Plasticization resistant carboxyl-functionalized 6FDA-polyimide of intrinsic microporosity (PIM-PI) for membrane-based gas separation

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ABSTRACT

A novel trimethyl-substituted carboxyl-containing polyimide was synthesized by a one-pot high temperature polycondensation reaction of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,5-diamino-2,4,6-trimethylbenzoic acid (TrMCA). The polyimide (6FDA-TrMCA) displayed Brunauer-Emmett-Teller (BET) surface area of $260 \text{ m}^2 \text{ g}^{-1}$ demonstrating intrinsic microporosity in contrast to the related low-free volume COOH-functionalized polyimide 6FDA-DABA. Compared to the non-functionalized 6FDA polyimide analog made from 2,4,6-trimethyl-*m*-phenylenediamine (TrMPD) — also known as 6FDA-DAM — carboxyl functionalization in 6FDA-TrMCA resulted in reduced surface area, lower fractional free volume, and tighter average chain spacing. Gas permeabilities of 6FDA-TrMCA were typical of functionalized polyimides of intrinsic microporosity (PIM-PIs). For example, at 2 atm and 35 °C, 6FDA-TrMCA showed pure-gas H_2 and CO_2 permeability of 193 and 144 barrer coupled with H_2/CH_4 and CO_2/CH_4 selectivity of 61 and 45, respectively. Notably, in mixed-gas permeation tests with an equimolar $\text{CO}_2\text{-CH}_4$ mixture at 12 atm CO_2 partial pressure, 6FDA-TrMCA demonstrated performance located on the 2018 mixed-gas upper bound with a CO_2 permeability of ~ 98 barrer and CO_2/CH_4 permselectivity of 38. As the first reported COOH-functionalized PIM-PI homopolymer, 6FDA-TrMCA revealed excellent resistance against CO_2 -induced plasticization at least up to a CO_2 partial pressure of 15 atm covering the range of typical wellhead CO_2 partial pressures (5–10 atm).

Keywords: polyimides, PIM-PIs, carboxyl functionalization, intrinsic microporosity, gas separation, mixed-gas permeation.

■ INTRODUCTION

Solution processible ladder polymers of intrinsic microporosity (PIMs), first introduced by Budd and McKeown in 2004, are a promising class of high-performance membrane materials for various gas separation applications.¹⁻⁵ The design concept of these polymers is based on the insertion of sites of contortion and bulky side substitutions (to lock local chain rotation) to significantly enhance free volume and boost gas permeability while maintaining moderate- to high gas-pair selectivity.¹⁻³ In 2008, McKeown's group introduced linear chain polyimides of intrinsic microporosity (PIM-PIs) from a spirobisindane (SBI) kinked dianhydride monomer as a microporosity generator.⁶ Although highly gas permeable, the original PIM-PIs displayed inferior gas-pair selectivity compared to commercial polymer membrane materials (e.g. cellulose triacetate), specifically for removal of CO₂ from natural gas and biogas. Based on a study of Baker and Lokhandwala, these applications become economically very attractive with membranes showing a mixed-gas CO₂/CH₄ selectivity value of ~40; hence, optimization of the permeability-selectivity properties of PIM-PIs is essential.^{7,8} To reach this objective, the incorporation of polar functionalities in the polymer backbone, such as hydroxyl (–OH) and carboxyl (–COOH) groups were demonstrated by Stern's group and confirmed by others for low-free-volume polyimides with CO₂/CH₄ permeability selectivities significantly higher than those of similar non-functionalized polyimides and 2 to 3 times higher than that of commercial cellulose triacetate.⁹⁻¹¹ Our group applied this approach by introducing hydroxyl-functionalization to various PIM-PIs, such spirobisindane¹²⁻¹⁴, spirobifluorene¹⁵, triptycene¹⁶⁻¹⁹ and Tröger's base.²⁰ Wang et al. recently reviewed PIM-PIs reported in the literature and found that OH-functionalized PIM-PIs are among the most promising membrane materials for CO₂ removal from natural gas with performance located on the 2018 mixed-gas CO₂/CH₄ upper bound.³

An alternative route to design functionalized polyimides can be pursued by carboxyl-functionalization. The well studied 6FDA-DABA polyimide obtained by reacting 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with 3,5-diaminobenzoic acid (DABA) and

copolymer variations thereof were introduced by Koros' group and have shown great promise for natural gas separation because of their ability of facile cross-linking by various methods.²¹⁻²⁸ For example, Qiu et al. combined an unfunctionalized sterically hindered building block, 2,4,6-trimethyl-*m*-phenylenediamine (TrMPD), with DABA to introduce carboxyl functionalization in co-polyimides.²⁵ A 6FDA-based polyimide copolymer with TrMPD:DABA molar ratio of 3:2 dried at 180 °C exhibited a CO₂ permeability of 144 barrers with CO₂/CH₄ selectivity of 34. To provide CO₂-plasticization resistant membranes sub-Tg crosslinking of the 6FDA-TrMPD:DABA (3:2) at 330 °C for 10 h gave an increased CO₂ permeability of 290 barrer with a CO₂/CH₄ selectivity of 28.²⁵

