Synthesis and characterization of 6FDA/3,5-diamino-2,4,6-trimethylbenzenesulfonic acid-derived polyimide for gas separation applications

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ABSTRACT

A sulfonic acid-functionalized trimethyl-substituted polyimide was synthesized by reacting 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,5-diamino-2,4,6-trimethylbenzenesulfonic acid (TrMSA). The properties of 6FDA-TrMSA were compared to the related 6FDA-derived polyimide analogues made from 2,4,6-trimethylbenzene-1,3-diamine (6FDA-TrMPD) and 3,5-diamino-2,4,6-trimethylbenzene benzoic acid (6FDA-TrMCA). Compared to 6FDA-TrMPD and 6FDA-TrMCA, sulfonic acid functionalization resulted in significantly lower surface area, reduced fractional free volume, and tighter chain *d*-spacing. Consequently, 6FDA-TrMSA displayed lower gas permeabilities with a commensurate increase in permeability-based gas-pair selectivities. The enhanced CO₂/CH₄ selectivity of 6FDA-TrMSA was caused exclusively by higher diffusion selectivity, which was promoted by strong hydrogen bonding induced by the -SO₃H functionalization. Permeation experiments of 6FDA-TrMSA with a 1:1 CO₂-CH₄ mixture revealed the occurrence of competitive sorption effects (depressing CO₂ gas permeability) and CO₂-induced polymer matrix plasticization, which reduced the polymer selectivity by enhancing CH₄ permeability. At ~20 atm total pressure, 6FDA-TrMSA showed a CO₂ permeability of ~15 Barrer and an equimolar CO₂/CH₄ mixed-gas selectivity of 55, which are ~2-fold higher performance values than those of the state-of-the-art polymer used for industrial scale natural gas sweetening, i.e., cellulose triacetate.

1. Introduction

Polyimides are attractive high-performance materials applied widely in industrial applications because of their variable processability, high thermal, mechanical and chemical stability [1]. Structure-property relationships of polyimides with respect to their gas transport properties have been extensively investigated. By proper choice of the polymer backbone substituents, the gas separation performance may be optimized by either disrupting the polymer chain packing to enhance permeability or promoting interchain interactions to boost permeability selectivity [2-13].

Introduction of methyl groups to phenylenediamine-derived polyimides has often been used as a simple and effective way to enhance the gas permeability by restricting the rotational mobility of the imide linkages and providing spacer groups for inefficient interchain packing [14]. Specifically, polyimides based on 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 2,4,6-trimethyl-1,3-phenylenediamine (TrMPD) or 2,3,5,6-tetramethyl-1,4-phenylenediamine (TeMPD) showed enhanced gas permeabilities compared to their unsubstituted 1,3-phenylene diamine (MPD) and 1,4-phenylenediamine (PPD) analogues; however, the boost in permeability also resulted in a significant commensurate drop in selectivity [15-17]. Because of its high permeability, TrMPD has been applied as a monomer for fine-tuning an appropriate balance between gas permeability and selectivity by designing a wide variety of co-polyimides [15-17].

Previous studies demonstrated that integrating polar groups in the polyimide backbone, e.g., hydroxyl (–OH) [10,11,18-27] and carboxyl (–COOH) [28-34] groups, can enhance their performance, specifically for CO₂/CH₄ separation [10,18,21-34]. The hydroxyl and carboxyl groups promote *interchain* hydrogen bonding and trigger charge transfer complex (CTCs) interactions, which typically lead to polyimides with tighter chain packing and enhanced gas-pair selectivity coupled with some loss in permeability [10,24,27]

