH₄ selectivities initially increased. Both mixed gas cases exhibited similar CO₂ permeability reductions, but gas/vapor mixed gas CH₄ permeability decreased more than ternary mixed gas CH₄ permeability in the presence of toluene. As a result, the increase in gas/vapor mixed gas CO₂/CH₄ selectivity (from 19.5 to 42) was greater than that in the ternary mixed gas case (from 21.4 to 24). After toluene was removed, over the time scale of the experiment, gas/vapor mixed gas CO₂/CH₄ selectivity was consistently higher than ternary mixed gas CO₂/CH₄ selectivity. Comparison of these transport properties indicates that the influence of toluene on ternary mixed gas permeation can be quite different from that on gas/vapor mixed gas transport properties. These trends are discussed further below, after a short discussion on toluene vapor sorption to assist in explaining these results.

3.4 Toluene sorption and desorption

To shed further light on the effect of toluene on the CO₂ and CH₄ transport properties, the sorption of toluene vapor was measured. Figure 7 presents toluene sorption and desorption isotherms. The isotherms are concave to the activity axis, which is consistent with dual mode sorption behavior typically observed in glassy polymers [22, 53]. The dual mode model (Equation (4)) was fit to the sorption data. In addition, Equation (4) was used to divide sorption into Langmuir and Henry's law contributions. At low toluene activities (≤ 0.3), the rapid increase in toluene sorption with penetrant activity is mainly attributed to toluene's occupation of Langmuir sites in HAB-6FDA TR450, although there is some contribution of Henry's law sorption, particularly at activities above 0.1. At higher toluene activities (> 0.3), the Langmuir sites were mostly filled, and sorption takes place mainly in the Henry's law sites. Typically, penetrant sorption in the Henry's law region correlates strongly with polymer swelling and conditioning effects [24, 62].

Figure 7: Toluene sorption and desorption isotherms in HAB-6FDA TR450 at 35 °C. Dual mode parameters were obtained by fitting Equation (4) to the experimental sorption data. The Langmuir and Henry's law contribution to the toluene sorption isotherm were determined using Equation (4).

Figure 7 shows some hysteresis, likely due to polymer conditioning, during desorption [63]. As the external toluene activity is gradually reduced, penetrant-conditioned polymer may not immediately return to its preconditioned state [27, 58]. Such long-lived changes in polymer structure could persist over the experimental time scales of interest in this study. Additionally, even after the sample was exposed to dynamic vacuum for six days, which was comparable to the time scale of the permeation recovery phase in mixed gas tests (cf., Figure 5B), some residual toluene ($\sim 14 \text{ cm}^3(\text{STP})/\text{cm}^3 \text{ polymer}$) remained in the film. Omole et al. reported a similar observation and attributed this behavior to slow toluene desorption [61]. In this case, high toluene affinity for the Langmuir sites and the large size of toluene may markedly slow the desorption process.

Table 4 compares toluene dual mode parameters with those of other penetrants in HAB-6FDA TR450 [41]. Smith et al. reported sorption isotherms of CO₂, CH₄, O₂, and N₂ in HAB-6FDA TR450 at 35 °C [41]. Even though a thicker film with a somewhat lower TR conversion (cf., Table 1) was used by Smith et al., we can at least qualitatively compare the dual mode parameters for different penetrants in the polymer. Because toluene is more condensable than either methane or carbon dioxide [5], toluene sorption in the Langmuir domains will be heavily favored relative to that of the other gases due to competitive sorption. This preferential sorption of toluene is demonstrated in Table 4, in which the Langmuir affinity parameter, b , of toluene (967 atm⁻¹) is much larger than that of CO₂ (0.53 atm⁻¹) or CH₄ (0.16 atm⁻¹). Penetrant solubility in polymers typically correlates strongly with their condensability (e.g., critical temperature or normal boiling point) [64]. When considering penetrants whose critical temperatures span broad ranges, solubility coefficients have been correlated with the critical temperature squared [65]. Such a correlation is shown in Figures 8A and 8B, which present the Langmuir affinity parameter and Henry's law constant as a function of critical temperature squared on semilog scales. A good correlation of these dual mode parameters with T_c^2 is observed, despite the somewhat different thicknesses and conversions of the samples used to gather the data.

