

# High-Performance Polybenzimidazole Membranes for Helium Extraction from Natural Gas

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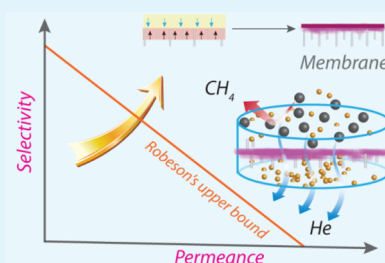
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## Supporting Information

**ABSTRACT:** Increasing helium use in research and production processes necessitates separation techniques to secure sufficient supply of this noble gas. Energy-efficient helium production from natural gas is still a big challenge. Membrane gas separation technology could play an important role. Herein, a novel poly(*p*-phenylene benzobisimidazole) (PBDI) polymeric membrane for helium extraction from natural gas with low He abundance is reported. The membranes were fabricated by a facile interfacial polymerization at room temperature. The thin and defect-free membrane structure was manipulated by the confined polymerization of monomers diffusing through the interface between two immiscible liquids. Both He/CH<sub>4</sub> selectivity and He permeance are competitive over those of other commercial perfluoropolymers. Even at low He content of 1%, separation performance of the PBDI membrane transcended the current upper bound. The unprecedented selectivity (>1000) together with the excellent stability (~360 h) endows PBDI membranes with a great potential for energy-efficient industrial recovery and production of this precious He resources from reservoirs with low abundance.

**KEYWORDS:** He separation, membrane, natural gas, interfacial polymerization, polybenzimidazole



## INTRODUCTION

Helium is a unique gas with a wide range of important medical, scientific, and industrial applications because of its extremely low boiling point (4.2 K), inert and nonflammable nature, and small atomic size.<sup>1–3</sup> The majority of helium is extracted by cryogenic liquefaction from natural gas (NG) sources with low He abundance.<sup>3–5</sup> The expensive capital investment and extensive energy consumption of this stripping and cryogenic distillation lead to a high He price.<sup>5</sup> Membrane gas separation is an energy-efficient and environmentally friendly alternative to the cryogenic gas separation processes.<sup>6–8</sup> Current commercial membrane separation involves nitrogen enrichment, hydrogen recovery, vapor separation, and NG upgrading;<sup>9–11</sup> the emerging application in olefin/paraffin separation and CO<sub>2</sub> capture is significantly promoted by the development of membrane materials.<sup>6,12,13</sup> However, the development of membranes for He separation is very limited.<sup>14,15</sup>

Since the emergence of commercial membranes in the 1960s, perfluoropolymer membranes have been proposed for He/CH<sub>4</sub> separation in a three-stage membrane process.<sup>16</sup> The energy consumption would be saved by 30–80% compared to the current thermal process for He production.<sup>2–4,17,18</sup> However, their development in the real application is actually impeded.<sup>18,19</sup> The perfluoropolymer membranes are fabricated

by melt press<sup>20</sup> or solution casting method.<sup>21,22</sup> A critical issue is the strong solvent retention property of perfluoropolymers, resulting in a fluctuated selectivity for the thick free-standing membranes.<sup>23</sup> The membrane selectivity was greatly improved by the newly emerging dioxolane-based perfluoropolymers.<sup>22,24,25</sup> On the point of the industrial application view, asymmetric perfluoropolymer membranes with a thinner layer are highly desired to improve the permeation flux, but only few achievements were reported.<sup>24–26</sup> Another issue is the physical aging property of thin perfluoropolymer membranes, which is generally several orders of magnitude more rapid than expected for a thick free-standing membrane.<sup>27,28</sup>

In this work, we developed a novel poly(*p*-phenylene benzobisimidazole) (PBDI) polymeric membrane with superior He/CH<sub>4</sub> selectivity and long-term stability. PBDI is a rodlike aromatic polymer and initially investigated as proton-exchange membranes for fuel cells by molecular simulation.<sup>29,30</sup> The free-standing polybenzimidazole membranes made by nonsolvent phase inversion are very brittle and difficult to handle.<sup>31–33</sup> Robust gas separation membranes were fabricated by coating commercial poly(2,2'-*m*-phenylene-