Here, we report a new solution-processable carboxyl-functionalized PIM-PI homopolymer prepared by polycondensation reaction of 6FDA and 3,5-diamino-2,4,6-trimethylbenzoic acid (TrMCA) in *m*-cresol at 200 °C (**Scheme 1**). 6FDA-TrMPD, a non-functionalized analog of 6FDA-TrMCA, was synthesized by reacting 6FDA with 2,4,6-trimethyl-*m*-phenylenediamine (TrMPD) and was included for comparison in this study (**Scheme 1**). Both 6FDA-TrMCA and 6FDA-TrMPD were fully characterized by ¹H NMR, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). Gas sorption and gas permeation studies were performed to demonstrate the potential of 6FDA-TrMCA for CO₂ removal from natural or biogas.

Scheme 1. Synthesis of 6FDA-TrMPD and 6FDA-TrMCA Polyimides. Structures of 6FDA-TrMPD:DABA (3:2), 6FDA-mPDA, and 6FDA-DABA are Included as Reference.

■ EXPERIMENTAL SECTION

Materials. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride, 2,4,6-trimethyl-*m*-phenylenediamine, 2,4,6-trimethylbenzoic acid (99%), nitric acid (HNO₃, 70%), sulfuric acid (H₂SO₄, 95-98%), hydrazine monohydrate (N₂H₄·H₂O, 64-65%), 10% palladium on carbon (Pd/C), *m*-cresol (99%), and isoquinoline (97%) were obtained from Merck and used as received without further purification.

Characterization and Methods. The infrared spectra were recorded for dense polyimide films using a Varian 670-IR FT-IR spectrometer. Nuclear Magnetic Resonance (NMR) spectra of the synthesized monomers and polymers were recorded with a Bruker AVANCE-III spectrometer at a frequency of 400 MHz in either deuterated chloroform (CDCl₃) or deuterated dimethylsulfoxide (DMSO-*d*₆) with 64 scans

for ^1H NMR and 512 scans for ^{13}C NMR and recorded in ppm. Mass spectrometry (MS) of the monomers was conducted on a Thermo UHPLC/MS Ultimate 3000. Molecular weight and polydispersity index (PDI) of 6FDA-TrMPD and 6FDA-TrMCA (with a concentration of 1 mg ml^{-1} in DMF solvent) were obtained by gel permeation chromatography (GPC) in an Agilent 1200 system (polystyrene was used as external standard). The decomposition temperatures of both polymers were acquired with a TGA Q5000 (TA Instruments) at a rate of $3\text{ }^\circ\text{C min}^{-1}$ and up to $800\text{ }^\circ\text{C}$ under N_2 gas (the temperature was initially held at $100\text{ }^\circ\text{C}$ for 30 min to remove any moisture). Brunauer-Emmett-Teller (BET) surface areas were determined from nitrogen adsorption isotherms (on polymer samples in fiber form) measured via a Micrometrics ASAP 2020 porosimetry analyzer; prior to these tests, all samples were degassed at $150\text{ }^\circ\text{C}$ for 12 h under high vacuum. Melting points (mp) of the monomers were obtained by differential scanning calorimetry (DSC, TA Instruments Q2000) with a ramp rate of $20\text{ }^\circ\text{C/min}$ to $350\text{ }^\circ\text{C}$. The densities of the polymers were measured geometrically using film thickness, area, and weight data.

Monomer Synthesis. The facile procedure for synthesis of 3,5-diamino-2,4,6-trimethylbenzoic acid (TrMCA) is shown in **Scheme 2**.

Scheme 2. Two-Step Synthesis of 3,5-Diamino-2,4,6-Trimethylbenzoic Acid (TrMCA).

Synthesis of 2,4,6-trimethyl-3,5-dinitrobenzoic acid (I). 2,4,6-Trimethylbenzoic acid (1 g, 6.1 mmol) was suspended in H_2SO_4 (13 ml), and then HNO_3 (20 ml) was added dropwise. The reaction was stirred overnight at room temperature. The reaction mixture was then poured into water, and the dinitro compound was precipitated, filtrated, washed three times with water, and then dried under vacuum at $100\text{ }^\circ\text{C}$ for 24 h to afford a white powder product (1.24 g, 80% yield); mp = $219\text{ }^\circ\text{C}$; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.19 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 12.9, 15.2, 122.4, 128.2, 137.6, 150.1, 167.7. MS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_6]^+$: 255.05; found: 255.06.

