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# Gas Separation Performance of Carbon Molecular Sieve Membranes Based on 6FDA-mPDA/DABA (3:2) Polyimide\*\*

Wulin Qiu, Kuang Zhang, Fuyue Stephanie Li, Ke Zhang, and William J. Koros\*[a]

6FDA-mPDA/DABA (3:2) polyimide was synthesized and characterized for uncross-linked, thermally crosslinked, and carbon molecular sieve (CMS) membranes. The membranes were characterized with thermogravimetric analysis, FTIR spectroscopy, wide-angle X-ray diffraction, and gas permeation tests. Variations in the *d* spacing, the formation of pore structures, and changes in the pore sizes of the CMS membranes were discussed in relation to pyrolysis protocols. The uncross-linked polymer membranes showed high CO<sub>2</sub>/CH<sub>4</sub> selectivity, whereas thermally crosslinked membranes exhibited significantly improved CO<sub>2</sub> permeability and excellent CO<sub>2</sub> plasticization resist-

ance. The CMS membranes showed even higher CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity. An increase in the pyrolysis temperature resulted in CMS membranes with lower gas permeability but higher selectivity. The 550 °C pyrolyzed CMS membranes showed CO<sub>2</sub> permeability as high as 14 750 Barrer with CO<sub>2</sub>/CH<sub>4</sub> selectivity of approximately 52. Even 800 °C pyrolyzed CMS membranes still showed high CO<sub>2</sub> permeability of 2610 Barrer with high CO<sub>2</sub>/CH<sub>4</sub> selectivity of approximately 118. Both polymer membranes and the CMS membranes are very attractive in aggressive natural gas purification applications.

## Introduction

Polymer membranes are attractive for gas separation, as they are more energy efficient with smaller capital cost and physical footprint and also cause less environmental concerns than thermally driven amine absorption processors.<sup>[1–3]</sup> Among all membrane materials, polyimides, particularly the (4,4'-hexafluoroisopropylidene)diphthalic anhydride (6FDA)-based polyimides have shown good separation performance, including high productivity, high selectivity (especially excellent intrinsic CO<sub>2</sub>/CH<sub>4</sub> selectivity), thermal and chemical stability, and robust mechanical properties under high-pressure natural gas feeds.<sup>[3–9]</sup> Furthermore, 6FDA-based polyimides can be dissolved in several common solvents, which allows easy fabrication of the polymer into a working device. However, one drawback in using polyimides is that they are plasticized under aggressive feed conditions (e.g., high pressure or high CO<sub>2</sub> content), which causes selectivity loss and thus separation efficiency loss.<sup>[3,6,10,11]</sup> This disadvantage can be overcome through crosslinking of the membranes.<sup>[6,8,9,12–18]</sup> Our group first investigated ester bond crosslinking of 3,5-diaminobenzoic acid (DABA)-based polyimide membranes by using a diol to form the ester bonds among the polyimide chains.<sup>[3,6,9,15,17,19–23]</sup> More recently, we also developed a new decarboxylation-induced thermal crosslinking approach to afford a DABA-based 6FDA family of polyimides,<sup>[8,12]</sup> and subsequently, elaborated that approach to a sub-*T*<sub>g</sub> (*T*<sub>g</sub> = glass transition temperature)

thermal-crosslinking method.<sup>[12]</sup> Unexpectedly, the decarboxylation-induced thermal crosslinking mechanism caused a significant increase in permeability for different gases, including He, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, and only a slight decrease in CO<sub>2</sub>/CH<sub>4</sub> selectivity, which was presumably due to reduced segmental packing. The selectivity of the cross-linked membrane was maintained even under very aggressive CO<sub>2</sub> operating conditions beyond those without crosslinking. Plasticization resistance was demonstrated even up to 700 psia (1 psia = 6.89 kPa) for pure CO<sub>2</sub> gas or up to 1000 psia for 50/50 CO<sub>2</sub>/CH<sub>4</sub> mixed gas.<sup>[12]</sup> The sub-*T*<sub>g</sub> thermal crosslinking approach<sup>[12]</sup> was further extended to 6FDA-DAM/DABA (3:2) (DAM = 2,4-diaminomesitylene) asymmetric hollow fiber membranes, which showed no damage of the delicate skin and porous substructure.<sup>[24]</sup>

Given that gas separation performance is inherently determined by the polymer's chemical structure, we first optimized the polymer's structure and found the most efficient uncross-linked precursor. We compared the gas separation performance of several 6FDA-based polyimides with different chemical structures, and correlated the chemical structures with gas transport properties with a special focus on CO<sub>2</sub> and CH<sub>4</sub> transport and plasticization stability of the polyimides membranes relevant to natural gas purification.<sup>[25]</sup> The results indicated that 6FDA-mPDA/DABA (mPDA = *m*-phenylenediamine) is a particularly attractive polyimide for natural gas separation among the investigated polyimides, in addition to the earlier reported 6FDA-DAM/DABA copolyimide.<sup>[25]</sup> The uncross-linked 6FDA-mPDA/DABA membrane showed much higher CO<sub>2</sub>/CH<sub>4</sub> selectivity (~57) than the 6FDA-DAM/DABA membrane (~34). Moreover, the permeability of 6FDA-mPDA/DABA was comparable to that of the commercial polyimide Matrimid, which has a CO<sub>2</sub> permeability of 5–10 Barrer (1 Barrer = 7.5 ×

[a] Dr. W. Qiu, Dr. K. Zhang, F. S. Li, Dr. K. Zhang, Prof. Dr. W. J. Koros  
School of Chemical and Biomolecular Engineering  
Georgia Institute of Technology  
778 Atlantic Drive, Atlanta, GA 30332-0100 (USA)  
E-mail: wjk@chbe.gatech.edu

[\*\*] 6FDA = (4,4'-hexafluoroisopropylidene)diphthalic anhydride; mPDA = *m*-phenylenediamine; DABA = 3,5-diaminobenzoic acid.

