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**Pure- and mixed-gas propylene/propane permeation properties of spiro-
and triptycene-based microporous polyimides**

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Abstract

Solution-processable polyimides of intrinsic microporosity (PIM-PIs) comprising relatively inflexible and contorted backbones have demonstrated outstanding molecular-sieving behavior in membrane-based separation of gas/gas pairs. In this work, the effects of systematically increasing intra-chain rigidity on the propylene/propane separation properties were compared for PIM-PIs made from 2,3,5,6-tetramethyl-1,4-phenylene diamine (TMPD) and (i) spiro-centered dianhydride (SPDA-TMPD or PIM-PI-1) and (ii) 9,10-diisopropyltritycene-based dianhydride (TPDA-TMPD or KAUST PI-1). Pure-gas experiments at 2 bar and 35 °C showed significant increases in C_3H_6 permeability and C_3H_6/C_3H_8 selectivity by transitioning from PIM-PI-1 ($P(C_3H_6)=393$ Barrer, $\alpha(C_3H_6/C_3H_8)=6$) to KAUST-PI-1 ($P(C_3H_6)=817$ Barrer, $\alpha(C_3H_6/C_3H_8)=16$), positioning KAUST-PI-1 considerably above the experimentally observed pure-gas C_3H_6/C_3H_8 polymer upper bound. However, 50:50 C_3H_6/C_3H_8 mixed-gas feeds induced significant losses in C_3H_6 permeability and C_3H_6/C_3H_8 selectivity relative to the 2 bar pure-gas data for PIM-PI-1 and KAUST-PI-1 as the C_3H_6/C_3H_8 selectivity dropped from 6 to 3 and 16 to 5, respectively, at 2 bar C_3H_6 partial pressure due to plasticization and competitive sorption.

1. Introduction

Propylene is the second most used feedstock in the petrochemical industry for the production of plastics (e.g. polypropylene) and chemicals (e.g. propylene oxide, isopropanol, and acrylonitrile) [1]. In 2009, approximately 13 million metric tons of propylene were produced in the US and this figure continues to rise [1]. To meet this current demand for propylene production, olefin and paraffin components are separated in industry using cryogenic distillation which is a highly energy intensive process often requiring tall fractionation towers with 200 trays or more and high reflux ratios due to the marginal difference in condensability of C_3H_6 and C_3H_8 [2]. A recent report by the U.S. Department of Energy recommended incorporation of a gas separation membrane in the process to reduce the separation load on the distillation columns and, therefore, the overall energy consumption and process economics [3].

Besides being a potentially lower energy intensive process to distillation technology, polymer membranes are attractive candidates for C_3H_6/C_3H_8 separation because the modular technology is amenable to retrofitting existing plants and they offer relatively simple and continuous operation [4]. Ideally, a polymer membrane should exhibit high permeability *and* high selectivity, but a tradeoff relationship exists such that increasing permeability is concomitant with decreasing selectivity as embodied by Robeson's upper bounds [5, 6]. An experimentally observed upper bound has also been identified for C_3H_6/C_3H_8 separation by Burns and Koros and was defined by two low-free-volume conventional polyimides, namely 6FDA-DDBT ($P(C_3H_6)=1.8$ Barrer, $\alpha(C_3H_6/C_3H_8)=20$) and 6FDA-TrMPD ($P(C_3H_6)=30$ Barrer, $\alpha(C_3H_6/C_3H_8)=11$) [7]. However, these upper bounds have been derived from idealistic pure-gas experiments, which neglect the

potentially significant effects of plasticization and competitive sorption often encountered in mixed-gas feeds involving highly condensable gases like C_3H_6 and C_3H_8 [8, 9]. Usually, approximately 30% reductions in the C_3H_6 permeability were observed in previous studies using 50:50 C_3H_6/C_3H_8 mixed-gas feeds relative to pure-gas conditions at similar C_3H_6 partial pressures due to competitive sorption with C_3H_8 [10-12]. In addition, plasticization compromises the ability of the membrane to sieve similarly sized gases, thereby increasing the mixed-gas permeability of the larger C_3H_8 gas and reducing selectivity under mixed-gas conditions [13]. Baker and Low stated that many processes would benefit from a membrane with a C_3H_6 permeance of 20-40 gas permeation units ($1 \text{ GPU} = 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$) and a C_3H_6/C_3H_8 selectivity of 6-10 [14].

