Bi-Functionalized Intrinsically Microporous Polyimides with Simultaneously Enhanced Gas Permeability and Selectivity

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Two novel intrinsically microporous co-polyimides, synthesized by condensation reaction of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5'-diamino-6,6'-diol (SBIDA) and 3,5-diaminobenzoic acid (DABA) with diamine ratios of 80-20 (Co-80/20) and 50-50 (Co-50/50) are reported. Unexpectedly, the Co-80/20 not only demonstrated higher microporosity ($300 \text{ m}^2/\text{g}$) than the PIM-6FDA-OH homopolymer ($190 \text{ m}^2/\text{g}$), but exhibited simultaneously enhanced CO_2 permeability (from 119 to 171 Barrer) and CO_2/CH_4 selectivity (from 35 to 41) after thermal annealing at 250°C . This higher permeability originated from enhanced diffusivity (D_{CO_2}) and the higher selectivity resulted from its increased diffusion selectivity ($D_{\text{CO}_2}/D_{\text{CH}_4}$). After crosslinking at 300°C , the Co-80/20 exhibited an even higher CO_2 permeability (261 Barrer) and almost unchanged CO_2/CH_4 selectivity.

Introduction

Polymer membranes are applied in a variety of industrial applications, such as hydrogen recovery in ammonia plants, on-site nitrogen generation from air, and natural gas sweetening, etc.^[1-2] Currently, only around ten polymers are used in 90% of the membrane-based gas separation market.^[3] Highly efficient membranes are especially demanding for further cost-effectiveness. However, the gas permeation properties of polymer membranes are typically restricted to a permeability/selectivity trade-off, first proposed by Robeson, and later theoretically analyzed by Freeman; that is, polymers with high permeability exhibit low selectivity and vice versa.^[4-6] Rational molecular design is an efficient way to improve the gas transport performance of advanced polymer membranes. The concept of introducing micropores ($< 20 \text{ \AA}$) or ultramicropores ($< 7 \text{ \AA}$) into rigid polymer structures by incorporation of bulky sites of contortion to form solution-processable ladder polymers of intrinsic microporosity (PIM) was first reported by Budd's and McKeown's groups in 2004.^[7,8] The corresponding PIM-1 demonstrated several orders higher permeability combined with modest selectivity as compared with conventional polymers.^[9] Thereafter, extensive investigations were performed on pristine and modified PIM-1 as well as structurally novel PIMs.^[10-17] Significant progress in the development of high-performance PIMs has been achieved for triptycene- and Tröger's base-based ladder PIMs, as their performance defines the 2015 upper bounds for O_2/N_2 , H_2/N_2 and H_2/CH_4 .^[17]

The introduction of intrinsic microporosity was successfully extended to polyimides by incorporating various contortion sites (e.g., spirobisindane, ethanoanthrance, spirobifluorene, triptycene and Tröger's base) to dianhydride or diamine building blocks. Some recently designed PIM-PIs exhibited extraordinary gas separation performance and reached the 2015 upper bound for several gas pairs.^[18-23] In addition, *o*-hydroxy-functionalized spirobisindane- and spirobifluorene-based PIM-PIs were designed to combine the properties of highly permeable PIMs and highly selective hydroxy-containing polyimides.^[24,25] Such hydroxy-

functionalized PIM-PIs demonstrated high CO₂/CH₄ selectivity (from 29 to 42) and CO₂ permeability about 10-25 fold higher than that of commercial membrane materials such as cellulose acetate.

Co-polyimides functionalized with carboxylic acid groups exhibit a good combination of permeability and selectivity and have shown advantages against physical aging and plasticization under aggressive high-pressure natural gas feed after solid-state crosslinking.^[26-33] Koros' group reported copolymers made from 6FDA, DABA and benzene-1,3-diamine or 2,4,6-trimethylbenzene-1,3-diamine. After crosslinking with different glycols at medium temperature (~ 200 °C), the resulting polymers exhibited enhanced permeability and slightly increased selectivity, combined with a remarkable plasticization resistance.^[31,32] In this study, we report for the first time bifunctional intrinsically microporous co-polyimides containing both OH and COOH groups. The structures of the polymers and their synthetic procedure are shown in **Figure 1**.