Table 4. Comparison of dual mode sorption parameters of gas penetrants in HAB-6FDA TR450 at 35 °C.

Sample	Penetrant	Dual mode sorption parameters			Reference
		k_d (cm ³ (STP)/(cm ³ polymer atm))	C_H' (cm ³ (STP)/cm ³ polymer)	b (atm ⁻¹)	
HAB-6FDA TR450	Toluene ^a	737	38	967	This study
	CO ₂ ^b	1.6	62	0.53	[41]
	CH ₄ ^b	0.49	36	0.16	
	O ₂ ^b	0.34	25	0.11	
	N ₂ ^b	0.25	21	0.084	

^a 6 μm film, 84% TR conversion

^b 40 μm film, 76% TR conversion

Figure 8: (A) The Langmuir affinity constant and (B) the Henry's law solubility constant of HAB-6FDA TR450 as a function of gas critical temperature squared. The dual mode parameters of CO₂, CH₄, O₂, and N₂ are from literature [41].

3.5 Influence of toluene activity on ternary mixed gas transport properties

Figure 9 presents the influence of toluene activity on ternary mixed gas CO_2 and CH_4 relative permeabilities in HAB-6FDA TR450 at 35 °C. Filled symbols indicate permeability coefficients measured as toluene activity in the feed was initially increased, and open symbols indicate permeability coefficients measured as toluene activity was subsequently decreased. The feed gas was an equimolar CO_2/CH_4 mixture at 4.7 atm CO_2 fugacity (9.9 atm total pressure). At each toluene activity, sufficient time was allowed for permeation to reach pseudo-steady state conditions (usually about 24 h, except at a toluene activity of 0 after toluene was desorbed from the film, when permeation required 7 days to reach a pseudo-steady state) before any permeation measurements were recorded. Therefore, the time to complete this experiment was about 7 days as toluene concentration in the feed increased and about 13 days as toluene concentration in the feed decreased. As presented in Figure 9, both ternary mixed gas CO_2 and CH_4 permeability coefficients initially decreased strongly with increasing toluene activity, up to an activity of 0.1. For example, CO_2 and CH_4 permeability coefficients decreased to about 16% of their pre-exposure values at a toluene activity of 0.03, and they decreased to about 7% at a toluene activity of 0.08. As shown in Figure 7, over the same range of toluene activity (0 - 0.1), the majority of the toluene sorbed resides in the Langmuir sites in the polymer matrix, consistent with competitive sorption contributing to reduced permeabilities in the presence of toluene.

Figure 9: Influence of toluene activity on normalized CO₂ (▲) and CH₄ (■) permeability (50/50 mol% CO₂/CH₄ feed) at 4.7 atm CO₂ fugacity (9.9 atm total pressure) and 35 °C. Filled symbols indicate permeabilities measured during toluene sorption, and open symbols indicate permeability measured during toluene desorption.

Another factor potentially contributing to the ternary mixed gas CO₂ and CH₄ permeability decrease is antiplasticization [14, 15, 17, 18]. To qualitatively describe the relative influence of competitive sorption and antiplasticiation by toluene on CO₂ or CH₄ permeability, the partial-immobilization dual mode model for binary penetrant mixtures was used [66]:

$$P_A = k_{D_A} D_{D_A} + C'_{H_A} D_{H_A} \frac{b_A}{1 + b_A f_A + b_B f_B} \quad (5)$$

where D_{D_A} and D_{H_A} are the diffusion coefficients associated with penetrant populations in the Henry's law and Langmuir modes, respectively. P_A is the permeability of species A, and f_A is the fugacity of A. C'_{H_A} , b_A , and k_{D_A} are the dual mode model parameters defined earlier. Table 5 presents projected dual mode parameters for an equimolar CO₂/CH₄ binary mixture in HAB-6FDA TR450 (84% TR conversion). The projected values were estimated based on reported dual mode parameters for HAB-6FDA TR polymers at lower TR conversions [39], and a detailed description of the estimation strategy is included in the Supplementary Information.