Polymers of intrinsic microporosity (PIMs) are a rapidly emerging class of high-performance materials which, on one hand, can readily offer high permeability attractive to the C_3H_6/C_3H_8 separation [15, 16]. Structurally, PIMs comprise relatively inflexible macromolecular architectures integrating contortion sites that help disrupt packing and trap microporous free volume elements ($< 20 \text{ \AA}$). Recently, solution-processable PIMs (ladder-type and PIM-polyimides (PIM-PIs)) have been designed and predominantly evaluated for gas/gas separations (i.e. O_2/N_2 , H_2/N_2 , H_2/CH_4 , CO_2/CH_4) [17-25]. Only a few studies on PIMs, specifically the prototypical ladder-type PIM-1, have revealed outstanding vapor/gas separation properties [26, 27]. Additionally, two studies investigated the C_3H_6/C_3H_8 separation properties of PIM-1 in its pristine, annealed, and covalently crosslinked states and demonstrated permeability-driven performance enhancements (ranging from 18 to ~8,000 Barrer) at the expense of selectivity (ranging from 2.5 to 9) [28, 29]. However, the latter studies reported only pure-gas data measured

at 1-2 bar. Mixed-gas data are critical to evaluating permeability- and selectivity-driving non-ideal phenomena including plasticization and competitive sorption.

Moreover, it has been recently demonstrated that PIMs and PIM-PIs can be rationally designed to merge high permeability with high selectivity for gas/gas separations. That is, replacing the spirobisindane contortion centers (single tetrahedral carbon atom shared by two rings) of the earliest reported solution-processable ladder PIMs [20, 30, 31] and PIM-PIs [17, 23, 32, 33] with bridged bicyclics (e.g., ethanoanthracene [34], Tröger's base [35, 36], and triptycene [18, 19, 21, 37]) enhanced the polymer intra-chain rigidity to simultaneously boost permeability *and* selectivity. For example, replacing only the relatively flexible spirobisindane (SPDA) contortion center of PIM-PI-1 with a shape-persistent 9,10-diisopropyltriptycene (TPDA) moiety (i.e., KAUST-PI-1) and barring any other changes in the backbone (Fig. 1) results in simultaneous four-fold increases in O₂ permeability and two-fold increases in O₂/N₂ selectivity, positioning KAUST-PI-1 significantly above the latest 2008 O₂/N₂ upper bound [19]. Using physisorption studies, this trend was attributed to the development of a size-sieving ultra-microporous polymer structure. However, no investigations of vapor/vapor separation properties using PIM-PIs have been reported to date.

Fig. 1. Chemical structures of a) KAUST-PI-1 and b) PIM-PI-1 highlighting the 9,10-diisopropyltritycene (red) and spirobisindane (blue) contortion centers.

In this paper, the C_3H_6/C_3H_8 separation properties of two high performance PIM-PIs (PIM-PI-1 and KAUST-PI-1) differing only in the contortion center of their dianhydride structures are explored for the first time in pure- and 50:50 C_3H_6/C_3H_8 mixed-gas feeds at 35 °C and compared to previously published permeation data for 6FDA-TMPD. Microstructural differences between PIM-PI-1 and KAUST-PI-1 were evaluated using physisorption isotherms (N_2 at -196 °C) and high-pressure sorption experiments for a structure/property discussion of the permeation results. A preliminary discussion on the potential for these high free-volume polymers to efficiently separate propylene from propane is provided in the context of repeat unit design principles.

2. Experimental

2.1. Polymer Synthesis

PIM-PI-1 and KAUST-PI-1 (Fig. 1) were synthesized and characterized according to previously reported procedures [17, 18]. Briefly, equimolar amounts of diamine and dianhydride monomers were stirred in *m*-cresol with isoquinoline. After 1 h, the temperature was raised to 200 °C and held for 4 h under a nitrogen atmosphere, during which water formed by the imidization reaction was removed by azeotropic distillation using anhydrous toluene. Fibrous polyimides were obtained by precipitation of the polymer solution in methanol. The resulting solids were filtered and purified by reprecipitation from chloroform in methanol.

