6FDA-DETDA: DABE polyimide-derived carbon molecular sieve hollow fiber membranes: Circumventing unusual aging phenomena

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A R T I C L E   I N F O

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Crosslinking
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A B S T R A C T

Transport properties are reported for asymmetric carbon molecular sieve (CMS) hollow fiber membranes based on polyimide precursors derived from a butanol esterified diamino benzoic acid (DABA) based polyimide, 6FDA-DETDA:DABE. Precursor fiber pretreatment with 10\% Ethenyl(trimethoxy)silane \(\text{[vinyltrimethoxysilane (VTMS)]}\) solution in hexane followed by pyrolysis at 550 °C in ultra-high purity argon created asymmetric CMS fibers with \(\text{CO}_2\) permeance above 1000 GPU and \(\text{CO}_2/\text{CH}_4\) selectivities > 25. Storage of the as-made modules for 72 days in 7 bar \(\text{CO}_2\) suppressed undesirable aging typically seen under vacuum or atmospheric pressure air and provided \(\text{CO}_2\) permeance and \(\text{CO}_2/\text{CH}_4\) selectivity of 780 GPU and 48 respectively. These results are in contrast to significant losses in \(\text{CO}_2\) permeance and \(\text{CO}_2/\text{CH}_4\) selectivity for CMS created under equivalent pyrolysis conditions from non-esterified 6FDA-DETDA: DABA variant, even under \(\text{CO}_2\) storage. The 6FDA-DETDA: DABA-derived CMS results were surprising, since dense film CMS samples from the same precursors did not show the undesirable permeance and selectivity changes. Moreover, other non-DABA containing precursors in dense film and asymmetric fiber forms can be effectively stabilized under \(\text{CO}_2\) storage. Such results suggest that high residual stress in the freshly formed thin selective layers of asymmetric structures in DABA-derived CMS causes undesirable micro-scale rearrangements. In dense films and even asymmetric skins of non-DABA derived CMS membranes, evidence of such undesirable rearrangements are not apparent. DABA-derived cross-links are presumably the cause of these effects. Mono-esterification of 6FDA-DETDA: DABA to form 6FDA-DETDA: DABE controls such crosslinking-derived stresses and resultant instabilities in the CMS fibers, thereby providing stable high performance gas separation properties under \(\text{CO}_2\) storage or use in mixed gas feeds.

1. Introduction

Natural gas, an attractive fossil fuel, often contains \(\text{CO}_2\) as a contaminant at levels over 50 mol\%[1]. Such high \(\text{CO}_2\) levels can cause corrosion of pipelines and downstream equipment, thereby making \(\text{CO}_2/\text{CH}_4\) separation a high priority research topic [2]. Gas separation membrane processes [3,4] have the potential to massively reduce separation energy costs compared to conventional separation process [5]. Polymer membranes enable economical processability into hollow fiber modules with desirable morphologies and high surface area per unit volume [6]. In aggressive streams, polymeric membranes tend to swell and lose selectivity [7,8]; however, use of more rigid materials such as carbon molecular sieves can avoid this problem.

CMS materials, formed by thermal decomposition of precursor polymers produces a carbon rich material [9] comprising 0.7–2 nm "micropores" connected by slit-like "ultramicropores" smaller than 0.7 nm. Micropores provide sorption sites, while ultramicropores enable molecular sieving, thereby making CMS materials both highly permeable and highly selective, with properties above the upper-limit of polymers [10,11]. Also CMS membranes maintain their performance in adverse environments including high pressure feeds of high \(\text{CO}_2\) concentrations that would undermine typical polymer membranes performance [12,13]. Despite many advantages, challenges must be overcome to enable large scale CMS membrane technology [14,15].

Recent dense film membrane research [16,17] on 6FDA-containing cross-linkable polyimides identified 6FDA-DETDA: DABA (3:2) as an attractive polyimide precursor for hollow fiber CMS applications. Here, we report details of 6FDA-DETDA: DABA spinning of hollow fiber precursors via dry-jet/wet-quench fiber spinning as well as fabrication and morphology of the hollow fiber CMS formed under well-controlled
pyrolysis conditions. Transport properties of the hollow fiber, including surprising new phenomena related to loss in selectivity with age, are not seen in dense films formed from the same precursor polymer, are reported and analyzed here.

DABA-derived cross-links were hypothesized to be the cause of the above mentioned effects, so mono-esterification of 6FDA-DETDA: DABA to form 6FDA-DETDA: DABE was pursued to moderate crosslinking-derived stresses. Transport properties and stability under use and under CO$_2$ storage are compared for CMS fibers created from both the 6FDA-DETDA: DABA and 6FDA-DETDA: DABE precursor fibers.