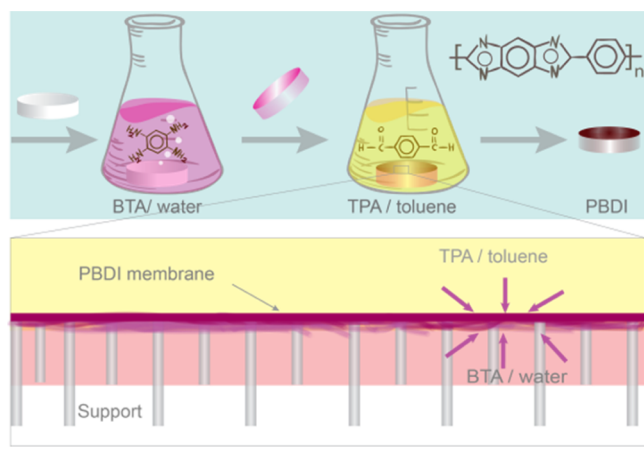
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5,5'-bibenzimidazole) on porous inorganic tubes.<sup>34</sup> Herein, we explored an interfacial polymerization method to fabricate PBDI membranes on porous ceramic supports (Scheme 1).

**Scheme 1. PBDI Membrane Preparation by Interfacial Polymerization in the Confined Space: The Porous Supports Were First Saturated with an Aqueous BTA Solution and Then Immersed in the TPA Toluene Solution for 0.1–3 h, Enabling the Formation of PBDI Membranes at the Interface**



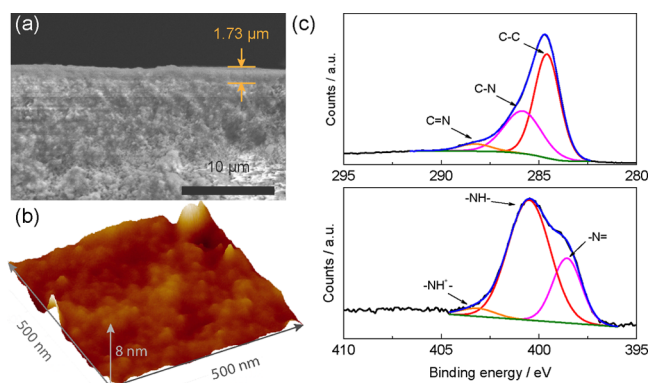
Typically, an aqueous 1,2,4,5-benzenetetramine (BTA) solution infused the pores of the support. After removing the excess BTA solution, the support was transferred to a terephthal aldehyde (TPA) toluene solution. Because of the immiscibility of the water and toluene phase,<sup>35,36</sup> the TPA and BTA monomers would diffuse toward and react in the confined interface of the two solutions forming a dense and uniform membrane layer on top of the support. Despite that the interfacial polymerization method was extensively investigated on polyamide-based membranes for seawater desalination<sup>37,38</sup> and solvent-resistant nanofiltration,<sup>39,40</sup> it is a newly emerging method for fabricating polybenzimidazole membranes for gas separation.

## RESULTS AND DISCUSSION

### PBDI Membrane Preparation and Characterization.

The condensation polymerization of TPA and BTA was well manipulated by the reaction time (Table S1). Smooth PBDI membranes with a thickness of 1.7  $\mu\text{m}$  were achieved after 3 h reaction (Figure 1a). The roughness of the membrane surface was determined to be less than 15 nm by atomic force microscopy (AFM, Figures 1b and S1). The chemical surface composition of the membrane surface was confirmed by X-ray photoelectron spectroscopy (XPS, Figures 1c and S2a). The binding energy at 398.6 eV ( $\text{N}_{1s}$ ) is assigned to the benzimidazole ring formation by the condensation reaction.<sup>41</sup> The protonated  $=\text{N}-$  functional groups evidenced by the low signal at 403.0 eV, would generate a conjugated bond system, leading to a slightly lower ratio between  $\text{C}-\text{N}/\text{C}=\text{N}$  (72:28) than in the ideal benzimidazole structure.<sup>42</sup>