Table 5. Estimated dual mode parameters for an equimolar CO₂/CH₄ binary mixture in HAB-6FDA TR450 (84% TR conversion). The dual mode values were estimated based on reported data for HAB-6FDA TR polymers at lower TR conversions [39], and the estimation strategy is described in more detail in the Supplementary Information.

Sample	Gas	$k_{D_A}D_{D_A}$ (Barrer)	$C'_{H_A}D_{H_A}$ (Barrer atm)	b (atm ⁻¹)
HAB-6FDA TR450 (84% TR conversion)	CO ₂	380	2300	0.16
	CH ₄	18.9	240	0.038

The first term on the right hand side of Equation (5) describes gas permeation in the Henry's law mode, and the second term describes gas permeation in the Langmuir mode. If toluene occupied all of the Langmuir sites, CO₂ or CH₄ would permeate only through the Henry's law mode and, according to Equation (5), penetrant permeability would approach a value of $k_{D_A}D_{D_A}$, which is 380 Barrer for CO₂ and 18.9 Barrer for CH₄ (cf., Table 5). For an equimolar CO₂/CH₄ mixture at 4.7 atm CO₂ fugacity, CO₂ and CH₄ binary mixed gas permeability coefficients (cf., Table 3) would decrease by about 33% and 21%, respectively, if the Langmuir domains were completely inaccessible to CO₂ or CH₄. However, as shown in Figure 9, at the lowest toluene activity considered (0.03), CO₂ and CH₄ permeability decreased

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4 by more than 80%, which is much more than might be expected based on competitive sorption
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6 alone. Thus, in addition to decreases in sorption coefficients due to toluene competitive
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8 sorption, the CO₂ and CH₄ diffusion coefficients were also likely decreased due to
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10 antiplasticization effects. Based on this analysis, at low toluene activities, antiplasticization is
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12 more important than competitive sorption.
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16 Omole et al. reported a similar observation in a study of toluene effect on mixed gas CO₂
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18 and CH₄ permeation properties of a crosslinked polyimide hollow fiber [5]. Omole et al.
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20 postulated that toluene-induced antiplasticization reduced polymer chain mobility and hindered
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22 the transient gap formation required for penetrants diffusion, thereby decreasing diffusion
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24 coefficients [5]. In another study investigating the contaminant influence on CO₂ and CH₄
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26 transport properties, White et al. reported that the gas permeation properties of a 6FDA-
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28 containing polyimide are more sensitive to contaminants, at saturation conditions, than that of
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30 cellulose acetate (CA) [6]. Additionally, White et al. speculated that diffusivity, which is
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32 sensitive to structural changes promoted by contaminant-induced plasticization at high activities,
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34 contributed more to gas selectivity of the polyimide than that of CA. Therefore, for highly size-
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36 selective materials such as the polyimide considered, plasticization appeared to be a more
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38 important factor than competitive sorption. This speculation is consistent with our findings,
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40 where at low toluene activities, antiplasticization appears to be more important than competitive
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51 In any case, determining precise competitive sorption and antiplasticization effects on gas
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53 transport properties is difficult. As mentioned earlier, there can be a variety of effects on gas
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55 permeation properties depending on both the contaminant and the polymer of interest [6], which
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57 highlights the complexity of the observed gas transport behavior. Additionally, an
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unambiguous determination of dual mode parameters, especially in a ternary mixture, can be difficult. Because verification of the dual mode model in such complex cases is not well-established, a quantitative analysis of antiplasticization and competitive sorption effects is beyond the scope of this study.

