1 Introduction

Membrane-based gas separation techniques are of great interest due to their flexibility, low energy consumption, high reliability, and lower operating costs.\(^1\)–\(^3\) Compared with other membrane materials, polymeric membranes have the advantages of easy fraction, low production cost, and excellent physical and mechanical properties.\(^4\)–\(^5\) Polymer membranes have been used in CO\(_2\) recovery during oil recovery, oxygen and nitrogen separation from air, and natural gas sweetening.\(^6\)–\(^9\) Among them, polyamide (PA) is considered as excellent material for gas separation.\(^10\)–\(^12\) For example, Parthasarathi \textit{et al.} have evaluated the gas transport properties for PAs containing a fluorinated biphenyl moiety.\(^13\) PA-I having a tert-butyl group showed the highest permeability CO\(_2\) \((P = 42.60\) barrer\) and CO\(_2\)/N\(_2\) selectivity \((\alpha = 20.29)\). PA membranes have also been indicated by Zhu \textit{et al.} to have 12.26 barrer for CO\(_2\) permeability at 25 °C and 1 bar.\(^14\) In a similar manner, José Luis \textit{et al.} reported that PAs containing a dibenzobarrelen pendant group show the lowest CO\(_2\) permeability \((P = 2.96\) barrer\) and CO\(_2)/N\(_2\) selectivity \((\alpha = 8.4)\), and the highest CO\(_2\) permeability \((P = 9.66\) barrer\) and CO\(_2)/N\(_2\) selectivity \((\alpha = 13.6)\).\(^15\) In another important work, R. Sulub-Sulub \textit{et al.} synthesized and characterized a series of polyimide containing tert-butyl moieties. The DPT-TMPD membrane showed better performance in terms of selectivity CO\(_2\) permeability \((2035\) barrer\).\(^16\) The above-mentioned comparison of copolymers demonstrates that polyamide is an excellent material for gas separation. Polydimethylsiloxane (PDMS) is a flexible rubbery polymer with a high free volume for gas transport. A very high permeability is hence expected for membranes prepared from PDMS. In order to enhance gas permeability, several approaches, including crosslinking or grafting of PDMS onto the polymer have been successfully applied. For instance, Yang \textit{et al.} synthesized and characterized a series of SBS-PDMS crosslinked membranes.\(^17\) The CH\(_4\) permeability of SBS-c-PDMS-co-PMHS-70 sample has notably enhanced to 443.6 barrer at 25 °C and 1 bar as compared to 37.6 barrer over the pure SBS membrane. Hyelim \textit{et al.} studied the crosslinked polyimide polydimethylsiloxane (PI-PDMS) copolymer membranes. These crosslinked copolymers exhibited excellent thermochemical stability and CO\(_2\) separation performance \((\text{PCO}_2 = 799\) barrer and CO\(_2)/\text{N}_2\) permselectivity of 15.7).\(^18\)

Based on the above design considerations, a series of PAs containing PDMS group were synthesized in the present work via polycondensation towards enhancing gas permeability. After FTIR, \(^1\)H NMR, and UV-visible absorption spectra characterizations, the single-gas (H\(_2\), O\(_2\), CO\(_2\), CH\(_4\), and N\(_2\)) permeation properties of the membranes were evaluated at 25 °C and 1.0 atm. In addition, the effect of PDMS content on single-gas separation properties of membranes was extensively discussed. The gas permeability of the optimum PA-PDMS-20 membrane was further explored in a wide temperature (25–55 °C) and pressure (1.0–3.0 atm) range.

2 Experimental

2.1 Materials

All chemicals and reagents were used without further purification. 4,4'-Oxybis (benzoic acid) (OBA, 98%) were purchased from Meryer Chemical Technology Co., Ltd., China.
Poly(dimethylsiloxane)bis(aminokyl) terminated (PDMS, $M_w = 2000$ g mol$^{-1}$) was obtained from Aladdin (China). 4,4′-(Fluorenylidene)dianiline (9FDA) was synthesized according to the reported procedure.$^{19}$ $N,N$-Dimethylformamide (DMF), $N,N$-dimethylacetamide (DMAc), triphenyl phosphite (TPP, 99%), pyridine (Py, 99%) and calcium chloride were supplied by Tianjin Reagent Co., Ltd., China. Cylinders of CO$_2$, CH$_4$ and N$_2$ gases (99.9%) were purchased from Gas Production Plant, Taiyuan, China.