Synthesis of 3,5-diamino-2,4,6-trimethylbenzoic acid (II). 2,4,6-Trimethyl-3,5-dinitrobenzoic acid (I) (0.64 g, 2.5 mmol) was suspended in methanol (10 ml) followed by the addition of Pd/C (10%) (0.1 g) and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (3 ml). The reaction was refluxed for two days, cooled to room temperature, filtered through Celite, and the solution was then concentrated in a Rotavap system. The solution was added to dichloromethane (DCM) to obtain a white precipitate. The obtained solid was filtered and placed in an oven at 90 °C for 24 h to afford the pure diamino compound (0.44 g, 90% yield); mp = 286 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.89 (s, 3H), 1.91 (s, 6H), 4.99 (br s, 4H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 11.6, 15.2, 103.6, 105.0, 141.9, 142.0, 176.1. MS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2]^+$: 195.11; found: 195.13.

General procedure for synthesis of polyimides. In a 25 ml Schlenk tube equipped with a mechanical stirrer, nitrogen inlet, and an oil bubbler, an equimolar amount of commercially available 4,4-(hexafluoroisopropylidene) diphtalic anhydride (6FDA) and TrMCA (or TrMPD) diamine were mixed with *m*-cresol and heated up to 80 °C; then, a catalytic amount of isoquinoline (0.1 ml) was added under continuous flow of nitrogen. The solution was gradually heated up to a temperature of 200 °C and stirred for 4 h. Water obtained as a by-product of the imidization step (i.e., the conversion of polyamic acid to polyimide) was removed by flushing with nitrogen gas. Subsequently, the reaction vessel was cooled down, and methanol was added; this induced precipitation of the polymer in a fiber-like form that was collected by filtration and purified two times by re-precipitation from their dimethylformamide (DMF) solutions into methanol. The off-white solid polymer fibers were finally dried under vacuum for 24 h at 150 °C.

Synthesis of 6FDA-TrMPD. Following the general procedure for polyimide synthesis, 6FDA-TrMPD was prepared by reacting 6FDA (0.59 g, 1.33 mmol) with TrMPD (0.2 g, 1.33 mmol) in 3 ml *m*-cresol to afford a white powder (92% yield) as a final product. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.91 (s, 3H), 2.13 (s, 6H), 7.32 (s, 1H), 7.92 (s, 4H), 8.17 (s, 2H). $M_n = 135,800 \text{ g mol}^{-1}$; PDI = 1.22; $\rho = 1.24 \text{ g cm}^{-3}$; $S_{\text{BET}} = 450 \text{ m}^2 \text{ g}^{-1}$; TGA analysis: $T_{d,5\%} = 502 \text{ °C}$.

Synthesis of 6FDA-TrMCA. 6FDA-TrMCA was prepared by reacting 6FDA (0.46 g, 1.03 mmol) with TrMCA (0.2 g, 1.03 mmol) in 3 ml *m*-cresol to afford white fiber (95% yield) as a final product. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.96 (s, 3H), 2.13 (s, 6H), 7.94 (br s, 2H), 8.19 (d, 4H, J = 7.92 Hz), 13.79 (br s, 1H). FT-IR (ν, cm⁻¹): 3200-3700 (br, str O-H), 1791 (C=O asym), 1714 (C=O sym, str), 1351 (C-N, str), 718 (imide ring deformation); M_n = 113,700 g mol⁻¹; PDI = 1.16; ρ = 1.31 g cm⁻³; S_{BET} = 260 m² g⁻¹; TGA analysis: T_{d,5%} = 404 °C.

Dense film preparation. Robust films were prepared by slow evaporation of polymer solution poured into flat glass Petri dishes after filtration through 0.45 μm PTFE filters. All polymer solutions had a concentration of 3 wt/vol% in DMF for 6FDA-TrMCA and CHCl₃ for 6FDA-TrMPD. The obtained membranes were dried at 200 °C for 24 h under vacuum. Complete solvent removal was confirmed by TGA. On average, coupons used for pure- and mixed-gas permeability measurements had an area of ~ 1 cm² and a thickness of ~85 μm. Film thickness was measured via a Mitutoyo 547-400S digital micrometer and sample areas were measured via digital image scan.

Molecular dynamic simulations. Molecular dynamic simulations were carried out using Materials Studio 8.0 software (the COMPASS force field was assigned to account for charge and force field parameters). The energy-minimized amorphous cells of the 6FDA-based PIs were constructed employing five chains of five repeat units each; the experimental geometric density of each polymer and the temperature of 298 K were used as simulations constrains. Long-range coulombic interactions were taken into account with the Ewald sum method, and the non-bonded energy was calculated with a cut-off distance of 9.5 Å. A probe radius of 1.65 Å was used to calculate the fractional free volume (FFV) using the following equation: $FFV = V_f / (V_f + V_o)$; where V_f and V_o are the free and occupied volume of the polymer chains in the amorphous cell, respectively. Hydrogen bonding between polymer chains was detected inside the optimized amorphous cells by setting a maximum range of 4 Å.

Fluorescence spectroscopy. Fluorescence spectroscopy measurements were conducted on a PerkinElmer LS45 setup in a 90° arrangement with fixed 10 nm slits to investigate the potential formation of charge-transfer complexes (CTCs) between the electron donor and electron acceptors atoms in the

polyimides backbone. Fluorescence excitation (excited at 380 nm) and emission spectra were collected against wavelength for polymer films with a thickness of ~15 μm .