As presented in Figure 9, as toluene desorbed from the film after reaching the maximum activity considered (0.7), ternary mixed gas CH₄ permeabilities were slightly higher than those measured during toluene sorption, possibly due to conditioning effects (i.e., swelling) induced by the ternary gas mixture. After toluene was removed from the feed gas mixture, CO₂ and CH₄ permeability coefficients returned to about 84% of their respective pre-exposure values and remained at that level for the duration of the experiment, which was about six days. Such permeability recovery behavior is somewhat different from that presented earlier (cf., Figure 5B), where within 24 h of toluene (activity ~ 0.28 in the feed gas) removal, both CO₂ and CH₄ ternary mixed gas permeability coefficients increased to levels above their pre-exposure values. Because toluene concentration in the Henry's law sites is linearly correlated with toluene activity (cf., Figure 7), toluene-induced conditioning should be more extensive at an activity of 0.7 than that at an activity of 0.28. Additionally, complete toluene desorption from the sample may require long time frames, so after reaching an activity of 0.7, some residual toluene might remain in the film over the experimental time scale of interest in this study (cf., Figure 7). Any residual toluene in the sample could continue to exert competitive sorption and antiplasticization effects, thereby inhibiting CO₂ and CH₄ permeabilities from returning to pre-exposure (or higher) values.

Figure 10 presents the influence of toluene sorption and desorption on ternary mixed gas CO₂/CH₄ selectivity values, which were calculated based on the data presented in Figure 9.

During toluene sorption, CO_2/CH_4 selectivity initially increased from 23.4 for a toluene-free binary mixed gas feed to 25.3 for a ternary mixed gas feed at a toluene activity of 0.08, and then decreased monotonically to 20.3 at a toluene activity of 0.7. The initial increase in selectivity may be due to antiplasticization and competitive sorption effects, both of which would decrease permeability more for the larger, less soluble molecule (i.e., CH_4) than for the smaller, more soluble molecule (i.e., CO_2), thereby increasing CO_2/CH_4 selectivity [14, 16, 39]. At higher toluene activities, the Langmuir domains become saturated and additional toluene sorption occurs mainly in the Henry's law mode (cf., Figure 7), promoting polymer swelling. Such swelling would tend to weaken the size-sieving ability of the polymer, leading to a decrease in CO_2/CH_4 selectivity. As toluene activity was reduced, the polymer chains remained in a more swollen, conditioned state, and selectivity was relatively unchanged. Finally, as toluene activity in the feed decreased to below 0.16 (< 1000 ppm), less toluene would be sorbed in the Langmuir sites, and conditioning-induced swelling would begin to relax. Both of these factors would increase CO_2/CH_4 selectivity, in this case back to essentially the pre-exposure level.

Figure 10: Influence of toluene sorption and desorption on CO_2/CH_4 selectivity (50/50 mol% CO_2/CH_4 feed) at 4.7 atm fugacity of CO_2 (9.9 atm total pressure) and 35 °C.

4. CONCLUSIONS

The influence of toluene on gas/vapor and ternary mixed gas CO_2 and CH_4 transport properties for HAB-6FDA TR450 was investigated. For toluene-free pure and mixed gas feed, CO_2 and CH_4 permeability coefficients decreased as fugacity increased, which is consistent with typical dual mode behavior. As a result of competitive sorption, CH_4 permeability was depressed in mixtures with CO_2 , which increased selectivity. Gas/vapor mixed gas CO_2 and CH_4 permeability coefficients decreased significantly in the presence of toluene, due to a combination of antiplasticization and competitive sorption effects. After toluene was removed from the feed, gas/vapor mixed gas CO_2 permeability recovered more rapidly than that of CH_4 and to a level higher than the pre-toluene exposure level, which is attributed to polymer

conditioning (i.e., matrix swelling) induced by the CO₂/toluene mixture. Upon removing toluene from the feed, CH₄ permeability in a ternary gas mixture recovered more quickly and increased to a higher level than in a gas/vapor mixture, indicating that the presence of all three penetrants led to more extensive polymer conditioning than in the CH₄/toluene mixture alone. Polymer conditioning was also observed via hysteresis in the toluene vapor sorption and desorption isotherms. Gas transport properties also depended strongly on toluene concentration in the feed. As toluene activity in the feed increased, ternary mixed gas CO₂ and CH₄ permeabilities decreased by more than 80% at toluene activities as low as 0.03. CO₂/CH₄ selectivity values in the ternary mixture initially increased from 23.4 to 25.3 at low toluene activities, and they then decreased to 20.3 at higher toluene activities. However, these effects in the ternary mixture were mostly reversed after toluene was removed from the feed.