Alternatively, sulfonic acid ($-\text{SO}_3\text{H}$) groups can be used to functionalize polyimides, which have been investigated extensively as ion-conducting membrane materials [35-40]. Furthermore, several studies reported the gas transport properties of sulfonated polyimides [41-48]. Tanaka et al. investigated polyimides made from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (BAPHF) and the sulfonated analogues bearing sulfonic acid ($-\text{SO}_3\text{H}$) or triethylamine sulfonate ($-\text{SO}_3\text{NHEt}_3$) groups [46]. When tested under pure-gas conditions at 35 °C and 1 atm, the sulfonic-acid-containing NTDA-BAPHFDA-H polyimide exhibited higher CO_2/CH_4 permeability selectivity than the triethylamine-sulfonate-based NTDA-BAPHFDS-A polyimide (81 vs. 35). At the same time, both polymers displayed about the same CO_2 permeability of 13-14 Barrer [46]. More recently, a series of sulfonated polyimides was reported by Zhang et al. [48]. TEA-*t*SPI (see structure in **Scheme 1**), prepared from 6FDA and the SO_3NHEt_3 salt of 3,5-diamino-2,4,6-trimethylbenzenesulfonic acid (TrMSA), displayed a CO_2 permeability of 52 Barrer with pure-gas CO_2/CH_4 selectivity of 33 (at 1 atm and 35 °C) [48].

Here, we report the sulfonated polyimide prepared by the polycondensation reaction of TrMSA with 6FDA in *m*-cresol (**Scheme 1**). We present the structural and physical polymer properties, including gas sorption, diffusion, and permeability of 6FDA-TrMSA. To elucidate the effects of specific functionalization groups on gas transport properties, we compared 6FDA-TrMSA with previously reported triethylamine-sulfonated- [48], carboxylated- [33] and non-functionalized 6FDA-TrMPD [33] analogues — i.e., TEA-*t*SPI, 6FDA-TrMCA and 6FDA-TrMPD polyimide. We also performed CO_2/CH_4 gas mixture permeation studies to investigate the potential of 6FDA-TrMSA for natural gas or biogas applications.

Scheme 1. Synthetic scheme for synthesis of 6FDA-TrMSA. Structures of previously reported 6FDA-TrMPD, 6FDA-TrMCA and TEA-tSPI polyimides are included for comparison [33,48].

2. Experimental

2.1. Materials and characterizations

6FDA (99%) and TrMSA (97%) were obtained from Tokyo Chemical Industry Co., Ltd. (JP) (TCI). Solvents were purchased from Sigma-Aldrich and used without further purification. All polymer characterizations were performed as described in our previous work [25] and are described in the Supporting Information of this work.

2.2. Polymer synthesis

6FDA-TrMSA was synthesized by reacting 6FDA (0.58 g, 1.3 mmol) and TrMSA (0.3 g, 1.3 mmol) in *m*-cresol (4 ml) in the presence of isoquinoline (0.1 ml), as shown in **Scheme 1**. The

solution was stirred for 20 min at room temperature under a continuous flow of nitrogen. The temperature was then gradually increased to 200 °C while stirring continued for 6 h. The water resulting from the reaction was continuously removed with a nitrogen stream. The highly viscous solution was cooled and precipitated in methanol (300 ml) at room temperature. The obtained light brown polymer was re-precipitated two times from dimethylformamide (DMF) solution into methanol and then dried under vacuum for 24 h at 200 °C; (92% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.93 (br s, 3H), 2.17 (br s, 6H), 7.95 (br m, 4H), 8.19 (br s, 2H). FT-IR (ν , cm⁻¹): 3100-3600 (br, str O-H), 1791 (C=O asym), 1718 (C=O sym, str), 1351 (C-N, str), 1191 and 1047 (O=S=O, str), 712 (imide ring deformation); M_n = 106,000 g mol⁻¹; PDI = 1.28; TGA analysis: $T_{d,5\%}$ = 316 °C; S_{BET} = 40 m² g⁻¹; ρ = 1.41 g cm⁻³.

2.3. Polymer film preparation

A 3 wt/vol% 6FDA-TrMSA solution in DMF was filtered through a 0.45 μ m PTFE filter in a glass Petri dish. The polymer solution was then heated at 80 °C for 24 h under continuous nitrogen flow to evaporate DMF. Finally, the pre-dried film was further heated at 200 °C for 24 h under vacuum. Films with a thickness of $\sim$ 45 μ m were used for the gas permeation measurements.