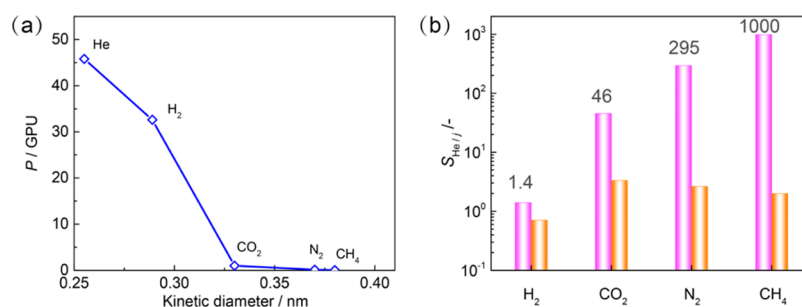
**Single Gas Permeation.** The membrane exhibits a typical size-selective property as based on the single gas permeance of He (0.255 nm),  $\text{H}_2$  (0.289 nm),  $\text{CO}_2$  (0.33 nm),  $\text{N}_2$  (0.364 nm), and  $\text{CH}_4$  (0.38 nm) employing the Wicke–Kallenbach technique.<sup>43</sup> Highest gas permeance was achieved for He (46 GPU), monotonically decreasing with increasing kinetic



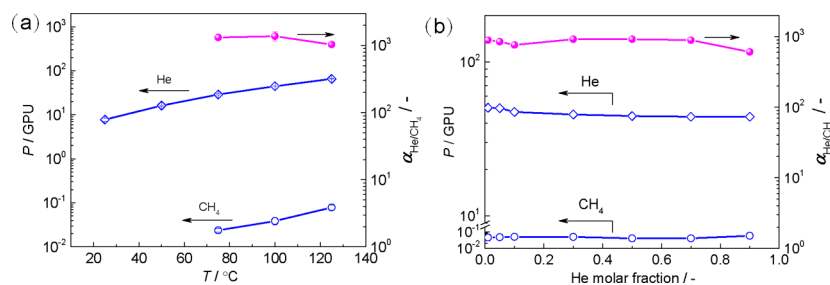
**Figure 1.** PBDI membrane characterization. (a) Cross-sectional SEM image; (b,c) 3D AFM image, C 1s and N 1s XPS spectra of the PBDI membrane surface.

diameter of the probe gas molecules (Figure 2a). Even though the adsorption selectivity favors  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{CH}_4$  over He for benzimidazole-linked polymers,<sup>44,45</sup> the ideal selectivity of He/ $\text{CO}_2$ , He/ $\text{N}_2$ , and He/ $\text{CH}_4$  were 46, 295, and 1000, respectively, and much higher than the corresponding Knudsen selectivity (Figure 2b). Considering the rigid and amorphous nature of PBDI, it can be envisaged that the He molecules can permeate through the pores that are too small for  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{CH}_4$ , resulting in the high selectivity. The molecular diffusivity dominates the overall separation selectivity, trending toward the molecular sieving limit. Polybenzimidazole of poly(2,2'-*m*-phenylene-5,5'-bibenzimidazole) was previously fabricated on stainless steel tubes by nonsolvent phase inversion as  $\text{H}_2$ -selective membranes, which exhibited a low permeance of 4.7 GPU.<sup>34</sup> Because of excess water inside porous supports, the initial PBDI oligomers prefer to form a stable hydrogen-bonded network as an intermediate layer rather than far advanced condensation polymerization.<sup>46</sup> A hierarchical membrane structure would be generated by interfacial polymerization, leading to an improved gas permeance.

