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Pure- and Mixed-Gas Permeation Properties of Highly Selective and Plasticization Resistant Hydroxyl-Diamine-Based 6FDA Polyimides for CO₂/CH₄ Separation

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Abstract

The effect of hydroxyl functionalization on the *m*-phenylene diamine moiety of 6FDA dianhydride-based polyimides was investigated for gas separation applications. Pure-gas permeability coefficients of He, H₂, N₂, O₂, CH₄, and CO₂ were measured at 35 °C and 2 atm. The introduction of hydroxyl groups in the diamine moiety of 6FDA-diaminophenol (DAP) and 6FDA-diamino resorcinol (DAR) polyimides tightened the overall polymer structure due to increased charge transfer complex formation compared to unfunctionalized 6FDA-*m*-phenylene diamine (*m*PDA). The BET surface areas based on nitrogen adsorption of 6FDA-DAP (54 m²g⁻¹) and of 6FDA-DAR (45 m²g⁻¹) were ~18% and 32% lower than that of 6FDA-*m*PDA (66 m²g⁻¹). 6FDA-*m*PDA had a pure-gas CO₂ permeability of 14 Barrer and CO₂/CH₄ selectivity of 70. The hydroxyl-functionalized polyimides 6FDA-DAP and 6FDA-DAR exhibited very high pure-gas CO₂/CH₄ selectivities of 92 and 94 with moderate CO₂ permeability of 11 and 8 Barrer,

respectively. It was demonstrated that hydroxyl-containing polyimide membranes maintained very high CO₂/CH₄ selectivity (~ 75 at CO₂ partial pressure of 10 atm) due to CO₂ plasticization resistance when tested under high-pressure mixed-gas conditions. Functionalization with hydroxyl groups may thus be a promising strategy towards attaining highly selective polyimides for economical membrane-based natural gas sweetening.

Keywords: polyimides, 6FDA, hydroxyl functionalization, natural gas, mixed-gas permeation, plasticization

1. Introduction

Natural gas processing and separation has grown to one of the largest scale industrial applications of membrane technology during the past 25 years. Introducing membrane technology to the natural gas industry is a major change in conventional gas processing plants [1-4]. However, it has been projected that natural gas processing will have a future potential for significant growth of membrane technology, focusing particularly on CO₂/CH₄ separation [2]. In this application, glassy polymeric membranes are used exclusively due to their good gas separation and mechanical properties as well as their solution processability for the production of either asymmetric or thin-film composite membranes [5-8]. The most commonly used commercial membrane materials for CO₂ removal from natural gas are based on cellulose diacetate, triacetate or blends thereof, which have pure-gas selectivity values of about 32-35 coupled with CO₂ permeability of 1.84 to 6.56 Barrer at 1 atm and 35 °C (1 Barrer = 10⁻¹⁰ cm³(STP)·cm/cm²·s·cmHg) depending on the degree of acetylation [9]. However, under high-pressure, mixed-gas conditions, the CO₂/CH₄ selectivity often drops to less than 15 making the process economics only marginally acceptable due to excessive methane loss [10, 11]. Baker and Lokhandwala proposed that novel membrane materials with a mixed-gas selectivity of higher than 40 would dramatically improve the overall economical feasibility of CO₂ removal from natural gas [2].

Over the past three decades, aromatic polyimides have been extensively investigated as potential membrane materials for natural gas separation [6, 8, 12-15]. However, many polyimides have

similar limitations in their practical use as cellulose acetate because of CO₂-induced plasticization, which often results in unacceptable loss in CO₂/CH₄ selectivity [16-19]. However, recent studies demonstrated that plasticization in polyimides can be mitigated to a large extent by various methods, such as: (i) Thermal annealing [20-23], (ii) chemical cross-linking [22, 24-30] and (iii) formation of charge transfer complexes [31].

