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Gas Permeation and Physical Aging Properties of Iptycene Diamine-Based Microporous Polyimides

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ABSTRACT

The synthesis and gas permeation properties of two 6FDA-dianhydride-based polyimides prepared from 2,6-diaminotriptycene (6FDA-DAT1) and its extended iptycene analog (6FDA-DAT2) are reported. The additional benzene ring on the extended triptycene moiety in 6FDA-DAT2 increases the free volume over 6FDA-DAT1 and reduces the chain packing efficiency. The BET surface area based on nitrogen adsorption in 6FDA-DAT2 ($450 \text{ m}^2 \text{ g}^{-1}$) is ~40% greater than that of 6FDA-DAT1 ($320 \text{ m}^2 \text{ g}^{-1}$). 6FDA-DAT1 shows a CO_2 permeability of 120 Barrer and CO_2/CH_4 selectivity of 38, whereas 6FDA-

DAT2 exhibits a 75% increase in CO₂ permeability to 210 Barrer coupled with a moderate decrease in selectivity (CO₂/CH₄ = 30). Interestingly, minimal physical aging was observed over 150 days for both polymers and attributed to the high internal free volume of the shape-persistent triptycene geometries. The aged polyimides maintained CO₂/CH₄ selectivities of 25-35 along with high CO₂ permeabilities of 90-120 Barrer up to partial CO₂ pressures of 10 bar of an aggressive 50:50 CO₂:CH₄ mixed-gas feed, suggesting potential application in membranes for natural gas sweetening.

Keywords: polyimides of intrinsic microporosity; triptycene; gas separation; natural gas; physical aging

1. Introduction

Membrane technology has been applied in recent years for industrial gas separations such as natural gas upgrading, onsite nitrogen production from air and hydrogen recovery [1]. Some advantages of membrane-based gas separation over conventional technologies, such as cryogenic distillation, adsorption and absorption include: simple modular design, cost effectiveness and small footprint, which is important for offshore natural gas processing operations [2, 3]. Ideal polymers for gas separation membranes should have the following properties: (i) high permeability, (ii) high selectivity, (iii) good chemical resistance and (iv) stable long-term separation properties. Unfortunately, an inherent trade-off exists between permeability and selectivity, that is, highly permeable polymers show low selectivity and vice versa. Robeson developed gas permeability/selectivity upper bound relationships for a variety of gas pairs based on a large database of published permeation data [4].

Recently developed polymers of intrinsic microporosity (PIM) have demonstrated excellent gas separation performance, often exceeding the latest 2008 upper bounds [5-11]. These amorphous glassy polymers are characterized by: (i) very high thermal stability; (ii) solubility in organic solvents; (iii) high BET surface area (up to $\sim 1000 \text{ m}^2/\text{g}$); (iv) microporosity (pore size $< 20 \text{ \AA}$) as well as ultra-microporosity ($< 7 \text{ \AA}$). One class of PIMs is based on high-free-volume aromatic polyimides (PIM-PIs) that contain rigid contortion sites either in their dianhydride and/or diamine moiety. Examples of such molecular building blocks are: (i) spirobisindane dianhydrides [7, 12, 13] and diamines [14, 15], ethanoanthracene dianhydride [6, 16], spirobifluorene dianhydride [17] and diamines [18, 19], Tröger's base diamines [20-22], and triptycene dianhydrides [10, 23] and diamines [15, 24, 25].

Triptycene is the simplest ipitycene and frequently used in polymer building units due to its unique rigid and contorted structure with phenyl rings attached to the [2,2,2] bicyclooctatriene bridgehead system. Triptycene, as shown in Figure 1a, has three phenyl rings bound by a single hinge, which provides a high energy barrier to molecular twisting or deformation which keeps the angle between aromatic rings at 120° . The rigid 3-dimensional, fully aromatic structure leads to poor polymer chain packing, which, in turn, results in high internal free volume (IFV) [26, 27].

Fig. 1. Chemical structures of a) triptycene and b) extended iptycene demonstrating internal free volume (IFV).

An extended iptycene building block, shown in Figure 1b, demonstrates even larger IFV than triptycene due to the addition of a benzene ring to the transverse aromatic arm in the 9,10-position of the triptycene unit.