2.4. Gas sorption and permeation experiments

Gravimetric gas sorption experiments were performed as previously reported [33]. Pure-gas permeation experiments were performed at 2 atm and 35 °C in the following order: H₂, N₂, O₂, CH₄, and CO₂; the details of the procedure are described in the Supporting Information. Furthermore, pure CO₂ and CH₄ permeation data were generated over a pressure range of 2-18

atm. Permeation experiments were also conducted with a 1:1 molar CO₂/CH₄ mixture with a total maximum pressure of up to 32 atm, as previously described [25].

2.5. Molecular Dynamics Simulation

Molecular dynamics simulations to estimate FFV and hydrogen bonding sites were performed by the same methodology as reported in previous work [33]. The occurrence of hydrogen bonding between the simulated polymer chains was elucidated by imposing a maximum bond distance of 4 Å between the donor and acceptor sites. The modeling results of 6FDA-TrMSA are displayed together with those of 6FDA-TrMPD and 6FDA-TrMCA polyimides in **Fig. S1**.

3. Results and discussion

3.1. Synthesis and characterization of the polyimides

The synthesis of the 6FDA-TrMSA polyimide was carried out using a conventional high-temperature polycondensation reaction of equimolar amounts of 6FDA and TrMSA in *m*-cresol at 200 °C. The ¹H NMR spectrum of 6FDA-TrMSA matched the expected chemical structure and is compared to that of 6FDA-TrMPD in **Fig. 1**. No signals were detected above 10 ppm, indicating full conversion of poly(amic acid) to polyimide.

The characteristic peaks of the imide group were detected at 1791 (asymmetric C=O stretching) and 1718 cm⁻¹ (symmetric C=O stretching) for 6FDA-TrMSA. The hydroxyl stretching frequency of the –SO₃H group was obtained as a wide band between 3100 and 3600 cm⁻¹, and the S–O and S=O stretching frequency was found at 1047 and 1191 cm⁻¹, respectively (**Fig. 2**).

Fig. 1. ^1H NMR spectra of 6FDA-TrMSA and 6FDA-TrMPD [33] in deuterated dimethylsulfoxide (DMSO-d_6).

Fig. 2. FT-IR spectra of 6FDA-TrMSA and 6FDA-TrMPD [33] polyimides. a) identification of O-H stretching and imide formation ($\text{C}=\text{O}$ stretching, $\text{C}-\text{N}$ stretching); b) identification of $-\text{SO}_3\text{H}$ group at 1047 and 1191 cm^{-1} .

Like the previously reported carboxylated 6FDA-TrMCA [33], the sulfonated 6FDA-TrMSA polyimide exhibited excellent solubility at 23 $^{\circ}\text{C}$ in high boiling point polar solvents but was

insoluble in chlorinated solvents, i.e., dichloromethane (DCM) and chloroform (CHCl₃) (**Table 1**).

Table 1

Solubility of 6FDA-TrMSA in common organic solvents.

Polymer	DCM	CH ₃ Cl	THF	NMP	DMF	DMAc	DMSO	<i>m</i> -cresol
6FDA-TrMPD [33]	++	++	++	++	++	++	++	++
6FDA-TrMCA [33]	--	--	++	++	++	++	++	++
6FDA-TrMSA [this study]	--	--	-+	++	++	++	++	++

--: insoluble, -+: soluble with heating, ++: soluble at room temperature.

6FDA-TrMSA displayed high M_n of 106,000 g mol⁻¹ and PDI of 1.28. Thermal gravimetric analysis of 6FDA-TrMSA, shown in **Fig. 3**, indicated decomposition of 6FDA-TrMSA in two steps: (i) the first started at ~270 °C and was primarily due to the thermal removal of the functional –SO₃H group; (ii) the second stage starting at ~ 400 °C marked the main chain degradation. A similar behavior was observed for the carboxyl-functionalized version of the 6FDA-TrMPD (i.e., 6FDA-TrMCA), where degradation of the –COOH group occurred at ~ 350 °C [33]. 6FDA-TrMPD, 6FDA-TrMCA and 6FDA-TrMSA displayed decomposition temperatures at 5% weight loss ($T_{d,5\%}$) of 502, 404 and 316 °C, respectively, under nitrogen atmosphere (**Table 2**).

Fig. 3. Thermal gravimetric analysis (TGA) of 6FDA-TrMSA polyimide.