2.2. Low-pressure physisorption and pore-size distribution analysis

Micromeritics ASAP 2020 with software version 4.02 was utilized to perform nitrogen sorption measurements at -196 °C up to 1 bar. Powder samples of PIM-PI-1 and KAUST-PI-1 were dried at 120 °C under high vacuum for 24 hours before initiation of the experiment.

2.3. Polymer film preparation

Solutions of 3-5 % w/w polymer in chloroform were filtered using 0.45 µm PTFE syringe-filters, cast on a leveled glass plate and covered to induce slow evaporation and formation of homogenous films. The freshly cast films were dried under vacuum at 120 °C for 24 hours, soaked in methanol (a non-solvent) at room temperature for 24 hours, and finally dried under vacuum at 120 °C for 24 hours. Soaking the film in methanol

swells the polymers and facilitates removal of residual solvent trapped in the micropores during casting [38]. Thermogravimetric analysis (TGA) confirmed complete solvent removal. The film thicknesses were determined by a digital micrometer to be ~130 μm for PIM-PI-1 and ~100 μm for KAUST-PI-1. The film areas were determined by calibrated scanning software.

2.4. High-pressure sorption

High-pressure propylene and propane sorption isotherms were collected up to 8 bar on powder samples of PIM-PI-1 and KAUST-PI-1 at 35 °C using a gravimetric Hiden IGA system. Samples were degassed under high vacuum for at least 24 hours until the mass of the sample had equilibrated before beginning collection of the isotherm points. The solubility coefficients, S (cm^3 (STP) cm^{-3} cmHg^{-1}), for C_3H_6 and C_3H_8 were determined at each pressure point from the gas concentration in the polymer, C (cm^3 (STP) cm^{-3}) and the pressure, p (cmHg), by:

$$S = \frac{C}{p}$$

$\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ solubility selectivities (α_S) were determined as the ratio of the solubility coefficients of C_3H_6 and C_3H_8 at each pressure point.

2.5. Pure-gas $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ permeation

Permeabilities were determined using the constant-volume/variable-pressure method. Membrane films were degassed in the permeation apparatus upstream and downstream at 35 °C. The change in permeate pressure per unit time was measured by a 100 torr MKS

Baratron transducer. C_3H_6 and C_3H_8 permeabilities measured at 2 bar and 35 °C were calculated by:

$$P = DS = 10^{10} \frac{V_d l}{p_{up} A R T} \frac{dp}{dt}$$

where P is the permeability coefficient (1 Barrer = 10^{-10} cm³(STP) cm/cm² s cmHg = 7.5×10^{-18} m³(STP) m m⁻² s⁻¹ Pa⁻¹), D is the diffusion coefficient, S is the solubility coefficient, dp/dt is the permeate-side pressure increase (cmHg/s), V_d is the downstream volume (cm³), l is the membrane thickness (cm), p_{up} is the upstream feed pressure (cmHg), A is the membrane area (cm²), R is the gas constant (0.278 cm³ cmHg cm⁻³(STP) K⁻¹), and T is the permeation temperature (K). The ideal selectivity for C_3H_6/C_3H_8 was calculated via:

$$\alpha_{A/B} = P_A/P_B$$

2.6. Mixed-gas (50:50) C_3H_6/C_3H_8 permeation measurements

Pressure-dependent mixed-gas testing was conducted at 35 °C with a 50:50 C_3H_6/C_3H_8 mixture using a setup comparable to that reported by O'Brien et al [39]. A stage-cut of less than 0.01 was used to avoid concentration polarization. The permeate composition was determined using a calibrated gas chromatograph (Agilent 3000A Micro GC) equipped with thermal conductivity detectors. The mixed-gas permeability was determined via:

$$P_i = 10^{10} \frac{y_i V_d l}{x_i p_{up} A R T} \frac{dp}{dt}$$

where y represents the mole fraction in the permeate and x represents the mole fraction in the feed. The mixed gas selectivity of C_3H_6/C_3H_8 was determined by:

$$\alpha_{ij} = (y_i/y_j)(x_j/x_i)$$

3. Results and discussion

3.1 Microstructural analysis

The microstructural differences associated with substituting the spirobisindane contortion site with the 9,10-diisopropyltriptycene moiety in the early PIM-PI platform can be qualitatively assessed with N₂ (-196 °C) physisorption isotherms. Maintaining the same diamine (TMPD), the results for PIM-PI-1 and KAUST-PI-1 are compared to those for a polyimide containing the conventional 6FDA dianhydride in Fig. 2. Two main observations may be made: Firstly, a steeper increase in gas sorption in the low-pressure region (inset) indicates a greater presence of finer microporosity (< 20 Å). N₂ uptake increases in the order 6FDA-TMPD < PIM-PI-1 < KAUST-PI-1, indicating the greatest presence of smallest micropores in KAUST-PI-1. Secondly, the BET surface areas – which serve as a qualitative measure of free volume in the polymer – increased in the order 6FDA-TMPD (500 m²/g) < PIM-PI-1 (660 m²/g) < KAUST-PI-1 (750 m²/g). As expected, the relatively flexible 6FDA moiety induced better packing in the solid state relative to the contorted and more rigid PIM-type dianhydrides.

Fig. 2. Physisorption isotherms for KAUST-PI-1 [18], PIM-PI-1 and 6FDA-TMPD using N_2 at -196°C ($p_o = 1$ bar). The inset is zoomed into the low-pressure region.

Indeed, the trends in low-pressure uptakes and surface area are consistent with the relative intra-chain rigidities of the dianhydrides. That is, as a first approximation, torsional freedoms available about select bonds in the backbones of each dianhydride (barring the fused-ring segments and the N-phenyl imide bond to TMPD common to all) are shown in Fig. 3 assuming the energy available at a temperature T is $\sim 3RT$. The systematic increase in free volume *and* narrow microporosity correlates well with the reduction in backbone torsional freedoms going from 6FDA to SPDA to TPDA, which inhibits efficient chain packing. This increased intra-chain rigidity is also consistent with the report of a 50% higher Young's modulus for KAUST-PI-1 (2460 MPa) relative to PIM-PI-1 (1620 MPa) [37].

Fig. 3. Degrees of torsional freedom available at 35 °C about the bold highlighted bonds in the 6FDA, SPDA and TPDA dianhydrides (Conformer's module, Materials Studio 7.0, Accelrys).

3.2 High-pressure sorption experiments: Dual-mode framework

The C_3H_6 and C_3H_8 pure-gas sorption isotherms for PIM-PI-1 and KAUST-PI-1 at 35 °C are illustrated in Fig. 4a and 4b, respectively. Sorption experiments were conducted gravimetrically for C_3H_6 and C_3H_8 with incremental increases in pressure taken upon achievement of steady-state mass uptake. The isotherms show minimal differences in the concentrations of C_3H_6 and C_3H_8 in the polymers with increasing pressure for both PIM-PI-1 and KAUST-PI-1, with C_3H_6 sorbing slightly more than C_3H_8 . This results in solubility selectivities of close to 1, in good agreement with previous literature [10-12, 40, 41]. Therefore, the separation of C_3H_6 from C_3H_8 is expected to be essentially diffusion-based.

Fig. 4. Pure-gas C_3H_6 and C_3H_8 sorption isotherms at 35 °C for a) PIM-PI-1 and b) KAUST-PI-1.

Moreover, the isotherms in Fig. 4 were fit using the dual-mode sorption model (Table 1), which for glassy polymers describes total gas sorption as the sum of sorption in the “frozen microvoids” of the Langmuir domain and in the densely packed region known as Henry’s domain. Sorption in the Langmuir domain is described by the C_H' parameter and correlated with free volume in a polymer under the dual-mode framework [13]. It is typical for observed C_H' values to be higher for C_3H_6 than for C_3H_8 due to the fact that C_3H_6 is slightly more condensable and compact, and therefore can access the microvoids more readily. KAUST-PI-1 showed higher C_H' values for C_3H_6 and C_3H_8 than for PIM-PI-1, reflecting its more microporous structure discussed in Section 3.1. Comparing these values of C_H' for the highly microporous KAUST-PI-1 with those of a more efficiently packing conventional low-free volume polyimide 6FDA-6FpDA [11] shows a difference in C_H' for C_3H_6 and C_3H_8 of 112% and 146%, respectively. The significant difference in C_H' between PIM-PIs including KAUST-PI-1 and PIM-PI-1 and the more conventional

polyimide 6FDA-6FpDA can be attributed to the higher free volume in PIM-PIs that is more easily accessible to large gases like C₃H₆ and C₃H₈.