$10^{-18} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$ ) with a  $\text{CO}_2/\text{CH}_4$  selectivity of only approximately 35,<sup>[26,27]</sup> and this is significantly higher than another commercial polyimide Torlon, which has a  $\text{CO}_2$  permeability of only  $0.7 \times 10^{-3}$ – $0.5$  Barrer with a  $\text{CO}_2/\text{CH}_4$  selectivity of approximately 52.<sup>[28,29]</sup> The gas permeation performance of copolyimides of 6FDA-mPDA/DABA can be tailored by adjusting the monomer ratio during synthesis. Most importantly, the 6FDA-mPDA/DABA family of copolyimides can also be cross-linked through the  $-\text{COOH}$  group by using ester bonds<sup>[23]</sup> or decarboxylation-based crosslinking, which is similar to the 6FDA-DAM/DABA copolymer.

Besides utilization as polyimide membranes, these materials are excellent precursors to make carbon molecular sieve (CMS) membranes with extraordinary thermal, chemical, and plasticization stability.<sup>[30]</sup> CMS membranes have super high permeability and high selectivity that can surpass the well-known upper bound limit of the separation performance of polymer membranes.<sup>[31,32]</sup> Through pyrolysis of the 6FDA-mPDA/DABA membrane to the CMS membrane, an even more enhanced separation performance is expected. Previous work on thermal crosslinking showed that as the temperature approached the decarboxylation temperature, microvoids and packing disruptions were created in the space previously occupied by  $-\text{COOH}$  groups, and moreover, the polymer chains may be locked in.<sup>[8,12]</sup> Assuming that such a microvoided cross-linked structure is maintained in the subsequent pyrolysis process, the resulting CMS membrane might have permeability that is super high relative to that of membranes derived from other polymer precursors. Clearly, a higher DABA group concentration in the polymer precursor structure (e.g., 3:2 versus 9:1) provides more decarboxylation points, that is, more cross-linkable sites, which benefits the separation performance of the CMS. The combination of the new decarboxylation-induced crosslinking and the major increase in cross-linkable site density illustrates that this family of 6FDA-based materials forms a platform with many possible directions for the development of membranes for separation.

In this manuscript, we synthesized the uncross-linked 6FDA-mPDA/DABA(3:2) copolymer, performed the decarboxylation-induced thermal crosslinking of the polymer membranes, and prepared CMS membranes. The gas transport properties of the uncross-linked membrane, the thermally cross-linked membrane, and the CMS membranes are all reported and discussed in this paper. The results demonstrated very good gas separation performance.

## Background and theory

Unlike polymer membranes, which are composed of characteristic polymer chains, CMS membranes are prepared from pyrolyzing polymer precursor membranes under controlled conditions. As a result, they consist of almost-pure carbon materials with a resulting “turbostatic” structure that comprises disordered,  $\text{sp}^2$ -hybridized, condensed carbon sheets<sup>[33]</sup> with pores formed from packing imperfections. The pore structure is described as a “slit-like” structure comprising both micropores (7–20 Å) and smaller ultra-micropores (< 7 Å), with a special bi-

nodal pore-size distribution.<sup>[34]</sup> The specific combination of micropores and ultra-micropores provides both high flux and high separation efficiency in gas separations through a molecular sieving function in the CMS membranes.

Similar to polymer membranes, the intrinsic productivity and separation capability of CMS membranes are also determined by the permeability and selectivity of a gas pair (A versus B). Permeability ( $P$ ), which has units of Barrer [Eq. (1)], is equal to the transmembrane fugacity difference ( $\Delta f$ ) and membrane thickness ( $l$ ) normalized to the penetrant diffusive flux ( $n$ ), as shown in Equation (2).

$$1 \text{ Barrer} [=] 10^{-10} \frac{\text{cm}^3 (\text{STP}) \text{ cm}}{\text{cm}^2 \text{ s cmHg}} \quad (1)$$

$$P_i = \frac{(n_i)l}{(\Delta f_i)} \quad (2)$$

The ideal selectivity between penetrants A and B is defined as the ratio of their permeability, as given in Equation (3).

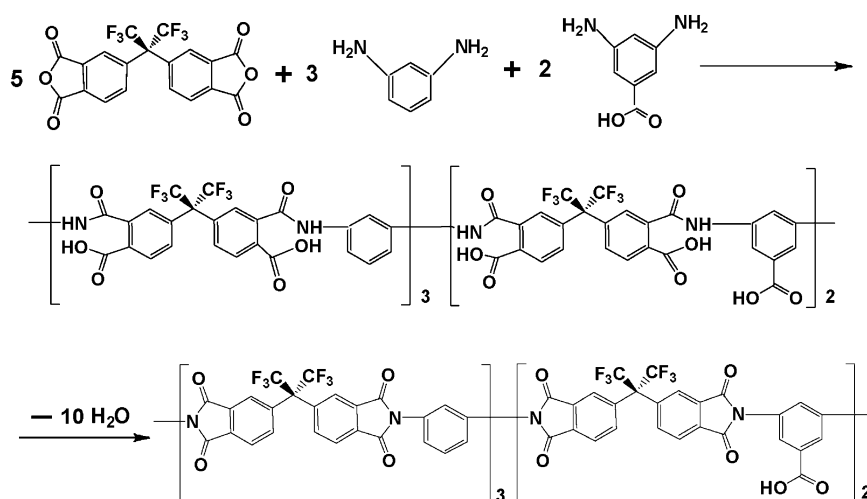
$$\alpha_{AB} = \frac{P_A}{P_B} \quad (3)$$

## Results and Discussion

As shown in Scheme 1, 6FDA-mPDA/DABA (3:2) copolyimide was synthesized. Usually, 6FDA-based polyimides can be dissolved in commonly used solvents such as tetrahydrofuran (THF) or *N*-methyl-2-pyrrolidone (NMP), which gives the polymer good processability. The introduction of the DABA backbone in the polymer provides reactive sites for crosslinking of membranes and thus yields a membrane with good  $\text{CO}_2$  plasticization resistance.<sup>[6,8,9,12,23]</sup> In addition, it is expected that the more compact mPDA backbone will provide higher  $\text{CO}_2/\text{CH}_4$  selectivity than less compact aromatic diamines owing to tighter segmental packing. The molecular weight of synthesized 6FDA-mPDA/DABA (3:2), which was measured by gel-permeation chromatography (GPC), was 208 000 ( $M_w$ ). The glass transition temperature, measured by differential scanning calorimetry (DSC), was 328 °C, and this was defined as the inflection point of the change in heat capacity during the second heating step in the DSC temperature change protocol.