Table 2

Physical properties of 6FDA-TrMSA. Data for 6FDA-TrMPD and 6FDA-TrMCA are included for comparison.

Polymer	$T_{d,5\%}$ (°C) ^a	Carbon (%) ^b	S_{BET} (m ² g ⁻¹) ^c	ρ (g cm ⁻³) ^d	FFV (-) ^e
6FDA-TrMPD [33]	502	66%	450	1.24	0.25
6FDA-TrMCA [33]	404	50%	260	1.31	0.21
6FDA-TrMSA [this study]	316	45%	40	1.41	0.14

^a Measured by TGA at 5% weight loss.

^b Obtained from TGA representing the residual carbon at 800 °C.

^c BET surface area determined from N₂ adsorption isotherms at -196 °C.

^d Geometric density.

^e Estimated FFV from MD simulations.

3.2. Microstructure of the $-SO_3H$ -functionalized polyimide

In this section, we discuss the difference between introducing $-SO_3H$ and $-COOH$ [33] functionalities to the polymer backbone. To this aim, it is helpful to identify the potential types of hydrogen bonding sites in the 6FDA-TrMSA polymer matrix, as derived by molecular dynamic simulations (**Fig. 4**).

Fig. 4. Possible hydrogen bonding sites in 6FDA-TrMSA identified by MD simulations.

The sulfonic acid group ($-\text{SO}_3\text{H}$) can create hydrogen bonds with both the carbonyl and imide groups (**Fig. 4a**) of neighboring polymer chains. Moreover, the $-\text{OH}$ donor sites are likely to create hydrogen bonds with the $-\text{SO}_2$ of the adjacent chains, as shown in **Fig. 4b** and **4c**. Hence, the sulfonic acid functionalization acts similarly to the carboxyl group in 6FDA-TrMCA, which also provides hydrogen bonding donor and acceptor sites [33]. However, the interchain interactions promoted by the sulfonic acid group are much stronger than those obtainable by the carboxylic acid functionality, as indicated by comparing the pK_a (i.e., the negative logarithm of the acid dissociation constant) of two acids bearing the sulfonic and carboxyl functionality, i.e., benzenesulfonic acid ($\text{pK}_a = -2.8$) is a much stronger acid than benzoic acid (pK_a of 4.2). Thus, the $-\text{SO}_3\text{H}$ group will induce stronger hydrogen bonding, which results in tighter interchain packing in 6FDA-TrMSA than the $-\text{COOH}$ -functionalized 6FDA-TrMCA and significantly more than the non-functionalized 6FDA-TrMPDA analogue. To support this hypothesis, it is informative to compare the BET surface area of 6FDA-TrMPD with the two acid-functionalized 6FDA-TrMPD-based polyimides. The intrinsically microporous, non-functionalized 6FDA-

TrMPD displayed a high BET surface area of $450 \text{ m}^2 \text{ g}^{-1}$ [33], while after $-\text{COOH}$ functionalization, the BET surface area decreased to $260 \text{ m}^2 \text{ g}^{-1}$ for 6FDA-TrMCA [33]. Introducing $-\text{SO}_3\text{H}$ to the polymer backbone led to an even much larger reduction in BET surface area to only $40 \text{ m}^2 \text{ g}^{-1}$ for 6FDA-TrMSA (**Fig. S2**), a value similar to other low-free-volume polyimides [25]. This result is also supported by the qualitative trends in other physical properties, in which 6FDA-TrMSA showed higher density and lower FFV values relative to 6FDA-TrMCA and 6FDA-TrMPD (**Table 2**).

To analyze the pore size distribution of 6FDA-TrMSA, NLDFT modeling of the CO_2 adsorption isotherm at 273 K permitted us to identify two groups of ultramicropores: the first with an average pore width of $\sim 3.6 \text{ \AA}$ and the second in the range 5-7.5 $\text{ \AA}$ (**Fig. S3a**). In agreement with this observation, the deconvolution of the X-ray diffraction spectrum of 6FDA-TrMSA displayed two groups of amorphous peaks, the first with an average d -spacing of 5.1 and 6.9 $\text{ \AA}$ (**Fig. 5, Fig. S4**) and the second consisting of two less pronounced peaks at 3.1 and 3.7 $\text{ \AA}$. Hence, the interchain hydrogen bonding associated with the $-\text{SO}_3\text{H}$ functionality tightens the polymer structure by creating diffusion domains with pore width of $\sim 3.5 \text{ \AA}$, which are tailored for diffusion-selective CO_2 permeation. **Fig. 5** displays how the X-ray diffraction spectrum of 6FDA-TrMSA shifted toward a tighter chain structure than for the unfunctionalized and $-\text{COOH}$ -functionalized polyimides. Indeed, 6FDA-TrMSA revealed the most pronounced size sieving character in this polyimide series, as discussed in Section 3.4.