## 2.2 Synthesis of PA-PDMS copolymers

Polyamide-poly(dimethylsiloxane)s containing PDMS groups (PA-PDMS-x, x: weight content (wt%) of PDMS) are successfully synthesized via condensation copolymerization as shown in Scheme 1. A typical procedure for the synthesis of PA-PDMS-20 has as follows: a mixture of OBA (0.294 g, 1.14 mmol), 9FDA (0.368 g, 1.05 mmol), PDMS (0.166 g, 0.09 mmol), 1.4 mL of Py, TPP (1.4 mL, 5.34 mmol), 5 mL of DMAc and calcium chloride (0.368 g, 1.05 mmol) were added to a round-bottom flask equipped with a reflux condenser and a nitrogen inlet. The reaction mixture was heated at 120 °C for 36 h under continuous stirring. Afterwards, it was poured slowly into 150 mL methanol to filter and washed several times with methanol followed by hot and cold deionized water to remove the adsorbed solvent and residual CaCl$_2$. The final products were dried in a vacuum oven at 60 °C for 24 h. A series of PA-PDMS-x (as show in Scheme 1) were successfully synthesized using the same procedure as described for synthesis of PA-PDMS-10. The reaction conditions and properties of copolymer are listed in Table 1.

## 2.3 Preparation of PA-PDMS copolymer membranes

PA-PDMS-x (0.2 g) was dissolved in DMAc (25 mL) to obtain an 8% solution. The solution was placed on a flat glass plate and dried in oven at 80 °C for 24 h to obtain a thin (50–70 μm thick), transparent and tough membrane.

### Table 1. Yield, inherent viscosity, density and fractional free volume (FFV) of PA-PDMS copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>OBA (g)</th>
<th>9FDA (g)</th>
<th>PDMS (g)</th>
<th>Yield (%)</th>
<th>$\eta_{inh}$ (dL g$^{-1}$)</th>
<th>$\rho$ (g mL$^{-1}$)</th>
<th>FFV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-PDMS-5</td>
<td>0.294</td>
<td>0.393</td>
<td>0.036</td>
<td>96.3</td>
<td>4.694</td>
<td>1.114</td>
<td>0.212</td>
</tr>
<tr>
<td>PA-PDMS-10</td>
<td>0.294</td>
<td>0.386</td>
<td>0.076</td>
<td>95.5</td>
<td>4.332</td>
<td>1.119</td>
<td>0.207</td>
</tr>
<tr>
<td>PA-PDMS-15</td>
<td>0.294</td>
<td>0.378</td>
<td>0.118</td>
<td>97.1</td>
<td>4.018</td>
<td>1.125</td>
<td>0.203</td>
</tr>
<tr>
<td>PA-PDMS-20</td>
<td>0.294</td>
<td>0.368</td>
<td>0.166</td>
<td>95.8</td>
<td>4.676</td>
<td>1.130</td>
<td>0.197</td>
</tr>
</tbody>
</table>

### Scheme 1. Synthesis of PA-PDMS copolymers.
polyamide segments and PPG segments, respectively; \( V_{w1} \) and \( V_{w2} \) are the van der Waals volumes for the two segments, respectively. Mechanical properties of the membranes were measured using a Shimadzu Autograph AGS-X 500 N tensile testing instrument with a strain rate of 5% min\(^{-1}\) at room temperature. The rectangular specimens were fabricated with an initial width of 8 mm, gauge length of 30 mm and thickness of 30–50 \( \mu \)m.

2.5 Gas permeability measurements

Gas permeability of the membranes was performed using a gas permeability device (VAC-V2, Labthink Instruments Company, China). Gas permeation properties of the membranes were determined using five gases, i.e. \( \text{CO}_2 \), \( \text{CH}_4 \) and \( \text{N}_2 \), at a feed pressure of 1.0 atm and different temperatures (25–55 °C). The permeability (\( P \)) of each gas was calculated by the eqn (2):\(^{21}\)

\[
P = \frac{1}{76} \frac{273.15 V}{T} \frac{1}{A} \frac{dp}{dt} \quad (2)
\]

where \( P \) is the gas permeability (barrer) (1 barrer = \( 1 \times 10^{-10} \) cm\(^3\) (STP) cm (cm\(^{-2}\) s\(^{-1}\) cmHg\(^{-1}\))), \( \Delta P \) is the trans-membrane pressure difference (Pa); \( A \) is the effective membrane area (cm\(^2\)); \( T \) is the operating temperature (K); \( l \) is the membrane thickness (cm); \( V \) is the downstream volume (cm\(^3\)) and \( dp/dt \) is the rate of the pressure rise under the steady state.