Introduction of pendant polar groups, such as -OH and -COOH has been used for the structural design of polyimides with enhanced CO₂/CH₄ selectivity and functionality for various cross-linking mechanisms [29]. Stern's group was the first to report hydroxyl- and carboxyl-containing polyimides with extremely high CO₂/CH₄ selectivity [32]. For example, 4,4-(hexafluoroisopropylidene) diphthalic anhydride-2,4-diaminophenol (6FDA-DAP) and 4,4-(hexafluoroisopropylidene) diphthalic anhydride-4,6-diamino resorcinol (6FDA-DAR) showed pure-gas CO₂/CH₄ selectivities of 94 and 75, respectively, combined with moderate CO₂ permeability of about 8 Barrer. Other groups later reported similar promising results with a variety of hydroxyl-diamine-based 6FDA polyimides [33-36]. A recent paper by Comesaña-Gándara et al. re-investigated the pure-gas permeation properties of 6FDA-DAP and 6FDA-DAR and their polybenzoxazole derivatives formed by thermal rearrangement as well as their non-functionalized counterpart polyimide (6FDA-*m*PDA) [37].

To the best of our knowledge systematic mixed-gas permeation studies are only available for 6FDA-2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF) in this burgeoning class of high-performance hydroxyl-functionalized polyimides for CO₂/CH₄ separation [31]. Therefore, in this study, 6FDA-DAP and 6FDA-DAR were evaluated in pure- and high-pressure mixed gas permeation experiments for CO₂/CH₄ separation. To qualitatively measure the performance enhancement due to hydroxyl-functionalization, a non-functional 6FDA-*m*PDA polyimide was evaluated under the same test conditions.

2. Experimental

2.1 Materials

4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA), 1,3-phenylenediamine (*m*PDA), 2,4-diaminophenol dihydrochloride (DAP), 4,6-diaminoresorcinol dihydrochloride (DAR), isoquinoline, acetone, chloroform, benzoic acid and trimethylamine were obtained from Aldrich and used as received. Only 6FDA and *m*PDA were 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.

2.2 Synthesis of the polyimides

Three polyimides were synthesized via the cycloimidization reaction between equimolar amounts of the commercially available 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and the corresponding diamine in *m*-cresol and in presence of trimethylamine and benzoic acid (Scheme 1). The polymers were fully characterized by ¹H-NMR, FT-IR, GPC, TGA and BET surface area and demonstrated good solubility in organic solvents from which self-supporting and transparent flexible films were cast.

Scheme 1. Synthesis of 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR. Note that the imide linkages of all polyimides are in meta position.

Synthesis of 6FDA-*m*PDA polyimide

Into a dry 10 mL Schlenk tube equipped with a nitrogen gas inlet and outlet, were added *m*-phenylenediamine (0.126, 1.17 mmol), 6FDA (0.52g, 1.17 mmol) and freshly distilled *m*-cresol (3.5ml). After stirring for 5 minutes and under a flow of nitrogen, the temperature was raised gradually to 200 °C and maintained at that temperature for 2 hours. During the heating, water produced by the imidization reaction was removed with a stream of nitrogen. After cooling, the reaction mixture was added to methanol. The resulting fibrous polymer was collected by filtration and purified by reprecipitation from chloroform into methanol and then dried under vacuum at 130 °C for 20 h to give white powder in 84% yield. ¹H-NMR (400MHz, CDCl₃) δ (ppm): 7.54 (dd, 2H), 7.65 (m, 2H), 7.86 (d, 2H), 7.96 (s, 2H), 8.04 (d, 2H). FT-IR (Membrane, ν , cm⁻¹): 1784 (asym C=O, str), 1718 (sym C=O, str), 1353 (C-N, str), 842 (imide ring deformation). Analysis by GPC (CHCl₃): M_n = 141000 g mol⁻¹, M_w = 166400 g mol⁻¹ relative to polystyrene, M_w/M_n = 1.2. BET surface area = 66 m² g⁻¹, total pore volume = 0.151 cm³ g⁻¹ at (P/P₀ = 0.98, adsorption). TGA analysis: (Nitrogen), Initial weight loss due to thermal degradation commences at T_d = 475 °C with 5% weight loss at $T_{d,5\%}$ = 475 °C.