Cho et al. reported the synthesis, characterization and gas permeation properties of a polyimide based on the reaction of 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA) and 2,6-diaminotriptycene (DAT1) that exhibited good performance for gas separation [24]. Swager's group communicated the synthesis and characterization of a polyimide series based on 2,6-triptycene diamine (DAT1) and its extended iptycene diamine derivative (DAT2) for optical applications [15].

Here, the pure-gas permeability, diffusivity, and sorption properties of 6FDA-DAT1 and extended 6FDA-DAT2 are reported and analyzed with respect to their chemical structures. In addition, CO₂/CH₄ mixed-gas permeation experiments were performed and

the effect of long-term physical aging on the gas permeation properties of the polymers was investigated. The polyimides were fully characterized by ^1H -NMR, FT-IR, GPC, and TGA. Nitrogen and carbon dioxide adsorption experiments were performed to elucidate the micropore structure of the PIM-PIs.

2. Experimental

2.1 Materials

6FDA, triptycene, 1,4-dihydro-1,4-epoxynaphthalene, hydrazine hydrate, Pd-C, isoquinoline, acetic anhydride, 2,6-diaminoanthraquinone and *o*-dichlorobenzene were obtained from Aldrich and used as received. 6FDA was purified by sublimation under vacuum prior to use. *m*-Cresol was distilled under reduced pressure and stored under nitrogen atmosphere in the dark over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used as received. 2,6-diaminotriptycene (DAT1) was prepared as previously reported by nitration of triptycene followed by reduction of the purified 2,6-dinitrotriptycene with Pd-C and hydrazine hydrate. The extended triptycene DAT2 was prepared by the conventional Diels-Alder reaction between 2,6-diaminoanthracene and 1,4-dihydro-1,4-epoxynaphthalene followed by dehydration in the presence of perchloric acid [15].

2.2 Polymer characterization

^1H -NMR (400 MHz) was recorded on a Bruker DRX 400 spectrometer in a suitable solvent using trimethylsilane as the internal standard. Chemical shifts (δ) are reported in ppm. Column chromatography was performed on silica gel 60A. Fourier transform infrared (FT-IR) measurements were performed using a Varian 670-IR FT-IR spectrometer. Gel permeation chromatography (GPC, Viscotek) was carried out using chloroform as an eluent. Thermogravimetric analysis (TGA, TA Q-5000) measurements were performed under nitrogen atmosphere. All TGA runs entailed a drying step at 100 °C for 30 minutes followed by a temperature ramp of 3 °C/min up to 800 °C. The BET surface area of the polymers was determined by N_2 sorption at -196 °C using a Micromeritics ASAP-2020. Powder polymer samples were degassed under high vacuum

at 120 °C for 15 hours prior to analysis. Analysis of the pore size distributions was performed using the NLDFT (Non-Local Density Functional Theory) model using N₂ (at -196 °C) and CO₂ (at 0 °C) sorption isotherms for carbon slit pore geometry provided by ASAP 2020 version 4.02 software.

2.3 Synthesis of polyimides

6FDA-DAT1 and 6FDA-DAT2 polyimides were synthesized via the cycloimidization reaction between equimolar amounts of 6FDA and the corresponding diamine (Scheme 1). To a dry 10 mL Schlenk tube equipped with nitrogen inlet and outlet were added the diamine monomer (1 mmol) and freshly distilled *m*-cresol (4 ml). After stirring for 5 min an equimolar amount of 6FDA (1.0 mmol) and isoquinoline (0.1 ml) was added. The mixture was stirred at ambient temperature for 15 minutes under a flow of nitrogen and then the temperature was raised gradually to 200 °C and kept at that temperature for 4 hours.

Scheme 1. Synthesis of 6FDA-DAT1 and 6FDA-DAT2. Polymer structures and their energy-minimized conformations are shown (Materials Studio 6.0, Accelrys).

After cooling, the polymer was precipitated by pouring the reaction mixture into an excess of methanol. The resulting fibrous polymer was collected by filtration and purified by reprecipitation from chloroform into methanol and then dried under vacuum at 120 °C for 20 h to give an off-white powder in quantitative yield.