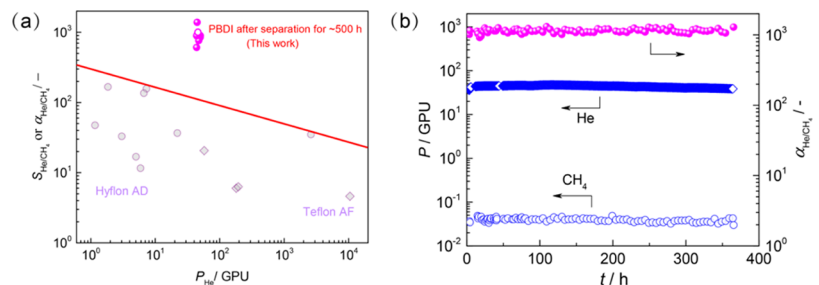
**Mixed Gas Separation Performance.** In order to gain further understanding of the separation behavior, the PBDI membrane performance for the binary He/ $\text{CH}_4$  system was evaluated at various temperatures and feed compositions. Both He and  $\text{CH}_4$  permeance monotonically increased with temperature (Figure 3a), yielding an estimated diffusivity activation energy of 21.0 and 46.2  $\text{kJ mol}^{-1}$ , respectively (Figure S3), indicating an activated diffusion of both He and  $\text{CH}_4$  molecules through PBDI membranes. Hence, the diffusion of the bigger  $\text{CH}_4$  molecule benefits more from a temperature increase than He. Therefore, a slight decrease of the He/ $\text{CH}_4$  separation factor was observed when the temperature increased further from 100 to 125  $^\circ\text{C}$  (1380 vs 1030). The He permeance of 45 GPU at 100  $^\circ\text{C}$  in the mixture is slightly lower than that for pure He feed, which is attributed to some competition with  $\text{CH}_4$ . The cost of He separation and purification from NG is strongly dependent on the feed gas composition.<sup>47,48</sup> Our PBDI membranes exhibit a constant He/ $\text{CH}_4$  selectivity even for a He molar fraction decreased down to 1% (>900, Figure 3b). The high He/ $\text{CH}_4$  selectivity is crucial for the membrane process. For example, the required minimum He/ $\text{CH}_4$  selectivity is 160 to achieve a purity of 99% from a feed of 1% He by a three-stage membrane process;<sup>47</sup> while a two-stage membrane process requires a selectivity of 175, as simulated by Scholes and Ghosh.<sup>47</sup> Along this line, a



**Figure 2.** Single gas permeance (a) and ideal selectivity (b) of the PBDI membrane; orange columns indicate Knudsen selectivity of He to other components.



**Figure 3.** (a) Temperature-dependent separation performance of the PBDI membrane for an equimolar He/CH<sub>4</sub> mixture; (b) effect of He molar fraction on He/CH<sub>4</sub> separation performance.



**Figure 4.** (a) Pure (open circle) and mixed (solid circle, 1–90% He composition) He/CH<sub>4</sub> separation performance comparison of PBDI membranes with commercial Hyflon AD and Teflon AF perfluoropolymers;<sup>20,21,24,26,49,50</sup> the red line represents the current upper bound for He/CH<sub>4</sub> separation; (b) long-term performance of the PBDI membrane for He/CH<sub>4</sub> mixture separation at 1 bara and 100 °C.

two-stage PBDI membrane process would be sufficient to produce 99% He.

**Long-Term Stability.** Our PBDI membranes possess a superior He/CH<sub>4</sub> selectivity in comparison with the commercial Hyflon AD and Teflon AF perfluoropolymers (Figure 4a)<sup>20,21,24,26,49,50</sup> and surpass Robeson's upper bound (Figure S5).<sup>19</sup> The *d*-spacing between the PBDI polymer chains is 3.4 and 6.8 Å (Figure S6), while that is 8.2 and 9.1 Å for Hyflon AD80 and Teflon AF1600, respectively.<sup>22</sup> The average free volume size of PBDI film is 4.3 Å as determined by positron annihilation lifetime spectroscopy (PALS, Table S3). The higher selectivity of PBDI membranes than commercial Hyflon AD and Teflon AF systems and the emerging dioxolane-based perfluoropolymers is attributed to a stricter size-exclusion property.<sup>22,24,25</sup> Even perfluoropolymers could achieve higher permeation flux with moderate selectivity, the CO<sub>2</sub> permeability is normally quite significant (Table S4) and therefore becomes an issue in the presence of CO<sub>2</sub> in NG.<sup>3</sup> The high selectivity of He over CO<sub>2</sub> and CH<sub>4</sub> renders the PBDI membrane process more competitive for He extraction, especially from crude NG with low helium abundance and CO<sub>2</sub> presence.