The k_d parameter describes sorption in the Henry's domain or densified equilibrium matrix of the polymer. KAUST-PI-1 showed k_d values for C₃H₆ and C₃H₈ of 7.9 and 6.1 cm³(STP) cm⁻³(polymer) bar⁻¹, respectively. PIM-PI-1 had higher k_d values for C₃H₆ and C₃H₈ of 9.9 and 9.0 cm³(STP) cm⁻³(polymer) bar⁻¹, respectively. One reason for the higher k_d values in PIM-PI-1 may be that its spirobisindane center facilitates chain mobility compared to triptycene (Fig. 3), which is structurally the only difference between their backbones. Therefore, the PIM-PI-1 chains may more readily rearrange themselves to accommodate increasing gas uptake under higher gas feed pressures. Accordingly, C₃H₆ and C₃H₈ sorb more in PIM-PI-1 than in KAUST-PI-1 as the feed pressure approaches 8 bar. The k_d values were, in contrast, significantly lower for the conventional low-free-volume polyimide 6FDA-6FpDA in which a more tightly packed structure cannot easily accommodate the large gases [11, 42].

Table 1. Pure-gas C₃H₆ and C₃H₈ dual-mode sorption parameters at 35 °C.

Polymer	Gas	k_d^a	$C_H'^b$	b^c	$\alpha_s(C_3H_6/C_3H_8), 2 \text{ bar}$
KAUST-PI-1	C ₃ H ₆	7.9	72	4.2	1.1
	C ₃ H ₈	6.1	70	4.4	
PIM-PI-1	C ₃ H ₆	9.9	69	2.6	1.1
	C ₃ H ₈	9.0	63	3.2	
6FDA-6FpDA ^d	C ₃ H ₆	3.8	20	3.5	1.6
	C ₃ H ₈	2.9	11	3.2	

^a Unit: k_d [=] cm³(STP) cm⁻³(polymer) bar⁻¹.

^b Unit: C_H' [=] $\text{cm}^3(\text{STP}) \text{cm}^{-3}(\text{polymer})$.

^c Unit: b [=] bar^{-1}

^d Adapted from Das et al. [11].

3.3 Pure-gas C_3H_6/C_3H_8 permeation

Fig. 5 is an upper bound plot for C_3H_6/C_3H_8 using reported pure-gas data accumulated from the literature based on steady-state measurement conditions on thick polymer films [7]. All data used to construct the upper bound had been collected between temperatures of 26 and 100 °C and at feed pressures between 2 and 4 bar. As recently emphasized by our group, data for PIMs are most appropriately reported at an “aging-knee” when the non-equilibrium free volume trapped by casting and solvent exchange steps relaxes and the transport properties change little on the experimental time-scale [43]. Accordingly, data at 2 bar and 35 °C are superimposed for 6FDA-TMPD [10], PIM-PI-1, and KAUST-PI-1 (red points). Fixing the diamine as TMPD and transitioning from 6FDA $\rightarrow$ SPDA $\rightarrow$ TPDA dianhydrides characteristic of PIM-PIs led to significant enhancements in permeability. Substituting the 6FDA dianhydride with spiro-based SPDA (i.e., PIM-PI-1), the C_3H_6 permeability increased by over one order of magnitude from 37 to 393 Barrer, and the C_3H_6/C_3H_8 selectivity decreased slightly from 8.6 to 6. Replacing the spirobisindane contortion center of PIM-PI-1 with the more rigid 9,10-diisopropyltritycene (i.e., KAUST-PI-1) elicited more than two-fold increases in *both* C_3H_6 permeability to 817 Barrer and C_3H_6/C_3H_8 selectivity to 16. KAUST-PI-1 has the highest reported pure-gas C_3H_6 permeability of any polyimide to date which, joined with a selectivity matching that of low-free-volume, low-permeability polyimides, positions it well above the experimentally observed upper bound. As observed for gas/gas

separations involving air and hydrogen [18, 37], the enhanced microporosity typically attributed to increased polymer intra-chain rigidity offers notable simultaneous gains in both C_3H_6 permeability and C_3H_6/C_3H_8 selectivity.