Fig. 5. Wide-angle X-ray diffraction (WAXD) spectrum of 6FDA-TrMSA polyimide and comparison with that of the unfunctionalized (6FDA-TrMPD) and $-\text{COOH}$ -functionalized versions (6FDA-TrMCA) [33].

3.3. Fluorescence spectra

In polyimides, the delocalization of the π -electrons induces charge-transfer complexes (CTCs) of electron withdrawing groups of the dianhydride and electron-donating groups of the diamine [24,25,49]. Integrating polar functional groups (i.e. OH, and COOH) to the polymer chains reduces the FFV of an amorphous polymer by promoting interchain interactions and, thus, CTC formation. Hence, the CTC interactions tightens the polymer chain structure. In general, the fluorescence emission intensity is proportional to the strength of CTCs within a polymer matrix. Previously, we showed how the inclusion of the carboxyl functionality into the 6FDA-TrMPD polyimide increased the interchain interactions and promoted CTCs formation [33]. These CTCs interactions were even further enhanced by introducing the $-\text{SO}_3\text{H}$ functionality, as the fluorescence emission intensity of the 6FDA-TrMSA was substantially higher than that observed for the carboxyl-functionalized 6FDA-TrMCA (**Fig. 6**). The higher fluorescence intensity is macroscopically visible by the coloration of the polyimide films, i.e., 6FDA-TrMSA and 6FDA-TrMCA displayed

dark brown and light-yellow colors, respectively, whereas 6FDA-TrMPD was essentially colorless.

Fig. 6. Fluorescence emission spectra of 6FDA-TrMSA (excitation at 380 nm) in comparison with related polyimides (film thickness 12 – 15 μm) [33] and typical trends of CTC formation on chain packing and gas permeation properties.

3.4. Pure-gas transport properties

The pure-gas permeation properties of 6FDA-TrMSA polyimide are summarized in **Table 3**; data for 6FDA-TrMPD, 6FDA-TrMCA [33], TEA-*t*SPI [48], and three reference polymers used for commercial gas separation membranes, i.e., cellulose triacetate (CTA) [50], polysulfone [51] and polyimide (Matrimid) [51], are included for comparison.

Compared to the non-functionalized 6FDA-TrMPD, the 6FDA-TrMSA polyimide was strongly size-selective due to tight chain packing resulting from the vast hydrogen bonding and CTCs interactions triggered by the $-\text{SO}_3\text{H}$ functionalization. However, the tightening of the polymer structure was also coupled with a decrease in gas permeability (**Table 3**). For example,

the introduction of the -SO₃H functionality to 6FDA-TrMPD led to a notable 3-fold enhancement in CO₂/CH₄ selectivity from 22 to 61 but was penalized by a ~25-fold decrease in CO₂ permeability, i.e., from 498 to 19 Barrer (**Table 3**). Moreover, the presence of -SO₃H in 6FDA-TrMSA boosted the H₂/CH₄ selectivity of 6FDA-TrMPD from 18 to 180 with ~7-fold reduction in H₂ permeability from 407 to 56 Barrer. Interestingly, 6FDA-*m*-phenylenediamine (6FDA-MPD), a related non-functionalized low-free-volume polyimide, without both -SO₃H functionality and trimethyl-substitution, exhibited similar pure-gas permeabilities and selectivities compared to 6FDA-TrMSA (**Table 3**). Importantly, the 6FDA-TrMPD polyimide displayed higher H₂ and CO₂ permeability as well as enhanced H₂/N₂, H₂/CH₄ and CO₂/CH₄ selectivity than commonly used commercial membrane materials, such as cellulose triacetate, polysulfone and polyimide (Matrimid).