The most significant concern with polymeric membranes for He separation is the susceptibility to physical aging and plasticization.<sup>9,23</sup> The separation performance of our PBDI membrane, however, did not show any deterioration for a He/CH<sub>4</sub> mixture during the 360 h operation at 100 °C (Figures 4b and S4). In comparison, a supported 6FDA-based polyimide membrane lost 30–60% He permeance after aging in a vacuum chamber at 35 °C for 1000 h.<sup>51</sup> The PBDI polymeric membrane shows no sign of aging. The superior anti-aging behavior is competitive to that of the commercial Hyflon AD60, which kept its permeance after 200 days storage in ambient air.<sup>24</sup>

## CONCLUSIONS

In conclusion, highly selective PBDI membranes were fabricated by interfacial polymerization at room temperature. The overall membrane selectivity is dominated by diffusion selectivity of He to CH<sub>4</sub> primarily due to the small free volume size. The He/CH<sub>4</sub> separation performance of the PBDI membrane is competitive to that of the commercial perfluoropolymers and surpassed Robeson's upper bound. Because of the benchmark selectivity and long-term stability

(~360 h), the PBDI membranes pave the way to direct extraction of this precious helium, especially from low-concentration NG resource.

## EXPERIMENTAL SECTION

**Materials.** BTA tetrahydrochloride, TPA (99%), toluene (anhydrous, 99.8%), *N,N*-dimethylformamide (anhydrous, 99.8%), and ethanol (95%) were purchased from Sigma-Aldrich. Deionized water was provided by the Department of Chemical Engineering, Applied sciences of the Delft University of Technology. Asymmetric  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, average pore size ~2.5  $\mu$ m;  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer on top, average pore size ~5.0 nm) with a diameter of 18 mm and a thickness of 2 mm were purchased from Fraunhofer-Institut für Keramische Technologien und Systeme IKTS. The substrate exhibits a He permeance of ~30 000 GPU and a He/CH<sub>4</sub> ideal selectivity of 1.4. All materials and solvents were used without further purification.

**Supported PBDI Membrane and Free-Standing PBDI Film Preparation.** An alumina substrate was first immersed in a clean Petri dish containing 1.5 wt % BTA aqueous solution under reduced pressure of 0.2 bar for 20 min, and then the substrate was taken out from the solution and dried with compressed air until no visible droplets were left on the surface. A 1.0 wt % TPA toluene solution was then poured onto the BTA saturated alumina substrate, leaving the reaction to run for 0.1–3 h. Afterward, the membrane was left in the fume hood overnight, washed with toluene, dried at room temperature, and finally put into a homemade permeation setup for performance testing at its fresh stage.<sup>36</sup>

Free-standing PBDI films were prepared in the same way for characterization. Briefly, a TPA toluene solution (1.0 wt %) was gently spread on top of a 1.5 wt % BTA aqueous solution in a Petri dish (or bottle). After few seconds, a brown film layer was formed at the water–toluene interface. The reaction was left to run for 0.1–3 h, and then the film was collected and washed. The resulting films were left to dry in the fume hood at ambient condition and then dried under vacuum at 373 K overnight.