Fig. 5. Pure-gas C_3H_6/C_3H_8 permeability/selectivity performance of TMPD-based 6FDA- and PIM-polyimides (shown in red). Solid line is the experimentally observed C_3H_6/C_3H_8 upper bound [7].

Pure-gas transport data including permeability, diffusion, and solubility coefficients and selectivities thereof are shown in Table 2 for 6FDA-6FpDA [11], 6FDA-TMPD [10], PIM-PI-1, and KAUST-PI-1. In general, the solubility coefficients in the high-free-volume PIM-PIs are two to threefold greater than those in the 6FDA polyimides, as typically observed with light gases. On the other hand, the C_3H_6 diffusion coefficient in KAUST-PI-1 is twofold greater than for PIM-PI-1 and almost eightfold greater than for 6FDA-TMPD (Table 2). Therefore, the large gain in C_3H_6 permeability for KAUST-PI-1 over the other polyimides is diffusion-driven. Likewise, the higher permselectivity of

KAUST-PI-1 results from its higher diffusivity selectivity of 16 versus 6 for PIM-PI-1 and 7 for 6FDA-TMPD. However, intra-chain rigidity does *not* necessitate simultaneous gains in permeability and selectivity: 6FDA-TMPD, with its rotation-restricted imide bond, has 52-fold higher C_3H_6 permeability than 6FDA-6FpDA, having a torsionable imide bond, but about half the selectivity. The latter emphasizes the potential of the PIM-PI platform and has been rationalized in microporous materials by the presence of a bimodal distribution in porosity whereby smaller pores are joined with larger pores [18, 27, 44]. While increasing the chain rigidity may be a contributing factor to this favorable sieving behavior, the theoretical ribbon-like geometry of triptycene-based KAUST-PI-1 – in contrast to the entangled chain geometry of spirobisindane-based PIM-PI-1 – may also play an important role [43].

Table 2. Pure-gas C_3H_6/C_3H_8 transport properties for KAUST-PI-1, PIM-PI-1, 6FDA-TMPD [10], and 6FDA-6FpDA [11] at 2 bar.

Polymer	$P(C_3H_6)^a$	α_P	$D(C_3H_6)^b$	α_D	$S(C_3H_6)^c$	α_S
KAUST-PI-1	817	16	155	16	0.53	1.1
PIM-PI-1	393	6.0	75.4	6.0	0.51	1.1
6FDA-TMPD ^d	37	8.6	18.5	7.0	0.20	1.3
6FDA-6FpDA ^e	0.7	19	0.412	12	0.17	1.6

^a Unit: Barrer [=] $10^{-10} \text{ cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$.

^b Unit: $10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

^c Unit: $\text{cm}^3(\text{STP}) \text{ cm}^{-3}(\text{polymer}) \text{ cmHg}^{-1}$.

^d Adapted from Tanaka et al. at 50 °C [10]

^e Adapted from Das et al. [11]

3.4 Mixed-gas $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ permeation

3.4.1 Pressure dependent mixed-gas permeation

Mixed-gas permeation experiments were conducted with 50:50 $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ feed at 35 °C for PIM-PI-1 and KAUST-PI-1 to further examine the pure-gas results under more realistic conditions. The feed pressure was incrementally increased once a quasi steady-state in permeabilities and selectivities was reached. The mixed-gas permeation results for PIM-PI-1 and KAUST-PI-1 are illustrated in Fig. 6 and 7, respectively. At 2 bar C_3H_6 partial pressure, there are three similar comparisons that can be made between the mixed-gas data and corresponding 2 bar pure-gas data for both PIM-PIs: (i) C_3H_6 permeability decreased from 393 Barrer (pure-gas) to 260 Barrer under mixed-gas conditions for PIM-PI-1, and from 817 Barrer (pure-gas) to 676 Barrer for KAUST-PI-1; (ii) C_3H_8 permeability *increased* from 65 Barrer (pure-gas) to 108 Barrer in the mixed-gas for PIM-PI-1, and from 57 Barrer (pure-gas) to 146 Barrer for KAUST-PI-1; and accordingly (iii) $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity decreased from 6 (pure-gas) to 2 in the mixed-gas for PIM-PI-1 and from 16 (pure-gas) to 5 for KAUST-PI-1.