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5. REFERENCES

- [1] R.W. Baker, K. Lokhandwala, Natural gas processing with membranes: an overview, *Industrial & Engineering Chemistry Research*, 47 (2008) 2109-2121.
- [2] D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B.D. Freeman, Energy-efficient polymeric gas separation membranes for a sustainable future: a review, *Polymer*, 54 (2013) 4729-4761.
- [3] R.W. Baker, B.T. Low, Gas separation membrane materials: a perspective, *Macromolecules*, 47 (2014) 6999-7013.
- [4] N. Tanihara, H. Shimazaki, Y. Hirayama, S. Nakanishi, T. Yoshinaga, Y. Kusuki, Gas permeation properties of asymmetric carbon hollow fiber membranes prepared from asymmetric polyimide hollow fiber, *Journal of Membrane Science*, 160 (1999) 179-186.
- [5] I.C. Omole, D.A. Bhandari, S.J. Miller, W.J. Koros, Toluene impurity effects on CO₂ separation using a hollow fiber membrane for natural gas, *Journal of Membrane Science*, 369 (2011) 490-498.
- [6] L.S. White, T.A. Blinka, H.A. Kloczewski, I.f. Wang, Properties of a polyimide gas separation membrane in natural gas streams, *Journal of Membrane Science*, 103 (1995) 73-82.
- [7] J.S. Lee, R.T. Adams, W. Madden, W.J. Koros, Toluene and n-heptane sorption in Matrimid[®] asymmetric hollow fiber membranes, *Polymer*, 50 (2009) 6049-6056.
- [8] J.S. Lee, W. Madden, W.J. Koros, Antiplasticization and plasticization of Matrimid[®] asymmetric hollow fiber membranes—Part A. Experimental, *Journal of Membrane Science*, 350 (2010) 232-241.
- [9] J.S. Lee, J. Leisen, R.P. Choudhury, R.M. Kriegel, H.W. Beckham, W.J. Koros, Antiplasticization-based enhancement of poly(ethylene terephthalate) barrier properties, *Polymer*, 53 (2012) 213-222.
- [10] B. Pereira, W. Admassu, Effects of chemical impurities on gas permeation and diffusion in polymeric membranes, *Separation Science and Technology*, 36 (2001) 3121-3140.
- [11] M. Al-Juaied, W.J. Koros, Performance of natural gas membranes in the presence of heavy hydrocarbons, *Journal of Membrane Science*, 274 (2006) 227-243.
- [12] C.J. Anderson, W. Tao, C.A. Scholes, G.W. Stevens, S.E. Kentish, The performance of carbon membranes in the presence of condensable and non-condensable impurities, *Journal of Membrane Science*, 378 (2011) 117-127.
- [13] C. Ma, W.J. Koros, Effects of hydrocarbon and water impurities on CO₂/CH₄ separation performance of ester-crosslinked hollow fiber membranes, *Journal of Membrane Science*, 451 (2014) 1-9.

