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Triptycene dimethyl-bridgehead dianhydride-based intrinsically microporous hydroxyl-functionalized polyimide for natural gas upgrading

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Abstract

The synthesis and gas permeation properties of a high-performance hydroxyl-functionalized PIM-polyimide (TDA1-APAF) prepared from a novel 9,10-dimethyl-2,3,6,7-triptycene tetracarboxylic dianhydride (TDA1) and a commercially available 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF) diamine monomer are reported. The microporous polymer had a BET surface area based on nitrogen adsorption of $260 \text{ m}^2 \text{ g}^{-1}$. A freshly prepared sample exhibited excellent gas permeation properties: (i) CO_2 permeability of 40 Barrer coupled

with a CO₂/CH₄ selectivity of 55 and (ii) H₂ permeability of 94 Barrer with a H₂/CH₄ selectivity of 129. Physical aging over 250 days resulted in significantly enhanced CO₂/CH₄ and H₂/CH₄ selectivities of 75 and 183, respectively with only ~ 25% loss in CO₂ and H₂ permeability. Aged TDA1-APAF exhibited 5-fold higher pure-gas CO₂ permeability (30 Barrer) and two-fold higher CO₂/CH₄ permselectivity over conventional dense cellulose triacetate membranes at 2 bar. In addition, TDA1-APAF polyimide had a N₂/CH₄ selectivity of 2.3, thereby making it potentially possible to bring natural gas with low, but unacceptable nitrogen content to pipeline specification. Gas mixture permeation experiments with a 1:1 CO₂/CH₄ feed mixture demonstrated higher mixed- than pure-gas selectivity and plasticization resistance up to 30 bar. These results suggest that intrinsically microporous hydroxyl-functionalized triptycene-based polyimides are promising candidate membrane materials for removal of CO₂ from natural gas and hydrogen purification in petrochemical refinery applications.

Keywords: polyimides, triptycene, hydroxyl functionalization, mixed-gas permeation, plasticization, physical aging, natural gas

1. Introduction

Worldwide demand for energy is projected to quickly expand caused by the continuing growth in global population. In the 2014 Annual Energy Outlook (AEO) report, total delivered energy consumption in the industrial sector was estimated to increase by 28% from 2012 to 2040 [1, 2]. Much of the growth will reflect natural gas use due to its relatively low carbon footprint, increased thermal efficiency, and cleaner burning benefits compared to other fossil fuels. Currently, natural gas accounts for about 23% of the world's energy consumption and the International Energy Agency predicts that the demand for natural gas will grow by approximately 44% through 2035 [3]. In spite of this promising projection, raw natural gas typically contains significant amounts of impurities such as water vapor, carbon dioxide (CO₂), hydrogen sulfide (H₂S), nitrogen (N₂) and other gases, which must be removed before pipeline

delivery to end-users. Currently, amine absorption dominates acid gas separation technology, which reduces the CO₂ content to meet the pipeline requirement (< 2%). However, absorption processes present environmental concerns besides high capital and maintenance costs of the large scrubber units [4]. It has been estimated that about 16% of all natural gas in the United States contains higher nitrogen content (up to 15%) than the allowable maximum value (< 3%) according to pipeline specifications [3, 5]. Removal of nitrogen by conventional separation technologies, such as cryogenic distillation, is extremely cost intensive [6]. One alternative technology is pressure-swing adsorption (PSA) using molecular sieves that preferentially adsorb nitrogen [7]. In principle, polymeric gas separation membranes can be applied in many processing steps during upgrading of natural gas, including simultaneous removal of CO₂ and N₂ [8]. Membrane processes can potentially offer more energy-efficient technology with low capital cost, small footprint, simple operation, and low maintenance, as well as minimal environmental impact [9, 10].

The main requirements for advanced polymeric membrane materials are: (i) high permeability, (ii) high selectivity, (iii) long-term durability and (iv) processability into thin-films [11]. In 1991, Robeson reported an inherent trade-off between permeability (P) and selectivity (α), that is, high permeability polymers typically have low selectivity and vice versa [12]. An updated version was reported in 2008 [13] where the trade-off curves moved upwards primarily due to the development of perfluorinated glassy polymers [14] and ladder polymers of intrinsic microporosity (PIMs) with pores < 20 Å [15-17].

