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Enhanced propylene/propane separation by thermal annealing of an intrinsically microporous hydroxyl-functionalized polyimide membrane

Ramy J. Swaidan, Xiaohua Ma, Eric Litwiller, Ingo Pinnau*

Advanced Membranes and Porous Materials Center (AMPMC), Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

*Corresponding author: Tel: +966-12-808-2406

E-mail address: ingo.pinnau@kaust.edu.sa (I. Pinnau)

Key words: polymers of intrinsic microporosity, polyimide, propylene/propane separation, plasticization, thermal annealing

Abstract

Effective separation of propylene/propane is vital to the chemical industry where C_3H_6 is used as feedstock for a variety of important chemicals. The purity requirements are currently met with cryogenic distillation, which is an extremely energy-intensive process. Hybrid arrangements incorporating highly selective membranes ($\alpha > 20$) have been proposed to “debottleneck” the process and potentially improve the economics. Selective and permeable membranes can be obtained by the design of polymers of intrinsic microporosity (PIMs). In this work, a 250 °C annealed polyimide (PIM-6FDA-OH) membrane produced among the highest reported pure-gas C_3H_6/C_3H_8 selectivity of 30 for a solution-processable polymer to date. The high selectivity resulted from enhanced diffusivity selectivity due to the formation of inter-chain charge-transfer-complexes. Although there were some inevitable losses in selectivity under 50:50 mixed-gas feed conditions due to competitive sorption, relatively high selectivities were preserved due to enhanced plasticization resistance.

1. Introduction

Purification of propylene from propane is one of the most important separation processes in the petrochemical industry due to the large demand of propylene as a feedstock for production of many common plastics and chemicals [1]. Worldwide production has grown to over 84 billion pounds per year and the current means of meeting this demand is separation by cryogenic distillation, which is an extremely energy-intensive process due to the marginal differences in relative volatility of C_3H_6 and C_3H_8 [2]. C_3 splitters typically comprise over 200 trays and are operated with reflux ratios greater than 10, making the distillation process very energy-intensive. One of the potential means of reducing the energy demands is incorporation of a highly selective membrane to “debottleneck” the process [2, 3]. However, development of highly permselective polymeric membranes for C_3H_6/C_3H_8 separations has proven to be challenging due to: i) very poor solubility selectivity due to a small difference in penetrant condensability (T_b C_3H_6 = -47.6 °C; T_b C_3H_8 = -42 °C) and ii) polymer plasticization and competitive sorption effects under mixed-gas conditions, which both reduce selectivity [4, 5].

A permeability/selectivity trade-off relationship exists for polymeric membrane materials for many common gas pairs [6,7]; the same trend has been observed for C_3H_6/C_3H_8 [6-8]. It is important to note that the C_3H_6/C_3H_8 permselectivity of polymers is generated almost exclusively by the diffusivity selectivity due to the relatively large difference size of the gases (D_{LJ} C_3H_6 = 4.68 Å; D_{LJ} C_3H_8 = 5.12 Å). To date, the best performing polymers, as gauged by 2 bar pure-gas experiments, are 6FDA-based polyimides [8]. However, while membrane material performance is typically judged by its position relative to the trade-off curve, Koros and Lively elucidated performance criteria necessary for a membrane to debottleneck the cryogenic distillation process.

According to their study, an economically acceptable process would require a membrane material with a minimum mixed-gas C_3H_6/C_3H_8 selectivity of 20 and C_3H_6 permeability of 10 Barrer; these properties are beyond those of materials currently defining the upper bound [2]. Consequently, to meet these requirements simultaneous enhancements in permeability and selectivity of novel membrane materials are necessary to make the process economics feasible. A critical attribute necessary for a membrane to preserve high selectivity under realistic mixed-gas feed conditions is strong plasticization resistance, which emanate from sorption-induced matrix dilations. A simple physical approach to mitigate plasticization to maintain high selectivity is thermal annealing of polymers functionalized with polar moieties like hydroxyl or carboxyl groups [5, 9, 10]. Thermal annealing leads to intra- and, even more importantly, inter-segmental chain immobilization [9] due the formation of charge transfer complexes (CTCs) by alternating arrangement of electron donor and acceptor molecules about the N-phenyl imide bond [11-17]. This technique has been effectively used by Das and Koros to mitigate plasticization for C_3H_6/C_3H_8 separation to preserve high selectivity under mixed-gas conditions [5].