6FDA-DAT1.

Following the above general procedure, 6FDA-DAT1 was prepared from 6FDA and DAT1 diamine. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 5.54 (H_1 , s, 2H), 7.06 ($\text{H}_{(2,6)}$, m, 4H), 7.42 (H_5 , dd, 2H), 7.45 (H_3 , s, 2H), 7.54 (H_4 , d, 2H), 7.84 (H_9 , d, 2H), 7.89 (H_7 , s, 2H), 7.99 (H_8 , d, 2H). FT-IR (membrane, ν , cm^{-1}): 1780 (asym C=O, str), 1720 (sym C=O, str), 1360 (C-N, str), 835 (imide ring deformation). Analysis by GPC (CHCl_3): $M_n = 16200 \text{ g mol}^{-1}$, $M_w = 33300 \text{ g mol}^{-1}$ relative to polystyrene, $M_w/M_n = 2.1$. BET surface area (N_2) = $320 \text{ m}^2 \text{ g}^{-1}$, total pore volume = $0.24 \text{ cm}^3 \text{ g}^{-1}$ at $p/p_0 = 0.98$, adsorption. TGA analysis: (N_2), initial weight loss due to thermal degradation commences at $T_d = 530^\circ\text{C}$.

6FDA-DAT2.

Following the above typical procedure, 6FDA-DAT2 was prepared from 6FDA and DAT2 diamine. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 5.66 (H_1 , s, 2H), 7.11 (H_2 , dd, 2H), 7.39 (H_6 , m, 2H), 7.50 (H_3 , d, 2H), 7.54 (H_4 , d, 2H), 7.71 (H_{10} , dd, 2H), 7.82 ($\text{H}_{(5,9)}$, m, 4H), 7.87 (H_7 , s, 2H), 7.97 (H_8 , d, 2H). FT-IR (membrane, ν , cm^{-1}): 1780 (asym C=O, str), 1720 (sym C=O, str), 1360 (C-N, str), 835 (imide ring deformation). Analysis by GPC (CHCl_3): $M_n = 38000 \text{ g mol}^{-1}$, $M_w = 67000 \text{ g mol}^{-1}$ relative to polystyrene, $M_w/M_n = 1.8$. BET surface area (N_2) = $450 \text{ m}^2 \text{ g}^{-1}$, total pore volume = $0.57 \text{ cm}^3 \text{ g}^{-1}$ at $p/p_0 = 0.98$,

adsorption. TGA analysis: (N₂), initial weight loss due to thermal degradation commences at T_d = 530 °C.

2.4 Polymer film preparation

Solutions of the polymers in chloroform (5 wt/vol%) were filtered through 0.45 µm polypropylene filters and isotropic films were obtained by slow evaporation of the solvent at room temperature from a levelled glass Petri dish. To remove any traces of residual solvent, the dry membranes were soaked in methanol for 10 h, air-dried, and then post-dried at 120 °C in a vacuum oven for 12 h. The resulting yellowish tough 6FDA–DAT1 and 6FDA–DAT2 films with thickness of 65 ± 5 µm were used for gas permeability measurements.

2.5 Pure- and mixed-gas permeation experiments

The pure-gas permeability of 6FDA-DAT1 and 6FDA-DAT2 was determined by using the variable pressure/constant volume method. Each 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 °C and 2 bar. Pressure-dependence of CO₂ and CH₄ permeability was determined from 2 to 15 bar. The gas permeability was calculated by:

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

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

where P is the permeability in Barrers (1 Barrer = 10⁻¹⁰ cm³(STP)·cm/cm²·s·cmHg = 7.5 × 10⁻¹⁸ m³ (STP) m m⁻²·s⁻¹·Pa⁻¹), p_{up} is the upstream pressure (cmHg), dp/dt is the steady-state permeate-side pressure increase (cmHg/s), V_d is the calibrated permeate volume (cm³), l is the membrane thickness (cm), A is the effective membrane area (cm²), T is the operating temperature (K), and R is the gas constant (0.278 cm³·cmHg /cm³(STP)·K). The ideal selectivity for a gas pair is given by the following relationship:

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

The apparent diffusion coefficient D (cm^2/s) was calculated by $D = l^2/6\theta$, where θ is the time lag of the permeability measurement and l is the membrane thickness. The solubility coefficient S ($\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{cmHg}$) was then calculated from the solution-diffusion gas transport relationship: $S=P/D$.