Lag method using the following equation:

\[
D = L^2/6 \theta \quad (3)
\]

where \( D \) is the diffusion coefficient (\( 10^8 \) cm\(^2\) s\(^{-1}\)), \( L \) is the membrane thickness, and \( \theta \) is the time lag, which is given by the intercept of the asymptotic line of time-pressure curve to the time axis.

The \( S \) value was calculated by using equation:

\[
S = P/D \quad (4)
\]

Fig. 1 FTIR spectra of PA-PDMS copolymers.

Fig. 2 \(^1\)H NMR spectra of PA-PDMS-10.
The ideal selectivity ($\alpha$) of one penetrant (A) over another (B) is given by:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

### 3 Results and discussion

#### 3.1 Synthesis and characterization of PA-PDMS copolymers

The PA-PDMS copolymers were synthesized by polycondensation reaction as illustrated in Scheme 1. The density and FFV values of polymers were summarized in Table 1. The density values of PA-PDMS copolymers were in the range of 1.114–1.130 g mL$^{-1}$, while their FFV values varied from 0.197 to 0.212. As expected, the FFV values of the PA-PDMS copolymers gradually decreased with the increase of PDMS content, due to the cracks of polymer chains filled with the flexible PDMS soft segments.

The chemical structure of the PA-PDMS-x samples was confirmed based on the FTIR spectra in Fig. 1. The bands at 1635, 1184, and 1163 cm$^{-1}$ belong to aromatic C=C stretching vibration, C–O–C stretching vibration of OBA, respectively. On the other hand, the swing at 1251 cm$^{-1}$ and 1009 cm$^{-1}$ can be attributed to –Si–O–Si– and –Si(CH$_3$)$_3$–O– in PDMS. The N–H and C=O stretching vibrations from amide groups were observed approximately at 3442 and 1668 cm$^{-1}$, respectively.

The chemical structure of the PA-PDMS-5 was further examined by $^1$H NMR with DMSO-$d_6$ as the solvent. The $^1$H-NMR spectra of PA-PDMS-5 sample is shown in Fig. 2. A group of peaks at 7.0–8.1 ppm are due to the aromatic protons of benzene ring.$^{23}$ The peaks at 1.2 ppm are assigned to –CH$_3$ groups protons of PDMS.$^{24}$ In addition, the peak at 10.2 ppm is originated by amide group proton, indicating the successful synthesis of PA-PDMS copolymers. The mechanical properties of the membranes were measured at room temperature (Table 2). The membranes samples of PA-PDMS-x showed higher tensile strength (18–23 MPa) and lower strain (30–51%). These data indicate these membranes are strong and tough enough to be applied as membrane for gas separation.

#### 3.2 UV-vis absorption analysis

UV-vis absorption spectrum is a useful method to analyze molecular interactions.$^{25}$ UV-vis absorption bands of PA-PDMS copolymers were performed in DMF solvent at room temperature and the results are presented in Fig. 3. As shown in Fig. 3, polymers exhibited similar absorption bands between 268 and 298 nm, indicating that the center of absorption bands is related to intramolecular and intermolecular charge-transfer interactions. Furthermore, the maximum absorption band ($\lambda_{max}$) of PA-PDMS copolymers tend to red-shifted towards higher wavelength with the increase in PDMS content. The short absorption band is generally found in the intramolecular charge-transfer complexes, whereas the intermolecular charge-transfer occurs in the long absorption band.$^{26}$ The following order, in relation to $\lambda_{max}$ values, was obtained: PA-PDMS-5 < PA-PDMS-10 < PA-PDMS-15 < PA-PDMS-20. Therefore, the order of the intermolecular interaction strength of polymers is PA-PDMS-5 < PA-PDMS-10 < PA-PDMS-15 < PA-PDMS-20.

![Fig. 3 UV-vis absorption bands of PA-PDMS copolymers.](image-url)

### Table 2 Mechanical properties of PA-PDMS-x membranes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>22</td>
<td>36</td>
</tr>
<tr>
<td>PA-PDMS-5</td>
<td>23</td>
<td>30</td>
</tr>
<tr>
<td>PA-PDMS-10</td>
<td>21</td>
<td>44</td>
</tr>
<tr>
<td>PA-PDMS-15</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>PA-PDMS-20</td>
<td>18</td>
<td>51</td>
</tr>
</tbody>
</table>

where $S$ is the solubility coefficient ($10^3$ cm$^3$ STP cm$^{-3}$ cmHg$^{-1}$).