Table 3

Pure-gas permeability and selectivity of 6FDA-TrMSA. Properties of related polyimides and commercial membrane polymers are provided for comparison.

Polymer	Permeability (Barrer) ^a					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-MPD ^b [25]	46	0.62	3.6	0.20	14	74	230	5.8	70
6FDA-TrMPD ^b [33]	407	25.3	91.4	23.0	498	16	18	3.6	22
6FDA-TrMCA ^b [33]	193	5.52	26.4	3.2	144	35	61	4.8	45
6FDA-TrMSA ^b [This work]	56	0.6	3.8	0.31	19	93	180	6.3	61
6FDA- <i>t</i> SPI (TEAsalt) ^c [48]	58	1.87	8.19	1.58	52.2	31	37	4.4	33
Cellulose triacetate [50]	15.5	0.23	1.46	0.20	6.6	67	78	6.3	33
Polysulfone [51]	14.0	0.25	1.40	0.25	5.6	56	56	5.6	22
Polyimide (Matrimid) [51]	18.0	0.32	2.10	0.28	10.0	56	64	6.6	36

^a 1 barrer = 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹.

^b Treated at 200 °C for 24 h under vacuum and tested at 2 atm and 35 °C.

^c Treated at 150 °C for 8 h under vacuum and tested at 1 atm and 35 °C [48].

To further investigate the effect of the $-\text{SO}_3\text{H}$ group on the pure-gas transport performance of 6FDA-TrMSA, we measured the gas uptake of CO_2 and CH_4 by gravimetric sorption at $35\text{ }^\circ\text{C}$ and up to $\sim 15\text{ atm}$ (**Fig. S4**). We then deduced the gas diffusion coefficients from the relationship $D = P/S$ (**Table 4**).

Introduction of the highly polar $-\text{SO}_3\text{H}$ group had a relatively small effect on the CO_2 and CH_4 sorption coefficients compared to the non-functionalized 6FDA-TrMPD polyimide; moreover, the CO_2/CH_4 solubility selectivity values varied only over a narrow range from 3.6 to 4.5 (**Table 5**), which is in the range of other previously reported polyimides (at 2 atm and $35\text{ }^\circ\text{C}$) [4,14]. On the other hand, functionalization with polar groups had significant impact on the diffusion coefficients — e.g., the CH_4 diffusion coefficients followed the order: 6FDA-TrMSA ($0.09 \times 10^{-8}\text{ cm}^2\text{ s}^{-1}$) < 6FDA-TrMCA ($0.66 \times 10^{-8}\text{ cm}^2\text{ s}^{-1}$) < 6FDA-TrMPD ($4.2 \times 10^{-8}\text{ cm}^2\text{ s}^{-1}$). This effect was less pronounced for CO_2 (**Table 4**); therefore, the high CO_2/CH_4 pure-gas permselectivity of 61 for 6FDA-TrMSA resulted primarily from its high CO_2/CH_4 diffusion selectivity. For comparison, 6FDA-TrMSA, 6FDA-TrMCA, and 6FDA-TrMPD displayed CO_2/CH_4 diffusion selectivity values of 17.2, 10 and 6.1, respectively (**Table 5**).

The gas permeability and selectivity of TEA-*t*SPI, the triethylamine sulfonate salt form of 6FDA-TrMSA (**Scheme 1**), along with other sulfonated polyimides were recently reported by Zhang et al. [48]. The TEA-*t*SPI polyimide showed a higher CO_2 permeability (52 vs. 19 Barrer) but lower CO_2/CH_4 selectivity (33 vs 61) than the 6FDA-TrMSA polyimide (**Table 3**). Interestingly, 6FDA-TrMSA and TEA-*t*SPI displayed similar H_2 permeability 56–58 Barrer; however, 6FDA-TrMSA demonstrated high H_2/CH_4 selectivity of 180, whereas TEA-*t*SPI displayed only a moderate selectivity of 37 [48]. This result may be attributed to less pronounced

hydrogen bonding after replacing $-\text{SO}_3\text{H}$ by the bulkier and less polar $-\text{SO}_3\text{NH}(\text{CH}_2\text{CH}_3)_3$ group in the TEA-*t*SPI polyimide.