The mixed-gas permeation properties of the membranes were measured using a feed gas mixture of 1:1 CO_2/CH_4 at 35 °C with a setup similar to that described by O'Brien et al. [28]. Both polyimides were tested at total pressures of 4, 10, 20 and 30 bar, respectively. The mixed-gas permeabilities were calculated by:

$$P_{\text{CO}_2} = 10^{10} \frac{y_{\text{CO}_2} V_d l}{x_{\text{CO}_2} P_{\text{up}} A R T} \frac{dp}{dt}$$

$$P_{\text{CH}_4} = 10^{10} \frac{y_{\text{CH}_4} V_d l}{x_{\text{CH}_4} P_{\text{up}} A R T} \frac{dp}{dt}$$

where y and x are the mole fractions in the permeate and feed, respectively. Because the downstream pressure was negligible, the mixed-gas CO_2/CH_4 selectivity was obtained from:

$$\alpha_{\text{CO}_2/\text{CH}_4} = \frac{y_{\text{CO}_2}/y_{\text{CH}_4}}{x_{\text{CO}_2}/x_{\text{CH}_4}}$$

3. Results and discussion

3.1 Physical properties and microstructures of 6FDA-DAT1 and 6FDA-DAT2

The physical properties of the polyimides from our study and previous reports are listed in Table 1. The molecular weights and molecular weight distributions of 6FDA-DAT1 vary significantly depending on the reaction conditions used for synthesizing the polyimide.

Table 1. Physical properties of 6FDA-DAT1 and 6FDA-DAT2.

Polymer	M_n (g mol ⁻¹)	PDI	T_d (°C)	BET surface area (N ₂) (m ² g ⁻¹)
6FDA-DAT1 ^a	21100	5.2	540	-
6FDA-DAT-1 ^b	29000	1.8	531	68
6FDA-DAT1 ^c	16200	2.1	530	320
6FDA-DAT2 ^b	17000	1.6	540	430
6FDA-DAT2 ^c	38000	1.8	530	450

^a [24]; ^b [15]; ^c this study.

The influence of the additional benzene ring in the three-dimensional extended iptycene moiety can be assessed from N₂ (-196 °C) and CO₂ (0 °C) physisorption isotherms (Figure 2 and 3). The corresponding NLDFT-derived pore size distributions (PSDs) are shown in Figure 4. The addition of a benzene ring increased the BET surface area from 320 m²g⁻¹ for 6FDA-DAT1 to 450 m²/g for 6FDA-DAT2, which is expected based on the geometric structures of triptycene and its extended iptycene derivative (Figure 1). Furthermore, N₂ sorption isotherms indicate the development of larger microporosity in the 6FDA-DAT2 polymer. Previously, Swager's group reported a BET surface area for 6FDA-DAT1 of only 68 m²g⁻¹; one possible reason for this lower surface area could be attributed to traces of residual solvent trapped in the micropores of the polymer.

Fig. 2. Physisorption isotherms for 6FDA-DAT1 and 6FDA-DAT2 using N_2 at $-196\text{ }^\circ\text{C}$. Closed symbols: adsorption; open symbols: desorption.

Fig. 3. Physisorption isotherms for 6FDA-DAT1 and 6FDA-DAT2 using CO_2 at $0\text{ }^\circ\text{C}$. Closed symbols: adsorption; open symbols: desorption.

The PSDs based on CO_2 isotherms (Figure 4) showed that the quantity of ultra-micropores ($< 7\text{ }\text{\AA}$) is similar in both polymers. However, PSDs deduced from N_2 isotherms qualitatively indicate that 6FDA-DAT2 contains an increased fraction of micropores larger than $7\text{ }\text{\AA}$ compared to 6FDA-DAT1. Furthermore, pore sizes within the range of 8 to $12\text{ }\text{\AA}$ in 6FDA-DAT1 shifted to sizes greater than $12\text{ }\text{\AA}$ in 6FDA-DAT2.