Synthesis of 6FDA-DAP polyimide

Into a dry 10 mL Schlenk tube equipped with a nitrogen gas inlet and outlet, were added diaminophenol (0.446g, 2.26 mmol), 6FDA (1.05g, 2.26 mmol), benzoic acid (1g), freshly

distilled *m*-cresol (7 ml) and triethylamine (0.63 ml). After stirring for 5 minutes under a flow of nitrogen, the temperature was raised gradually to 200 °C and maintained at that temperature for 2 hours. During the heating, water produced by the imidization reaction was removed with a stream of nitrogen. After cooling, the reaction mixture was added to methanol. The resulting polymer was collected by filtration and purified by reprecipitation from acetone into methanol-water (50:50 v/v) and then dried under vacuum at 130 °C for 20 h to give a white powder in 83% yield. ¹H-NMR (400MHz, CDCl₃) δ (ppm): 7.21 (d, 1H), 7.52(d, 1H), 7.76 (m, 1H), 7.90 (m, 2H), 7.98-7.8.12(m, 4H), 9.28 (s, 1H). FT-IR (Membrane, ν , cm⁻¹): 1784 (asym C=O, str), 1718 (sym C=O, str), 1361 (C-N, str), 845 (imide ring deformation), 3400 (OH stretching). Analysis by GPC (CHCl₃): M_n = 98200 g mol⁻¹, M_w = 176600 g mol⁻¹ relative to polystyrene, M_w/M_n = 1.8. BET surface area = 54 m² g⁻¹, total pore volume = 0.135 cm³ g⁻¹ at (p/p_o = 0.98, adsorption). TGA analysis: (Nitrogen), Initial weight loss due to thermal degradation commences at T_d = 450 °C with 5% weight loss at $T_{d,5\%}$ =450 °C.

Synthesis of 6FDA-DAR polyimide

Into a dry 10 mL Schlenk tube equipped with a nitrogen gas inlet and outlet, were added diaminophenol (0.211 g, 1.0 mmol), 6FDA (0.439 g, 1.0 mmol), benzoic acid (0.5 g), freshly distilled *m*-cresol (4 ml) and triethylamine (0.274 ml). All following conditions were the same as described for 6FDA-DAP. The polymer was obtained as a white powder in 77% yield. ¹H-NMR (400MHz, CDCl₃) δ (ppm): 6.76 (s, 1H), 7.35 (s, 1H), 7.9(s, 2H), 8.04 (d, 2H), 8.11 (d, 2H), 9.20 (br s, 2H). FT-IR (Membrane, ν , cm⁻¹): 1783 (asym C=O, str), 1710 (sym C=O, str), 1370 (C-N, str), 845 (imide ring deformation), 3300-3500 (OH stretching). Analysis by GPC (CHCl₃): M_n = 99300 g mol⁻¹, M_w = 158900 g mol⁻¹ relative to polystyrene, M_w/M_n = 1.6. BET surface area = 45 m² g⁻¹, total pore volume = 0.093 cm³ g⁻¹ at (p/p_o = 0.98, adsorption). TGA analysis: (Nitrogen), Initial weight loss due to thermal degradation commences at T_d = 425 °C with 5% weight loss at $T_{d,5\%}$ =425 °C.

2.3 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 for 6FDA-*m*PDA and gel permeation chromatography (GPC, Agilent) was carried out using tetrahydrofuran (THF) as an eluent for 6FDA-DAP and 6FDA-DAR. 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 N₂ sorption at -196 °C using a Micromeritics ASAP-2020. Powder polymer samples were degassed under high vacuum at 150 °C for 24 hours prior to analysis. CO₂ sorption isotherms of the polymers were obtained at 0 °C up to 1 atm.