A relatively new approach to developing high-performance gas separation membranes is to introduce sterically hindered contortion sites into a rigid polymer structure, which lead to inefficient chain packing to form polymers of intrinsic microporosity (PIMs) [9, 18-28]. By designing selective free volume into the polymer structure PIMs have been shown to simultaneously boost permeability and gas/gas selectivity. Recently, our group reported the performance of highly permeable triptycene (KAUST-PI-1)- and spirobisindane (PIM-PI-1)-based polyimides for propylene/propane separation [29]. KAUST-PI-1 exhibited a C_3H_6/C_3H_8 selectivity of 16 with the highest C_3H_6 permeability of any polyimide reported to date of 817

Barrer, positioning it well above the experimentally observed upper bound. The only other reported works using PIMs for C_3H_6/C_3H_8 separation were conducted with pristine, aged, annealed, and covalently cross-linked variations of ladder-type PIM-1 showing permeability-driven performance, with low to moderate selectivities in the range of 2.5 to 9 [30] [31]. Furthermore, their mixed-gas performance was adversely affected by plasticization and competitive sorption, which resulted in an additional drop in selectivity. Traditional PIM design principles strive for enhancing intra-chain rigidity but lack the emphasis on inter-chain interactions, which is a potential way to create plasticization resistant membranes. Excellent mixed-gas stability of PIM-polyimides (PIM-PIs) under CO_2/CH_4 feeds was demonstrated via thermal annealing of PIMs containing polar hydroxyl groups, supplementing strong inter-chain hydrogen-bonding with CTCs that further draw the polymer chains closer together [9].

In this work, thermal annealing of a hydroxyl-functionalized polyimide, PIM-6FDA-OH (Fig. 1), was carried out to tune its microporosity for C_3H_6/C_3H_8 separation. Microstructural characterization of the resulting membranes was performed using fluorescence spectroscopy and high-pressure gas sorption. As a preliminary assessment of performance, 2 bar pure-gas transport properties of the membranes are reported at 35 °C. These results are followed up with pressure dependent mixed-gas testing using 50:50 C_3H_6/C_3H_8 feeds because while insightful, pure-gas tests do not give an adequate assessment of the membrane's performance under non-ideal conditions where contributions of plasticization and competitive sorption can be observed.

Fig. 1. Chemical structure of PIM-6FDA-OH.

2. Experimental

2.1. Polymer Synthesis

PIM-6FDA-OH was prepared as a light yellow powder according to a previously reported procedure by our group [20]. Gel permeation chromatography (Agilent GPC 1200) indicated number- and weight-averaged molecular weights of 8.54×10^4 and 1.65×10^5 g/mol, respectively.

2.2. Polymer film preparation

Dense polymer films were formed by slow evaporation of filtered 3-5 weight percent tetrahydrofuran (THF) solutions cast on a leveled glass plate. The freshly cast films were dried under vacuum at 120 °C for 24 h, soaked in a mixture of *n*-hexane/dichloromethane (90/10) at room temperature for 24 h, and finally dried in vacuum at 120 °C for 24 h. Soaking the film in *n*-hexane/dichloromethane swells the polymer and facilitates removal of residual casting solvent trapped in the micropores [32]. Thermal gravimetric analysis (TGA) confirmed complete solvent

removal. Annealed films were made by heating the pristine PIM-6FDA-OH under vacuum at 250 °C for 24 hours. The film thicknesses and areas were determined by a digital micrometer and by calibrated scanning software, respectively.

2.3. Fluorescence spectroscopy

Fluorescence spectroscopy was used to assess the formation of CTCs between the 120 and 250 °C treated PIM-6FDA-OH films. CTCs can form in polyimides due to the formation of a conjugated system of p-orbitals with delocalized electrons between polymer repeat units of adjacent chains and/or the same chain. Inter-chain interactions are enhanced due to the alternating arrangement of electron donor and acceptor molecules, which arise across the N-phenyl imide bonds. Upon formation of CTCs, densification of polymer chains occurs, which manifests itself by higher intensity peak emissions upon fluorescent excitation [11, 12, 14, 16]. In this study excitation of the films was performed at 325 nm.