2. Experimental

2.1. Materials

The 6FDA-DETDA: DABA (3:2) polymer (repeating unit shown in Fig. 1) used in this study was purchased from Akron Polymer Systems, and other chemicals for spinning dope preparation, NMP, THF, ethanol, and lithium nitrate, were purchased from Sigma Aldrich. For solvent exchange of as-spun fibers, deionized water was produced in-house, methanol, and hexane were purchased from BDH Chemicals Co. Ethynyl (trimethoxysilyl) or vinyltrimethoxysilane for the post-treatment of precursors, and 1-butanol for mono-esterification were purchased from Sigma Aldrich.

2.2. Dope preparation

Dope formation used the protocol described for our prior polyimide spinning work [18]. Either 6FDA-DETDA: DABA or 6FDA-DETDA: DABE polymer and lithium nitrate were dried in a vacuum oven for at least 12 h at 120 °C. NMP, ethanol and lithium nitrate were placed in a 1 L Gorpak® glass bottle to produce a clear solution. After adding the THF and appropriate polymer, the bottle was sealed with a Teflon® lined cap, and placed on a roller under a heat lamp (about 50 °C) until the solution became clear and homogenous (typical time was 2 weeks).

2.3. Formation of hollow fiber polymeric fibers

Asymmetric hollow fibers of 6FDA-DETDA: DABA were formed via the standard dry-jet/wet-quench fiber spinning setup identical to that of previously reported systems [18]. The spinning dope and a bore fluid comprising NMP/H$_2$O in a desired 80:20 ratio were extruded via an ISCO syringe pump after overnight degassing. The dope and bore fluid were filtered in-line between the pumps and the spinneret with 90 μm and 2 μm sintered metal filters, respectively. Thermocouples were attached to the dope pump and the spinneret. The dope (180 cm$^3$/h) and the bore fluid (at 60 cm$^3$/h) were co-extruded through an adjustable air gap into the water quench bath at 50 °C, passed over a Teflon® guide in the quench bath and collected onto a rotating take up drum. The take up drum was partially immersed in an additional water bath at room temperature to promote residual solvent removal. Once removed from the take up drum, the fibers were soaked in deionized water baths (changing water once a day) for 3 days to remove all traces of solvent, and then solvent exchanged in sequence for 20 min, 3 times, with methanol and hexane each. Fibers were dried overnight in a fume hood, in a vacuum oven for 2 h at 70 ℃, and cooled to room temperature. These hollow fibers provided the precursors to create CMS asymmetric fibers. The same procedure was followed for spinning 6FDA-DETDA: DABE polymer dope, including minor optimization adjustments in spinning parameters noted in Section 4.

2.4. Formation of CMS hollow fiber membranes

Hollow fiber CMS membranes were formed by pyrolysis of precursor fibers in a setup identical to that of previously reported systems [19]. Pyrolysis was carried out with a controlled temperature protocol under a continuous inert gas (Ultra High Purity Argon) purge at 200 cm$^3$/min (for about 8 h when oxygen meter read < 1 ppm before starting). A 3-zone tube furnace (Thermcraft, Inc., model XST-3-0-24-3C) was fitted with a multi-channel PID temperature controller (Omega Engineering, Inc., model CN1507TC) to achieve uniform temperature profile inside the quartz tube (55 mm ID × 59 mm OD, National Scientific Company, GE Type 214 Quartz). The tube was sealed with a metal flange with two silicon O-rings (MTI Corporation, model EQ-FI-60) on both ends.

Precursor fibers were placed parallel to each other on a quartz plate inside the quartz tube. After completing the pyrolysis protocol, the furnace was allowed to cool naturally to room temperature (~50 ℃) under flowing UHP argon. The resulting CMS fibers were then removed from the furnace and used for subsequent characterization.

After each pyrolysis, the quartz tube and support plate were rinsed with acetone and heated to 800 ℃ with a 120 min soak under 500 cm$^3$/min air flow to remove any residue that might affect subsequent pyrolysis runs. All the tube fittings are inspected and cleaned periodically or replaced if the fittings are difficult to clean. An oxygen meter (Rapidox 2100), calibrated after cleaning and reassembly, and was used to monitor oxygen levels (< 1 ppm) during pyrolysis cycle. Since the 6FDA-DETDA: DABA polymer undergoes cross linking reactions prior to pyrolysis, the temperature protocol for all pyrolysis trials included a cross-linking step (# 3) at 370 ℃ as shown below:

1. 50 – 250 ℃ at a ramp rate of 13.33 ℃/min
2. 250 – 370 ℃ at a ramp rate of 3.85 ℃/min
3. 60 min soak for cross-linking reaction at 370 ℃
4. 370 – 550 ℃ at a ramp rate of 3.85 ℃/min
5. 120 min soak at 550 ℃

2.5. Vinyltrimethoxysilane treatment of precursors

Ethynyl(trimethoxysilyl) or vinyltrimethoxysilane (VTMS) treatment is a useful pre-pyrolysis treatment that restricts asymmetric support morphology collapse during pyrolysis to form CMS fibers. The technique uses a sol-gel crosslinking reaction between an organic alkoxysilane and moisture, thereby coating the support structure “struts” with negligible reaction with the polymer matrix [20]. The treatment process optimization uses a hexane solution of vinyltrimethoxysilane with concentration of VTMS from 0% to 100% [21]. The preference for hexane as a non-solvent for the VTMS-hexane combination of V-treatment is due to the existing post spinning solvent exchange process for the precursor [21].