The concept of PIMs was first reported by Mckeown and Budd in 2004 using spirobisindane-based ladder polymers [15-17]. For example, PIM-1 (**Fig. 1**) showed high permeability with moderate selectivity for the separation of O₂/N₂ and CO₂/N₂ [17-20]. Thereafter, significant advances were achieved with the development of ladder polymers derived from AB-type triptycene- (TPIM-1 and TPIM-2) [21] and Tröger's base-building blocks [22, 23] that significantly outperformed all polymers listed on the 2008 Robeson upper bound for O₂/N₂, H₂/N₂ and H₂/CH₄ separation [24]. Polyimides of intrinsic microporosity (PIM-PIs) designed with contorted and inflexible backbones also showed promising gas separation properties [25-33]. Ghanem et al. [29, 34] and Rogan et al. [30] reported spirobisindane dianhydride-based PIM-PIs which displayed significantly improved permeability among all known polyimides. The first PIM-PI derived from a triptycene diamine showed higher selectivity but at the cost of lower

permeability; e.g. 6FDA-2,6-diaminotriptycene (6FDA-DAT1) had a CO₂ permeability of 120 Barrer and a CO₂/CH₄ selectivity of 38 [35]. Recently, Ghanem et al. and Swaidan et al. [25, 36] reported a series of PIM-PIs made from 9,10-bridgehead-substituted triptycene dianhydrides with excellent gas separation performance, which significantly surpassed the 2008 upper bound for several gas pairs (O₂/N₂, H₂/N₂, H₂/CH₄) due to their strong size-sieving ultramicroporous structures. However, their applicability for efficient CO₂/CH₄ separation was limited by their relatively low selectivity.

Previous work demonstrated that 6FDA-derived PI membranes made from hydroxyl-containing diamines, such as 6FDA-APAF (Fig. 1), showed the *highest* CO₂/CH₄ selectivities reported to date; however, the CO₂ permeability of these hydroxyl-functionalized polyimides was relatively low (< ~10 Barrer) [37, 38]. Recently, our group synthesized the first PIM-PI containing hydroxyl groups (PIM-6FDA-OH) (Fig. 1), which exhibited notable performance for CO₂/CH₄ separation [31].

Fig. 1. Structures of ladder PIM-1 and OH-functionalized 6FDA-APAF and PIM-6FDA-OH.

Furthermore, it was demonstrated that a PIM-PI-OH made from 9,10-triisopropyl-bridgehead triptycene dianhydride (TPDA) and 2,2-bis(3-amino-4-hydroxy-phenyl)-hexafluoropropane (APAF) exhibited enhanced CO₂/CH₄ selectivity relative to a TPDA-based polyimide derived from a related, purely hydrocarbon-based diamine (5,5'-(hexafluoroisopropylidene)-di-*o*-toluidine (ATAF)) [39]. The effect of hydroxyl-functionalization was elucidated with fluorescence spectroscopy, which clearly indicated the formation of a strong charge transfer complex (CTC). As a result, the OH-based polyimide exhibited more efficient intermolecular chain packing which led to lower CO₂ sorption capacity but significantly enhanced gas sieving capability, as indicated by high diffusion selectivity [39].

Here, we report the synthesis and gas transport properties of a newly developed high-performance triptycene-based hydroxyl-functionalized PIM-PI membrane material by a one-step

polycondensation reaction between a new 9,10-dimethyl-2,3,6,7-triptycene tetracarboxylic dianhydride (TDA1) monomer and APAF, as shown in **Scheme 1**. The polyimide was fully characterized by ^1H NMR, FTIR, GPC, XRD, BET surface area, and TGA measurements.

Scheme 1. Synthesis of TDA1-APAF polyimide.

Additionally, pure-and mixed-gas permeation properties of fresh and physically aged membranes were analyzed to identify key structure/property relationships that could guide the rational design of highly selective *and* permeable PIM-PIs for natural gas sweetening and petrochemical refinery applications.