<Figure 1>

Results and Discussion

The PIM homopolymers and copolymers were synthesized by condensation reaction of 6FDA, SBIDA^[24] and DABA in *m*-cresol with catalytic amount of isoquinoline at 180 °C for several hours. The detailed synthesis and characterization of the homopolymers and copolymers are shown in the supporting information. By changing the diamine ratio, pure PIM-6FDA-OH, Co-80/20 (SBIDA to DABA ratio of 80/20), Co-50/50 (SBIDA to DABA ratio of 50/50), and pure 6FDA-DABA were obtained. The copolymer structures and the monomer ratio were confirmed and identified by NMR as shown in **Figure 1**, as evidenced by a clear peak of the COOH group at 13.6 ppm and OH group at 9.6 ppm. The physical properties of the

polyimides are shown in **Table 1**. Information about the densities of PIM-6FDA-OH, Co-80/20 and Co-50/50 before and after heat-treatment is provided in **Table S1**.

<Table 1>

All polymers exhibited excellent thermal stability as shown in **Figure 2**. The online mass spectroscopy (MS) of the Co-80/20 polyimide was very similar to that of PIM-6FDA-OH,^[24] characterized by a CO₂ and H₂O peak around 430 to 510 °C, respectively (**Figure 1a**). The decomposition of the Co-50/50 polyimide was more complex due to multi-decomposition stages. It is noteworthy that ~1.5% weight loss of water, as confirmed by online MS, was observed in the TGA curve around 290 °C (**Figure 2b**). This weight loss is very close to the theoretical weight loss of 1.37%, caused by the *in-situ* solid-state esterification reaction of OH (from SBIDA) and COOH (from DABA), respectively. Importantly, unlike PIM-6FDA-OH, the Co-80/20 and Co-50/50 polyimides could not be dissolved in any solvent after treatment at 300 °C for 1 hr under N₂ atmosphere (**Table S2**), providing evidence of crosslinking. Previous work reported a self-crosslinking reaction of copolymers containing only DABA to form anhydride, which occurred at or above 330 °C for more than 20 hrs.^[29]

<Figure 2>

All polymer membranes were treated under two different conditions, that is, 250 °C annealed under vacuum for 24 hrs and 300 °C heat-treated under N₂ atmosphere for 1 hr. It is noteworthy that all polymers annealed at 250 °C under vacuum were soluble in NMP and DMF (**Table S2**).

Unexpectedly, the bi-functionalized Co-80/20 polyimide exhibited distinctly higher N₂ BET surface area compared with PIM-6FDA-OH (**Figure 2c**). The Co-80/20 polyimide

demonstrated a remarkable ~50% enhancement in the BET surface area to 300 m²/g from 190 m²/g for PIM-6FDA-OH. This may be due to the incorporation of the DABA moiety which may give rise to extra hydrogen bonding (V-shaped hydrogen bond compared with linear hydrogen bond in PIM-6FDA-OH, **Figure 2e**) in either intra- or inter-molecular chains between the COOH (from DABA) and OH group (from SBIDA), which created additional free volume. However, the Co-50/50 polyimide exhibited very low porosity, possibly due to: (i) smaller contortion center density and (ii) excessive hydrogen bonding compromising the micropore formation ability. It is noteworthy that after heat-treatment of the copolymers to 300 °C no hysteresis in the N₂ sorption isotherms of the pristine and crosslinked copolymers were observed, as shown in **Figure 2d**.