2.4. High-pressure sorption

High-pressure propylene and propane sorption isotherms were collected up to 8 bar on powder samples of PIM-6FDA-OH 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 (cm³ (STP) cm⁻³ cmHg⁻¹), for C₃H₆ and C₃H₈ were determined at each pressure point from the gas concentration in the polymer, C (cm³ (STP) cm⁻³) and the pressure, p (cmHg), by:

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

C_3H_6/C_3H_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 C_3H_6/C_3H_8 permeation

Permeabilities were evaluated using the constant-volume/variable-pressure method. PIM-6FDA-OH films were degassed in the permeation apparatus at 35 °C for at least 24 h. 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 (Barrer), D is the diffusion coefficient, S is the solubility coefficient, V_d is the downstream volume (cm^3), dp/dt is the permeate-side pressure increase ($cmHg/s$), l is the membrane thickness (cm), p_{up} is the upstream feed pressure ($cmHg$), A is the membrane area (cm^2), R is the gas constant ($0.278 \text{ cm}^3 \text{ cmHg cm}^{-3}(\text{STP}) \text{ K}^{-1}$), and T is the permeation temperature (K). The ideal selectivity for C_3H_6/C_3H_8 was calculated via:

$$\alpha_{C_3H_6/C_3H_8} = P(C_3H_6)/P(C_3H_8)$$

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

Pressure-dependent mixed-gas testing was evaluated at 35 °C with a 50:50 C_3H_6/C_3H_8 mixture using a setup similar to that reported by O'Brien et al. [33]. A stage-cut (permeate to feed flow rate) 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:

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

where y represents the mole fraction in the permeate, x represents the mole fraction in the feed.

The mixed-gas selectivity of C_3H_6/C_3H_8 was determined by:

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

3. Results and discussion

3.1. High-pressure sorption experiments

The C_3H_6 and C_3H_8 pure-gas sorption isotherms at 35 °C for thermally treated PIM-6FDA-OH films at 120 and 250 °C are illustrated in Fig. 2. 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 that C_3H_6 sorbs only slightly more than C_3H_8 at all pressures. This results in solubility selectivities of approximately 1, in good agreement with previous studies [4, 5, 34-36]. The separation of C_3H_6 from C_3H_8 is thus expected to be only governed by size-sieving diffusivity selectivity.

Fig. 2. Pure-gas C₃H₆ and C₃H₈ sorption isotherms at 35 °C for PIM-6FDA-OH. Fits are drawn to guide the eye.

The dual-mode sorption model for glassy polymers describes total gas sorption as the sum of sorption in the “frozen microvoids” of the Langmuir domain (low pressure region) and the densely packed region known as Henry’s domain (high pressure region). Sorption in the Langmuir domain correlates with free volume in a polymer under the dual-mode framework [37]. It is typical to observe greater sorption uptake of C₃H₆ than C₃H₈ due to the fact that C₃H₆ is slightly more condensable and compact, and therefore can access the microvoids more readily. There was a slight decrease in concentration of C₃H₆ and C₃H₈ upon annealing at 250 °C, likely due to a tightening of the pore structure. That is, annealing of polyimides typically enhances CTC interactions and can contract free volume elements [10].

3.2. Fluorescence spectroscopy

Inherent to polyimide structures are intra- or inter-chain charge-transfer complexes (CTCs), which are electrostatic interactions due to the alternating arrangement of electron donor and

acceptor molecules across the N-phenyl imide bonds [14, 16]. A schematic showing the expected inter-chain interactions due to the formation of charge transfer complexes upon annealing of PIM-6FDA-OH is illustrated in Fig. 3. CTC formation in thermally annealed polyimides has been indicated via an increase in the intensity of the emission spectra collected by fluorescence spectroscopy [9, 11, 12, 15]. Fig. 4 is a plot of the emission spectra (325 nm excitation) for 120 and 250 °C treated PIM-6FDA-OH films of the same thickness. The intensity of the emission band increased upon annealing at 250 °C by about 50%, thereby indicating a greater concentration of CTCs. While it is unclear whether these enhancements in CTC formation emanate from intramolecular or intermolecular interactions, previous work has suggested a dominant effect of inter-chain interactions in solid-state polyimides [14]. That is, it is often visualized that a thermally-induced coplanarization of the chains increases packing density and molecular aggregation. Ultimately, the resulting inter-chain interactions help suppress inter-chain motions and are thus promising for plasticization suppression.

Fig. 3. Schematic diagram showing the inter-chain interactions due to the formation of charge transfer complexes upon annealing of PIM-6FDA-OH polyimide.

Fig. 4. Solid-state fluorescence emission spectra (excitation at 325 nm) of PIM-6FDA-OH heat-treated at 120 and 250 °C.