The chemical structure of the PA-PDMS-x samples was further confirmed based on the FTIR spectra in Fig. 1. The bands at 1635, 1184, and 1163 cm$^{-1}$ belong to aromatic C=C stretching vibration, C–O–C stretching vibration of OBA, respectively. On the other hand, the swing at 1251 cm$^{-1}$ and 1009 cm$^{-1}$ can be attributed to –Si–O–Si– and –Si(CH$_3$)$_3$–O– in PDMS. The N–H and C=O stretching vibrations from amide groups were observed approximately at 3442 and 1668 cm$^{-1}$, respectively.

The chemical structure of the PA-PDMS-5 was further examined by $^1$H NMR with DMSO-$d_6$ as the solvent. The $^1$H-NMR spectra of PA-PDMS-5 sample is shown in Fig. 2. A group of peaks at 7.0–8.1 ppm are due to the aromatic protons of benzene ring.$^{23}$ The peaks at 1.2 ppm are assigned to –CH$_3$ groups protons of PDMS.$^{24}$ In addition, the peak at 10.2 ppm is originated by amide group proton, indicating the successful synthesis of PA-PDMS copolymers. The mechanical properties of the membranes were measured at room temperature (Table 2). The membranes samples of PA-PDMS-x showed higher tensile strength (18–23 MPa) and lower strain (30–51%). These data indicate these membranes are strong and tough enough to be applied as membrane for gas separation.

### Table 3 Gas permeability of PA-PDMS copolymer membranes at 25 °C and 1.0 atm$^a$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$P$(H$_2$)</th>
<th>$P$(CO$_2$)</th>
<th>$P$(O$_2$)</th>
<th>$P$(CH$_4$)</th>
<th>$P$(N$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>8.09 ± 0.19</td>
<td>6.58 ± 0.11</td>
<td>1.31 ± 0.03</td>
<td>0.32 ± 0.05</td>
<td>0.26 ± 0.01</td>
</tr>
<tr>
<td>PA-PDMS-5</td>
<td>10.53 ± 0.38</td>
<td>8.87 ± 0.42</td>
<td>1.55 ± 0.11</td>
<td>0.37 ± 0.08</td>
<td>0.29 ± 0.01</td>
</tr>
<tr>
<td>PA-PDMS-10</td>
<td>13.92 ± 0.21</td>
<td>11.65 ± 0.51</td>
<td>2.14 ± 0.09</td>
<td>0.45 ± 0.03</td>
<td>0.37 ± 0.05</td>
</tr>
<tr>
<td>PA-PDMS-15</td>
<td>17.67 ± 0.59</td>
<td>14.31 ± 0.72</td>
<td>2.61 ± 0.06</td>
<td>0.53 ± 0.01</td>
<td>0.43 ± 0.02</td>
</tr>
<tr>
<td>PA-PDMS-20</td>
<td>22.14 ± 0.93</td>
<td>18.02 ± 0.86</td>
<td>3.19 ± 0.15</td>
<td>0.66 ± 0.12</td>
<td>0.51 ± 0.09</td>
</tr>
</tbody>
</table>

$^a$ Gas permeability ($P$) in barrer. 1 barrer = $10^{-10}$ cm$^3$ (STP) cm$^{-1}$ cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$. 

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polymer chains, and hence to a decrease of FFV values. Obviously, the order of $\lambda_{\text{max}}$ values is opposite to that of FFV values.

### 3.3 Effect of PDMS groups on gas permeability

Permeation measurements were carried out using pure H₂, O₂, CO₂, N₂ and CH₄ at different pressures and temperatures. To investigate the effect of PDMS groups on gas permeability, a series of polyamide-poly(dimethylsiloxane)s containing PDMS groups were fabricated. The permeability of all gases at different PDMS contents is shown in Table 3. We can see that the gas permeability of the membrane increased with the increase of PDMS content, which is due to the high flexibility of $-\text{O-Si-O-}$ bonds of PDMS. As the PDMS content increases from 5% to 20%, an increase in the CO₂ permeability was observed for the PA-PDMS-x membranes. For instance, PA-PDMS-20 membrane exhibits a permeability of 18.02 barrer at 25°C and 1.0 atm, which is much higher than that of PA-PDMS-5 membrane (8.87 barrer). A similar permeability behavior was observed for the rest gases (H₂, O₂, N₂, CH₄).