- [14] Y. Maeda, D.R. Paul, Effect of antiplasticization on gas sorption and transport. I. Polysulfone, *Journal of Polymer Science Part B: Polymer Physics*, 25 (1987) 957-980.
- [15] J.S. Vrentas, J.L. Duda, H.C. Ling, Antiplasticization and volumetric behavior in glassy polymers, *Macromolecules*, 21 (1988) 1470-1475.
- [16] Y. Maeda, D.R. Paul, Effect of antiplasticization on selectivity and productivity of gas separation membranes, *Journal of Membrane Science*, 30 (1987) 1-9.
- [17] Y. Maeda, D.R. Paul, Effect of antiplasticization on gas sorption and transport. II. Poly(phenylene oxide), *Journal of Polymer Science Part B: Polymer Physics*, 25 (1987) 981-1003.
- [18] Y. Maeda, D.R. Paul, Effect of antiplasticization on gas sorption and transport. III. Free volume interpretation, *Journal of Polymer Science Part B: Polymer Physics*, 25 (1987) 1005-1016.
- [19] N.M. Larocca, L.A. Pessan, Effect of antiplasticisation on the volumetric, gas sorption and transport properties of polyetherimide, *Journal of Membrane Science*, 218 (2003) 69-92.
- [20] W.C. Madden, The performance of hollow fiber gas separation membranes in the presence of an aggressive feed stream (Doctoral dissertation, Georgia Institute of Technology, Atlanta, GA, USA), (2005).
- [21] J.S. Lee, Fundamentals of transport in advanced barrier materials based on engineered antiplasticization (Doctoral dissertation, Georgia Institute of Technology, Atlanta, GA, USA), (2011).
- [22] B. Freeman, Y. Yampolskii, I. Pinnau, *Materials science of membranes for gas and vapor separation*, John Wiley and Sons, 2006.
- [23] S. Zhou, S.A. Stern, The effect of plasticization on the transport of gases in and through glassy polymers, *Journal of Polymer Science Part B: Polymer Physics*, 27 (1989) 205-222.
- [24] J.S. Chiou, J.W. Barlow, D.R. Paul, Plasticization of glassy polymers by CO₂, *Journal of Applied Polymer Science*, 30 (1985) 2633-2642.
- [25] R.T. Chern, C.N. Provan, Gas-induced plasticization and the permselectivity of poly(tetrabromophenolphthalein terephthalate) to a mixture of carbon dioxide and methane, *Macromolecules*, 24 (1991) 2203-2207.
- [26] A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, CO₂-induced plasticization phenomena in glassy polymers, *Journal of Membrane Science*, 155 (1999) 67-78.
- [27] S.M. Jordan, W.J. Koros, G.K. Fleming, The effects of CO₂ exposure on pure and mixed gas permeation behavior: comparison of glassy polycarbonate and silicone rubber, *Journal of Membrane Science*, 30 (1987) 191-212.

- [28] H.D. Kamaruddin, W.J. Koros, Sorption of methanol/MTBE and diffusion of methanol in 6FDA–ODA polyimide, *Journal of Polymer Science Part B: Polymer Physics*, 38 (2000) 2254-2267.
- [29] I. Pinnau, C.G. Casillas, A. Morisato, B.D. Freeman, Hydrocarbon/hydrogen mixed gas permeation in poly(1-trimethylsilyl-1-propyne) (PTMSP), poly(1-phenyl-1-propyne) (PPP), and PTMSP/PPP blends, *Journal of Polymer Science Part B: Polymer Physics*, 34 (1996) 2613-2621.
- [30] D.F. Sanders, Z.P. Smith, C.P. Ribeiro Jr, R. Guo, J.E. McGrath, D.R. Paul, B.D. Freeman, Gas permeability, diffusivity, and free volume of thermally rearranged polymers based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), *Journal of Membrane Science*, 409-410 (2012) 232-241.
- [31] H.B. Park, C.H. Jung, Y.M. Lee, A.J. Hill, S.J. Pas, S.T. Mudie, E. Van Wagner, B.D. Freeman, D.J. Cookson, Polymers with cavities tuned for fast selective transport of small molecules and ions, *Science*, 318 (2007) 254-258.
- [32] R. Guo, D.F. Sanders, Z.P. Smith, B.D. Freeman, D.R. Paul, J.E. McGrath, Synthesis and characterization of thermally rearranged (TR) polymers: influence of ortho-positioned functional groups of polyimide precursors on TR process and gas transport properties, *Journal of Materials Chemistry A*, 1 (2013) 262-272.
- [33] R. Guo, D.F. Sanders, Z.P. Smith, B.D. Freeman, D.R. Paul, J.E. McGrath, Synthesis and characterization of thermally rearranged (TR) polymers: effect of glass transition temperature of aromatic poly(hydroxyimide) precursors on TR process and gas permeation properties, *Journal of Materials Chemistry A*, 1 (2013) 6063-6072.
- [34] D.F. Sanders, R. Guo, Z.P. Smith, K.A. Stevens, Q. Liu, J.E. McGrath, D.R. Paul, B.D. Freeman, Influence of polyimide precursor synthesis route and ortho-position functional group on thermally rearranged (TR) polymer properties: pure gas permeability and selectivity, *Journal of Membrane Science*, 463 (2014) 73-81.
- [35] D.F. Sanders, R. Guo, Z.P. Smith, Q. Liu, K.A. Stevens, J.E. McGrath, D.R. Paul, B.D. Freeman, Influence of polyimide precursor synthesis route and ortho-position functional group on thermally rearranged (TR) polymer properties: conversion and free volume, *Polymer*, 55 (2014) 1636-1647.
- [36] Y. Jiang, F.T. Willmore, D. Sanders, Z.P. Smith, C.P. Ribeiro, C.M. Doherty, A. Thornton, A.J. Hill, B.D. Freeman, I.C. Sanchez, Cavity size, sorption and transport characteristics of thermally rearranged (TR) polymers, *Polymer*, 52 (2011) 2244-2254.
- [37] C.H. Park, E. Tocci, S. Kim, A. Kumar, Y.M. Lee, E. Drioli, A simulation study on OH-containing polyimide (HPI) and thermally rearranged polybenzoxazoles (TR-PBO): relationship between gas transport properties and free volume morphology, *The Journal of Physical Chemistry B*, 118 (2014) 2746-2757.
- [38] H.B. Park, S.H. Han, C.H. Jung, Y.M. Lee, A.J. Hill, Thermally rearranged (TR) polymer membranes for CO₂ separation, *Journal of Membrane Science*, 359 (2010) 11-24.