### Thermal analysis of polymer membranes

In addition to ester-bond-based crosslinking of DABA-based polyimides, decarboxylation-induced thermal crosslinking was performed for the 6FDA-DAM/DABA polymers.<sup>[8,12]</sup> For the 6FDA-mPDA/DABA (3:2) polymer, two membrane samples were used to study the relationship between membrane status and thermal behavior. One membrane was dried at 180 °C for 24 h, which was uncross-linked; another was dried at 370 °C for 1 h, which was proven to cause crosslinking, as will be discussed below. Figure 1a shows the thermogravimetric analysis (TGA) profile for the membrane dried at 180 °C. A slow weight loss was observed starting at approximately 290 °C until ap-



**Scheme 1.** Synthesis of 6FDA-mPDA/DABA (3:2) copolyimide.

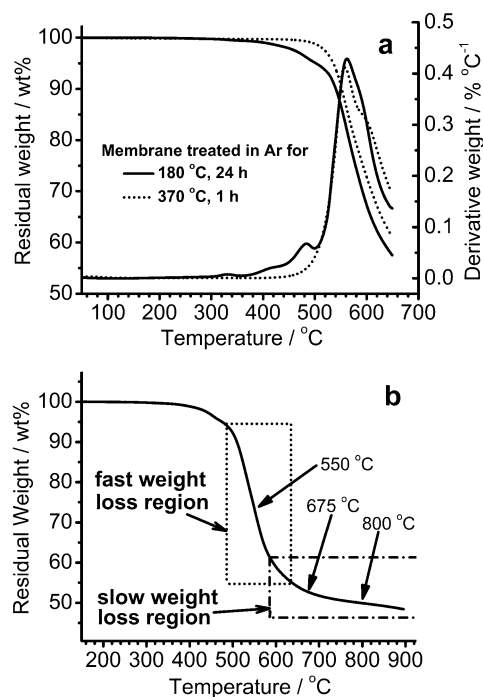
proximately 430 °C in the TGA curve, whereas a very small positive derivation peak appears at approximately 330 °C followed by the appearance of a shoulder peak at approximately 410 °C in the derivative weight curve. This small weight loss (~1.3 wt%) is a result of the removal of a trace amount of solvent remaining from the membrane preparation step and/or emission of water from the completion of polymer imidization. Given that the decarboxylation of 6FDA-DAM/DABA (3:2) was found to initiate near 300 °C,<sup>[12]</sup> this trace weight loss might also contain some CO<sub>2</sub> from decarboxylation of the pendant –COOH group in the 6FDA-mPDA/DABA (3:2) polymer. The

larger weight loss (~3.3 wt%) started between 430 and 500 °C in the TGA curve with a corresponding peak at 484 °C in the derivative weight curve. This larger weight loss is attributed to decarboxylation of the DABA moieties. The theoretical weight loss of decarboxylation is 3.5 wt% for the 6FDA-mPDA/DABA (3:2) polymer, which was calculated by assuming that two DABA species formed an anhydride, followed by complete removal of the anhydride.<sup>[8]</sup> Furthermore, degradation of the polymer backbone may initiate in this temperature range. The major fast weight loss starting at approximately 500 °C in the TGA

curve is caused by degradation of the polymer backbone, with a large derivative weight at 560 °C.

For the polymer membrane thermally treated at 370 °C, the TGA curve shows results that are quite different from those obtained with the uncross-linked sample dried at 180 °C. This sample annealed at higher temperature has only one major weight loss that is caused by degradation of the polymer backbone. The smaller peaks that are observed in the lower temperature range in the 180 °C dried membranes were not observed here. This indicates that decarboxylation of the DABA moieties occurred upon treating the membrane at 370 °C. In our previous research on studying crosslinking of DABA-based polymers, we found that neither the small weight loss in the TGA curve nor the small peak in the derivative weight curve (owing to decarboxylation) was observed in thermally cross-linked membranes.<sup>[12,35]</sup> Therefore, the TGA results in Figure 1a indicate that the 6FDA-mPDA/DABA (3:2) membrane thermally treated at 370 °C was thermally cross-linked. This was also confirmed by solubility tests. The 370 °C thermally treated membrane was insoluble even in hot NMP over one week, whereas the membrane dried at 180 °C remained uncross-linked and could be dissolved easily in THF or NMP at room temperature. This also indicates that the cross-linked membrane has good chemical resistance. The gas permeation and CO<sub>2</sub> plasticization properties of the polymer membranes will be discussed below.

For the TGA curves in Figure 1b, the 6FDA-mPDA/DABA (3:2) polymer is stable until 430 °C, at which point decarboxylation happens, and the polymer starts to decompose at approximately 500 °C. A large weight loss of approximately 50 wt% was found up to 700 °C under an argon atmosphere. Beyond 700 °C, the weight loss is very small. The maximum degradation rate was found at approximately 550 °C; the degradation rate slows clearly at approximately 670 °C, and beyond 800 °C, the degradation rate was quite slow. On the basis of the decomposition behavior, the final pyrolysis temperatures to make a CMS membrane was chosen to be 550, 675, and 800 °C. The

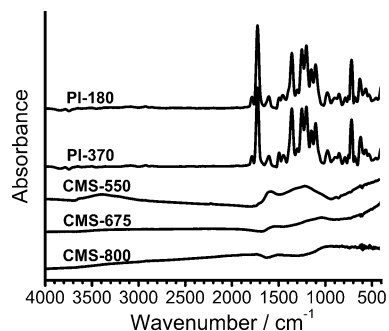


**Figure 1.** TGA analysis of polymer membranes: a) under different thermal treatment conditions and b) degradation behavior of the 180 °C dried sample over an extended temperature range.

heating protocols to prepare the CMS membranes at different pyrolysis temperatures are given in the Experimental Section.