The selectivity of PA-PDMS-x membranes in relation to relevant gas-pairs is listed in Table 4. As shown in Table 4, the selectivity increases monotonously with increasing PDMS content. The PA-PDMS-20 membrane exhibits higher selectivity for the CO₂/N₂ (35.33) and O₂/N₂ (6.25) gas-pairs. This can be explained by kinetic diameter that the easier diffusion of CO₂ and O₂, due to their lower kinetic diameter (H₂ 2.89 Å, CO₂ 3.3 Å, O₂ 3.46 Å, N₂ 3.64 Å, CH₄ 3.69 Å),

#### Table 4 Selectivity of PA-PDMS copolymer membranes at 25 °C and 1.0 atm

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$a$(H₂/N₂)</th>
<th>$a$(H₂/CH₄)</th>
<th>$a$(CO₂/N₂)</th>
<th>$a$(CO₂/CH₄)</th>
<th>$a$(O₂/N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>31.16 ± 1.91</td>
<td>25.28 ± 1.02</td>
<td>25.31 ± 0.98</td>
<td>20.56 ± 1.29</td>
<td>5.04 ± 0.21</td>
</tr>
<tr>
<td>PA-PDMS-5</td>
<td>36.31 ± 1.35</td>
<td>28.46 ± 1.02</td>
<td>30.57 ± 1.24</td>
<td>23.97 ± 0.98</td>
<td>5.35 ± 0.25</td>
</tr>
<tr>
<td>PA-PDMS-10</td>
<td>37.62 ± 0.97</td>
<td>30.93 ± 1.34</td>
<td>31.47 ± 1.11</td>
<td>25.89 ± 1.51</td>
<td>5.78 ± 0.23</td>
</tr>
<tr>
<td>PA-PDMS-15</td>
<td>40.09 ± 1.58</td>
<td>33.34 ± 1.26</td>
<td>33.28 ± 1.23</td>
<td>27.00 ± 1.37</td>
<td>6.07 ± 0.22</td>
</tr>
<tr>
<td>PA-PDMS-20</td>
<td>43.41 ± 1.46</td>
<td>33.55 ± 1.08</td>
<td>35.33 ± 1.16</td>
<td>27.30 ± 1.12</td>
<td>6.25 ± 0.23</td>
</tr>
</tbody>
</table>

#### Table 5 Permeation activation energy ($E_k$) of PA-PDMS-20 membrane

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CO₂</th>
<th>H₂</th>
<th>O₂</th>
<th>N₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPA-PPG (20%)</td>
<td>11.29</td>
<td>13.37</td>
<td>13.99</td>
<td>16.31</td>
<td>17.97</td>
</tr>
</tbody>
</table>
and CH₄ 3.8 Å). The permselectivity for the relevant gas pairs, CO₂/N₂ and O₂/N₂ versus P(CO₂) and P(O₂) of PA-PDMS-x membranes are plotted in the Robeson permeability/selectivity trade-off plots, as shown in Fig. 4. The fabricated PA-PDMS-x membranes exhibited very promising results; for CO₂/N₂ gas pairs, the data point of PA-PDMS-20 was close to the Robeson line in 2008 and for O₂/N₂ gas pairs which was close to the Robeson line in 1991.

### 3.4 Effect of operating temperature

The temperature dependence of gas permeability and selectivity of PA-PDMS-20 was investigated in the temperature range of 25–55 °C at a constant pressure of 1.0 atm. The PA-PDMS-20 membrane was selected for further investigation, since it exhibited the best separation performance. The corresponding results are presented in Fig. 5. As shown in Fig. 5, the permeability of PA-PDMS-20 gradually increased with the increase of operating temperature. For instance, the CO₂ gas permeability has increased by ca. 40%, i.e. from 18.02 to 29.83 barrer (Table 5). These results are in accordance with the Arrhenius equation (6):

\[
P = P_0 \exp \left( \frac{-E_P}{RT} \right)
\]

where \( P \) is gas permeability coefficient; \( P_0 \) is the pre-exponential coefficient; \( R \) is 8.314 J mol⁻¹ K⁻¹; \( E_P \) is the apparent activation energy for permeation process; and \( T \) is the absolute temperature (K). The improvement in gas permeability was mainly attributed to the following reasons: (i) the thermodynamic energy of gas molecules is increased with temperature, resulting in an increase of jumping frequency; (ii) the mobility between polymer chains is increased with temperature increase, resulting in an increase of fractional free volume and molecules transport.