The precursor fibers are soaked in the solution for at least 12 h and then placed in a glove bag containing 100% humid air for 24 h. The fibers are then dried for 24 h in a vacuum oven at 150 ℃ to obtain V-treated fibers, with the designation 10VT to signify fibers treated with 10% VTMS solution.
2.6. Mono-esterification of 6FDA-DETDA: DABA (Acid) to 6FDA-DETDA: DABE (Ester)

The mono-esterification reaction, shown in Fig. 2, is conducted as described elsewhere [22] by reacting 6FDA-DETDA: DABA with an alcohol to produce an ester, 6FDA-DETDA: DABE at 110 °C. Mono-esterification using 1-butanol was chosen for convenience in this work to facilitate easy reactions, but other alcohols could also clearly be used for the mono-esterification.

2.7. Permeation measurements

2.7.1. Hollow fiber module construction

To test the gas permeation of hollow fibers, small lab-scale modules were constructed as described in previous work [23]. A typical precursor fiber module contained 4–5 fibers with active membrane length of 15 – 20 cm. Single fiber modules were potted in the case of CMS fibers with active membrane length of 10 – 15 cm. Single-fiber modules were tested in triplicate and/or trials repeated to assess experimental uncertainty (±10%).

2.7.2. Pure gas permeance measurement (Method 1 & 2)

In method 1, pure gas permeation measurements using a constant-pressure system were conducted in a temperature-controlled enclosure at 35 °C using pure gas feed at 2 bar. In method 2, modules were mounted in a constant-volume permeation system and tested at 35 °C and a feed pressure of 2 bar as described elsewhere [17]. Both upstream and downstream cell chambers were typically evacuated for at least 30 min, which greatly exceeded the nominal time required to degas the thin skinned asymmetric membrane. Then the upstream was pressurized with the test gas, and the pressure rise in the downstream was recorded using LabVIEW until steady state was achieved. If a different testing gas was to be applied, the whole system was evacuated again until the outgassing rate met the above criteria. The results from either Method 1 or 2 gave equivalent results. For fiber age calculation the “time zero” is at the removal of CMS from the furnace after pyrolysis. Generally, the permeation test is conducted after a day (age 1 day).

2.7.3. Mixed gas permeance measurement using constant pressure system (Method 3)

Mixed gas permeation tests were performed in a set up similar to the constant pressure pure gas test with a constant pressure of 21 bar mixed gas feed on shell side. A premixed 50 mol% CO2 and 50 mol% CH4 binary mixture was used as a feed gas. The permeate flow was measured by a bubble meter, and composition was analyzed by a gas chromatograph to calculate the selectivity. The stage cut was set to be lower than 1% to eliminate any effects of concentration polarization.

3. Characterization

3.1. Molecular weight and PDI

For the samples purchased from Akron Polymer Systems (APS), the weight average molecular weight and PDI were tested and reported by APS.

3.2. Thermo-gravimetric analysis (TGA)

Thermal stability and polymer degradation during heating were characterized using thermo-gravimetric analysis (TGA: Q500, TA Instrument) under inert atmosphere (UHP Argon) at a heating rate of 10 °C/min. The maximum temperature was 900 °C. The temperature at which polymer experiences 5% mass loss is termed the Tg: polymer degradation temperature. Samples were dried in the oven at 120 °C overnight under vacuum, and cooled to room temperature before loading to the TGA. After loading, the sample chamber was flushed with argon for 2 h before heating. Crosslinking is carried out by holding sample for 60 min at 370 °C in the TGA chamber, which is below 388 °C Tg of the polymer (Table 1). Argon flow was 40 cm3/min for the “balance stream” and 60 cm3/min for the sample stream. The chamber exhaust was connected to the vent hood with 3 mm SS tubing of length ~ 1 m.

3.3. Differential scanning calorimeter (DSC)

A TA Q200 differential scanning calorimeter (DSC) was used to measure the glass transition temperature of samples with a heating rate of 10 °C per minute. Samples were dried in an oven at 120 °C overnight.