Fig. 4. NLDFT-based estimated pore size distribution obtained from N_2 and CO_2 isotherms for 6FDA-DAT1 and 6FDA-DAT2 assuming carbon slit-pore geometry.

3.2 Pure-gas permeation properties of 6FDA-DAT1 and 6FDA-DAT2

The pure-gas permeation properties of 6FDA-DAT1 and 6FDA-DAT2 are shown in Table 2. Gas permeabilities of 6FDA-DAT1 obtained in our study were lower and selectivities higher for all gas pairs compared to previously reported data by Cho et al. [24]. Possible reasons for the different gas permeation properties may include: (i) different polymerization protocols; (ii) different film formation, post-treatment and drying conditions; (iii) different permeation test conditions. To obtain meaningful structure/gas permeation property relationships between 6FDA-DAT1 and the extended 6FDA-DAT2, we applied exactly the same film preparation and permeation test protocols for each polymer (Table 2). 6FDA-DAT2 exhibited higher permeability for all gases than 6FDA-DAT1 coupled with lower selectivity. For example, 6FDA-DAT1 showed a CO_2 permeability of 120 Barrer and CO_2/CH_4 selectivity of 38, whereas 6FDA-DAT2 exhibited a 75% increase in CO_2 permeability to 210 Barrer coupled with a moderate decrease in selectivity ($CO_2/CH_4 = 30$). This result is qualitatively consistent with the BET and PSD results discussed above. Adding a benzene ring to the iptycene moiety in 6FDA-DAT2 reduces efficient chain packing, which, in turn, leads to an increase in the internal free volume (IFV), and, hence, gas permeability.

Table 2. Pure-gas permeabilities and ideal selectivities for 6FDA-DAT1 and 6FDA-DAT2.

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	O ₂ /N ₂
6FDA-DAT1 ^a	198	257	8.1	39.0	6.2	189	30	41	4.8
6FDA-DAT1 ^b	161	198	4.7	25.4	3.2	120	38	62	5.4
6FDA-DAT1 ^c	148	170	4.0	21.4	2.7	102	38	63	5.4
6FDA-DAT2 ^d	204	281	9.0	43.3	7.1	210	30	40	4.8
6FDA-DAT2 ^e	175	229	7.7	40.7	5.3	160	30	43	5.3

Test and preparation conditions:

^a T=35 °C, 1 bar; 2 hrs methanol soaked; dried under vacuum at 100 °C for 24 hrs [24].

^b T=35 °C, 2 bar; 10 hrs methanol soaked; dried under vacuum at 120 °C for 12 hrs. Fresh sample tested one day after drying.

^c same as b after 150 days of aging.

^d T=35 °C; 2 bar, 10 hrs methanol soaked; dried under vacuum at 120 °C for 12 hrs. Fresh sample tested one day after drying.

^e same as d after 150 days of aging.

The pure-gas diffusion (D) and solubility (S) coefficients of 6FDA-DAT1 and 6FDA-DAT2 for N₂, O₂, CH₄ and CO₂ were calculated by the time-lag method and shown in Table 3. The higher gas permeabilities in 6FDA-DAT2 are generally caused by increased diffusivity coefficients, whereas the solubility coefficients remain essentially constant. Faster diffusion again indicates the formation of a more open and interconnected microporosity by the bulkier DAT2 diamine (Figure 4). Relative to ~60-70% increases in the diffusivity coefficients of O₂ ($k_D=3.46 \text{ \AA}$), N₂ ($k_D=3.64 \text{ \AA}$) and CO₂ ($k_D=3.3 \text{ \AA}$), more than 100% increases were observed in that of the larger CH₄ gas ($k_D=3.8 \text{ \AA}$) which is most impacted by the newly accessible diffusion pathways. Indeed, the overall reduction in CO₂/CH₄ permselectivity from 38 in 6FDA-DAT1 to 30 in 6FDA-DAT2 (Table 2) is governed by a reduction in CO₂/CH₄ diffusivity selectivity (i.e., $D(\text{CO}_2)/D(\text{CH}_4)$).