Physisorption and gas permeation measurements. All procedures for physisorption analysis, pure-, and mixed-gas permeation tests are detailed in the Supporting Information of this work. Briefly, pure-gas sorption of CO_2 and CH_4 was performed using a gravimetric Hiden Isochema system at 305 K over a pressure range of 0 to 15 atm. Pure-gas permeation data were generated for H_2 , O_2 , and N_2 at 2 atm using the constant volume/variable pressure method.²⁹ In the case of CO_2 and CH_4 , permeability was determined over a pressure range of 2 to 15 atm. Mixed-gas permeation tests were carried out with an equimolar CO_2/CH_4 feed up to 30 atm using a previously reported method.³⁰

■ RESULTS AND DISCUSSION

Monomers and Polymers Characterization. 3,5-Diamino-2,4,6-trimethylbenzoic acid (TrMCA) was prepared by a two-step synthetic route that started with a nitration reaction of 2,4,6-trimethylbenzoic acid using nitric acid (HNO_3) in the presence of H_2SO_4 at room temperature. Then, the dinitro compound was reduced to diamine via reaction with hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) and palladium on carbon (Pd/C, 10%) in methanol under reflux. The molecular structures of the dinitro and the diamino compounds were confirmed by ^1H NMR, ^{13}C NMR, and MS.

Two polyimides were prepared by a one-step high-temperature polycondensation reaction between 6FDA and the two diamines (i.e., TrMPD and TrMCA) in *m*-cresol at 200 $^\circ\text{C}$ and in the presence of isoquinoline in a catalytic amount. Total conversion of polyamic acids to polyimides was confirmed by FT-IR (**Figure 1**) and ^1H NMR (**Figure S1** and **S2**). As shown in **Figure 1**, the characteristic absorption bands of the imide group were obtained at about 1791 and 1714 cm^{-1} (imide asymmetric and symmetric C=O stretching) and 1351 cm^{-1} (C-N, stretching frequency). The broadband absorption of the hydroxyl group of the $-\text{COOH}$ functionality was found between 3200 and 3700 cm^{-1} .

Figure 1. FT-IR spectra of 6FDA-TrMPD (in blue) and 6FDA-TrMCA (in red) polyimides.

Both PIM-PIs were mechanically robust (**Figure S3**; **Table S1**) and showed excellent solubility in various common organic solvents, such as THF, DMF, DMSO, DMAc, NMP, and *m*-cresol (**Table 1**).

Table 1. Solubilities of 6FDA-TrMPD and 6FDA-TrMCA Polyimides in Organic Solvents.

Polymer	CH ₃ Cl	THF	DMF	NMP	DMAc	DMSO	<i>m</i> -cresol
6FDA-TrMPD	++	++	++	++	++	++	++
6FDA-TrMCA	--	++	++	++	++	++	++

++: soluble; --: insoluble.

TGA was used to evaluate the thermal stability of the newly designed carboxyl-functionalized PIM-PI. The carboxyl-functionalized polyimide decomposed in two stages, where the first stage (in the range 350 to 450 °C) resulted from the thermal degradation of –COOH sites, whereas the second stage marked the decomposition of the main chain.³¹ The degradation temperature at 5% weight loss ($T_{d,5\%}$) of the 6FDA-TrMCA polyimide was 404 °C (**Figure 2**), which was lower than that of its non-functionalized form. In fact, 6FDA-TrMPD exhibited an outstanding $T_{d,5\%}$ of 502 °C.

In the case of 6FDA-TrMCA no glass transition temperature was detected before the initial decomposition temperature of ~ 360 °C by DSC and DMA, as shown in **Figure S4 and S5**. 6FDA-TrMPD displayed a glass transition temperature of 397 °C measured by DMA (**Figure S5**) that is in general agreement with previously reported values in the literature, e.g., $T_g = 395$ °C.³¹

Figure 2. Thermal gravimetric analysis (TGA) under N_2 atmosphere of 6FDA-TrMPD and 6FDA-TrMCA film polyimides that were dried at 200 °C for 24 h under vacuum.

For both PIM-PIs studied in this work, the GPC characterization revealed high number average molecular weight M_n and low polydispersity indexes (PDI), as listed in **Table 2**. 6FDA-TrMPD and 6FDA-TrMCA showed M_n of 135,800 $g\ mol^{-1}$ and 113,700 $g\ mol^{-1}$ with PDI of 1.22 and 1.16, respectively.

Table 2. Physical Properties of 6FDA-TrMPD and 6FDA-TrMCA Polyimides. Weight (M_w) and Number (M_n) Average Molecular Weights, Polydispersion Index (M_w/M_n), Degradation Temperature at 5% Weight Loss ($T_{d,5\%}$), Surface Area (S_{BET}), Polymer Density (ρ), and Fractional Free Volume (FFV).