3.3. Pure-gas C_3H_6/C_3H_8 transport properties

The pure-gas permeation properties of heat-treated PIM-6FDA-OH membranes are shown in Table 1. Fig. 5 shows the experimentally observed C_3H_6/C_3H_8 upper bound plot developed by Koros and Burns [8]. The “golden” region of the plot was suggested by Koros and Lively to indicate the membrane performance demands for debottlenecking a distillation process [2]. It is defined by having a minimum selectivity of 20 and C_3H_6 permeability greater than 10 Barrer. As can be seen in Fig. 5, the 250 °C annealed PIM-6FDA-OH shows excellent performance for a solution-processable polymer as its performance is well above the defined tradeoff curve with a combination of high selectivity (30) and moderate permeability ($P(C_3H_6) = 3.5$ Barrer). To date, it has among the highest pure gas C_3H_6/C_3H_8 selectivity reported for solution-processable polymers. Another polymer, which defines the upper bound is 6FDA-DDBT, shows similar performance. Tanaka et al. [34] and Okamoto et al. [38] reported C_3H_6/C_3H_8 selectivities ranging from 27 to 20 with C_3H_6 permeabilities between 0.76 to 1.8 Barrer measured at 50 °C. Upon annealing PIM-6FDA-OH at 250 °C, there was a 60% increase in C_3H_6/C_3H_8 selectivity from 19

to 30 at the expense of a ~30% reduction in C_3H_6 permeability, a trend commonly observed upon annealing of polyimides at high temperature [5, 9, 10]. Table 1 shows that the greater selectivity upon treating at 250 °C is derived exclusively from an enhancement in the diffusion selectivity by about 80%. On the other hand, the permeability reductions are due to drops in both diffusion and solubility coefficients. In general, the transport data are consistent with a more sieving and *tighter* microstructure, as indicated in Section 3.1. Compared with the other PIM materials (KAUST-PI-1, PIM-PI-1, and PIM-1) and even commercial low-free-volume Matrimid examined for the separation, PIM-6FDA-OH showed very promising performance.

Fig. 5. Pure-gas C_3H_6/C_3H_8 permeability/selectivity performance of the 120 and 250 °C treated PIM-6FDA-OH films. The solid line is the experimentally observed C_3H_6/C_3H_8 upper bound [8].

In addition to improving the size-sieving properties of polyimides, thermal annealing has also been used as a tool to improve their plasticization resistance. As a preliminary investigation of the effects of annealing, pure-gas pressure dependent C_3H_6 studies were carried out on the 120 and 250 °C treated PIM-6FDA-OH films. Fig. 6 shows a plot of the C_3H_6 permeability isotherms

at 35 °C. The 250 °C annealed film showed no up-turn in the C_3H_6 permeability isotherm, and instead demonstrated a dual-mode-like 20% drop with C_3H_6 feed pressure up to 5 bar. In contrast, the 120 °C-treated film showed an upturn between 2 and 3 bar. These preliminary pure-gas results indicate an improved plasticization resistance in the 250 °C film, consistent with formation of inter-chain CTCs discussed earlier. While this is a promising result, mixed-gas pressure dependence studies are necessary to assess the impact one component has on the transport behavior of the other [39].

Fig. 6. Pressure dependence of the pure-gas C_3H_6 permeabilities (35 °C) for PIM-6FDA-OH films treated at 120 and 250 °C. Fits are drawn to guide the eye.

Table 1. Pure-gas C₃H₆/C₃H₈ transport properties of 120 and 250 °C heat-treated PIM-6FDA-OH films at 2 bar and 35 °C.

Treatment	P(C ₃ H ₆) ^a	α_P	D(C ₃ H ₆) ^b	α_D	S(C ₃ H ₆) ^c	α_S
120 °C	5.1	19	2.0	15	0.25	1.3
250 °C	3.5	30	1.6	27	0.22	1.1

^a Unit: Barrer [=] 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹.

^b Unit: 10⁻⁹ cm² s⁻¹.

^c Unit: cm³(STP) cm⁻³(polymer) cmHg⁻¹.