2.4 Polymer film preparation

Solutions (5 wt/vol%) of 6FDA-*m*PDA in chloroform and 6FDA-DAP or 6FDA-DAR in acetone, were filtered through 0.45 µm polypropylene filters and isotropic films were obtained by slow evaporation of the solvents at room temperature from a levelled glass Petri dish. To remove any traces of residual solvent, the dry membrane of 6FDA-*m*PDA was soaked in methanol for 12 h, air-dried, and then post-dried at 120 °C in a vacuum oven for 24 h. 6FDA-DAP and 6FDA-DAR films could not be soaked in methanol due to excessive swelling. Therefore, films dried at 120 °C were post-dried at 200 °C in a vacuum oven for 24 h. The resulting tough films with thickness of 55 ± 5 µm were used for gas permeability measurements. Prior to any gas permeation test, TGA experiments were performed to confirm that the polyimide films were solvent-free. Film thickness and effective area for gas permeation measurements were determined by a digital micrometer and scanner, respectively.

2.5 Physisorption measurement

Nitrogen (-196 °C) and carbon dioxide (0 °C) sorption measurements were performed up to 1 atm using a Micromeritics ASAP-2020 apparatus equipped with a micropore upgrade. Powder samples of 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR were dried at 150 °C under high vacuum

for 24 h before measurement. All data were collected and analyzed using ASAP 2020 software version 4.02. The BET surface area was obtained from the N₂ isotherm at -196 °C at relative pressures of 0.1 < p/p₀ < 1.0, where p₀ = 1 atm is the saturation pressure for N₂ and p is the gas pressure. Maximum pore volumes were identified at p/p₀ < 0.99 of the N₂ isotherm. NLDFT (non-local density functional theory) analysis of the N₂ isotherms permits qualitative assessments of structural changes that occur upon hydroxyl functionalization of 6FDA-DAP and 6FDA-DAR.

2.6 Fluorescence spectroscopy

Fluorescence excitation (excited at 350 nm) and emission spectra were collected against wavelength for dense polymer films (~55 μm) on a PerkinElmer LS45 setup in a 90° arrangement with fixed 10 nm slits. These measurements were conducted to investigate the potential formation of charge transfer complexes in the polyimides.

2.7 Pure-gas permeation measurements

The pure-gas permeation measurements were conducted with a custom-designed permeation system using the constant-volume/variable-pressure method. The permeability was calculated from the steady-state rate of increase in pressure of the gas (dp/dt) in the permeate reservoir using the following equation:

$$P = \frac{VL}{ATp_{up} \times 0.278} \times \frac{dp}{dt} \times 10^{10}$$

where P , V , L , A , T , p_{up} are the permeability coefficient in Barrers (1 Barrer = 10^{-10} cm³(STP)·cm/cm²·s·cmHg), volume of the downstream gas reservoir, membrane thickness, membrane area, operating temperature and the upstream pressure, respectively. The pure-gas permeability of He, H₂, N₂, O₂, CH₄, and CO₂ was measured at 35 °C and 2 atm. The standard deviations in the gas permeation experiments were in the range of ±2-5%. The pressure-dependence of CO₂ and CH₄ permeability was determined from 2 to 20 atm.

2.8 Mixed-gas permeation measurements

The mixed-gas permeation measurements of 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR were performed at 35 °C using a custom-designed mixed-gas permeation system similar to that described by O'Brien et al. [38]. The feed gas mixture contained 50 vol.% CH₄/50vol.% CO₂ and the total feed pressure was varied between 4 and 40 atm; the permeate pressure was less than 0.01 atm. The stage cut, that is, the permeate flow rate to feed flow rate, 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 P is the permeability (Barrers) (1 Barrer = 10^{-10} cm³(STP)·cm/cm²·s·cmHg), p_{up} is the upstream pressure (cmHg), dp/dt is the steady-state permeate-side pressure increase (cmHg/s), V_d is the 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), and 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