Table 1

<table>
<thead>
<tr>
<th>Row</th>
<th>Sample I. D.</th>
<th>Tg (°C)</th>
<th>Ts (°C)</th>
<th>Δ = Ts - Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dense Film Precursor 6FDA-DETDA: DABA</td>
<td>388</td>
<td>452</td>
<td>71</td>
</tr>
<tr>
<td>1B</td>
<td>Dense Film Precursor 6FDA-DETDA: DABA Cross linked</td>
<td>398</td>
<td>454</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>Dense Film Precursor 6FDA-DETDA: DABE</td>
<td>394</td>
<td>470</td>
<td>76</td>
</tr>
</tbody>
</table>
under vacuum and cooled to room temperature before loading in the DSC sample pan. Three pinholes were made in the lid of the sample pan to allow free flow of gases. The sample was first heated to 420 °C (a temperature beyond its glass transition temperature, 388 °C), but below its decomposition temperature determined from TGA) and then cooled down to 50 °C before a second heating cycle at a rate of 10 °C/min to 420 °C was done. The double heating cycle eliminated the effects of thermal history, and the glass transition temperature (T_g) was taken to be the inflection point of the change in the heat flow during the second heating cycle.

3.4. Scanning Electron Microscope (SEM)

The morphology of precursors and CMS fiber membranes were examined using a high resolution scanning electron microscope (Zeiss Ultra60). The precursor fibers were soaked in hexane and then shear fractured in liquid nitrogen to preserve fiber morphology. Since CMS fibers are brittle, samples were prepared by bending and breaking. The precursor fiber samples were mounted on a SEM mount and sputter-coated with gold before being examined.

3.5. Energy Dispersive X-Ray Spectroscopy (EDS)

Energy Dispersive X-Ray Spectroscopy (EDS) was carried out in the scanning electron microscope (Zeiss Ultra60) using high energy beam (20 kV) with full aperture width. A standard silicon wafer with Si content 95 wt% was used for calibration. The wt% are based off of elements Si, C, O, F, and N in the sample. VTM's treatment introduces Si in the fiber wall, and a line scan was carried out across the wall from skin to bore to analyze Si distribution.

4. Results and discussion

4.1. Thermal properties of the dense film precursor

Thermal properties of the dense film precursor properties are shown in Table 1. The weight average molecular weight and PDI of the 6FDA-DETDA: DABA (3:2) polymer were 167 kDa and 2.2, respectively. The glass transition temperature (T_g) of the 6FDA-DETDA: DABA precursor film is 388 °C, and increases to 398 °C for a cross-linked precursor. The degradation temperature (T_d) remained almost the same ∼ 452 °C, and the difference between the glass transition temperature, so the degradation temperature indicated as A (T_d - T_g) is lower in the case of the cross-linked precursor. The cross-linked product is insoluble in THF.

The glass transition temperature of the 6FDA-DETDA: DABA dense film precursor is 394 °C (6 °C higher than the T_g of the 6FDA-DETDA: DABA precursor, 388 °C), and the thermal degradation temperature of the 6FDA-DETDA: DABA dense film precursor is 470 °C. The difference between glass transition temperature and the degradation temperature T_d indicated by A relates to the substructure collapse and formation of the separation layer [17].

4.2. Transport properties of the dense film precursor and CMS

Transport properties of the 6FDA-DETDA: DABA dense film precursor and CMS (pyrolyzed at 550 °C) reported in our earlier studies [17] are summarized in Table 2 along with the 6FDA-DETDA: DABA dense film studied now. The permeability of 6FDA-DETDA: DABA precursor is higher than the 6FDA-DETDA: DABA precursor. This fact suggests that the packing density of the 6FDA-DETDA: DABA precursor is smaller than in the 6FDA-DETDA: DABA precursor. On the other hand the permeability of 6FDA-DETDA: DABA CMS is higher than 6FDA-DETDA: DABA possibly due to the pre-pyrolysis cross-linking in case of 6FDA-DETDA: DABA. The carboxylic group in DABA provides a cross-link which also appears to open up the CMS structures compared to the DABA-free precursor case. The suggested mechanism of decarboxylation-induced crosslinking involves two −COOH groups in DABA moieties reacting to form an anhydride by releasing one water molecule followed by creation of phenyl free radicals by decarboxylation of the anhydride. The phenyl radicals are capable of crosslinking with formation of the bulky crosslinked structure that strongly inhibits chain packing and provides high permeability [17]. Normally, high permeability membranes should show high degrees of aging, and it appears that the cross-links play significant and complex role in the aging trend of 6FDA-DETDA: DABA CMS; however aging is slowed down for the 6FDA-DETDA: DABA CMS.