2. Experimental

2.1 Materials

The compounds 1,2-dimethoxybenzene, 2-aminobenzoic acid, trifluoromethanesulfonic anhydride, acetic anhydride, 1,1'-bis(diphenylphosphino)ferrocene, tris(dibenzylideneacetone)dipalladium(0), boron tribromide (BBr_3), zinc cyanide, potassium hydroxide, and isoquinoline were obtained from Aldrich and used as received. 9,10-Dimethyl-2,3,6,7-triptycene tetracarboxylic dianhydride (TDA1) monomer was synthesized and characterized as described in the supporting information. The monomer 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF) was purchased from Aldrich and purified by vacuum sublimation at 220 °C. *m*-Cresol was distilled under reduced pressure and stored under nitrogen in the dark over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used as received.

2.2 Polymer Characterization

^1H Nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker DRX 400 (400 MHz) spectrometer in a suitable solvent using tetramethylsilane as the internal standard. Column chromatography was performed on silica gel 60A. Fourier transform infrared (FTIR) measurements were carried out using a Varian 670-IR FTIR spectrometer. Gel permeation chromatography (GPC, Agilent 1200) was carried out using tetrahydrofuran (THF) as an eluent. Thermogravimetric analysis (TGA, TA Q-5000) measurement was done under nitrogen atmosphere with heating rate of $3\text{ }^\circ\text{C}/\text{min}$ up to $800\text{ }^\circ\text{C}$. Wide-angle X-ray diffraction (WAXD) spectra of fresh and aged polymer film samples were recorded on a Bruker D8 Advance diffractometer in a 2θ range of 10° to 55° and the d-spacings were calculated with Bragg's law. The Brunauer-Emmett-Teller (BET) surface area of the polymer was determined by N_2 sorption at $-196\text{ }^\circ\text{C}$ using a Micromeritics ASAP-2020. The polymer powder was degassed under high vacuum at $150\text{ }^\circ\text{C}$ for 16 hours prior to analysis. Maximum pore volume was identified at $p/p_0 < 0.96$ of the N_2 isotherm.

2.3 Synthesis of TDA1-APAF Polymer

A mixture of TDA1 (0.23 g, 0.54 mmol), APAF (0.2 g, 0.54 mmol) and 3 ml *m*-cresol was stirred in a Schlenk tube for 30 minutes under nitrogen at room temperature. The mixture was heated at $80\text{ }^\circ\text{C}$ for 1 hour and catalytic amount of isoquinoline was added and the temperature was raised gradually to $200\text{ }^\circ\text{C}$ and kept at that temperature until the mixture became very viscous. Water formed during imidization was removed with a stream of nitrogen. After cooling, the polyimide solution was added into methanol (250 ml) and the crude fibrous polymer was filtered, washed with methanol and dried. Re-precipitation by a THF-methanol mixture was carried out twice for further purification and the polymer was finally dried at $120\text{ }^\circ\text{C}$ in a vacuum oven for 24 hours to give 86% yield. ^1H NMR (400 MHz, DMSO- d_6): $\delta_{\text{H}} = 2.49$ (br s, 6H), 7.07-7.46 (br m, 10H), 7.84 (s, 4H), 10.42 (s, 2H). FTIR (Membrane, ν , cm^{-1}): 1779 (asym C=O, str), 1710 (sym C=O, str), 1374 (C-N, str), 846 (imide ring deformation). GPC (THF): $M_n = 42,000\text{ g mol}^{-1}$, $M_w = 106,000\text{ g mol}^{-1}$ relative to polystyrene, $M_w/M_n = 2.5$. TGA analysis: (nitrogen), thermal degradation commences at $T_d \sim 480\text{ }^\circ\text{C}$. BET surface area = $260\text{ m}^2\text{ g}^{-1}$, total pore volume = $0.30\text{ cm}^3\text{ g}^{-1}$ (at $p/p_0 = 0.96$, adsorption).

2.4 Polymer film preparation

A polymer solution (5 wt/vol%) in THF was filtered twice through 0.45 μm polypropylene filters, poured onto a flat glass Petri dish and slowly evaporated at room temperature for one day. The obtained film was then dried at 120 $^{\circ}\text{C}$. To remove any traces of residual solvent, the membrane was soaked in methanol for 10 h, air-dried, and then post-dried at 250 $^{\circ}\text{C}$ in a vacuum oven for 12 h. Tough films with thickness of 70 ± 5 μm were used for gas permeability measurements. Prior to the gas permeation tests, TGA experiments were performed to confirm that the polyimide film was solvent free. Film thickness and effective area for gas permeation measurements were determined by a digital micrometer and scanner, respectively.