### FTIR spectra of polymer membranes and CMS membranes

Figure 2 shows the attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectra of 6FDA-mPDA/DABA (3:2) polyimide membranes and the corresponding CMS membranes pyrolyzed at 550, 675, and 800 °C. The spectra of un-



**Figure 2.** FTIR spectra of polyimide uncross-linked (PI-180), cross-linked at 370 °C (PI-370), and CMS membranes pyrolyzed at 550, 675, and 800 °C.

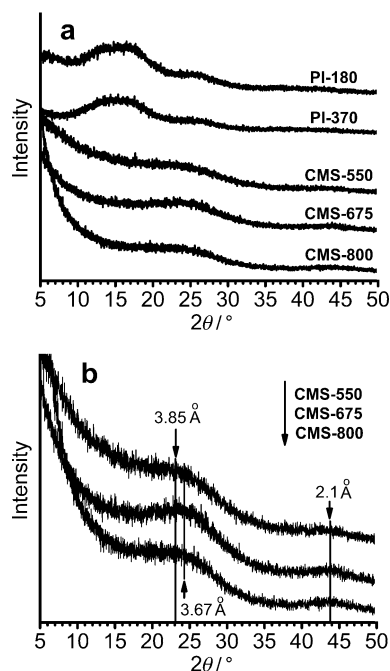
cross-linked polymer membrane PI-180 (notation: PI-*T*, PI = polyimide, *T* = drying temperature–change ok?) showed typical characteristic imide absorbance bands at 1785 (symmetric C=O stretching vibration), 1725 (asymmetric C=O stretching vibration), 720 (deformation of imide ring band of OC–N–CO), and 1357 cm<sup>−1</sup> (C–N–C stretching). No characteristic bands for the amide group at 1650 and 1550 cm<sup>−1</sup>, which come from C=O and N–H bending of the amide group, were observed. This result indicates that complete imidization of the polymer had occurred. The absorption bands at 1250, 1203, and 1150 cm<sup>−1</sup> were assigned to the C–F bond of the hexafluoroisopropylidene group on the 6FDA moiety. After the membrane was thermally cross-linked at 370 °C for 1 h, there was not a clear difference in its FTIR spectrum relative to that of PI-180. Although the TGA results showed that decarboxylation occurred for PI-370, the vibration band of the –OH group in the DABA moiety at 3200–3500 cm<sup>−1</sup><sup>[36]</sup> was very weak. The band for the carbonyl stretching of the acid group in the DABA moiety overlaps the bands for carbonyl stretching of the imide group. Therefore, the structure change caused by the decarboxylation-induced thermal crosslinking of the 6FDA-mPDA/DABA (3:2) polyimide membrane was not detected by ATR-FTIR spectroscopy.

Even though there was no clear change in the FTIR spectra before and after thermal crosslinking, the resulting CMS membranes showed FTIR spectra that were quite different from those of their precursor polymer membranes after pyrolysis. The intensities of the characteristic bands, including C=O, C–N, and aromatic C=C in the precursor polymer sample, decreased significantly and even disappeared at a higher pyrolysis temperature. The TGA results indicate that the polymer experienced a maximum degradation rate at a pyrolysis temperature of approximately 550 °C, at which temperature the degradation

of the imide ring was dominant, and this was confirmed by a decrease in the intensity of the band for the imide group in the FTIR spectrum (Figure 2). In the spectrum of the CMS-550 sample, the broad weak absorbance between 1740 and 1400 cm<sup>−1</sup> may result from an overlap of the C=O stretching vibration, skeletal vibration of the graphitic domains, and aromatic ring stretching vibrations; the absorption between 1400 and 950 cm<sup>−1</sup> was weak but still showed the presence of a –C–OH structure; and the broad weak absorption bands from 3690 to 2890 cm<sup>−1</sup> are indicative of the presence of a –OH group from –COOH and/or the –C–OH structure in the CMS-550 materials. This means that for the 6FDA-mPDA/DABA (3:2) polyimide pyrolyzed at 550 °C, the imide ring might be opened with residual –COOH and –C–OH groups in the process of forming the more graphite-like carbon structure. The absorption bands for the CMS-550 sample became weaker or disappeared for the CMS-675 and CMS-800 samples. As expected, this indicates that higher pyrolysis temperatures resulted in increased degrees of carbonization.

### Wide-angle X-ray diffraction patterns of polymer membranes and CMS membranes

The wide-angle X-ray diffraction (WAXD) patterns of the polymer and CMS membranes are shown in Figure 3, which were used to characterize the *d* spacing of the precursor polymer and CMS membranes pyrolyzed under different temperatures. Theoretically, the *d* spacing is expected to be the average spacing between the centers of the chains in the molecular materials. The average interchain distance (*d* spacing) values were calculated from Bragg's law ( $d = \lambda / 2 \sin \theta$ ) by using the maximum  $2\theta$  values of the broad peaks and the 1.54 Å wave-



**Figure 3.** WAXD patterns of polyimide uncross-linked, cross-linked at 370 °C, and CMS membranes pyrolyzed at 550, 675, and 800 °C.