- [39] K.L. Gleason, Z.P. Smith, Q. Liu, D.R. Paul, B.D. Freeman, Pure- and mixed-gas permeation of CO₂ and CH₄ in thermally rearranged polymers based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), *Journal of Membrane Science*, 475 (2015) 204-214.
- [40] C.A. Scholes, B.D. Freeman, S.E. Kentish, Water vapor permeability and competitive sorption in thermally rearranged (TR) membranes, *Journal of Membrane Science*, 470 (2014) 132-137.
- [41] Z.P. Smith, D.F. Sanders, C.P. Ribeiro, R. Guo, B.D. Freeman, D.R. Paul, J.E. McGrath, S. Swinnea, Gas sorption and characterization of thermally rearranged polyimides based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), *Journal of Membrane Science*, 415-416 (2012) 558-567.
- [42] G.L. Tullos, J.M. Powers, S.J. Jeskey, L.J. Mathias, Thermal conversion of hydroxy-containing imides to benzoxazoles: polymer and model compound study, *Macromolecules*, 32 (1999) 3598-3612.
- [43] H. Wang, T.-S. Chung, D.R. Paul, Physical aging and plasticization of thick and thin films of the thermally rearranged ortho-functional polyimide 6FDA-HAB, *Journal of Membrane Science*, 458 (2014) 27-35.
- [44] A. Bondi, van der Waals volumes and radii, *The Journal of Physical Chemistry*, 68 (1964) 441-451.
- [45] H. Lin, B.D. Freeman, Permeation and diffusion, *Springer Handbook of Materials Measurement Methods*, (2006) 371-387.
- [46] J.H. Dymond, E.B. Smith, *The virial coefficients of pure gases and mixtures: a critical compilation*, Clarendon Press, 1980.
- [47] J.S. Lee, P. Chandra, S.K. Burgess, R. Kriegel, W.J. Koros, An advanced gas/vapor permeation system for barrier materials: design and applications to poly(ethylene terephthalate), *Journal of Polymer Science Part B: Polymer Physics*, 50 (2012) 1262-1270.
- [48] J.W. McBain, A.M. Bakr, A new sorption balance, *Journal of the American Chemical Society*, 48 (1926) 690-695.
- [49] A. Singh, B.D. Freeman, I. Pinnau, Pure and mixed gas acetone/nitrogen permeation properties of polydimethylsiloxane [PDMS], *Journal of Polymer Science Part B: Polymer Physics*, 36 (1998) 289-301.
- [50] J.M. Smith, H.C. Van Ness, M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, 2005.
- [51] M.D. Abràmoff, P.J. Magalhães, S.J. Ram, Image processing with ImageJ, *Biophotonics international*, 11 (2004) 36-42.