2.5 Pure-gas permeation experiments

The pure-gas permeabilities of TDA1-APAF were determined by using the constant volume/variable pressure method. The polymer film sample was degassed in the permeation cell under vacuum for at least 24 hours. The pure-gas permeability of He, H₂, N₂, O₂, CH₄, and CO₂ was measured at 35 $^{\circ}\text{C}$ and 2 bar. The gas permeability was calculated by:

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

where P is the permeability in Barrers (1 Barrer = 10^{-10} $\text{cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$), p_{up} is the upstream pressure (cmHg), dp/dt is the steady-state permeate-side pressure increase (cmHg s^{-1}), V_d is the calibrated permeate volume (cm^3), l is the membrane thickness (cm), A is the effective membrane area (cm^2), T is the operating temperature (K), and R is the gas constant ($0.278 \text{ cm}^3 \text{ cmHg cm}^{-3}(\text{STP}) \text{ K}^{-1}$). The ideal pure-gas selectivity for a gas pair is given by the following relationship:

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

2.6 Mixed-gas permeation experiments

The mixed-gas permeation measurements of TDA1-APAF were performed at 35 $^{\circ}\text{C}$ using a custom-designed mixed-gas permeation system similar to that described by O'Brien et al. [40]. The feed gas mixture contained 50 vol.% CH₄/50 vol.% CO₂ and the total feed pressure was varied between 4 and 30 bar; the permeate pressure was less than 0.01 bar. The permeate flow

rate to feed flow rate, i.e. the stage-cut, was set at 0.01. Applying these conditions, the residue composition was essentially equal to that of the feed gas. CO₂ and CH₄ permeate concentrations were detected with a gas chromatograph (Agilent 3000A Micro GC) equipped with a thermal conductivity detector. The mixed-gas permeability was calculated by:

$$P_{CH_4} = 10^{10} \frac{y_{CH_4} V_d L}{x_{CH_4} p_{up} A R T} \frac{dp}{dt}$$

$$P_{CO_2} = 10^{10} \frac{y_{CO_2} V_d L}{x_{CO_2} p_{up} A R T} \frac{dp}{dt}$$

where y and x are the mole fractions in the permeate and feed, respectively.

The mixed-gas CO₂/CH₄ selectivity was obtained from:

$$\alpha_{CO_2/CH_4} = \frac{y_{CO_2}/y_{CH_4}}{x_{CO_2}/x_{CH_4}}$$

3. Results and discussion

Our previous study on a PIM-PI derived from the new 9,10-dimethyl-2,3,6,7-triptycene tetracarboxylic dianhydride (TDA1) monomer and 3,3'-dimethylnaphthidine (DMN) showed that the triptycene building block with bridgehead methyl side groups offered a polyimide with high BET surface area of 760 m² g⁻¹ and very high gas permeabilities (e.g. CO₂ = 3700 Barrer) but with only moderate selectivities (e.g. CO₂/CH₄ selectivity = 17) [41]. In this study, we report a new polyimide synthesized from TDA1 and a commercial hydroxyl-containing diamine monomer (APAF). The chemical structure of the polyimide was confirmed by FTIR and ¹H NMR spectroscopy. The FTIR spectrum of the polyimide film (**Fig. 2a**) contained absorption bands at approximately 1779 and 1710 cm⁻¹ (C=O asymmetric and symmetric stretching), 1374 cm⁻¹ (C-N stretching) and 846 cm⁻¹ (imide ring deformation).

Fig. 2. (a) FTIR spectrum; (b) ¹H NMR of TDA1-APAF.

In the proton NMR spectrum (**Fig. 2b**), the absorption band at 2.49 ppm was assigned to the two aliphatic methyl groups in the bridgehead carbons, while the aromatic protons appear in the range of 7.07-7.46 ppm. The absorption band at 10.42 ppm confirmed the presence of hydroxyl functional groups. The polymer exhibited high molecular weight ($M_w = 106,000 \text{ g mol}^{-1}$) as determined by GPC and good solubility in THF from which tough dense films were cast for permeation studies.

3.1 Physical properties and microstructure of TDA1-APAF

The polymer showed high thermal stability in N₂ atmosphere with an onset decomposition temperature of 480 °C determined by thermal gravimetric analysis, as shown in **Fig. 3**.