Polymer	M_w^a ($g\ mol^{-1}$)	M_n^a ($g\ mol^{-1}$)	PDI ^a	$T_{d,5\%}^b$ (°C)	S_{BET} ($m^2\ g^{-1}$)	Density ^c ($g\ cm^{-3}$)	FFV ^d (-)
6FDA-TrMPD	165,700	135,800	1.22	502	450	1.24	0.25 ^d (0.251) ^e
6FDA-TrMCA	131,900	113,700	1.16	404	260	1.31	0.21 ^d (0.218) ^e

^aMeasured by GPC with polystyrene as the calibration standard; ^bmeasured by TGA with a ramp rate of 3 °C min⁻¹ to 800 °C; ^cmeasured geometrically using weight, thickness, and area of the films; ^destimated via MD modeling; ^ecalculated using group contribution method.

Polymer Film Properties and Microstructure. In this section, we first briefly clarify the effect of the trimethyl substitution on the phenylenediamine building blocks that promoted the PIM-like transport properties of 6FDA-TrMPD and 6FDA-TrMCA; then, we elucidate the effect of the –COOH functionalization on the porosity and microstructure of 6FDA-TrMCA.

The well studied low-free-volume 6FDA-mPDA polyimide^{11,32} provides a baseline case to investigate structural effects on the properties of the microporous trimethyl-substituted 6FDA-TrMPD polyimide. Because the presence of the methyl groups *ortho* to the imide linkage severely hinders local rotation, efficient chain packing of 6FDA-TrMPD is disrupted, leading to higher free volume³² with FFV value of 0.25 (**Table 2**) than 6FDA-mPDA (FFV = 0.165) — a similar trend was observed for the BET surface areas of the two polymers with values of 450 and 66 m² g⁻¹, respectively.¹¹

The discussion is now extended to the effect of the –COOH functionalization of 6FDA-TrMCA on its physical and gas transport properties. To achieve this aim, we found it instructive to visualize the different types of hydrogen bonding within 6FDA-TrMCA via molecular dynamics simulations, as shown in **Figure 3**. The carboxyl group can act as a hydrogen bonding donor and acceptor at its –OH and C=O sites, respectively (**Figure 3a**). In addition, the hydrogen atom of the –COOH group can create hydrogen bonds with the fluorine atoms of the –CF₃ groups (**Figure 3b**) and with the carbonyl and imide groups (**Figure 3c**) of adjacent polymer chains.

Figure 3. Hydrogen bonding sites in 6FDA-TrMCA detected via molecular dynamics simulations.

Previous work demonstrated that polar groups are capable of hydrogen bonding between donor and acceptor atoms and can induce charge-transfer complex formation that tighten chain packing and increase the interchain rigidity of the polymer matrix, thus reducing polymer free volume and enhancing size sieving capability.^{16,33,34} In fact, our BET analysis based on N₂ sorption at -196 °C (**Figure 4**) for 6FDA-TrMPD gave a surface area of about 450 m² g⁻¹ that was 1.7-fold higher than that of carboxyl-functionalized 6FDA-TrMCA (i.e., 260 m² g⁻¹). Note that, as compared to 6FDA-TrMPD, the tighter interchain packing of 6FDA-TrMCA also explains its higher geometric density (**Table 1**) as well as lower fractional free volume (FFV) calculated from MD simulations, as shown in **Figure 5**.

Figure 4. N_2 physisorption isotherms (at $-196\text{ }^{\circ}\text{C}$) of 6FDA-TrMPD and 6FDA-TrMCA (measured in the range 0 to 1 relative pressure).

Figure 5. Molecular dynamics simulation of 6FDA-TrMPD and 6FDA-TrMCA polyimides in an amorphous cell with their corresponding calculated FFV. The blue areas are the x, y, z sections of the free volume elements.

To assess the effect of $-\text{COOH}$ groups on the average d-spacing of the polymer microstructure, we conducted X-ray diffraction (XRD) analysis on 6FDA-TrMPD and 6FDA-TrMCA film samples.

Coherent with similar polyimides, 6FDA-TrMPD and 6FDA-TrMCA demonstrated amorphous features, as shown in their XRD spectra (**Figure 6**). The d-spacings of the main amorphous peaks for 6FDA-TrMCA and 6FDA-TrMPD are 5.3 and 6.1 Å, respectively. The tightening of the main-chain spacing in 6FDA-TrMCA compared to 6FDA-TrMPD is consistent with decreased BET surface area (from 450 m² g⁻¹ in 6FDA-TrMPD to 260 m² g⁻¹ in 6FDA-TrMCA) and reduced fractional free volume (from 0.25 in 6FDA-TrMPD to 0.21 in 6FDA-TrMCA) predicted from molecular dynamics simulations.

Figure 6. X-ray diffraction spectra of 6FDA-TrMPD and 6FDA-TrMCA.