The pure-gas permeability of H₂, N₂, O₂, CH₄ and CO₂ was determined by the constant-volume/variable-pressure method and the results are summarized in **Table 2**. The 250 °C annealed PIM-6FDA-OH homopolymer demonstrated a lower CO₂ permeability (119 vs 265 Barrer) but higher CO₂/CH₄ selectivity (35 vs 29) compared with the same polymer membrane treated at 120 °C.^[24] Surprisingly, the Co-80/20 polyimide treated at 250 °C demonstrated both higher permeability *and* selectivity for several gas pairs than the PIM-6FDA-OH, e.g., the permeability of CO₂ increased over 50% from 119 to 173 Barrer and the selectivity of CO₂/CH₄ was enhanced from 35 to 42. This performance is an improvement compared to previously reported DABA-containing polyimides such as 6FDA-DAM:DABA (3:2) treated at 180 °C for 24 hrs (P_{CO2} = 144 Barrer, α_{CO2/CH4} = 34.4)^[29] and 6FDA-6FpDA:DABA (2:1) (P_{CO2} = 34 Barrer, α_{CO2/CH4} = 45).^[31] The Co-50/50 polyimide exhibited about the same H₂ permeability (171 Barrer) as PIM-6FDA-OH (181 Barrer) but its H₂/CH₄ selectivity increased to 118 as compared to 53 for the homopolymer.

<Table 2>

The gas permeability results of the 300 °C crosslinked Co-80/20 and Co-50/50 polyimides are also summarized in **Table 2**. Higher temperature (300 °C) and shorter thermal treatment time (1 hr) resulted in higher permeability coupled with a slightly lower selectivity. For example, the 300 °C crosslinked Co-80/20 membrane demonstrated a further enhancement of CO₂ permeability from 173 to 261 Barrer compared with the 250 °C annealed co-polyimide, while the CO₂/CH₄ selectivity of ~40 was essentially unaffected. This result is very promising as the performance for CO₂/CH₄ separation lies very close to the 2008 Robeson upper bound (**Figure S1**). It is also notable that the copolymer crosslinked at 300 °C demonstrated very stable performance after aging for more than one month. Only 10% permeability drop was observed coupled with a slight increase in selectivity (**Table S3**).

To better understand the effect of introducing DABA on the CO₂/CH₄ gas transport properties of OH-functionalized PIM-PI copolymers, the solubility coefficients of the membranes were measured by gravimetric sorption and the diffusion coefficients were then obtained by applying the relationship: $D = P/S$. The results are summarized in **Table S4**. The Co-80/20 polyimide membrane annealed at 250 °C demonstrated both higher permeability and selectivity than the PIM-6FDA-OH homopolymer. The major contribution to the higher permeability originated from its enhanced diffusion coefficient, that is, the diffusion coefficient of CO₂ increased by 56% from 5.56×10^{-8} to 8.69×10^{-8} cm²/s, which follows the trend of increased BET surface area of the Co-80/20 polyimide. Concurrently, the increase in CO₂/CH₄ permselectivity from 35 to 42 resulted from an increase in the diffusion selectivity ($D_{\text{CO}_2}/D_{\text{CH}_4}$ increased from 9.6 to 11.3). This was probably caused by hydrogen bonding between the OH group of SBIDA and COOH group of DABA (**Figure 2e**), where V-type hydrogen bonding sites created a stronger size-sieving effect compared with the linear hydrogen bonding in PIM-6FDA-OH.

The Co-50/50 polyimide showed a lower permeability than PIM-6FDA-OH due to a decrease in diffusion coefficient from 5.56×10^{-8} to 3.87×10^{-8} cm²/s. It is suggested that

hydrogen bonding and a lower spiro-center concentration resulted in tighter polymer chain packing, and, hence, lower diffusion coefficient and permeability.

Conclusions

Two bi-functionalized PIM-PIs were obtained by co-polymerization of 6FDA with SBIDA and DABA with different monomer ratios (80/20 and 50/50). These polyimides demonstrated good solubility and high thermal stability. Compared with the PIM-6FDA-OH homopolymer, the Co-80/20 polyimide demonstrated not only larger BET surface area but also higher CO₂ permeability and CO₂/CH₄ selectivity. The higher CO₂ permeability resulted from an enhanced diffusion coefficient and the higher CO₂/CH₄ permselectivity originated from a higher diffusion selectivity (α_D). The Co-50/50 polyimide exhibited higher selectivity than the PIM-6FDA-OH due to enhanced diffusion selectivity (α_D).