Fig. 3. Thermogravimetric analysis of TDA1-APAF polyimide film.

The BET surface area of TDA1-APAF derived from the N₂ sorption isotherm at -196 °C was 260 m² g⁻¹ (**Fig. 4**).

Fig. 4. Physisorption isotherms for TDA1-APAF using N₂ at -196 °C. Closed symbols: adsorption; open symbols: desorption.

Wide-angle X-ray diffraction (WAXD) measurements were conducted on a fresh and 250 days aged TDA1-APAF film to investigate *qualitative* changes in the average polymer chain spacing. Both membranes exhibited an amorphous halo centered around $d \approx 5.3$ Å (**Fig. 5**). In comparison with the fresh sample, the physically aged sample had one additional shoulder diffraction peak at $d \approx 3.7$ Å. This implies that a fraction of the larger free volume elements in the aged polymer densified, which resulted in the development of smaller pores in the low ultramicroporous range. This shift was expected to result in higher selectivities associated with lower gas permeabilities and confirmed by the results shown below.

Fig. 5. WAXD spectra of fresh and 250 days aged TDA1-APAF films.

3.2 Fresh and physically aged pure-gas permeation properties

Pure-gas permeation experiments were performed on a fresh, one-day old sample of TDA1-APAF at 2 bar and 35 °C (**Table 1**). The gas permeability decreased in the order: $H_2 > He > CO_2 > O_2 > N_2 > CH_4$ which confirmed the molecular sieving behavior of the polymer by the fact that the He and H_2 permeability was larger than that of CO_2 , opposite to the trend normally observed for high BET surface area PIMs materials [18]. Microporous glassy polymers undergo a physical aging process in which the chains slowly arrange into a more tightly packed configuration towards their equilibrium glassy state [42, 43]. Thus, pure-gas permeation experiments were also performed on an aged sample after 250 days at 2 bar and 35 °C (**Table 1**). The permeabilities for all gases decreased by only ~ 25% for H_2 and CO_2 ($P_{H_2} = 73$ Barrer and $P_{CO_2} = 30$ Barrer) but selectivities increased *significantly* for H_2/CH_4 and CO_2/CH_4 with values of 183 and 75, respectively. **Table 1** shows the data from this work in comparison to previously reported literature data for three commercial glassy membrane materials, e.g. cellulose triacetate, Matrimid and polysulfone. It is noteworthy that the aged TDA1-APAF sample had both higher permeabilities (He, H_2 , CO_2 , O_2) and selectivities for all gas pairs relative to those of commercial gas separation membrane materials.

Table 1. Pure-gas permeabilities and ideal selectivities for fresh and physically aged of TDA1-APAF membranes (at 2 bar; 35 °C).

Polymer	Pure-Gas Permeability (Barrer)						Ideal Selectivity (α)			
	He	H ₂	N ₂	O ₂	CH ₄	CO ₂	CO ₂ /CH ₄	H ₂ /CH ₄	N ₂ /CH ₄	O ₂ /N ₂
TDA1-APAF ^a	92	94	1.5	8.5	0.73	40	55	129	2.1	5.7
TDA1-APAF ^b	(70)	(73)	(0.90)	(6.4)	(0.40)	(30)	(75)	(183)	(2.3)	(7.1)
Cellulose acetate (DS 2.85) [44]	19.6	15.5	0.23	1.46	0.20	6.6	33	78	1.1	6.3
Matrimid [45]	-	17.5	0.22	1.46	0.21	7.3	35	83	1.1	6.6
Polysulfone [46]	13	14	0.25	1.40	0.25	5.6	22	56	1.0	5.6

^a Membrane was soaked in methanol for 10 hrs; dried under vacuum at 250 °C for 12 hrs. Tested after 1 day.

^b Tested after 250 days.

The pure-gas diffusion (D) and solubility (S) coefficients of the fresh and physically aged TDA1-APAF membranes for N₂, O₂, CH₄ and CO₂ were calculated by the time-lag method and are shown in **Table 2**. As expected, the tighter aged membrane displayed lower D and S values compared to the fresh sample. Concurrently, the enhanced ultramicroporosity in the aged TDA1-APAF sample resulted in improved size-sieving properties and, therefore, higher O₂/N₂, N₂/CH₄ and CO₂/CH₄ diffusion selectivity values than those of the fresh sample (**Table 3**).