In comparison with a relevant commercial membrane material (e.g., cellulose triacetate), 6FDA-TrMSA exhibited a notably improved performance for all gas pairs (**Table 3**). The 6FDA-TMSA polyimide exhibited about two-fold higher CO_2 permeability (19 vs. 6.6 Barrer) and ~85% higher CO_2/CH_4 selectivity (61 vs. 33) than cellulose triacetate [50].

Finally, we briefly discuss the aging behavior of 6FDA-TrMSA. Physical properties and separation performance of low-free-volume polyimides are *de-facto* only mildly affected by the extremely slow densification of the polymer matrix — i.e., physical aging. This behavior was also confirmed for our $-\text{SO}_3\text{H}$ -functionalized polyimide. In fact, a second sample of 6FDA-TrMSA (heat treated at 120 °C for 24 h followed by 200 °C for 2 h under vacuum) was tested after 3 months and displayed both CO_2 permeability and CO_2/CH_4 permeability selectivities adherent to values obtained for the fresh sample.

Table 4

Diffusion coefficients and solubility coefficients of CO_2 and CH_4 for 6FDA-TrMSA (2 atm and 35 °C).

Polymer	Diffusion coefficient ^a		Solubility coefficient ^b	
	(10 ⁻⁸ cm ² s ⁻¹)		(10 ⁻² cm ³ (STP) cm ⁻³ cmHg ⁻¹)	
	CO_2	CH_4	CO_2	CH_4
6FDA-TrMSA [this study]	1.55	0.09	12.3	3.45
6FDA-TrMCA [33]	6.8	0.66	16	3.6
6FDA-TrMPD [33]	25	4.2	15	4.2

^a Determined from $D = P/S$. ^b Measured by gravimetric sorption at 35 °C and 2 atm.

Table 5CO₂/CH₄ diffusion selectivity and solubility selectivity for 6FDA-TrMSA (2 atm and 35 °C).

Polymer	Diffusion selectivity	Solubility selectivity
	(α) _D	(α) _S
	CO ₂ /CH ₄	CO ₂ /CH ₄
6FDA-TrMSA [this study]	17.2	3.6
6FDA-TrMCA [33]	10	4.5
6FDA-TrMPD [33]	6.1	3.6

3.5. High-pressure pure- and mixed-gas transport properties

In a first set of experiments, we determined the CO₂ and CH₄ permeability in pure-gas measurements up to 18 atm. As observed for other glassy polymers, the CO₂ and CH₄ permeability decreased with increasing pressure due to competitive sorption effects [52,53]. The CO₂ permeability dropped from 18 to 14.5 Barrer, while CH₄ permeability declined from 0.287 to 0.190 Barrer over a feed pressure range of 2 to 18 atm (**Fig. 7a**). Based on pure gas testing, the CO₂/CH₄ selectivity was ~60 at 2 atm but increased to a stable value of ~ 80 up to 18 atm (**Fig. 7b**).

In a second series of experiments, the gas permeation properties of 6FDA-TrMSA were evaluated with a 1:1 CO₂/CH₄ mixture at 35 °C and up to 36 atm feed pressure. Recent studies on CO₂/CH₄ *mixed-gas sorption* in glassy polyimides and cellulose triacetate demonstrated *higher* CO₂/CH₄ solubility selectivities in mixtures than obtained with pure gases obtained at the same partial gas pressure [54-56]. This positive effect on mixed-gas permeability selectivity due to competitive sorption effects is unfortunately overcome in most glassy polymers by a highly undesirable drop in mixed-gas diffusion selectivity, which leads to a net drop in CO₂/CH₄ permselectivity [54,56]. In rare cases, however, higher mixed-gas than pure-gas CO₂/CH₄ permeability selectivities have been reported where the positive effect of enhanced mixed-gas solubility selectivity dominated over the reduced mixed-gas diffusion selectivity [21,23,55,57].