After 30 days aging in vacuum the 6FDA-DETDA: DABA CMS dense film permeability decreased by roughly 50% (rows 2A, and 3A), whereas 6FDA-DETDA: DABA CMS permeability decreased by only ~10% (rows 2B, and 3B). After aging, the CO2/CH4 selectivities increased for both the 6FDA-DETDA: DABA and 6FDA-DETDA: DABA CMS (normal tendency). Interestingly, after 30 days vacuum aging, both the dense film 6FDA-DETDA: DABA and 6FDA-DETDA: DABA CMS have similar transport properties.

Based on the estimated dense film CMS properties: CO2 permeability > 10,000 Barrer, the hollow fiber CMS permeance was expected to be > 10,000 GPU if the skin thickness is ~1 µm. Expecting very high CO2 permeance of ~10,000 GPU we proceeded to fabricate asymmetric hollow fiber CMS

4.3. Spinning hollow fiber precursors and their transport properties

Spinning dope compositions, preparation protocols of spinning dopes, and spinning parameters were optimized to form hollow fiber membrane precursors using the dry-jet/wet-quench fiber spinning technique as summarized in Table 3.

Optimized conditions for the dope and spinning of 6FDA-DETDA: DABA and 6FDA-DETDA: DABA are similar, with the only difference being in the air-gap (3 cm for 6FDA-DETDA: DABA versus 10 cm for 6FDA-DETDA: DABA fiber to form similar selective skin on the fiber as shown in the SEM pictures later). Since the dense film precursor transport properties of 6FDA-DETDA: DABA and 6FDA-DETDA: DABA are similar we expected similarity in spinning hollow fiber precursor. Keeping all other parameters of spinning the same, the only difference is in the air-gap in order to get similar skin thickness and selectivities.

The transport properties of the hollow fiber precursors are shown in Table 4. The selectivities of the hollow fiber precursors are also quite close to the dense film precursors shown in Table 2. Prior work with 6FDA-derived CMS showed that the precursors need to be defect free to avoid artifacts and provide optimum properties [24]. The precursor is nominally assumed to be defect free for an O2/N2 selectivity more than 90% of dense film selectivity. Moreover, as a further verification, the CO2/CH4 selectivity remained almost unchanged (±10%) after PDMS (Polydimethylsiloxane) treatment (rows 1 A & 1B; 2 A & 2B), thereby indicating the precursor fibers are free of pin-hole defects or non-selective substrate resistance.

4.4. Hollow fiber CMS membranes and transport properties

4.4.1. Pure gas permeance

The transport properties of the CMS fiber produced at a pyrolysis temperature of 550 °C for pure gas permeation measurements with 30 psig feed gas pressure gave results reported in Fig. 3. The untreated 6FDA-DETDA: DABA CMS fiber (Fig. 3A) exhibited CO2 permeance 147 GPU versus 340 GPU for the 6FDA-DETDA: DABA 10VT CMS fiber (Fig. 3B) when both were tested 1 day after potting the module.

When tested within 4 h of potting the module, the CO2 permeance of the 6FDA-DETDA: DABA 10VT CMS was more than 1000 GPU (Fig. 3B) but decreased rapidly to 340 GPU after a day, and to 40 GPU after 20 days aging even with storage in CO2 at 7 bar, which are the conditions that stabilize CMS from non-DABA containing precursors. Even more surprising, the CO2/CH4 selectivity also decreased from 33 to 6 in 20
days, which is highly unusual compared to “standard CMS” where selectivity increases with age. The drop in pure-gas permeance for DABA 10VT CMS for initial 10 days is < 10% whereas between 10 and 20 days ~90%. We believe that initial settling and relieving stresses is slower due to resistance offered by the cross-links to deform and break away, and once that resistance is overcome the settling is faster during the later time period (described later in Section 5).

VTMS treatment restricts asymmetric support morphology collapse during pyrolysis and decreases skin thickness in the resulting CMS, which increases the permeance as described in [20,21]. The morphology as well as the unusual phenomenon occurring in the skin, which was noted, clearly affect the degree of aging of CMS. Selectivity decrease versus aging reflects this unusual phenomenon, seen in hollow fiber CMS based on 6FDA-DETDA: DABA with or without VTMS treatment. The degree of this unusual phenomenon is higher in the case of VTMS treated samples, presumably due to thinner skin thickness resulting in stress concentration.

Both the 6FDA-DETDA: DABA and 6FDA-DETDA: DABE CMS decreased by 54% (from 37 to 17) while the 6FDA-DETDA: DABA CMS decreases by 23% (from 26 to 20) in 30 days, indicating that V-treatment imparts some stability. Surprisingly, the CO2/CH4 selectivity decreases with aging, which is highly unusual, indicating some new phenomena at play.