Table 3. Pure-gas diffusion and solubility coefficients of N₂, O₂, CH₄ and CO₂ for 6FDA-DAT1 and 6FDA-DAT2 based on time-lag method (35 °C; 2 bar).

Polymer	Diffusion coefficient (10 ⁻⁸ cm ² /s)				Solubility coefficient (10 ⁻² cm ³ (STP)/(cm ³ ·cmHg))			
	N ₂	O ₂	CH ₄	CO ₂	N ₂	O ₂	CH ₄	CO ₂
6FDA-DAT1 ^a	5.5	23	1.5	13	1.5	1.7	4.1	14.5
6FDA-DAT1	4.0	15	0.77	8.15	1.2	1.7	4.2	14.8
6FDA-DAT2	6.4	24.1	1.61	14.4	1.4	1.8	4.4	14.6

^a Ref.24

3.3. Pure-and mixed-gas CO₂/CH₄ permeation properties after physical aging

Microporous glassy polymers typically undergo physical aging, or a physical densification of the polymer matrix in which the chains gradually assume a tighter packing arrangement [29, 30]. Non-equilibrium excess free volume resulting from casting procedures or methanol treatment is dissipated and large reductions in permeability along with increases in selectivity are often reported. Our group has previously demonstrated that thick films (~70-100 μm) undergo a rapid aging phase until an “aging knee” around 10-15 days at which quasi-steady-state transport properties may be observed even until 150 days [23]. Accordingly, 6FDA-DAT1 and 6FDA-DAT2 were aged for 150 days and their resulting pure-gas permeabilities and ideal selectivities are reported in Table 2. Relative to the data for the freshly cast and dried films, roughly 15-20 % reductions in gas permeability coefficients were generally observed with negligible changes in selectivities. We hypothesize that the relatively flexible imide linkages (i.e., no ortho substituents in the diamine to sterically interfere with the nearby carbonyl groups and restrict rotation) to the DAT1 and DAT2 diamines permit the chains to assume a well-packed arrangement soon after casting and drying. Thereafter, the main contributor to the free volume and microporosity characteristics observed in Figures 2-4 are the relatively “frozen” internal free volume pockets induced by the shape-persistent geometry of the triptycene moiety. Accordingly, minimal densification occurs with time.

Although an auspicious resilience against physical aging is evidenced in the time-dependence of the pure-gas transport data, high sorption of condensable gases including CO_2 can induce chain mobility, plasticize the matrix, alter the pore structure and significantly affect the separation properties observed in ideal pure-gas experiments. The pure- and mixed-gas permeabilities (Figure 5 and 6) and selectivities (Figure 7) were measured with 1:1 CO_2/CH_4 mixtures at increasing CO_2 partial pressures (2, 5, 10 and 15 bar) for the aged polymers. The pure-gas CO_2 permeabilities in 6FDA-DAT1 and 6FDA-DAT2 initially decreased with increasing feed pressure (Figure 6). This can be rationalized by a decrease in CO_2 solubility coefficients with pressure as is typically observed in glassy polymers. Aged 6FDA-DAT2 showed ~60% greater CO_2 permeability attributed to its larger free volume. However, both polymers exhibit an up-turn in the pure CO_2 permeability isotherms around ~10 bar attributed to plasticization of the matrices by the highly sorbing CO_2 gas. Moreover, competitive sorption occurs between CO_2 and CH_4 for available sorption sites, which may reduce the overall sorbed concentration of CO_2 in the polymer. Across the entire investigated pressure range, the mixed-gas CO_2 permeabilities were thus lower than pure-gas CO_2 permeabilities and did not exhibit an upturn at 10 bar.

Fig. 5. Pressure-dependence of pure- and mixed-gas CO₂ permeabilities for 6FDA-DAT1 and 6FDA-DAT2 (50:50 CO₂:CH₄ mixture; 35 °C). Lines are drawn to guide the eye. Open symbols: pure-gas; closed symbols: mixed-gas.