Optical properties. To elucidate the strength of the charge transfer complexes in 6FDA-TrMCA and 6FDA-TrMPD, we conducted solid-state fluorescence spectroscopy experiments. Previous work showed how polyimides that can efficiently pack their polymer chains benefit from enhanced delocalization of the π -electrons through conjugations; this increases the potential for charge transfer complex (CTC) formation between the electron-withdrawing groups of the aromatic dianhydride and the electron-donor moieties of the aromatic diamine moiety.^{16,33-35} CTC-induced interchain tightening has been used as a design tool to improve gas-pair selectivity of polyimides.¹⁶ Similar to the effect of hydroxyl-

functionalization in polyimides on CTC formation, the carboxyl-functionalized polyimide 6FDA-TrMCA demonstrated higher fluorescence emission intensity at an excitation wavelength of 380 nm as compared to the unfunctionalized 6FDA-TrMPD (**Figure 7**). The stronger delocalization of π -electrons increased the coloration of the 6FDA-TrMCA that displayed a yellowish color, whereas the 6FDA-TrMPD was essentially colorless.

Figure 7. Solid-state fluorescence emission spectra (excitation at 380 nm) of 6FDA-TrMPD and 6FDA-TrMCA.

Pure-gas sorption and permeation. CO₂ and CH₄ pure-gas sorption uptakes in 6FDA-TrMPD and 6FDA-TrMCA are displayed in **Figure 8a** and **b**. We found our 6FDA-TrMPD data in good agreement with those reported by Hölck et al.³⁶; moreover, both carboxyl-functionalized PIM-PIs offered significantly higher sorption capacity for CO₂ and CH₄ than cellulose triacetate (CTA), the most commonly used membrane material for CO₂/CH₄ separation, reported by Puleo et al.³⁷ Compared to 6FDA-TrMPD, the introduction of the carboxyl functionality in 6FDA-TrMCA did not lead to significant differences in CO₂ and CH₄ uptakes (**Figure 8a** and **b**) and had only a small effect on CO₂/CH₄ solubility

selectivity (**Figure 8c**), indicating that preferential interactions of CO₂ with the COOH group did not occur.

The pure-gas solubility selectivity of 6FDA-TrMCA and 6FDA-TrMPD was inferior to that of CTA at all explored pressures. For example, the CO₂/CH₄ solubility selectivity of ~4 at 2 atm for both 6FDA-TrMPD and 6FDA-TrMCA was 2-fold lower than that of CTA (**Figure 8c**).

Figure 8. (a) CO₂ and (b) CH₄ pure-gas sorption isotherms measured gravimetrically. (c) CO₂/CH₄ pure-gas solubility selectivity of 6FDA-TrMPD (blue squares), 6FDA-TrMCA (red diamonds), and CA (black squares). Cellulose triacetate (CA, with a degree of substitution of 2.84) data were digitalized from the literature.³⁷ All curves were drawn via dual-mode sorption model analysis (not discussed).³⁸

The gas sorption results indicated that any significant changes in CO₂/CH₄ permeability selectivity must be related to changes in diffusion selectivity of the two gases, as discussed below. The pure-gas permeation properties of the two polyimides were measured at 35 °C and 2 atm in the following order:

H₂, N₂, O₂, CH₄ and CO₂ and are listed in **Table 3**; previously reported data for 6FDA-TrMPD³², 6FDA-TrMPD:DABA (3:2)²⁵, 6FDA-DABA¹³, 6FDA-mPDA¹¹, and CTA³⁷ are included for comparison. 6FDA-TrMPD and 6FDA-TrMCA exhibited high gas permeability due to the introduction of the trimethyl substitution that severely hinders rotational freedom of the imide linkage. For example, the trimethyl-substituted 6FDA-TrMPD and the unsubstituted 6FDA-mPDA showed CO₂ permeability values of 498 and 14 barrer, respectively (**Table 3**); likewise, the carboxyl-functionalized trimethyl-substituted 6FDA-TrMCA displayed 13-fold higher CO₂ permeability (144 barrer) than its unsubstituted counterpart 6FDA-DABA (11.1 barrer). 6FDA-TrMCA exhibited ~3-fold lower CO₂ permeability (144 barrer) than 6FDA-TrMPD (498 barrer) which can be ascribed to its tighter chain structure induced by the presence of –COOH groups due to hydrogen bonding and CTC formation. On the other hand, compared to 6FDA-TrMPD the carboxyl-functionalization improved all gas-pair selectivities of 6FDA-TrMCA by fine-tuning its size-sieving properties; e.g., CO₂/CH₄ and H₂/CH₄ permeability selectivities increased from 22 to 45 and from 18 to 61, respectively (**Table 3**). The lower permeability and increased gas-pair selectivity observed for 6FDA-TrMCA compared to 6FDA-TrMPD agreed qualitatively well with the lower BET surface area (260 vs. 450 m² g⁻¹) and smaller average main-chain spacing (5.3 vs. 6.1 Å), as discussed above.