- [52] W.R. Vieth, J.M. Howell, J.H. Hsieh, Dual sorption theory, *Journal of Membrane Science*, 1 (1976) 177-220.
- [53] T.A. Barbari, W.J. Koros, D.R. Paul, Gas transport in polymers based on bisphenol-A, *Journal of Polymer Science Part B: Polymer Physics*, 26 (1988) 709-727.
- [54] Z.P. Smith, R.R. Tiwari, M.E. Dose, K.L. Gleason, T.M. Murphy, D.F. Sanders, G. Gunawan, L.M. Robeson, D.R. Paul, B.D. Freeman, Influence of diffusivity and sorption on helium and hydrogen separations in hydrocarbon, silicon, and fluorocarbon-based polymers, *Macromolecules*, 47 (2014) 3170-3184.
- [55] H. Wang, T.-S. Chung, D.R. Paul, Thickness dependent thermal rearrangement of an ortho-functional polyimide, *Journal of Membrane Science*, 450 (2014) 308-312.
- [56] J.K. Ward, W.J. Koros, Crosslinkable mixed matrix membranes with surface modified molecular sieves for natural gas purification: II. Performance characterization under contaminated feed conditions, *Journal of Membrane Science*, 377 (2011) 82-88.
- [57] Y. Huang, D.R. Paul, Physical aging of thin glassy polymer films monitored by gas permeability, *Polymer*, 45 (2004) 8377-8393.
- [58] B.W. Rowe, B.D. Freeman, D.R. Paul, Effect of sorbed water and temperature on the optical properties and density of thin glassy polymer films on a silicon substrate, *Macromolecules*, 40 (2007) 2806-2813.
- [59] N.R. Horn, D.R. Paul, Carbon dioxide plasticization and conditioning effects in thick vs. thin glassy polymer films, *Polymer*, 52 (2011) 1619-1627.
- [60] N.R. Horn, D.R. Paul, Carbon dioxide plasticization of thin glassy polymer films, *Polymer*, 52 (2011) 5587-5594.
- [61] I.C. Omole, Crosslinked polyimide hollow fiber membranes for aggressive natural gas feed streams (Doctoral dissertation, Georgia Institute of Technology, Atlanta, GA, USA), (2008).
- [62] G.K. Fleming, W.J. Koros, Carbon dioxide conditioning effects on sorption and volume dilation behavior for bisphenol A-polycarbonate, *Macromolecules*, 23 (1990) 1353-1360.
- [63] M. Galizia, M.G. De Angelis, E. Finkelshtein, Y.P. Yampolskii, G.C. Sarti, Sorption and transport of hydrocarbons and alcohols in addition-type poly(trimethyl silyl norbornene). I: Experimental data, *Journal of Membrane Science*, 385-386 (2011) 141-153.
- [64] K. Toi, G. Morel, D.R. Paul, Gas sorption and transport in poly(phenylene oxide) and comparisons with other glassy polymers, *Journal of Applied Polymer Science*, 27 (1982) 2997-3005.
- [65] A.Y. Alentiev, V.P. Shantarovich, T.C. Merkel, V.I. Bondar, B.D. Freeman, Y.P. Yampolskii, Gas and vapor sorption, permeation, and diffusion in glassy amorphous Teflon AF1600, *Macromolecules*, 35 (2002) 9513-9522.

[66] W.J. Koros, R.T. Chern, V. Stannett, H.B. Hopfenberg, A model for permeation of mixed gases and vapors in glassy polymers, Journal of polymer science: Polymer Physics Edition, 19 (1981) 1513-1530.