3.1 Physical properties of the polyimides

The thermal stability of 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR was determined by thermal gravimetric analysis, as shown in Figure 1. All polymers were thermally very stable with onset decomposition temperatures of 475 °C for 6FDA-*m*PDA, 450 °C for 6FDA-DAP and 425 °C for 6FDA-DAR. As expected for polyimides with hydroxyl groups in ortho position to the imide linkage, 6FDA-DAP and 6FDA-DAR decomposed in two stages, where the first stage resulted from thermal rearrangement of the polyimide to a polybenzoxazole and the second stage involved decomposition to graphitic carbon [39]. Because of lack of hydroxyl functionality, 6FDA-*m*PDA did not undergo any thermal rearrangement but simply degraded into its carbon structure in a single stage process.

Fig. 1. Thermogravimetric analysis (TGA) of 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR films.

The effect of the hydroxyl group in the diamine moiety on the polyimide microstructure was assessed from N_2 ($-196\text{ }^{\circ}\text{C}$) and CO_2 ($0\text{ }^{\circ}\text{C}$) physisorption isotherms (Figure 2 and 3). The introduction of hydroxyl groups decreased the BET surface area determined with nitrogen from $66\text{ m}^2\text{g}^{-1}$ for 6FDA-*m*PDA to $54\text{ m}^2\text{g}^{-1}$ for 6FDA-DAP and to $45\text{ m}^2\text{g}^{-1}$ for 6FDA-DAR (in all cases $\pm 3\text{ m}^2\text{g}^{-1}$), which was anticipated based on the effect of interchain hydrogen bonding due to the introduction of hydroxyl groups to the polymer backbone [31]. Similar N_2 -based BET surface areas have previously been reported for other moderate-free-volume glassy polymers, such as poly(phenylene oxides) and polyimides [39-42].

Fig. 2. Adsorption isotherms for 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR using N_2 at $-196\text{ }^{\circ}\text{C}$.

Interestingly, the gravimetric CO_2 sorption uptake increased in the reverse order of the BET surface areas of the polymers, that is, 6FDA-DAR > 6FDA-DAP > 6FDA-*m*PDA, indicating that (i) hydroxyl functionalization increases CO_2 sorption and (ii) higher OH concentration per polymer repeat unit also leads to increased CO_2 uptake. The same order in CO_2 sorption capacity was confirmed by indirect determination of gas solubility by time-lag-based measurements as discussed below.

Fig. 3. Physisorption isotherms for 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR using CO₂ at 0 °C. Closed symbols: adsorption; open symbols: desorption.

To investigate potential interchain charge transfer complex (CTC) formation of the polar hydroxyl-functionalized polyimides in the solid state, fluorescence spectroscopy measurements were carried out. Fig. 4 shows the results of the emission spectra for the 6FDA-*m*PDA, 6FDA-DAP, and 6FDA-DAR membranes. CTCs are typically formed between the nucleophilic five-member rings and electrophilic six-member rings in polyimides [20, 21, 43]. The hydroxyl groups are likely to form hydrogen bonds, thereby tightening the polymer interchain structure to strengthen inter-chain CTCs, as evidenced by a previous study, which showed that hydroxyl moieties increased the intersegmental cohesive energy density (CED) in OH-functionalized polyimides [44]. The hydroxyl-containing polyimides, 6FDA-DAP and 6FDA-DAR, had emission spectra bands at 515 nm when excited at 350 nm. The fluorescence intensity of the hydroxyl-functionalized polyimides increased significantly compared to that of the 6FDA-*m*PDA, which suggests formation of a strong charge transfer complex in the hydroxyl-containing polyimides.

Fig. 4. Solid-state fluorescence emission spectra (excitation at 350 nm) of 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR.