Table 2. Pure-Gas Permeabilities and Ideal Permeability Selectivities for 6FDA-TrMPD and 6FDA-TrMCA Measured at 2 atm and 35 °C. 6FDA-TrMPD:DABA (3:2), 6FDA-mPDA, 6FDA-DABA and CTA are Included for Comparison.

Polymer	Permeability (Barrers)					Ideal selectivity ($\alpha_{X/Y}$)			
	H ₂	N ₂	O ₂	CH ₄	CO ₂	H ₂ /N ₂	H ₂ /CH ₄	O ₂ /N ₂	CO ₂ /CH ₄
6FDA-TrMPD ^a [This work]	407	25.3	91.4	23.0	498	16	18	3.6	22
6FDA-TrMPD ^b	516	31.6	109	26.1	431	16	20	3.4	17
6FDA-TrMCA ^a [This work]	193	5.52	26.4	3.2	144	35	61	4.8	45

6FDA-TrMPD:DABA (3:2) ^c	-	7.0	32.0	4.2	144	-	-	4.6	34
6FDA-DABA ^d	49.0	0.42	2.86	0.15	11.1	117	327	6.8	74
6FDA-mPDA ^e	46.0	0.62	3.60	0.20	14.0	74	230	5.8	70
CTA (2.84 d.s.) ^f	15.5	0.23	1.46	0.2	6.56	67	78	6.3	33

^a Treated at 200 °C for 24 h under vacuum; ^b dried at 200 °C for 20 h under vacuum, H₂, CO₂, CH₄ measured at 10 atm, O₂ and N₂ measured at 2 atm³²; ^c dried at 180 °C for 24 h under vacuum and tested at 6.8 atm²⁵; ^d treated at 250 °C for 24 h under vacuum¹³; ^e treated in methanol for 12 h and then dried at 120 °C under vacuum for 24 h¹¹; ^f ref. 37.

Table 3 compares the permeability and selectivity values of 6FDA-TrMPD and 6FDA-TrMCA to commercial CTA at 2 atm and 35 °C. Both 6FDA-TrMPD and 6FDA-TrMCA were significantly more permeable than commercial cellulose triacetate due to overall higher values of both CO₂ and CH₄ diffusion and solubility coefficients (**Table 3**); moreover, 6FDA-TrMCA displayed better CO₂/CH₄ permselectivity than CA with values of 45 and 33, respectively, because of its diffusion selectivity advantage (10 vs. 4.1 as shown in **Table 3**).

Table 3. Carbon Dioxide and Methane Solubility Coefficients (S) and CO₂/CH₄ Solubility Selectivities at 2 atm and 35 °C Obtained By Gravimetric Gas Sorption. CO₂ and CH₄ Diffusion Coefficients (D) Calculated from $D = P/S$ along with their CO₂/CH₄ Diffusion Selectivities.

	S, CH ₄	S, CO ₂	D, CH ₄	D, CO ₂	α_S	α_D
	(cm ³ (STP) cm ⁻³ atm ⁻¹)		(cm ² s ⁻¹)		(-)	(-)
6FDA-TrMPD	4.2	15	4.2E-08	2.5E-07	3.6	6.1
6FDA-TrMCA	3.6	16	6.6E-09	6.8E-08	4.5	10
CTA (2.84 d.s.) ³⁷	0.5	4.2	2.9E-09	1.2E-08	8.1	4.1

High pressure pure- and mixed-gas permeation and selectivity properties. CO₂ and CH₄ pure-gas permeability vs. pressure data for 6FDA-TrMPD are shown in **Figure 9a** and **b**, respectively. The comparison of CO₂ and CH₄ pure-gas permeability data of microporous 6FDA-TrMPD with low-free-volume 6FDA-mPDA (**Table 3** and **Figure 9 a** and **b**) demonstrated that the trimethyl substitution in the repeat unit of TrMPD allowed an increase of at least one order of magnitude in CO₂ permability. The same trend was found by comparing the trimethyl-substituted carboxyl-functionalized microporous polyimide 6FDA-TrMCA and 6FDA-DABA (**Table 3**). However, the increase in CO₂ permeability of 6FDA-TrMCA was coupled with a commensurate decrease in CO₂/CH₄ selectivity compared to its low-free-volume 6FDA-DABA analog, following the typical permeability/selectivity trade-off observed in polymeric membrane materials.³⁹