3.4. Mixed-gas C₃H₆/C₃H₈ permeation

Mixed-gas permeation experiments were conducted with a 50:50 C₃H₆/C₃H₈ feed at 35 °C for 120 and 250 °C treated PIM-6FDA-OH films to examine the separation performance under more realistic conditions. The feed pressure was incrementally increased once steady-state in permeability *and* selectivity were reached. The C₃H₆ and C₃H₈ mixed-gas permeability isotherms and C₃H₆/C₃H₈ selectivity isotherms are illustrated in Figs. 7-9. As observed in pure-gas testing, annealing PIM-6FDA-OH at 250 °C led to a reduction in the C₃H₆ permeability due to tightening of the pore structure [5]. However, there was also a marked improvement in plasticization resistance as the C₃H₆ permeability decreased up to 5 bar total feed pressure. On the other hand, it increased for the 120 °C treated membrane at ~3 bar. Previous work by Krol et al. suggested that annealed Matrimid hollow fibers displayed similar trends in C₃H₆ permeance compared to untreated fibers: i) There was a reduction in C₃H₆ permeance compared to the untreated fibers

attributed to densification of the chain packing from enhanced CTC interactions and ii) the C_3H_6 permeance decreased or remained constant with increasing feed pressure. Based on these observations, the authors claimed a suppression of plasticization [10].

However, the only conclusive way to evaluate plasticization is by examination of the permeability isotherm of the *slower* permeating component (i.e., C_3H_8). For the 250 °C annealed PIM-6FDA-OH, the C_3H_6 permeability decreased with pressure and the C_3H_8 permeability was essentially independent of pressure. This was a marked improvement in plasticization resistance over the 120 °C film for which C_3H_8 permeability increased by ~40 % from 1 bar to 2.5 bar feed pressure. The mixed-gas selectivity from 2 bar to 4 bar feed pressure was consistently 50-70% higher for the 250 °C film than the 120 °C film, ranging from 22 to 15 versus 13 to 10. The loss in selectivity for the 120 °C film can be attributed to contributions of *both* plasticization (i.e., a pressure-dependent increase in C_3H_8 mixed-gas permeability) and competitive sorption (i.e., a drop in C_3H_6 mixed-gas permeability relative to pure-gas). In addition, plasticization may also maintain the C_3H_6 mixed-gas permeability (i.e., even a slight upturn appears) (Fig. 7). This results in a relatively stable selectivity (i.e., 10-13), albeit lower than in the 250 °C film. On the other hand, selectivity losses in the annealed 250 °C film were attributed primarily to dual-mode-like pressure-dependent drops in C_3H_6 permeability.

The enhanced mixed-gas selectivities and plasticization resistance for thermally annealed polyimide films have also been demonstrated by Das and Koros [5]. Report of the permeation properties of unannealed 6FDA-6FpDA by Staudt-Bickel and Koros showed pure-gas C_3H_6/C_3H_8 selectivity at 2 bar of 16 and C_3H_6 permeability of 0.89 Barrer [4]. However, under mixed-gas

conditions the C_3H_6/C_3H_8 selectivity and C_3H_6 permeability at 2 bar C_3H_6 partial pressure dropped to 7 and 0.68 Barrer, respectively. The large decrease in selectivity was mainly attributed to plasticization as the C_3H_8 permeability increased with pressure at a faster rate than that of C_3H_6 . Upon annealing this membrane, Koros and Das [5] observed a 20% increase in pure-gas C_3H_6/C_3H_8 selectivity from 16 to 19, but more importantly a preservation of the mixed-gas C_3H_6/C_3H_8 selectivity as it was 14 at 2 bar C_3H_6 partial pressure. To date, annealed PIM-6FDA-OH and 6FDA-6FpDA have demonstrated the highest mixed-gas selectivities (15 and 14 at 2 bar C_3H_6 feed pressure, respectively) among all polymers reported. The more significant increase in pure-gas selectivity (i.e. 50% versus 20%) upon annealing PIM-6FDA-OH over 6FDA-6FpDA can likely be attributed to enhanced hydrogen bonding between the hydroxyl moieties in PIM-6FDA-OH upon thermally-induced polymer densification.

Fig. 7. Pressure dependence of mixed-gas C_3H_6 permeability isotherms at 35 °C for PIM-6FDA-OH films treated at 120 and 250 °C. Fits are drawn to guide the eye.

Fig. 8. Pressure dependence of mixed-gas C_3H_8 permeability isotherms at 35 °C for PIM-6FDA-OH films treated at 120 and 250 °C. Fits are drawn to guide the eye.

Fig. 9. Pressure dependence of mixed-gas C_3H_6/C_3H_8 selectivity isotherms at 35 °C for PIM-6FDA-OH films treated at 120 and 250 °C. Fits are drawn to guide the eye.