3.2 Pure-gas permeation properties

To investigate the effect of the hydroxyl functionalization and hydroxyl concentration of the *m*-phenylene diamine moiety in the polyimide series pure-gas permeation experiments were performed at 2 atm and 35 °C in the order He, H₂, N₂, O₂, CH₄ and CO₂. Table 1 shows the data from this work in comparison to previously reported literature data for the same series of polyimides [9, 32, 37, 45-47]. Permeation data of three commercial glassy membrane materials, that is, cellulose triacetate, polysulfone and tetrabromo-polycarbonate are also shown for comparison. In all cases, for a given gas at the same feed pressure, the polyimides showed permeabilities in the following order: 6FDA-*m*PDA > 6FDA-DAP > 6FDA-DAR indicating that introducing the hydroxyl group reduced the gas permeability. Moreover, in all three polyimides

the gas permeabilities decrease in the order: $\text{He} > \text{H}_2 > \text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{CH}_4$ which follows the order of the kinetic diameters of the gases. The gas permeability of the hydroxyl-containing polyimides also depends to a small extent on the hydroxyl concentration in 6FDA-DAP and 6FDA-DAR.

Table 1. Pure-gas permeabilities and ideal selectivities for 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR (at 2 atm; 35 °C) and commercial polymer membrane materials.

Polymer	Pure-gas Permeability (Barrer)						Ideal Selectivity (α)			Reference
	He	H ₂	N ₂	O ₂	CH ₄	CO ₂	CO ₂ /CH ₄	H ₂ /CH ₄	O ₂ /N ₂	
6FDA- <i>m</i> PDA	59	46	0.62	3.6	0.2	14	70	230	5.9	This work
	81	-	0.87	5.4	0.35	20.3	58	-	6.2	[47]
	46	-	0.29	2.1	0.1	7.3	76	-	7.3	[37]
6FDA-DAP	45	38	0.37	2.5	0.12	11	92	317	6.8	This work
	-	40	0.34	2.4	0.09	8.5	94	444	7.0	[32]
	62	-	0.43	2.9	0.11	11	100	-	6.8	[37]
6FDA-DAR	43	34	0.28	1.9	0.085	8	94	400	6.8	This work
	-	-	0.30	2.2	0.11	8	73	-	7.4	[32]
	43	-	0.29	2.1	0.08	8.2	102	-	7.3	[37]
Cellulose acetate (DS 2.85)	19.6	15.5	0.23	1.46	0.20	6.6	33	78	6.3	[9]
Polysulfone	13	14	0.25	1.40	0.25	5.6	22	56	5.6	[46]
Tetrabromo-polycarbonate	17.6	-	0.182	1.36	0.13	4.2	32	-	7.5	[45]

All polyimides reported in this study exhibited moderate permeability coupled with extremely high permselectivity for H_2/CH_4 and CO_2/CH_4 . The data show that introduction of hydroxyl groups in the polyimide repeat unit leads to a significant increase in the selectivity (i.e CO_2/CH_4 selectivity was enhanced from 70 for non-hydroxyl functionalized 6FDA-*m*PDA to 94 for 6FDA-DAR). This 34% increase in selectivity was due to the existence of interchain hydrogen bonding and CTC formation that tightened the interchain polymer structure. As expected for a denser polymer structure, CO_2 permeability decreased from 14 Barrers for 6FDA-*m*PDA to 11 and 8 Barrers for FDA-DAP and 6FDA-DAR, respectively. This 22-43% decrease in the CO_2 permeability is qualitatively consistent with the N_2 BET results discussed above.

The reported data for this work is in agreement with previously published data for 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR, as shown in Table 1. Small differences in permeability and selectivity maybe due to different synthetic procedures and different test conditions.

It is important to note that 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR exhibited notably better intrinsic performance than currently used commercial membrane materials (cellulose acetate, polysulfone and tetrabromo-polycarbonate) listed in Table 1. Particularly for H₂ and CO₂ separations, the polyimides showed higher permeabilities and *significantly* higher H₂/CH₄ and CO₂/CH₄ selectivity. For example, 6FDA-DAR combined a H₂ permeability of 34 Barrer with an extremely high H₂/CH₄ selectivity of 400. For air separation, specifically production of onsite nitrogen, the hydroxyl-functionalized polyimides also have excellent commercial potential as their O₂ permeabilities are higher and O₂/N₂ selectivities are comparable to that of tetrabromo-polycarbonate, as shown in Table 1.