Table 2. Pure-gas diffusion and solubility coefficients of N₂, O₂, CH₄ and CO₂ for fresh and physically aged TDA1-APAF films.

Diffusion coefficient (10 ⁻⁸ cm ² s ⁻¹)	Solubility coefficient (10 ⁻² cm ³ (STP) cm ⁻³ cmHg ⁻¹)

Polymer	Diffusion selectivity (α_D)				Solubility selectivity (α_S)			
	N ₂	O ₂	CH ₄	CO ₂	N ₂	O ₂	CH ₄	CO ₂
TDA1-APAF ^a	0.82	4.5	0.12	1.9	1.8	1.9	6.1	21.1
TDA1-APAF ^b	(0.60)	(4.0)	(0.08)	(1.6)	(1.5)	(1.6)	(5.0)	(18.5)

^a Tested after 1 day.

^b Tested after 250 days.

Table 3. Diffusion selectivities and solubility selectivities of fresh and physically aged TDA1-APAF films (2 bar; 35 °C).

Polymer	Diffusion selectivity (α_D)			Solubility selectivity (α_S)		
	O ₂ /N ₂	N ₂ /CH ₄	CO ₂ /CH ₄	O ₂ /N ₂	N ₂ /CH ₄	CO ₂ /CH ₄
TDA1-APAF ^a	5.5	6.83	15.8	1.06	0.30	3.5
TDA1-APAF ^b	6.7	7.5	20	1.07	0.30	3.7

^a Tested after 1 day.

^b Tested after 250 days.

3.3 Fresh and physically aged mixed-gas permeation properties

Commonly, high sorption uptake of condensable gases like CO₂ can dilate the polymer matrix and induce increased chain mobility, which significantly affects the gas transport properties of glassy polymers. The pure- and mixed-gas permeabilities (**Figs. 6 and 7**) and selectivities (**Fig. 8**) were measured using a 1:1 CO₂/CH₄ feed mixture with increasing CO₂ partial pressure (2, 5, 7, 10, 12 and 15 bar) for fresh and aged TDA1-APAF samples. Previously reported mixed-gas permeation data for cellulose triacetate (CTA) are included for comparison [47]. The pure-gas CO₂ permeabilities in both fresh and aged TDA1-APAF membranes decreased with increasing partial CO₂ feed pressure from 2 to 15 bar (**Fig. 6**), similar to the behavior of related PIM-PIs previously reported [35, 39, 47, 48]. This can be rationalized by a decrease in CO₂ solubility coefficient with pressure as is typically observed in glassy polymers due to dual-mode gas sorption behavior. In addition, competitive sorption is expected to occur between CO₂ and CH₄

for available sorption sites, which may reduce the overall sorbed concentration of CO_2 in the polymer. As a result, the mixed-gas CO_2 permeabilities were lower than the pure-gas CO_2 permeability values determined at the same partial pressure.

Fig. 6. Pressure-dependence of pure- and mixed-gas CO_2 permeabilities for CTA [47], fresh and physically aged TDA1-APAF polyimide (1:1 CO_2/CH_4 mixture; 35 °C). Lines are drawn to guide the eye. Open points: pure-gas; closed points: mixed-gas.

The mixed-gas CH_4 permeability was also lower than the pure-gas value over the entire pressure range, most likely due to partial blocking of the micropores by preferential sorption of CO_2 , as shown in **Fig. 7**. Similar behavior has previously been observed for related PIM-PIs [39] and polybenzoxazoles derived from thermally-rearranged polyimides [49, 50].

Fig. 7. Pressure-dependence of pure- and mixed-gas CH₄ permeabilities for CTA [47], fresh and physically aged TDA1-APAF (1:1 CO₂/CH₄ mixture, 35 °C). Lines are drawn to guide the eye. Open points: pure-gas; closed points: mixed-gas.