Fig. 6. Mixed-gas C_3H_6/C_3H_8 permeability and selectivity pressure dependence for PIM-PI-1 at 35 °C using a 50:50 C_3H_6/C_3H_8 feed. The fits are drawn to guide the eye.

Fig. 7. Mixed-gas C_3H_6/C_3H_8 permeability and selectivity pressure dependence for KAUST-PI-1 at 35 °C using a 50:50 C_3H_6/C_3H_8 feed. The fits are drawn to guide the eye.

The trends noted above indicate strong overlapping contributions of competitive sorption and plasticization to the mixed-gas permeation properties of both PIM-PI-1 and KAUST-PI-1. In general, competitive sorption was evident for both polymers given the reduction in C_3H_6 permeability in the mixed-gas relative to pure-gas values. This is expected based on the nearly identical and high gas uptakes observed in sorption measurements (Fig. 4). The high gas uptakes also resulted in plasticization-induced matrix dilations in both polymers that caused (i) almost two-fold increases in the mixed-gas permeability of the larger C_3H_8 penetrant relative to pure-gas and (ii) more than 65% losses in mixed-gas relative to pure-gas C_3H_6/C_3H_8 selectivity. Additionally, plasticization caused pressure-dependent increases in *both* the mixed-gas C_3H_6 and C_3H_8 permeabilities such that the mixed-gas C_3H_6/C_3H_8 selectivity dropped with pressure (Fig. 6 and 7): In PIM-PI-1, $\alpha(C_3H_6/C_3H_8)$ decreases from ~ 3.4 at 1 bar C_3H_6 partial pressure to ~ 2 at 2.5 bar C_3H_6 partial pressure; in KAUST-PI-1, from ~ 7 to ~ 5 . Interestingly, the plasticization effects were more severe for KAUST-PI-1 than for PIM-PI-1 as it exhibited a greater increase in permeabilities of both gases with pressure in the mixed-gas. Specifically, $P(C_3H_6)$ increased by 33% in KAUST-PI-1 versus 7% in PIM-PI-1, and $P(C_3H_8)$ increased by 87% for KAUST-PI-1 versus 53% for PIM-PI-1, from 1 bar to 2 bar C_3H_6 partial pressure. This unexpected extent of plasticization was previously demonstrated for KAUST-PI-1 in the context of CO_2/CH_4 mixed-gas separation and was explained by examination of the results observed in the physisorption-based characterization of the microstructure [43]. That is, the larger concentration of finer microporous elements in KAUST-PI-1, which must contribute significantly to its high pure-gas selectivity, makes

the permeation properties more susceptible to the effects of plasticization (e.g., selectivity loss).

Fig. 8 demonstrates the changes in pure-gas separation properties of polyimides defining the pure-gas upper bound under a mixed-gas feed with 2 bar C_3H_6 partial pressure. Losses in C_3H_6 permeability and, particularly, C_3H_6/C_3H_8 selectivity are observed for both the low-free-volume conventional 6FDA-based polymers as well as the high-free-volume PIM-PIs that are the subject of this work. Interestingly, KAUST-PI-1 retains selectivities similar to those obtained for most of the low-free-volume polymers, except with up to two orders of magnitude higher C_3H_6 permeability. Indeed, KAUST-PI-1 is the most permeable polyimide to C_3H_6 reported to date. Das et al. reported a mixed-gas C_3H_6/C_3H_8 selectivity of about 14 at 2 bar C_3H_6 partial pressure, for the annealed 6FDA-6FpDA, but it is not illustrated in the plot because a mixed-gas C_3H_6 permeability was not available. The advantages of bridged-bicyclic, in-plane contortion sites (e.g., 9,10-diisopropyltritycene in KAUST-PI-1) over spiro centers (e.g., in PIM-PI-1) are again reinforced in this study [34, 37].

Fig. 8. Permeability/selectivity map showing pure-gas data measured at 2 bar (unfilled markers) and mixed-gas data measured at 2 bar C_3H_6 partial pressure (filled markers) with 50:50 C_3H_6/C_3H_8 mixtures. Solid line is the experimentally observed pure-gas C_3H_6/C_3H_8 upper bound.