The pressure-dependence of pure CO₂ and CH₄ permeability and CO₂/CH₄ selectivity of the three polyimides are shown Fig. 5 and 6, respectively. As typical for glassy polymers, CO₂ permeability decreased slightly with increased pressure over a range of 2 to 20 atm. In contrast, the pure CH₄ permeability of the polyimides was essentially constant over the whole pressure range. As a result, only a small decrease (< 10%) was observed in the pure-gas CO₂/CH₄ selectivity, as shown in Figure 6. At 20 atm, the pure-gas CO₂/CH₄ selectivities of 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR were 67, 84 and 86, respectively.

Fig. 5. Pressure dependence of pure-gas CO_2 and CH_4 permeability for 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR at 35 °C.

Fig. 6. Pressure dependence of pure-gas CO_2/CH_4 selectivity for 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR at 35 °C.

The effect of hydroxyl-functionalization on the diffusion and solubility coefficients of the polyimides is shown in Table 2. As expected based on the increased tightness of the polymer chains due to CTC formation by introduction of hydroxyl groups, the diffusion coefficients of all gases decreased for 6FDA-DAP and 6FDA-DAR relative to those of 6FDA-*m*PDA.

Table 2. Pure-gas diffusion and solubility coefficients of N₂, O₂, CH₄ and CO₂ for 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR based on the time-lag method (2 atm; 35 °C).

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-<i>m</i>PDA	0.46	2.6	0.07	0.92	1.59	1.62	3.8	20.2
6FDA-DAP	0.05	0.32	0.03	0.47	4.46	4.69	5.41	29.1
6FDA-DAR	0.05	0.29	0.02	0.37	5.5	5.6	5.8	31

The diffusivity and solubility selectivities of the three polyimides for O₂/N₂ and CO₂/CH₄ are shown in Table 3. Clearly, the high permselectivities of the 6FDA-DAP and 6FDA-DAR hydroxyl-based polyimides are primarily due to higher diffusivity selectivities than those of the unfunctionalized 6FDA-*m*PDA. For example, the CO₂/CH₄ diffusivity of 6FDA-*m*PDA of 13 increased to ~17 by introduction of hydroxyl groups, whereas the CO₂/CH₄ solubility selectivity varied only between 5.3 - 5.4 (Table 3).

Table 3. Diffusivity selectivities and solubility selectivities for 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR (2 atm; 35 °C).

Polymer	Diffusivity Selectivity (α) _D		Solubility Selectivity (α) _S	
	O ₂ /N ₂	CO ₂ /CH ₄	O ₂ /N ₂	CO ₂ /CH ₄
6FDA-<i>m</i>PDA	5.7	13.2	1.02	5.32
6FDA-DAP	6.45	17.0	1.05	5.4
6FDA-DAR	6.48	17.4	1.05	5.4

3.3 High-pressure mixed-gas CO_2/CH_4 permeation properties

The mixed-gas permeation properties of the three polyimides were determined at 35 °C with a feed containing 50 vol% CO_2 /50 vol% CH_4 . The feed pressure was varied between 4 to 40 atm to obtain the same partial pressures used for the pure-gas pressure dependence experiments. For all three polyimides, CO_2 mixed-gas permeability was lower than that determined for the pure gas at the same partial CO_2 pressure, as shown in Figure 7a-c. This difference is most likely caused by competitive sorption between CO_2 and CH_4 under mixed-gas permeation conditions [48, 49]. On the other hand, the mixed-gas CH_4 permeability was essentially constant up to a feed pressure of 40 atm.

Fig. 7. Pressure-dependence of pure and mixed-gas CH_4 and CO_2 permeabilities for: a) 6FDA-*m*PDA; b) 6FDA-DAP; c) 6FDA-DAR. Feed: 50:50 CO_2 : CH_4 mixture; 35 °C). Lines are drawn to guide the eye: open points, pure-gas; closed points, mixed-gas.