As a result, the mixed-gas permselectivities of CO₂/CH₄ were slightly higher than those determined under pure-gas conditions (**Fig. 8**) due to a reduction of the mixed-gas CH₄ permeability by co-permeation of CO₂, as previously observed in TPDA-APAF, and some thermally-rearranged polyimides [49, 50]. Under typical natural gas sweetening conditions, where the partial pressure of CO₂ is often near 5-10% in a 60-70 bar feed, the aged membrane exhibited a very high CO₂/CH₄ selectivity of ~75. This high selectivity significantly benefits the membrane process economics as it mitigates the amount of CH₄ loss into the permeate [51]. The pure vs. mixed-gas permeation properties of CTA are different than those of TDA1-APAF as the mixed-gas CO₂/CH₄ selectivity is lower than the pure-gas value (**Fig. 8**). This behavior is indicative of CO₂-induced plasticization of CTA.

Fig. 8. Pressure-dependence of mixed-gas CO₂/CH₄ selectivities for CTA [47], fresh and physically aged TDA1-APAF samples (1:1 CO₂/CH₄ mixture, 35 °C). Lines are drawn to guide the eye: open points, pure-gas; closed points, mixed-gas.

The *mixed-gas* performance of the TDA-APAF polyimide for CO₂/CH₄ separation is compared to related PIMs and TR polymers evaluated under the same test conditions (35 °C; 10 bar CO₂ partial pressure) in **Fig. 9**. The aged intrinsically microporous TDA1-APAF polyimide (surface area of 260 m² g⁻¹) exhibited similar mixed-gas CO₂/CH₄ selectivity with two- to four-fold higher CO₂ permeability compared to low free volume 6FDA-based hydroxyl-functionalized polyimides (6FDA-APAF, 6FDA-DAP).

Fig. 9. CO₂/CH₄ mixed-gas permeability/selectivity trade-off curve for TDA1-APAF (this study), KAUST-PI-1 [47], AO-PIM-1 [52], 6FDA-DAT1 [35], 6FDA-DAT2 [35], TPDA-APAF [39], 6FDA-DAP [48], 6FDA-APAF [39], 6FDA-*m*PDA [48], TR 6FDA-HAB [49], TR PIM-6FDA-OH [50] and CTA [47]. All experiments were performed with a 50/50 (v/v) CO₂/CH₄ mixture at 20 bar feed pressure and 35 °C using the constant volume/variable pressure technique.

4. Conclusions

In this study, a new TDA1-APAF polyimide was synthesized from 9,10-dimethyl-2,3,6,7-triptycene tetracarboxylic dianhydride (TDA1) and a commercial hydroxyl-diamine (APAF) *via* one-step high-temperature solution imidization reaction. This polymer exhibited high molecular weight, good solubility and high thermal stability. The pure-gas permeation data showed that introducing hydroxyl groups to the polyimide leads to high permselectivity due to high diffusion selectivity for a variety of gas pairs, most notably CO₂/CH₄ and H₂/CH₄. The aged triptycene-based hydroxyl-containing polyimide showed a CO₂ permeability of 21 Barrer under binary 1:1 CO₂/CH₄ mixed-gas feed with a selectivity of 72 at a partial CO₂ pressure of 10 bar. These properties are significantly better than those of commercial cellulose triacetate used for natural gas sweetening, which exhibits P_{CO_2} = 8 Barrer and CO₂/CH₄ selectivity of 25 when tested under the same conditions. Moreover, aged TDA1-APAF polyimide had a N₂/CH₄ selectivity of 2.3, thereby making it potentially possible to simultaneously treat CO₂- and low concentration nitrogen-contaminated natural gas. These enhanced properties make TDA1-APAF polyimide an

excellent candidate material for development of asymmetric or thin-film composite membranes for industrial natural gas sweetening.

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Appendix A. Supplementary materials

Supplementary information associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2016.xx.xxx>.

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Graphical Abstract

Highlights

- New OH-functionalized polyimide was developed based on 9,10-dimethyl-2,3,6,7-triptycene tetracarboxylic dianhydride.
- Aged membrane (250 days) showed excellent gas separation performance for CO₂/CH₄ separation.
- TDA1-APAF polyimide offers simultaneous removal of CO₂ and N₂ from raw natural gas.
- Mixed-gas plasticization resistance up to 30 bar (1:1 CO₂/CH₄ feed; 35 °C)
- 10-20% increase in mixture CO₂/CH₄ selectivity over pure-gas values up to 30 bar.