We test the module and then store it in CO2 at 7 bar. We have observed that storage of the as-made modules in 7 bar CO2 suppresses undesirable aging typically seen under vacuum or atmospheric pressure air. But during the testing period in the absence of CO2 as a supporting gas during pure CH4 permeation measurement aging can occur. Testing involves pre-purging with the test gas, permeation of test gas, and post-purging with the next gas or CO2 for storage. In the case of pure gas, the testing steps are doubled since two gases are involved compared to only one in the mixed gas case. Hence pure gas test results [Fig. 2] showed increased aging effects compared to mixed gas test results [Fig. 4]. Moreover, in case of 6FDA-DETDA: DABA CMS, the unusual phenomenon would have enhanced.

To test the idea that crosslinks known to occur during heating of the DABA containing polymer [24] are responsible for the surprising trends, an esterified variant, 6FDA-DETDA: DABE precursor was formed and investigated. As with the non-esterified variant, hollow fiber CMS membranes were fabricated and tested (shown in Figs. 4C and 4D). The 6FDA-DETDA: DABA CMS as well as 10VT CMS exhibited more normal aging behavior in which permeance decreased and selectivity increased with the age. For storage under 7 bar CO2 with periodic testing, the 6FDA-DETDA: DABA 10VT CMS exhibited CO2 permeance > 1000 GPU for a week with a CO2/CH4 selectivity of 25. For storage under 7 bar CO2 for 72 days, the selectivity almost doubled to 48 and the CO2

4.4.2. Mixed gas permeance

The transport properties of the CMS fiber were tested in a constant pressure system with 50 mol% CO2 and 50 mol% CH4 feed gas mixture at 21 bar pressure (Method 3). The results are given in Fig. 4. As shown in Figs. 4A and 4B, the untreated 6FDA-DETDA: DABA CMS exhibited CO2 permeance of 104 GPU versus 300 GPU for the 6FDA-DETDA: DABA 10VT CMS. Permeance of the untreated 6FDA-DETDA: DABA CMS decreased (by 70%) from 104 to 32 GPU after 30 days storage in CO2 at 7 bar, while permeance of the 6FDA-DETDA: DABA 10VT CMS decreased (by 30%) from 300 to 214 GPU after 30 days even with storage in CO2 at 7 bar. The CO2/CH4 selectivity of the untreated 6FDA-DETDA: DABA CMS decreases by 54% (from 37 to 17) while the 6FDA-DETDA: DABA 10VT CMS decreases by 23% (from 26 to 20) in 30 days, indicating that V-treatment imparts some stability. Surprisingly, the CO2/CH4 selectivity decreases with aging, which is highly unusual, indicating some new phenomena at play.

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Table 2
Transport properties of the dense film precursor and CMS.

<table>
<thead>
<tr>
<th>Row</th>
<th>Pure gas feed at pressure 2 bar (Method 2)</th>
<th>Age</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In Days</td>
<td>P&lt;sub&gt;CO2&lt;/sub&gt;</td>
<td>P&lt;sub&gt;CH4&lt;/sub&gt;</td>
</tr>
<tr>
<td>1A</td>
<td>6FDA-DETDA: DABA Precursor Film</td>
<td>2</td>
<td>253</td>
<td>10</td>
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<tr>
<td>1B</td>
<td>6FDA-DETDA: DABA Precursor Film</td>
<td>2</td>
<td>304</td>
<td>12</td>
</tr>
<tr>
<td>2A</td>
<td>6FDA-DETDA: DABA CMS Film</td>
<td>2</td>
<td>21,740</td>
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<td>6FDA-DETDA: DABA CMS Film</td>
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<td>12,043</td>
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<td>3A</td>
<td>6FDA-DETDA: DABA CMS Film</td>
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<tr>
<td>3B</td>
<td>6FDA-DETDA: DABA CMS Film</td>
<td>30</td>
<td>11,071</td>
<td>346</td>
</tr>
</tbody>
</table>

The isotropic dense films are of thickness ~ 50 µm.

Table 3
Spinning dope composition and spinning conditions.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Dope Composition</th>
<th>wt%</th>
<th>Spinning Conditions</th>
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<td></td>
<td></td>
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<tr>
<td>6FDA-DETDA: DABA</td>
<td>Polymer</td>
<td>NMP</td>
<td>THF</td>
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<tr>
<td>1A</td>
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<td>9.5</td>
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<tr>
<td>1B</td>
<td>6FDA-DETDA: DABA</td>
<td>24</td>
<td>9.5</td>
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</table>