As a result of the decrease in mixed-gas CO_2 permeability with pressure, the CO_2/CH_4 selectivity dropped continuously from 4 to 40 atm total pressure for all polyimides, as shown in Fig. 8. For 6FDA-*m*PDA, a 40% reduction in CO_2/CH_4 selectivity was observed from 70 to 41 as the feed pressure was increased from 4 to 40 atm.

Fig. 8. Pressure-dependence of pure and mixed-gas CO_2/CH_4 selectivities for 6FDA-*m*PDA, 6FDA-DAP and 6FDA-DAR (50:50 CO_2/CH_4 mixture, 35 °C). Lines are drawn to guide the eye: open points, pure-gas; closed points, mixed-gas.

The hydroxyl-functionalized polyimides, 6FDA-DAP and 6FDA-DAR, showed very similar trends in mixed-gas pressure dependence of permeability and selectivity. The CO_2/CH_4 selectivity of both polymers dropped by ~30% by increasing the feed pressure from 4 to 40 atm. However, both polymers showed excellent mixed-gas selectivity of ~ 75 at a partial CO_2 pressure of 10 atm, respectively. It is worth noting that the typical partial pressure of CO_2 in the majority of natural gas wells is around 5-10 atm [1]. In summary, our study provides further evidence of previous work [31, 50] that polyimides with strong polar OH groups can mitigate plasticization when tested under high-pressure binary CO_2/CH_4 mixed-gas conditions due to strong chain interactions by interchain hydrogen bonding and CTC formation. Further work,

however, is required to evaluate the mixed-gas permeation properties of hydroxyl-functionalized polyimides with multi-component feeds including condensable C_{3+} hydrocarbons to fully demonstrate their potential in industrial natural gas sweetening [51].

4. Conclusions

In this study, the effects of hydroxyl functionalization on high-pressure pure- and mixed-gas permeation properties were investigated for a non-hydroxyl-containing 6FDA-based polyimide (6FDA-*m*PDA) and hydroxyl-containing 6FDA-based polyimides (6FDA-DAP and 6FDA-DAR). Pure-gas permeation data showed that introducing hydroxyl groups to 6FDA-*m*PDA leads to a significant increase in permselectivity due to a large increase in diffusivity selectivity for a variety of gas pairs, most notably H_2/CH_4 and CO_2/CH_4 . Mixed gas permeation experiments were performed using a binary 50%:50% CO_2/CH_4 feed up to a total pressure of 40 atm. 6FDA-based hydroxyl-containing polyimides showed excellent plasticization resistance under binary CO_2/CH_4 mixed gas feed with a selectivity of 75 at a partial CO_2 pressure of 10 atm. The intrinsic mixed-gas permeation properties of 6FDA-DAP and 6FDA-DAR determined with thick isotropic films are significantly better than those of commercial cellulose acetate-based membranes. Therefore, hydroxyl-functionalized polyimides are excellent candidate materials for development of asymmetric or thin-film composite membranes for industrial natural sweetening.

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Highlights

- Hydroxyl-functionalized 6FDA-DAP and 6FDA-DAR polyimides showed very high pure-gas CO₂/CH₄ permselectivity (92-94 at 2 atm; ~ 85 at 20 atm).
- Enhanced pure-gas CO₂/CH₄ permselectivity of OH-functionalized polyimides was primarily due to higher diffusivity selectivity compared to that of 6FDA-*m*PDA.
- Mixed-gas selectivity at 10 atm partial CO₂ pressure was reduced to 75 most likely due to competitive sorption.
- Plasticization was mitigated by introduction of hydroxyl groups at least up to 20 atm partial CO₂ pressure.

Pure- and Mixed-Gas Permeation Properties of Highly Selective and Plasticization Resistant Hydroxyl-Diamine-Based 6FDA Polyimides for CO₂/CH₄ Separation

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