In this study, the CO₂ permeability of 6FDA-TrMSA dropped when tested under gas mixture conditions (**Fig. 7a**); furthermore, the sulfonated polyimide exhibited lower mixed-gas CO₂/CH₄ selectivity than obtained for pure gases at the same partial pressures (**Fig. 7b**). This drop in mixed-gas selectivity was clearly evident by a continuous *decrease* in mixed-gas CO₂ and an *increase* in CH₄ permeability with increasing feed pressure (**Fig. 7a**). The enhanced CH₄ mixed-gas permeability was an indication of CO₂-induced plasticization; consequently, the CO₂/CH₄ mixed-gas permeability selectivity dropped significantly from ~60 to ~38 by increasing the partial CO₂ pressure from 2 to 18 atm. Hence, although the –SO₃H functionalization tightened the polyimide matrix by hydrogen bonding and improved the diffusion selectivity of the 6FDA-TrMSA polyimide under ideal pure-gas conditions, it could not prevent the CO₂-induced polymer plasticization.

Fig. 7. (a) CO₂ and CH₄ pure- and mixed-gas permeability vs. gas partial pressure of 6FDA-TrMSA at 35 °C. (b) Pure- and mixed-gas CO₂/CH₄ selectivity of 6FDA-TrMSA vs. CO₂ partial pressure.

From a mixed-gas performance perspective, at ~20 atm total pressure, 6FDA-TrMSA showed an equimolar CO₂/CH₄ mixed-gas selectivity of 55, which was ~twofold higher than that of cellulose triacetate, the state-of-the-art polymer used for membrane-based natural gas sweetening

[58], and 1.4 times that of the carboxyl-functionalized polyimide counterpart. However, the –COOH-functionalized polyimide (6FDA-TrMCA) presented a superior combination of permeability vs. permselectivity, with performance located closer to the 2008 pure- [59] and 2018 mixed-gas [11] trade-off curves than 6FDA-TrMSA, as shown in **Fig. 8**.

Fig. 8. Pure- (at 2 atm – open symbols) and mixed-gas (~10 atm partial CO₂ pressure – closed symbols) CO₂/CH₄ selectivity vs. CO₂ permeability of 6FDA-TrMSA at 35 °C relative to 2008 pure- [59] and 2018 mixed-gas CO₂/CH₄ upper bounds (valid for ~10 atm partial CO₂ pressure at 35 °C) [11]. Mixed-gas performance of a commercial membrane polymer (e.g., cellulose triacetate [58]) is included for comparison.

4. Conclusions

A sulfonic-acid-functionalized polyimide was synthesized by a high-temperature one-step polycondensation reaction of 6FDA and TrMSA. The 6FDA-TrMSA polyimide properties were compared to the carboxylic acid- (6FDA-TrMCA) and the non-functionalized (6FDA-TrMPD) analogue polyimides. Incorporation of the highly polar –SO₃H group promoted charge transfer

complex formation and increased hydrogen bonding interactions, which led to significantly tighter chain packing (as demonstrated by lower BET surface area and fractional free volume), smaller chain *d*-spacing, and enhanced ideal gas-pair selectivity with undesirable decrease in gas permeability. The –SO₃H-substituted 6FDA-TrMSA polyimide presented a notable pure-gas CO₂ diffusion selectivity of 17.2 at 2 atm and 35 °C. 6FDA-TrMSA suffered from CO₂-induced plasticization under mixed-gas conditions, as evidenced by enhanced CH₄ permeability and continuous loss in CO₂/CH₄ selectivity with increased feed pressure. However, at ~20 atm total pressure, it still maintained an excellent mixed-gas CO₂/CH₄ selectivity of 55, which is twofold higher than that of cellulose triacetate, which is the state-of-the-art membrane material used for industrial natural gas separation.

Declaration of competing interest

The authors declare no competing financial interests.

CRediT authorship contribution statement

Mahmoud A. Abdulhamid: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. **Giuseppe Genduso:** Methodology, Data curation, Visualization, Writing - review & editing. **Xiaohua Ma:** Data curation. **Ingo Pinnau:** Conceptualization, Resources, Methodology, Writing - review & editing, Visualization, Supervision, Funding acquisition, Project administration.

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Appendix A. Supplementary data

Supplementary data to this article can be found at <https://doi.org/10.1016/--->.

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