The selectivity of PA-PDMS-20 membrane gradually decreased with the increase of temperature as shown in Fig. 6. The permeation activation energy (\( E_P \)) of PA-PDMS-20 membrane for H₂, O₂, CO₂, CH₄ and N₂ is shown in Table 5. As illustrated in Table 5, the order of permeation activation energy was \( E_P(CO₂) < E_P(H₂) < E_P(O₂) < E_P(N₂) < E_P(CH₄) \). This order is exactly opposite to the permeability coefficient: \( P(CO₂) > P(H₂) > P(O₂) > P(N₂) > P(CH₄) \). Gas penetrant with higher permeation activation energy led to an enhanced permeability with the increase in operating temperature, which in turn resulted in a decreased selectivity.

### 3.5 Effect of operating pressure

The impact of pressure was assessed by employing H₂, O₂, CO₂, CH₄, and N₂ at 35 °C in a pressure range of 1.0–3.0 atm [Fig. 7]. It is evident that the permeability of all gases (H₂, O₂, CO₂, CH₄, N₂) increases with pressure. This phenomenon was observed for glassy materials at high pressure, where the contribution of the Langmuir region to the overall permeability diminishes and gas permeability approaches a constant value associated with simple dissolution (Henry's law) transport. Koros and Paul suggested the immobilization theory for the correlation between permeability and temperature.

### Table 6 The effects of pressure on diffusivity coefficient and solubility coefficient of PA-PDMS-20

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>H₂</th>
<th>CO₂</th>
<th>O₂</th>
<th>CH₄</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>6.04</td>
<td>4.10</td>
<td>1.65</td>
<td>0.32</td>
<td>0.27</td>
</tr>
<tr>
<td>2.0</td>
<td>7.66</td>
<td>5.37</td>
<td>2.27</td>
<td>0.39</td>
<td>0.31</td>
</tr>
<tr>
<td>3.0</td>
<td>9.19</td>
<td>6.69</td>
<td>2.85</td>
<td>0.45</td>
<td>0.36</td>
</tr>
</tbody>
</table>

\( ^a \) Diffusivity coefficient, 10⁻⁸ cm² s⁻¹. \( ^b \) Solubility coefficient, 10⁻⁷ cm³ STP cm⁻³ cmHg⁻¹.
pressure and solubility and diffusivity coefficients. This model indicates in general that the CO$_2$ and CH$_4$ diffusivity coefficients increased with pressure whereas their solubility coefficients decreased upon increasing pressure.\textsuperscript{3,14} The diffusion coefficients at different pressures obtained in the present work are shown in Table 6. As shown in Fig. 7 and Table 6, the N$_2$ and CO$_2$ permeability of PA-PDMS-20 membrane increased by about 11.4 and 33.0%, respectively, by increasing the pressure from 1.0 to 3.0 atm. On the other hand, the diffusion coefficient declined by about 38.7% and 25% for CO$_2$ and N$_2$, respectively, by increasing the pressure from 1.0 to 3.0 atm. A similar behaviour was observed for the rest gases. Fig. 8 shows the effect of pressure on ideal selectivity at 35 °C, which is increased upon pressure increase. This is because gas penetrants with smaller diameter offer higher permeability upon pressure increase, which consequently leads to a higher selectivity.

4 Conclusions

In summary, a series of copolymers with different PDMS content were synthesized though polycondensation reaction. The chemical structure of PA-PDMSs was characterized by FTIR and $^1$H NMR. The gas permeability of PA-PDMSs was investigated in a wide temperature and pressure range. CO$_2$ permeability gradually increased upon increasing operating temperature and PDMS content, while CO$_2$/N$_2$ selectivity progressively decreased. The best performance was obtained for PA-PDMS-20, which showed the highest selectivity (CO$_2$/N$_2$ = 41.84 and O$_2$/N$_2$ = 7.01) at 35 °C and 3 atm, accompanied by CO$_2$ and O$_2$ permeability values as high as 29.29 and 4.91 barrer, respectively.

Conflicts of interest

There are no conflicts to declare.

References