Table 4
Transport properties of the precursor.<sup>a</sup>

<table>
<thead>
<tr>
<th>Row</th>
<th>LD</th>
<th>Pure gas feed at pressure 2 bar (Method 1)</th>
<th>Permeance</th>
<th>Selectivity</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>(P/L) &lt;sub&gt;CO2&lt;/sub&gt; GPU</td>
<td>(P/L) &lt;sub&gt;CH4&lt;/sub&gt; GPU</td>
<td>(P/L) &lt;sub&gt;O2&lt;/sub&gt; GPU</td>
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<tr>
<td>1A</td>
<td>6FDA-DETDA: DABA Precursor</td>
<td>289</td>
<td>11.2</td>
<td>46.3</td>
</tr>
<tr>
<td>1B</td>
<td>After PDMS treatment</td>
<td>178</td>
<td>7.2</td>
<td>32.9</td>
</tr>
<tr>
<td>2A</td>
<td>6FDA-DETDA: DABA Precursor</td>
<td>403</td>
<td>14.0</td>
<td>61.9</td>
</tr>
<tr>
<td>2B</td>
<td>After PDMS treatment</td>
<td>343</td>
<td>12.6</td>
<td>44.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Precursor fiber module contained 4-5 fibers.
permeance only decreased moderately to 780 GPU, similar to other CMS materials derived for precursors without the DABA cross-linkable groups. Clearly, mono-esterification of 6FDA-DETDA: DABA to 6FDA-DETDA: DABE, successfully eliminates the unusual aging problem and maintains the CO\textsubscript{2} permeance at attractive levels.
4.5. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) pictures of the precursor, CMS, and 10VT CMS for 6FDA-DETDA: DABA and 6FDA-DETDA: DABE in Fig. 5 show apparent precursor skin thickness of only ~ 0.5 µm for both the precursors (Figs. 5A and 5B).

Untreated CMS have skin thickness slightly more than 1 µm (Figs. 5C and 5D). After V-treatment of the precursors, the CMS produced have apparent skin thickness less than 0.5 µm (Figs. 5E and 5F) for both materials. VTMS treatment restricts asymmetric support morphology collapse during pyrolysis, and this leads to decreased skin thickness in the resulting CMS compared to an untreated one [20]. The V-treatment technique enables restricting the microscale morphology collapse in asymmetric CMS membranes without having a chemical reaction with the polymer precursor material. This unusually thin skin may cause unusual stress concentrations when combined with the crosslinking present in the DABA variant, may motivate the undesirable aging seen for this case. The details of the phenomena involved are clearly complex; however, the moderation of cross linking clearly avoids its impact.

Based on the dense film permeability values (~10,000 Barrer for CO₂ in Table 2) and permeance of CO₂ (1000 GPU in Fig. 4) of the fiber, the calculated skin thickness is 10 µm. This calculated thickness is much higher than the apparent skin thickness of 0.5–1 µm obtained from SEM pictures. The surprising disagreement between SEM & transport values may provide an insight into the cause of the large aging seen as is discussed later in Section 5.

4.6. Energy Dispersive X-Ray Spectroscopy (EDS)

An Energy Dispersive X-Ray Spectroscopy (EDS) line scan shows (Fig. 6) that Si is present throughout the fiber wall of the 10VT CMS fiber that restricted the structure collapse during pyrolysis. The highest concentration measured was 16 wt% at the outermost layer of the skin for both 6FDA-DETDA: DABA 10VT CMS fiber and 6FDA-DETDA: DABE 10VT CMS fiber (Figs. 6A and 6B). On the other hand, the average concentration of Si in the wall 6FDA-DETDA: DABA 10VT CMS fiber was 5.5 wt%, and 7 wt% in 6FDA-DETDA: DABE 10VT CMS fiber. The above results indicate that the 6FDA-DETDA: DABE retains more Si than 6FDA-DETDA: DABA in CMS fiber possibly due to the structural differences and micro-voids in the precursors. The aging tendency in the CO₂/CH₄ selectivity 25–50 for 10VT verses 30–50 for 0VT) is similar, but appear to exceed experimental uncertainty. In any case both of the DABE fibers show selectivities more than for the simple dense film 30–35). This issue requires additional analysis, and we prefer to avoid speculation about it at this time.

4.7. Mechanical properties of hollow fiber CMS

The hollow fiber CMS are mechanically robust, and sufficient flexible to prepare modules for permeation test or commercial application, and even capable to make a loop as shown in the Fig. 7. Normally we do not conduct tensile test on the asymmetric hollow fiber CMS. However we did tensile test on CMS. Tensile testing was done on individual filaments using RSA III solids analyzer (Rheometric Scientific, Co.) at a gauge length of 25 mm and the strain rate was 0.1% per second. The results (average of 5 specimens shown in Table 5) indicate that 6FDA-DETDA: DABA based CMS has higher tensile modulus, tensile strength (attributed to cross-links), and strain at break than its...
Fig. 7. Hollow fiber CMS bent into a loop.

Table 5
Tensile properties of hollow fiber CMS.

<table>
<thead>
<tr>
<th>ID unit</th>
<th>Tensile Modulus GPa</th>
<th>Tensile Strength GPa</th>
<th>Strain %</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FDA-DETDA: DABA CMS</td>
<td>243 ± 47</td>
<td>2.4 ± 0.4</td>
<td>0.92 ± 0.17</td>
</tr>
<tr>
<td>6FDA-DETDA: DABE CMS</td>
<td>170 ± 53</td>
<td>2.2 ± 0.2</td>
<td>0.24 ± 0.17</td>
</tr>
</tbody>
</table>

DABA variant.