Supporting Information

Details of the polymer synthesis, membrane formation procedure, polymer density, solubility of the polymers, gravimetric gas sorption, permeation data for aged 300 °C treated copolymers and the CO₂/CH₄ and H₂/CH₄ performance curves are provided in the supporting information. The Supporting Information is available from the Wiley Online Library or from the corresponding author.

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Figure 1.

Figure 1. Synthetic procedure and the structures of the homo- and co-polyimides (**PIM-6FDA-OH**, **6FDA-DABA**, **Co-80/20** and **Co-50/50**), as well as the ^1H NMR of the co-polyimides.

Figure 2.

Figure 2. a) TGA-QMS of the **Co-80/20** polyimide; b) TGA-QMS of the **Co-50/50** polyimide; both membranes were heated to 800 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C}/\text{min}$ under N_2 atmosphere; c) N_2 adsorption/desorption isotherms of 250 $^{\circ}\text{C}$ treated **PIM-6FDA-OH**, **Co-80/20**, and **Co-50/50** polyimides; d) N_2 adsorption/desorption isotherms of the pristine and 300 $^{\circ}\text{C}$ treated **Co-80/20** and **Co-50/50** co-polyimides; e) proposed structure of hydrogen bonding and crosslinking reaction in the bi-functionalized PIM-PIs.

Table 1. Basic properties of the homo and co-polyimides.

Polymers	$M_n \times 10^{-4}$ (g/mol) ^{a)}	PDI	T _d (°C) ^{c)}	S _{BET} (m ² /g)
PIM-6FDA-OH ^{b)}	8.54	1.94	380	190
Co-80/20	3.52	1.65	380	300
Co-50/50	4.00	1.68	300	9
6FDA-DABA	3.26	3.6	380	-

^{a)}Measured by GPC using THF as solvent and polystyrene as external standard. ^{b)}Data from reference 24, except BET surface area which was determined with N₂ in this study ^{c)} Onset decomposition temperature from the TGA curve.

Table 2. Permeability and ideal selectivity of the polyimides and co-polyimides heat-treated under different conditions.

Polymer	Permeability (Barrer)					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
PIM-6FDA-OH ^{a)}	181	5.5	23.8	3.4	119	33	53	4.3	35
Co-80/20 ^{a)}	285	6.8	32.6	4.1	173	42	70	4.8	42
Co-50/50 ^{a)}	171	2.85	16.3	1.45	77	60	118	5.7	53
6FDA-DABA ^{a)}	49	0.42	2.86	0.15	11.1	115	327	6.7	72
PIM-6FDA-OH ^{b)}	228	7.15	33.6	5.3	168	32	43	4.7	32
Co-80/20 ^{b)}	380	10.2	49.1	6.7	261	37	57	4.8	39
Co-50/50 ^{b)}	155	2.5	14.5	1.3	67	62	119	5.8	52

^{a)}The polymer films were heated at 250 °C under vacuum for 24 hrs. ^{b)}The polymer films were heated at 300 °C for 1 hr under nitrogen.

Table of Contents

An intrinsically microporous co-polyimide was synthesized by condensation reaction of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with 80 mol% 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5'-diamino-6,6'-diol (SBIDA) and 20 mol% 3,5-diaminobenzoic acid (DABA). Unexpectedly, the copolymer not only demonstrated higher microporosity (300 m²/g) than the 6FDA-SBIDA (PIM-6FDA-OH) homopolymer (190 m²/g), but exhibited simultaneously enhanced CO₂ permeability (from 119 to 171 Barrer) and CO₂/CH₄ selectivity (from 35 to 41) after thermal annealing at 250 °C. In-situ solid-state esterification reaction of OH (from SBIDA) and COOH (from DABA) at 300 °C resulted in crosslinking of the co-polyimide that further enhanced the CO₂ permeability to 261 Barrer with almost unchanged selectivity.