length of the  $\text{CuK}\alpha$  X-ray source. Changes in the  $d$  spacing are indicators of changes in the packing density of the polymer chains and the average distance between atoms in the neighboring planes, which affect the ability of small molecules to penetrate through the glassy matrix. It is clear from Figure 3 that both the polymer membranes and the CMS membranes were amorphous. As can be seen in Figure 3a, the 6FDA-mPDA/DABA (3:2) polymer samples of both PI-180 and PI-370 showed a broad diffraction peak at approximately  $2\theta = 16^\circ$  and a small peak at approximately  $2\theta = 26^\circ$ . Usually, the average interchain distances of amorphous polymers would decrease if the polymer was thermally treated near or above its glass transition temperature owing to transition from a non-equilibrium state to an equilibrium state, which would result in increased chain packing density.<sup>[37]</sup> In contrast to annealing and physical aging, the  $d$ -spacing value at  $2\theta = 16^\circ$  for the decarboxylation-induced thermally cross-linked 6FDA-DAM/DABA (3:2) polymer membrane studied earlier increased, which indicated a larger free volume within the thermally cross-linked membrane.<sup>[12]</sup> However, Figure 3a shows that for 6FDA-mPDA/DABA (3:2), the change in the value of the  $d$  spacing at  $2\theta = 16^\circ$  is small between the uncross-linked membrane of PI-180 and the thermally cross-linked membrane of PI-370. However, as will be discussed below, the gas permeation results show that the thermally cross-linked membrane has higher free volume.

After pyrolysis, the peak near  $2\theta = 16^\circ$  disappeared in the CMS samples. As can be seen in Figure 3b, a broad peak was observed at approximately  $2\theta = 24^\circ$  for the CMS membranes. The  $d$ -spacing values were 3.85 (for CMS-550), 3.77 (for CMS-675), and 3.67 Å (for CMS-800), which are in agreement with the  $d$  spacing for a polymer char that can vary from 5 to 3.35 Å depending on the extent of carbonization and atomic organization.<sup>[38]</sup> The average interlayer distance for a perfect graphite crystal is 3.35 Å.<sup>[38]</sup> These results indicate that the average  $d$ -spacing values decrease with increasing pyrolysis temperatures; thus, the CMS membrane pyrolyzed at higher temperature has lower free volume. Furthermore, a small broad peak at approximately  $44^\circ$  with a  $d$  spacing of 2.1 Å was observed, which demonstrates the (110) plane of carbon-carbon spacing on graphitic planes.<sup>[38]</sup> The intensity of this peak is stronger at higher pyrolysis temperatures, and this is indicative of a more orderly packed structure of CMS membranes at higher pyrolysis temperatures. These results indicate that the CMS membranes have a conjugated aromatic graphite structure, and the CMS structure becomes more ordered with a high selectivity.

### Gas permeation properties of polymer membranes

The gas permeability of the polymer membranes was tested in the sequence of He,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ . The purity of the

feed gas was  $>99.999\%$ . Table 1 summarizes the permeability of the pure gases measured under 100 psia at  $35^\circ\text{C}$ , and the ideal selectivities are listed in Table 2. Note that the polymer membrane dried at  $180^\circ\text{C}$  remained uncross-linked, whereas

**Table 1.** Gas permeability of polymer membranes thermally treated under different conditions at 100 psia and  $35^\circ\text{C}$ .

Conditions	He	Gas permeability [Barrer]			
		$\text{O}_2$	$\text{N}_2$	$\text{CH}_4$	$\text{CO}_2$
$180^\circ\text{C}$ , 24 h (uncross-linked)	42.74	2.51	0.40	0.16	9.14
$370^\circ\text{C}$ , 1 h (cross-linked)	100.88	7.92	1.40	0.51	26.80

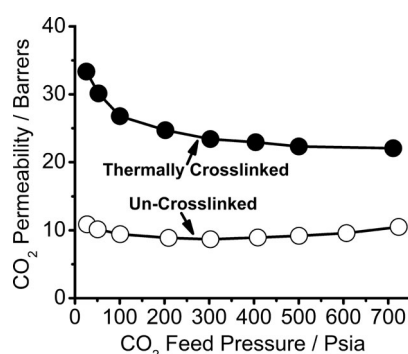
**Table 2.** Gas selectivities of membranes thermally treated under different conditions at 100 psia and  $35^\circ\text{C}$ .

Conditions	He/ $\text{CH}_4$	He/ $\text{N}_2$	$\text{O}_2/\text{N}_2$	Gas selectivity			
				$\text{O}_2/\text{CH}_4$	$\text{CO}_2/\text{CH}_4$	$\text{CO}_2/\text{N}_2$	$\text{N}_2/\text{CH}_4$
$180^\circ\text{C}$ , 24 h (uncross-linked)	267.1	106.9	6.3	15.7	57.1	22.9	2.5
$370^\circ\text{C}$ , 1 h (cross-linked)	197.8	72.1	5.7	15.5	52.5	19.1	2.7

the membrane thermally treated at  $370^\circ\text{C}$  was cross-linked. Table 1 shows that the uncross-linked 6FDA-mPDA/DABA (3:2) membrane had lower permeability to all measured gases; however, the  $\text{CO}_2$  permeability was still comparable to that of the commercial polyimide membrane Matrimid, which showed a  $\text{CO}_2$  permeability of 5–10 Barrer,<sup>[26,27]</sup> and it was still much higher than that of another commercial polyimide membrane Torlon, which has a  $\text{CO}_2$  permeability of  $\leq 0.5$  Barrer.<sup>[28,29]</sup> As can be seen in Table 2, the 6FDA-mPDA/DABA (3:2) membrane showed a  $\text{CO}_2/\text{CH}_4$  selectivity of 57, which is comparable to that of the Torlon membrane of approximately 52<sup>[28,29]</sup> and higher than that of the Matrimid membrane of approximately 35<sup>[26,27]</sup> and the uncross-linked 6FDA-DAM/DABA (3:2) membrane of approximately 34.<sup>[12]</sup> The permeability of all measured gases increased in the cross-linked 6FDA-mPDA/DABA (3:2) membrane, as shown in Table 1. Consistent with an increased  $d$ -spacing value results in the cross-linked membrane, the increase in the permeability also reflects a more open structured matrix after crosslinking. This trend in the values of the permeability is different from the general observations for rubbery polymers, for which the permeability usually decreases in cross-linked polymer membranes.<sup>[39]</sup> Crosslinking of other DABA-containing polyimides with diols generally led to an increase in the permeability for the dense film,<sup>[6,22,23]</sup> including the thermally cross-linked 6FDA-DAM/DABA membrane.<sup>[8,12]</sup> The selectivities of the measured gas pairs decreased or remained almost unchanged in the cross-linked samples, as can be seen in Table 2. In comparison with membranes annealed at  $180^\circ\text{C}$ , the  $\text{CO}_2$  permeability of the membrane thermally cross-linked at  $370^\circ\text{C}$  increased from 9.14 to 26.80 Barrer, whereas the  $\text{CO}_2/\text{CH}_4$  selectivity decreased only slightly from 57.1 to 52.5. Under the same annealing and thermal-crosslink-