5. Hypothesis about the unusual behavior of 6FDA-DETDA: DABA-based hollow fiber CMS

The loss in permeance and selectivity during 6FDA-DETDA: DABA aging, which is not seen in 50 µm dense film cases or in other non-DABA derived CMS or under 6FDA-DETDA: DABA derived CMS is, as noted, surprising. In this section, we hypothesize possible causes related to rearrangements that may be triggered by ultrahigh stresses localized in the thin selective CMS layer of the DABA variant.

Also as noted above, prior work shows that DABA moieties present in the 6FDA-DETDA: DABA precursor, cross-link at about 370 °C [25]; and we believe such a cross-linked structure behaves differently during pyrolysis, ramp, soak, and cooling than non DABA precursors. Moreover, in the thicker non-asymmetric case, stresses can be tolerated better than in the case of the thin selective layer of the DABA-derived asymmetric CMS, thereby causing undesirable microscale rearrangements in this critical asymmetric skin layer. In the context of prior discussion of the complex aromatization and fragmentation believed to occur during the ramp and soak periods [26], we hypothesize that the crosslinked precursor affects this process. Specifically, we envision the rearrangement to create an unusual strand fragmentation array, with inhibited highly stressed packing units being present, besides regular linear strands typical in non DABA precursors. Such a dual population formed during the stress induced fragmentation of the initial long semiflexible polyimide during aromatization in the pyrolysis may set the stage for the unusual asymmetric aging seen for the DABA variant. Under the driving force to minimize free volume by elimination of excess volume left after aromatization and fragmentation, such a strand array may collapse to pack even tighter while also leading to regions with defective packing to create a complex mosaic. “Tie strands” between cells probably facilitate this process. Such an undesirable outcome could create simultaneously low selectivity and low permeability in the asymmetric DABA variant not seen in other cases.

A schematic to describe the hypothesis about the unusual behavior of 6FDA-DETDA: DABA-based hollow fiber CMS is shown in Fig. 8. In the case of standard CMS dm3 and du4 represent micropores and ultra micropores in the as made condition (at the end of pyrolysis after cooling). After aging, sheets consolidate, so pores are smaller as represented by dm1 and du2. This fact results in decreased permeance and increased selectivity. In the case of 6FDA-DETDA: DABA based CMS, we envision cross links distorting micropores and ultra micropores represented by dm3 and du3. After aging, sheets consolidate, distorted more due to cross links represented by dm4 and du4, which results in decreased permeance as well as decreased selectivity.

The hypothesis that minimizing or moderating cross-links may eliminate the unusual behavior of 6FDA-DETDA: DABA led to our successful strategy to esterify the DABA units in the precursor. While other esterifying agents (e.g. methanol, ethanol, etc.) may be viable, this proof of concept study is consistent with the above picture. Further work to probe and verify this picture is underway.

6. Conclusions

- The 6FDA-DETDA: DABA polyimide-derived carbon molecular sieve hollow fiber modules showed very high CO2 permeance > 1000 GPU with CO2/CH4 selectivity 25, and exhibited usual aging behavior wherein permeance decreases and selectivity increases as the fiber ages.
- An unusual problematic phenomenon (loss in selectivity with age) encountered in the CMS derived from non-esterified 6FDA-DETDA: DABA variant was successfully eliminated in the 6FDA-DETDA: DABA CMS hollow fiber membranes while maintaining initial permeance of CO2 > 1000 GPU.
- The unusual problematic phenomenon was not observed in 6FDA-DETDA: DABA derived dense film CMS, consistent with the hypothesis that high residual stress in the freshly formed CMS produces nonstandard skin formation and aging behavior for CMS from 6FDA-DETDA: DABA fiber precursors.
- The application of the above hypothesis could apply to any precursor containing a cross-linkable moiety. While the discovery has been described in detail with respect to the DABA variant, many other variants can be envisioned and are under investigation.

Acknowledgment

The authors acknowledge the support from American Air Liquide and US Department of Energy Grant No. DE-FG02-04ER15510 for the funding of this project. Based on research work and the invention discussed in this report a patent application has been filed: U.S. Patent Application No. 62/476,065, “Hollow Fiber Carbon Molecular Sieve (CMS) Based on 6FDA-DETDA: DABA Polymer” Filed on March 24, 2017; GTRC Reference Number: 7540.

Fig. 8. A scheme to describe the hypothesis about the unusual behavior of 6FDA-DETDA: DABA-based hollow fiber CMS (B) compared to standard CMS (A).
References