Although the mixed-gas CO₂ permeability isotherms do not upturn with pressure, Figure 6 indicates a similar increase in mixed-gas CH₄ permeabilities relative to the pure-gas CH₄ permeabilities from ~5 bar for both polymers. This is a direct indication of matrix dilation by sorbed CO₂ molecules, which facilitates diffusion of the larger CH₄ gas and thereby increases its permeability. This is expected even in relatively rigid-backbone polymers lacking sufficient physical or covalent interactions between chains [31-33].

Fig. 6. Pressure-dependence of pure- and mixed-gas CH₄ permeabilities for 6FDA-DAT1 and 6FDA-DAT2 (50:50 CO₂:CH₄ mixture, 35 °C). Lines are drawn to guide the eye. Open symbols: pure-gas; closed symbols: mixed-gas.

Given the decrease in CO₂ permeabilities and increase in CH₄ permeabilities with pressure in the mixed-gas relative to the pure-gas experiments, the mixed-gas permselectivities (i.e., $P(\text{CO}_2)/P(\text{CH}_4)$) are lower than the pure-gas permselectivities (Figure 7). In the context of typical natural gas sweetening conditions, where the partial pressure of CO₂ is often near 5-10 mol% in a 60-70 bar feed, 6FDA-DAT1 exhibits a high selectivity of ~35 near to the target of 40 set for membranes that would have the

potential to replace current amine-absorption technology in the industry [1]. That is, high selectivity mitigates the extent of CH_4 -loss into the permeate, reducing the need for recompression of the product CH_4 in a second stage and improving the economics of the separation [34]. While the higher permeabilities of the 6FDA-DAT2 polymer reduce membrane area requirements for a given feed flow, the use of the bulkier DAT2 diamine also reduces the apparent selectivity to ~ 25 . Overall, selectivities were similar to thick-film cellulose acetate membranes [35], where cellulose acetate is the commercial standard, but joined with CO_2 permeabilities more than 10-fold greater.

Fig. 7. Pressure-dependence of mixed-gas CO_2/CH_4 selectivities for 6FDA-DAT1 and 6FDA-DAT2 (50:50 $\text{CO}_2:\text{CH}_4$ mixture, 35 °C). Lines are drawn to guide the eye. Open symbols: pure-gas; closed symbols: mixed-gas.

4. Conclusions

In summary, two aromatic polyimides were synthesized by polycondensation reaction of 6FDA with 2,6-diaminotriptycene (6FDA-DAT1) and its bulkier, extended analog (6FDA-DAT2). The effects of the additional benzene ring in the DAT2 diamine on the polymer microstructure and its gas transport properties were studied using low-pressure N_2 and CO_2 physisorption and pure- and mixed-gas permeation experiments, respectively. An increase in free volume ($\sim 40\%$ increase in BET surface area to $450 \text{ m}^2/\text{g}$) was observed in 6FDA-DAT2, which NLDFT-based pore-size distributions indicated were

due to the bigger presence of large pores created by the bulkier DAT2 diamine. Accordingly, the gas permeability coefficients were about 75% higher than in 6FDA-DAT1 owing primarily to increases in gas diffusion coefficients. However, small gas-sieving pores were also maintained in 6FDA-DAT2 such that the ideal permselectivities were similar in both polymers. Moreover, the iptycene-based polyimides demonstrated minimal physical aging over 150 days as evidenced by small 15-20% drops in permeability coefficients with negligible changes in selectivities. In 1:1 CO₂:CH₄ mixed-gas experiments, both polymers exhibited upturns in mixed-gas CH₄ permeabilities with pressure, suggesting CO₂-induced plasticization. However, CO₂/CH₄ selectivities of 25-35 were maintained near typical wellhead CO₂ partial pressures and joined with high CO₂ permeabilities exceeding 90 Barrer, deeming these polymers potential candidate materials for membrane-based gas separation when compared to the existing commercial polymers such as cellulose acetate.

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Highlights

- Intrinsically microporous polyimides from triptycene and extended triptycene analog
- Additional ring causes increase in permeability with minor changes in selectivity
- Both polyimides demonstrate slight ~15% losses in permeability after 150 days
- Selectivities were stable after 150 days physical aging
- Plasticized at ~10 bar CO₂ partial pressure under 50:50 CO₂/CH₄ feed