**Membrane Performance Evaluation.** The single gas permeation and mixed gas separation performance were evaluated by the Wicke–Kallenbach technique. The effective membrane diameter was 1.3 cm. The temperature, controlled by a convection oven, ranged between room temperature and 125 °C. The absolute feed gas pressure was controlled from 1.0 to 5.0 bara by a back-pressure controller on the retentate line. Argon was used as sweep gas with a constant volumetric flow rate of 20 mL/min to eliminate concentration polarization and carry the permeate to a gas chromatograph (Interscience Compact GC) equipped with an MXT-MSieve 5A column and a thermal conductivity detector to separate and analyze the mixture. Mixed gas permeation performance was determined with and without the presence of hydrocarbon or water vapor. For the single gas measurement of He, H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>, the feed flow rate was 20 mL/min. For the He/CH<sub>4</sub> mixture gas separation, the total feed flow rate was 50 mL/min. The feed gas could be saturated with water vapor by bubbling through a water container before passing to the membrane. The effect of higher hydrocarbon on He/CH<sub>4</sub> separation was conducted by introducing 5% *i*-butane to the feed gas. At each permeation condition, the system was allowed to stabilize for more than 2 h and the gas chromatography analysis was repeated at least 10 times. The permeance ( $P$ ,  $3.3928 \times 10^{-10}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> = 1 GPU), ideal selectivity ( $S_{ij}$ -based on the single component permeation), and separation factor ( $\alpha_{ij}$ -based on the mixture permeation) are defined by the following equations:

$$P_i = \frac{J_i}{\Delta p_i} \quad (1)$$

$$S_{ij} = \frac{P_i}{P_j} \quad (2)$$

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \quad (3)$$

where  $J_i$  is the permeation flux through the membrane, mol·m<sup>-2</sup>·s<sup>-1</sup>;  $\Delta p_i$  is the transmembrane partial pressure difference of component  $i$ , Pa; and  $x_i$ ,  $x_j$  and  $y_i$ ,  $y_j$  are the molar fractions of the mixture components  $i$  and  $j$  at the feed side ( $x$ ) and permeate side ( $y$ ), respectively.

**Characterization.** The membrane morphology was analyzed by emission scanning electron microscopy (SEM, JSM-6010LA, JEOL). Powder X-ray diffraction (PXRD) pattern of the membrane was recorded in a Bruker-D8 ADVANCE diffractometer using Co  $K\alpha$  radiation ( $\lambda = 0.178897$  nm). The  $2\theta$  range of 5°–50° was scanned using a scan rate of 0.05 deg·s<sup>-1</sup>. Because of the non-adsorbing property of He,<sup>52</sup> no isotherm could be recorded. XPS measurements were performed on a K-Alpha Thermo Fisher Scientific spectrometer using monochromatic Al  $K\alpha$  radiation at ambient temperature and chamber pressure of about 10<sup>-8</sup> mbar. The X-ray gun was operated at 3 mA and 12 kV, and the spot size was set to 400  $\mu$ m. All the spectra measured were corrected by setting the reference binding energy of carbon (C<sub>1s</sub>) at 284.6 eV.

PALS was used to measure the average free-volume size within PBDI. The PBDI was packed to 1.5 mm either side of the <sup>22</sup>NaCl positron source which was enclosed in a Mylar envelope (source correction 1.418 ns and 3.5%). The samples were placed under vacuum, and lifetimes were collected on EG&G Ortec spectrometers set for coincidence with a full width at half-maximum at 220 ns. The spectra were deconvoluted using LT-v9<sup>53</sup> software and fitted to two lifetimes. The first lifetime was fixed to 0.125 ns and was attributed to para-positronium formation (the bound state of an electron and a positron in opposite spin), and the second component was attributed to free annihilation with free electrons within the PBDI. There was no ortho-positronium formation (the bound state of an electron and a positron in the same spin) due to inhibition; therefore, the second component was used to determine the average free volume element size within the material using the adapted Tao–Eldrup equation.<sup>54</sup>

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b05548.

AFM images and XPS spectra of the PBDI membrane surface; Arrhenius representation for the He and CH<sub>4</sub> permeance of the PBDI membrane; long-term performance of the membrane; comparison of PBDI membranes with the state-of-the-art in He/CH<sub>4</sub> mixture separation; PXRD patterns; He/CH<sub>4</sub> separation performance summary; data points for He/CH<sub>4</sub> separation; physical properties of PBDI and commercial perfluoropolymers; and He/CO<sub>2</sub> separation performance comparison between PBDI and perfluoropolymer membranes (PDF)

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### Author Contributions

X.W., M.S., and X.L. contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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