ing conditions, the 6FDA-DAM/DABA (3:2) membrane showed a  $\text{CO}_2$  permeability that increased from 144 to 485 Barrer, with  $\text{CO}_2/\text{CH}_4$  selectivity decreasing from 34.4 to 26.8. Although crosslinking usually improves selectivity and plasticization resistance of a polymer membrane at the expense of productivity, in the rigid backbone polymers studied, permeability can rise as a result of packing disruptions during crosslinking. There are small molecules released during the decarboxylation-induced thermal crosslinking treatment, and this results in a change in the polymer structure and also produces microvoids, which thus cause an increase in the free volume. Systemic investigations of this feature were performed with the 6FDA-DAM/DABA (3:2) membrane.<sup>[12]</sup> Given that the monomer price of mPDA is approximately 17 times lower in cost than that of DAM,<sup>[40]</sup> 6FDA-mPDA/DABA is clearly an important polyimide with potential applications in natural gas separation.

In addition to acceptable  $\text{CO}_2$  permeability and good  $\text{CO}_2/\text{CH}_4$  selectivity, the cross-linked 6FDA-mPDA/DABA (3:2) membrane exhibited enhanced plasticization resistance for high  $\text{CO}_2$  feed pressures. As can be seen in Figure 4, the uncross-linked membrane showed a noticeable plasticization response near 300 psia, which was reflected by an upswing in  $\text{CO}_2$  permeability, whereas the  $\text{CO}_2$  permeability of the cross-linked membrane decreased monotonically with increasing feed pressure. Although the uncross-linked membrane showed a higher plasticization pressure than the other polyimides as a result of hydrogen bonds among the DABA groups, the cross-linked membrane gained good plasticization resistance. The excellent plasticization-resistant performance is apparent throughout the feed range that our equipment could test up to 700 psia. Furthermore, the thermally cross-linked membrane showed a higher  $\text{CO}_2$  permeability than the uncross-linked material. Even higher  $\text{CO}_2$  permeability is expected at higher crosslinking temperatures,<sup>[12]</sup> however, for use as asymmetric structures, lower crosslinking temperatures are more desirable to maintain the delicate porous structure.



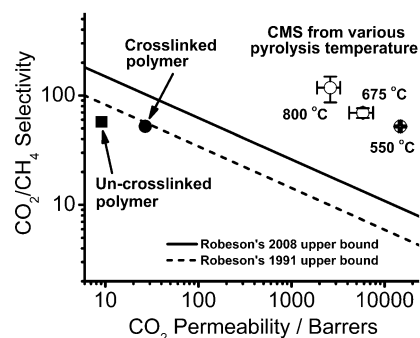
**Figure 4.**  $\text{CO}_2$  permeability as a function of feed pressure for uncross-linked and thermally cross-linked polymer membranes.

#### Gas permeation properties of carbon molecular sieve membranes

CMS membranes have excellent separation properties that often exceed the upper bound limit of the separation performance of polymer membranes. CMS membranes are formed

by pyrolysis of precursor polymer membranes at high temperatures, in inert purge gas, or under vacuum conditions. The final separation performance of a CMS membrane is determined by the following key parameters: the nature of the polymer precursor, pyrolysis temperature, heating rate, thermal soak time, and pyrolysis atmosphere. Herein, only pyrolysis temperature was investigated, and the CMS membranes were made at 550, 675, and 800 °C under a controlled flow of high-purity argon (> 99.99%) by using the heating protocols described in the Experimental Section.

The  $\text{CO}_2$  permeability and  $\text{CO}_2/\text{CH}_4$  selectivity were tested by using pure  $\text{CO}_2$  and  $\text{CH}_4$ ; the results are plotted against the experimental upper bound limit,<sup>[31,32]</sup> as shown in Figure 5. As seen in Figure 5, the separation performance of the CMS



**Figure 5.** Separation properties of  $\text{CO}_2/\text{CH}_4$  for the 6FDA-mPDA/DABA (3:2) based polymer and CMS membranes.

membranes was significantly higher than that of the precursor polymer membrane, including both uncross-linked and cross-linked, and exceeded the polymer upper bound limit for  $\text{CO}_2/\text{CH}_4$  separation, although the performance of the cross-linked polymer membrane was also at the Robeson's 1991 upper bound limit. The CMS membranes from a lower pyrolysis temperature such as 550 °C showed much higher  $\text{CO}_2$  permeability but lower  $\text{CO}_2/\text{CH}_4$  selectivity. An increase in pyrolysis temperature led to higher  $\text{CO}_2/\text{CH}_4$  selectivity but lower  $\text{CO}_2$  permeability. However, it is noted that even for the CMS membrane made at 800 °C, the  $\text{CO}_2$  permeability was still significantly higher than that of the precursor polymer membranes. The CMS membrane from 800 °C showed a  $\text{CO}_2$  permeability of  $(2610 \pm 730)$  Barrer with a  $\text{CO}_2/\text{CH}_4$  selectivity of  $118 \pm 31$ . The CMS membrane pyrolyzed at 550 °C showed a  $\text{CO}_2$  permeability of  $(14\,750 \pm 610)$  Barrer with a  $\text{CO}_2/\text{CH}_4$  selectivity of approximately  $52 \pm 2$ . Both the  $\text{CO}_2$  permeability and  $\text{CO}_2/\text{CH}_4$  selectivity of the CMS membranes from 550 to 800 °C were attractive; however, as expected, the selectivity of the 800 °C pyrolyzed sample was the highest.