The data of the mixed-gas experiments can be evaluated relative to what has been reported to date by plotting them relative to the experimentally observed C_3H_6/C_3H_8 mixed-gas upper bound

4. Conclusions

In this work, the introduction of microporosity and hydroxyl-functionality was explored as a means of simultaneously boosting permeability and selectivity in PIM-6FDA-OH polyimide for propylene/propane separation. By thermally treating PIM-PI-OH, performance well above the experimentally observed trade-off curve approaching an industrially attractive “golden region” was observed. All films treated at temperatures at 250 °C demonstrated stable performance in mixed-gas environments, with no observable plasticization. Thermal annealing at 250 °C of PIM-6FDA-OH contributed to approximately 50% increase in C_3H_6/C_3H_8 selectivity in both pure-gas and mixed-gas feeds. Pure-gas selectivity improved from 19 to 30 at 2 bar, and mixed-gas selectivity improved from 10 to 15 at 2 bar C_3H_6 partial pressure. Improved plasticization resistance was consistent with CTC formation observed in fluorescence spectroscopy.

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Nomenclature

PIMs	polymers of intrinsic microporosity
PIM-PIs	polyimides of intrinsic microporosity
PIM-1	polymer of intrinsic microporosity 1
6FDA	hexafluoroisopropylidene bisphthalic dianhydride
SPDA	bis(carboxylic anhydride)
TPDA	9,10-diisopropyl-triptycene-based dianhydride

TMPD	2,3,5,6-tetramethyl-1,4-phenylene diamine
DDBT	dimethyl-3,7-diaminodibenzothiophene-5,5-dioxide
TrMPD	2,4,6-trimethyl-1,3-phenylenediamine
6FpDA	4,4'-(hexafluoro-isopropylidene) dianiline
C ₃ H ₆	propylene
C ₃ H ₈	propane
O ₂	oxygen
N ₂	nitrogen
H ₂	hydrogen
CO ₂	carbon dioxide
CH ₄	methane
P	permeability coefficient (Barrer [=] 10 ⁻¹⁰ cm ³ (STP) cm cm ⁻² s ⁻¹ cmHg ⁻¹)
S	solubility coefficient (cm ³ (STP) cm ⁻³ (polymer) cmHg ⁻¹)
D	diffusion coefficient (cm ² s ⁻¹)
P(C ₃ H ₆)	propylene permeability coefficient
P(C ₃ H ₈)	propane permeability coefficient
□(C ₃ H ₆ /C ₃ H ₈)	propylene/propane selectivity
GPU	gas permeation units (cm ³ (STP)/cm ² ·s·cmHg)
dp/dt	steady-state permeate-side pressure increase (cmHg/s)
p_{up}	upstream pressure (cmHg)
V_d	calibrated permeate volume (cm ³)
l	membrane thickness (cm)
A	effective membrane area (cm ²)

T	operating temperature (K)
R	gas constant ($0.278 \text{ cm}^3\text{cmHg}/\text{cm}^3(\text{STP})\text{K}$)
y_i	mol fraction of component in the permeate
x_i	mol fraction of component in the feed
$\square_S$	solubility selectivity
$\square_D$	diffusion selectivity
p	pressure (bar)
C	concentration ($\text{cm}^3 (\text{STP}) \text{ cm}^{-3}$)
C_H'	Langmuir sorption parameter ($\text{cm}^3(\text{STP}) \text{ cm}^{-3}(\text{polymer})$)
k_d	Henry's Law sorption parameter ($\text{cm}^3(\text{STP}) \text{ cm}^{-3}(\text{polymer}) \text{ bar}^{-1}$)
b	Langmuir hole affinity parameter (bar^{-1})
PTFE	polytetrafluoroethylene
TGA	thermal gravimetric analysis
T_b	normal boiling point
D_{LJ}	Lennard Jones diameter
CTC	charge transfer complex
THF	tetrahydrofuran

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Enhanced propylene/propane separation by thermal annealing of an intrinsically microporous hydroxyl-functionalized polyimide membrane

Ramy J. Swaidan, Xiaohua Ma, Eric Litwiller, Ingo Pinnau*

Highlights

- Thermal annealing of a hydroxyl functionalized PIM-PI was used to achieve enhanced pure- and mixed-gas C_3H_6/C_3H_8 selectivity and plasticization suppression.
- Annealing effects on the microstructure and C_3H_6/C_3H_8 transport properties were examined.
- Discussion on the effects of plasticization and competitive sorption in C_3H_6/C_3H_8 transport.
- ~50% increase in pure-gas C_3H_6/C_3H_8 selectivity to 30 upon annealing.