3.4.2 Mixed-gas time dependence

Numerous data in the literature pertaining to C_3H_6/C_3H_8 separation have been reported with unreproducibly high selectivities due to non-steady-state experiments involving transient C_3H_8 data [45, 46]. Additionally, in the event of plasticization, permeabilities may continue to steadily rise over time [47] and thus it is important to consider the time-dependence of the data. In this work, the highly microporous structures of the PIM-PIs permitted quasi-steady-state conditions to be obtained in a reasonable timeframe. That is, relatively slight changes in the permeabilities *and* selectivities were evident beyond a certain time. Fig. 8 is a representative series of plots showing the time dependence of the C_3H_6 and C_3H_8 permeabilities and C_3H_6/C_3H_8 selectivities of KAUST-PI-1 in the mixed-gas experiments. Briefly, after the first 2 bar exposure to the mixture, the time required to reach a quasi steady-state was reduced from 120 hours to less than 70 hours. Although the selectivities appeared to become constant earlier on, the permeabilities required more time as the gases gained more access to the plasticized matrix. Analogous behavior was observed for PIM-PI-1.

Fig. 9. Time dependence of mixed-gas a) C_3H_6 and C_3H_8 permeabilities and b) C_3H_6/C_3H_8 selectivities for KAUST-PI-1 at various total feed pressures (50:50 C_3H_6/C_3H_8 , 35 °C). Fits are drawn to guide the eye.

4. Conclusions

PIM-PI films were evaluated for C_3H_6/C_3H_8 separation under non-ideal mixed-gas conditions. The effects of systematically increasing intra-chain rigidity on the C_3H_6/C_3H_8 separation properties were investigated upon transitioning from a conventional 6FDA dianhydride to a PIM-type spiro-centered dianhydride (SPDA) (i.e., in PIM-PI-1) and then its 9,10-diisopropyltriptycene-based analog (TPDA) (i.e., in KAUST-PI-1), all while maintaining a rotation-restricted TMPD diamine. The results of this study can be summarized as follows:

- 1. Microstructural characterization:** The increase of polymer intra-chain rigidity in PIM-PIs over conventional 6FDA-based polyimides resulted in a shift towards

finer microporosity *and* an increase in free volume in the fashion of 6FDA-TMPD < PIM-PI-1 < KAUST-PI-1, the diamine being the same for all polyimides.

2. **High-pressure sorption:** C_3H_6/C_3H_8 solubility selectivities of ~ 1 were observed for the PIM-type polymers as typically observed for low-free-volume polyimides, suggesting diffusion-governed separation. The PIM-polyimides showed a significantly higher capacity for C_3H_6 and C_3H_8 uptake compared to 6FDA-based polyimides, consistent with the higher free volume evidenced in low-pressure and low-temperature physisorption experiments.
3. **Pure-gas permeation:** Pure-gas experiments showed a significant increase in C_3H_6 permeability in the PIM-polyimides compared to 6FDA-TMPD (37 Barrer (6FDA-TMPD) [10] $\rightarrow$ 393 Barrer (PIM-PI-1) $\rightarrow$ 817 Barrer (KAUST-PI-1)) coupled with a significant increase in selectivity from 6 to 16 by replacing the spirobisindane contortion center with a 9,10-diisopropyltritycene, paralleling a systematic increase in backbone intrachain rigidity.
4. **Mixed-gas (50:50 C_3H_6/C_3H_8) permeation:** In more realistic mixed-gas experiments with 50:50 C_3H_6/C_3H_8 feed, significant losses in C_3H_6/C_3H_8 selectivity and C_3H_6 permeability in the PIM-polyimides were incurred due to plasticization and competitive sorption, respectively. However, compared with the performance of several 6FDA-based polyimides, KAUST-PI-1 offered similar or higher selectivity concurrent with up to two orders of magnitude greater C_3H_6 permeability.

Research is currently ongoing in our group to further exploit the potential of the PIM-PI platform in C_3H_6/C_3H_8 separation, with particular attention to mitigating the plasticization response and preserving the size-sieving capacity of the membranes.

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- High PIM-PI *intra*-chain rigidity insufficient for plasticization suppression
- Significant losses in permeability and selectivity in 50:50 mixed-gas feed