Separation performance of CMS from other polyimides is summarized in Table 3<sup>[41,42]</sup> for comparison. These results confirmed that the CMS membranes from the 6FDA-mPDA/DABA (3:2) polymer showed higher permeability than most CMSs from other reported polymers.

It is reasonable to question why CMS membranes from the 6FDA-mPDA/DABA (3:2) polymer have such high  $\text{CO}_2$  permea-

**Table 3.** Gas separation performance of CMS membranes derived from other polyimide precursors at 35 °C.

Polyimide precursor	Pyrolysis temperature [°C]	CO <sub>2</sub> permeability [Barrer]	CO <sub>2</sub> /CH <sub>4</sub> selectivity	Testing pressure [psia]	Reference
Matrimid	800	300.9	67.1	–	[41]
Matrimid	800	66	209	100	[42]
Matrimid	550	1264	65	100	[42]
6FDA/BPDA-DAM	800	94	122	100	[42]
6FDA/BPDA-DAM	550	4864	54	100	[42]
Torlon	800	43.1	18.3	–	[41]
P84	800	144.2	67.1	–	[41]

bility. Apparently, the high CO<sub>2</sub> permeability results from the DABA moieties in the precursor polymer. As the temperature approaches the decarboxylation temperature, microvoids and packing disruptions are created in the space previously occupied by –COOH groups, and moreover, the polymer chains may be locked in.<sup>[8,12]</sup> Such a microvoided cross-linked structure may be maintained in the subsequent pyrolysis process, which would thereby prevent the formation of an ordered graphite-like region, but this forms disordered structures (the broad peak at approximately 44° with a *d* spacing of 2.1 Å was very weak in Figure 3). Increasing gas permeability by the DABA moieties was also observed in CMS membranes from BTDA-ODA/DABA polymers (BTDA = benzophenone tetracarboxylic dianhydride, ODA = 4,4'-oxydianiline).<sup>[43]</sup> The CO<sub>2</sub> permeability was increased from 1674 to 2863 Barrer for the 700 °C pyrolyzed CMS membranes if the precursor BTDA-ODA/DABA (8:2) polymer was replaced by BTDA-ODA/DABA (5:5).<sup>[43]</sup> Clearly, these results indicate that CMS membranes made from 6FDA-mPDA/DABA (3:2) are especially attractive in natural gas purification to separate CO<sub>2</sub> and CH<sub>4</sub>, and DABA-based polymers might render high permeability in general to the resulting CMS membranes. The separations of other gas pairs including paraffins/olefins by using the 6FDA-mPDA/DABA-derived CMS membranes are also of potential interest, and we are planning to explore these systems in the future.

It is not easy to get perfectly flat CMS membranes from dense films of polymers, especially if they are pyrolyzed under an inert gas purge and/or under higher pyrolysis temperatures. Intrinsic stress or a unique polymer chain orientation might result in a “crinkled or curled” configuration at the periphery of a CMS membrane; however, the center area is flat, smooth, and homogeneous. CMS membranes are usually somewhat brittle, which makes it difficult to mask and/or to test for CMS membranes made from most polymers we investigated. Thus, a flat CMS membrane is necessary to be masked. Fortunately, we found that even the periphery “crinkled or curled” 6FDA-mPDA/DABA (3:2) based CMS membranes could still be masked and tested without failing, and this indicates that these CMS membranes have good intrinsic mechanical properties. These intrinsic mechanical properties make it easy to assemble CMS hollow fibers modules for large-scale separation applications.

The above separation results also indicate that a CMS membrane pyrolyzed at a lower temperature has a larger pore size than a membrane pyrolyzed at a higher temperature. There is

a competition between the creation of pores and the reduction of ultra-micropore size (or densification) of a CMS membrane during pyrolysis process. As shown in Figure 1b, the pyrolysis temperature can be considered in two regions: a fast weight-loss region and a slow weight-loss region. With a pyrolysis temperature in the fast weight-loss region, the creation

of pores is dominant, whereas in the slow weight-loss region, the reduction of pore size is dominant. At a lower pyrolysis temperature, which is in the fast weight-loss region, the polyimide experienced a sharp weight loss with the evolution of a large volume of gas. For the PMDA-ODA (PMDA = pyromellitic dianhydride) polymer, CO and CO<sub>2</sub> were detected from 500 to 600 °C as a result of imide ring cleavage, and CH<sub>4</sub> was generated at approximately 600–700 °C, although the quantity was very small.<sup>[44]</sup> For 6FDA-DAM/DABA (3:2), CO<sub>2</sub> was detected starting at approximately 400 °C, and CF<sub>3</sub> was found between 400 and 550 °C.<sup>[12]</sup> Degradation of the polymer chain and evolution of a large volume of gas resulted in a significant structure transition and pore formation. In the higher pyrolysis temperature region, the weight loss became slower, which was due to the evolution of a smaller volume of molecular gases such as H<sub>2</sub>.<sup>[44]</sup> Within this higher pyrolysis temperature range, the carbonized CMS membranes were transformed into a more graphite-like structure, as observed from the WAXD results, with continuous pore shrinkage and densification of the porous CMS membrane through structure adjustment. Therefore, CMS membranes pyrolyzed at temperatures in the fast weight-loss region (lower pyrolysis temperatures) have higher permeability with lower selectivity; in contrast, a higher pyrolysis temperature usually results in CMS membranes with lower permeability but higher selectivity. Therefore, the pyrolysis temperatures can be optimized based on different separation applications.