In pure-gas tests, CO₂ and CH₄ permeabilities decreased with pressure due to the progressive saturation of the Langmuir's sites of glassy 6FDA-TrMPD and 6FDA-TrMCA (**Figure 9 a-d**).³⁸ When we tested these PIM-PI polymers using a 50:50 molar CO₂-CH₄ mixture, the permeability vs. partial pressure behavior was preserved; in addition, we found that for both polymers over the entire pressure range, CO₂ and CH₄ mixed-gas permeabilities were lower than the corresponding pure-gas values (**Figure 9 a-d**). This is a consequence of the *competitive* sorption phenomenon by which CO₂ tends to acquire part of the sorption sites for CH₄ and *vice versa* (the extent of this competition depends on the affinity with the polymer of the involved gases). Hence, because gas permeability depends both on diffusion and solubility coefficients (as given by the solution diffusion theory⁴⁰), CO₂ and CH₄ were less permeable when tested in mixed-gas than in pure-gas conditions. Furthermore, it is important to consider the polymer matrix plasticization capability of CO₂ in mixed-gas environment. In fact, the presence of CO₂ locally dilates the glassy polymer matrix, thereby enhances the methane diffusion coefficient leading to faster CH₄ diffusion in mixed-gas conditions than obtained in pure-gas tests.⁴¹⁻⁴³ Thus, CO₂-induced plasticization depresses the diffusion selectivity of glassy polymers; this counteracts with the fact that solubility selectivities of CO₂-CH₄ mixtures are *higher* than those obtained under ideal pure-gas conditions — as demonstrated and quantified in several examples.⁴¹⁻⁴³ Generally, the negative effect of the presence of CO₂ on diffusion

selectivity is predominant and lowers the CO₂/CH₄ mixed-gas permeability selectivity of a polymer membrane material relative to its respective pure-gas value.⁴¹⁻⁴³ However, some polymers that can better resist CO₂-induced plasticization demonstrated CO₂/CH₄ mixture permselectivity matching or even slightly outperforming their respective pure-gas values.^{16,25} This is also the case for 6FDA-TrMCA and 6FDA-TrMPD, (**Figure 10**), some hydroxyl-functionalized polyimides and their thermally rearranged derivatives such as 6FDA-HAB⁴⁴ and TDA1-APAF⁴⁵.

Fig. 9. (a) CO₂ and (b) CH₄ pure- and mixed-gas (50:50 molar) permeabilities vs. partial pressure for 6FDA-TrMPD; (c) CO₂ and (d) CH₄ pure- and mixed-gas (50:50 molar) permeabilities vs. partial pressure for 6FDA-TrMCA. Pure-gas permeability vs. pressure dependence data for 6FDA-mPDA were retrieved from the literature.¹¹

Figure 10. CO₂/CH₄ permeability selectivity vs. CO₂ partial pressure for 6FDA-TrMPD (in blue) and 6FDA-TrMCA (in red). Open-points and closed points represent pure- and mixed-gas data, respectively.

The performance of 6FDA-TrMCA at a partial pressure of ~12 atm and 35 °C is shown on the 2018 *mixed-gas* CO₂/CH₄ upper bound in **Figure 11**.³ Similar to various previously reported 6FDA-DAM:DABA copolymers, the carboxyl-functionalized 6FDA-TrMCA homopolymer demonstrated excellent performance with location on the upper bound with a CO₂ permeability of 98 barrer and CO₂/CH₄ selectivity of 38, thereby making it a promising membrane material for CO₂ removal from natural gas or biogas applications.

Figure 11. Mixed-gas performance of 6FDA-TrMCA and 6FDA-TrMPD (light blue symbols) relative to the 2018 mixed-gas CO_2/CH_4 upper bound at a partial CO_2 pressure of ~ 10 atm and 35°C .³ Commercial membrane materials (CTA, Matrimid and P84) are highlighted in green symbols; carboxyl-functionalized copolymers are labeled in grey.

■ CONCLUSIONS

In this work, a trimethyl-substituted carboxyl-functionalized 6FDA-TrMCA polyimide was synthesized by a high temperature one-pot reaction of 3,5-diamino-2,4,6-trimethylbenzoic acid (TrMCA) with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). The 6FDA-TrMCA polyimide was soluble in numerous common organic solvents. 6FDA-TrMCA was compared with the unsubstituted 6FDA-TrMPD analog (also known as 6FDA-DAM) that does not contain the COOH functionality of TrMCA. The trimethyl substitution of both TrMPD and TrMCA diamine building blocks promoted the formation of large unrelaxed free volumes that were demonstrated via BET surface area analysis; the novel 6FDA-TrMCA displayed a surface area of $260 \text{ m}^2 \text{ g}^{-1}$ that is typical of polyimides of intrinsic microporosity (PIM-PIs). The presence of the $-\text{COOH}$ functionality promoted interchain hydrogen bonding and encouraged charge transfer complex (CTC) formation. Hence, the structure of 6FDA-TrMCA was tighter

and more size-selective than that of 6FDA-TrMPD. Of particular interest was the CO₂-CH₄ mixed-gas behavior of 6FDA-TrMCA and 6FDA-TrMPD. Both PIM-PIs were resistant to CO₂-induced plasticization up to a partial pressure of at least ~ 15 atm. CO₂/CH₄ mixed-gas permeability selectivities of 6FDA-TrMCA and 6FDA-TrMPD were slightly higher than those obtained under pure-gas conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Gas sorption and permeation testing procedures, NMR, mechanical and thermal properties, WXR and table of CO₂ and CH₄ pure- and mixed-gas permeation data (PDF).

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Notes

The authors declare no competing financial interest.

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Graphic abstract