## Conclusions

6FDA-mPDA/DABA (3:2) polyimide is a very attractive candidate for gas separation, and it can be used as an uncross-linked polymer membrane, cross-linked polymer membrane, or CMS membrane, on the basis of the application requirement. The polymer membranes showed higher CO<sub>2</sub>/CH<sub>4</sub> selectivity than commercial polyimides, in addition to comparable CO<sub>2</sub> permeability. The thermally cross-linked polymer membrane showed improved permeability with good CO<sub>2</sub> plasticization resistance. The resulting CMS membranes showed very high CO<sub>2</sub> permeability and high CO<sub>2</sub>/CH<sub>4</sub> selectivity, and the separation performance exceeded the experimental upper bound limit for all CMS membranes within experimental pyrolysis conditions. For a given precursor polymer, the pyrolysis temperature influenced the *d* spacing, pore structure, and pore sizes of the CMS membranes. Higher pyrolysis temperature yielded



a CMS membrane with higher selectivity but lower permeability, whereas lower pyrolysis temperature delivered membranes with higher permeability. Finally, DABA moieties in the precursor polymers, through which pre-crosslinking can occur in the polymer, improved the permeability of the resulting CMS membranes.

## Experimental Section

### Materials

The (4,4'-hexafluoroisopropylidene)diphthalic anhydride (6FDA), *m*-phenylenediamine (mPDA), and 3,5-diaminobenzoic acid (DABA) monomers were purchased from Aldrich. The monomers were purified through sublimation or recrystallization and stored separately under high vacuum before synthesis. Solvents and reagents, 1-methyl-2-pyrrolidinone (NMP), acetic anhydride (AcAn), and  $\beta$ -picoline were dehydrated with molecular sieves before use to remove any water.

### Polymer synthesis

The 6FDA-mPDA/DABA (3:2) copolyimide was synthesized by the well-known condensation of the dianhydride with diamine, as shown in Scheme 1. The first step produced a high-molecular-weight polyamic acid (PAA) at low temperature ( $\sim 5^\circ\text{C}$ ) followed by a second ring-closing imidization step. In the first step, stoichiometric amounts of monomers were agitated and treated with a 20 wt% NMP solution under  $\text{N}_2$  purge for 24 h to produce the PAA solution. Chemical imidization was achieved in the presence of  $\beta$ -picoline and acetic anhydride at ambient temperature for 24 h under  $\text{N}_2$  purge, and the resulting polyimide (PI) was precipitated, washed with methanol, and dried at  $210^\circ\text{C}$  under vacuum for 24 h. The FTIR and TGA results of the obtained polyimide showed essentially complete imidization.

### Polymer-dense film formation

The polymer dense film was cast on a Teflon-coated glass plate from a THF solution inside a glove bag under a controlled atmosphere to achieve slow evaporation of the solvents. A casting knife with a 12 mil clearance was used for film casting, and after evaporation of the THF solvent, the membrane was removed from the plate and dried at  $180^\circ\text{C}$  for 24 h under vacuum.

### Crosslinking of polymer-dense film and CMS dense-film formation

A Thermcraft three-zone split-tube furnace was outfitted with internal thermocouples connected to a multichannel temperature controller; an argon purge was controlled with a mass flow controller, and the oxygen concentration inside the tube was monitored by an oxygen analyzer ( $10^{-20}$  ppm to 100%  $\text{O}_2$ ) during the thermal treatment process. Polymer membranes were put on a quartz plate with equally spaced channels and loaded inside a quartz tube, and then the tube was placed in the furnace. Argon was purged at  $200\text{ mL min}^{-1}$  until the system reached steady state prior to thermal treatment, and the purge was continued during the thermal treatment and pyrolysis process.

Thermal crosslinking of the polymer membrane was performed at  $370^\circ\text{C}$ . The procedure comprised heating from  $50^\circ\text{C}$  at  $10\text{ K min}^{-1}$  to  $320^\circ\text{C}$ , followed by heating at  $1\text{ K min}^{-1}$  to the  $370^\circ\text{C}$ , and

dwelling for 1 h; the membrane was allowed to cool to room temperature naturally. The cross-linked membranes were removed from the furnace for masking.

The formation of the CMS membranes was performed at the desired temperatures ( $T_{\text{des}}$ ) of 550, 675, and  $800^\circ\text{C}$  by using a heating protocol that involved heating from 50 to  $250^\circ\text{C}$  at  $10\text{ K min}^{-1}$ , then to a temperature of " $T_{\text{des}}-15^\circ\text{C}$ " at  $3\text{ K min}^{-1}$ , followed to  $T_{\text{des}}$  at  $0.25\text{ K min}^{-1}$ , and finally soaked at  $T_{\text{des}}$  for 2 h. The furnace was then cooled down naturally with continuous argon purge below  $50^\circ\text{C}$  before unloading the resulting CMS membranes. The resulting CMS membranes were denoted as CMS-550, CMS-675, and CMS-800, respectively.

### Characterization

The molecular weight of the polymer was determined by GPC by using a Waters 2410 Separations Module equipped with Stryagel HR 4,3 and 1 columns. The detection was performed by a Waters 410 refractive index detector. The samples were dissolved in THF at 1 wt% concentration. Thermogravimetric analysis (TGA) and derivative weight data were recorded with a TA Q-5000 analyzer at a heating rate of  $10\text{ K min}^{-1}$  under a nitrogen atmosphere by using approximately 10 mg of the sample. Differential scanning calorimetry (DSC) was performed with a TA Q-200 at a heating rate of  $10\text{ K min}^{-1}$  under a nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) was also measured with a PAnalytical X'pert Pro diffractometer operating with  $\text{CuK}_\alpha$  radiation at a wavelength of  $1.54\text{ \AA}$  in a  $2\theta$  range from  $5$  to  $45^\circ$  to consider segmental packing and to verify the lack of crystallinity. Polymer membranes of uncross-linked, cross-linked, and CMS membranes were used for gas permeation tests. The membrane was masked by using impermeable aluminum tape to define the permeable area, and epoxy was applied at the interface of the tape and the open area of the membrane to insure against bypassing the membrane. The masked membranes were loaded into a permeation cell and assembled to a permeation system for testing. We usually chose perfect CMS membranes without crinkling for easy masking in our experiments. The testing procedure and testing conditions of all membranes were the same as those for other polymeric membranes reported earlier in our previous work.<sup>[12]</sup>

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