Solvent-induced microstructure of polyimide membrane to enhance CO$_2$/CH$_4$ separation

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ABSTRACT
Membrane technology, a successful technology for separating gases such as CO$_2$/CH$_4$ mixture, has attracted much attention because of its low energy consumption, and membrane performance is an important factor affecting its industrial application. Herein, the solvent-induced microstructure of a polyimide membrane was employed to enhance its CO$_2$/CH$_4$ separation performance. The effect of solvents on the membrane structure and gas separation performance was investigated by using different solvents (such as tetrahydrofuran, N,N-dimethylacetamide) to dissolve a newly synthesized polyimide polymer, which was fabricated into a membrane. Various characterization methods, such as positron annihilation lifetime spectroscopy (PALS) and X-ray diffractometry (XRD), were conducted to reveal changes in the microstructure of membranes prepared with different solvents. The interaction of solvents with groups of polymer backbones was also analyzed for the explanation of the effect of solvents on the membrane performance for the separation of different gas pairs, such as CO$_2$/CH$_4$ mixture. The results showed that a membrane with optimal separation performance was obtained by optimizing the solvent composition, which exceeded the 2018 mixed-gas CO$_2$/CH$_4$ upper bound. The induced effect of solvents on the polymer membrane structure provides a new research path for the optimization of polymer membranes to enhance separation performance.

1. Introduction
Carbon dioxide (CO$_2$) is primarily found in natural gas, biogas, and landfill gas. However, the presence of CO$_2$ decreases the combustion calorific value of these gases and causes them to have a certain corrosivity and toxicity [1,2], which increases the risk of pipeline transportation, and anti-corrosion materials used for prevention increase the cost. Therefore, the separation of CO$_2$ from natural gas is of great importance [3,4]. General methods for separating CO$_2$ include adsorption [5], absorption [6], cryogenic condensation [7], and membrane separation [8]. Membrane technology can be a powerful tool for the CO$_2$ capture process because of its high energy efficiency, low cost, and good scalability [2,7,9].

The nature of a membrane material is the key factor for improving separation performance and promoting the application of membrane technology. Common membrane materials include ceramics [10], molecular sieves [11], metal-organic frameworks (MOFs) [12,13], and organic polymers [14]. Among them, organic glassy polyimide (PI) is an ideal membrane material owing to its good thermal stability, chemical resistance, and mechanical strength [15]. In addition, the presence of abundant electron-rich N and O atoms in the polyimide result in its strong affinity to CO$_2$ molecules via dipole-quadrupole interactions [16], which makes PI a prospective membrane material in the field of CO$_2$ capture. However, traditional PI membrane separation performance needs to be further improved to make it more competitive for commercialization.

Polymer molecular design is an ideal method for improving the performance of polymer membranes [2,17]. In 2004, Budd et al. [18] introduced twisted nodes and bulky side groups into polymers to limit the rotation and aggregation of chains and obtained polymers of intrinsic microporosity (PIMs) with high free volume and permeability. In 2008, Ghanem et al. [19] prepared polyimides of intrinsic microporosity (PIM-PIs) using the same strategy, which takes advantage of the properties of both PIMs and PI. Compared with traditional polyimide with a low free volume, PIM-PI has abundant micro pores, a higher free volume fraction, and an ultra-high gas permeability, with a CO$_2$ permeability of 3700 Barrer.

In addition to the synthesis of different membrane materials to...
enhance membrane performance, fabrication conditions, such as the choice of solvent in the polymer membrane-forming process, can also affect membrane performance because the shape or conformation of polymer chains can be affected by the used solvents owing to their different properties [20]. The choice of solvent has become an important focus for the optimization of conditions [21–25], and has been studied by many researchers, who have found that solvent effects have a significant influence on membrane structure. Different membrane separation performance can thus be observed when different solvents are used for the dissolution of a polymer. Zhao et al. [24] used acetic acid and n-butanol to explore the influence of solvent on the permeability of polyether block amide (PEBA). It was found that when acetic acid was used as the solvent, partial hydrolysis of the amide group occurred, which increased the number of amorphous regions in the membrane, leading to enhanced permeability. Hill et al. [21] found that the casting solvent affected the degree of entanglement of PIM-1 polymer chains. When tetrahydrofuran (THF) was used, chain entanglement was enhanced and gas selectivity was higher, whereas when a mixed solution of dimethylformamide/mesitylene was used, the degree of entanglement of polymer chain was lower, and higher gas permeability was observed. Furthermore, the solvent effect also affects the interface effect in the mixed-matrix membranes, thus changing the separation performance and anti-aging performance of the membrane [26]. Previous studies have demonstrated the importance of solvents in membrane formation. Meanwhile, much attention has been paid to analyzing the influence of solvents on membrane structure and separation performance, whereas less attention has been paid to the mechanism. Different polymers may require different solvents to endow the formed membranes with the best separation performance.

In this study, a PIM-PI polymer was first synthesized. Solvents such as N, N-dimethylacetamide (DMAC), dichloromethane, chloroform, THF, N, N-dimethylformamide (DMF), and N-methylpyrrolidone (NMP), as examples of commonly used solvents, were employed for the dissolution of polyimide [27], in order to study their effect on membrane structure. Different characterization methods, such as dynamic light scattering, X-ray diffraction, physical adsorption, and positron annihilation were used to investigate changes in membrane structure. The effect of the solvent on membrane performance was explored by analyzing the properties of the solvent and polymer chains. The diffusion coefficient and solubility coefficient were then investigated, and the separation performance and aging performance were investigated for the separation of gas pairs, such as CO₂/CH₄ mixtures. This work highlights the importance of the solvent and provides guidance for the membrane fabrication process.

2. Experimental

2.1. Materials

The chemicals m-Cresol (purity: 98%), N,N-dimethylacetamide (DMAC, 99.8%), N,N-dimethylformamide (DMF, 99.5%), and N-methylpyrrolidone (NMP, 99.5%) were purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd. Isoquinoline (97%), tetrahydrofuran (THF, 99%), and 2,2′-bis(trifluoromethyl)benzidine (TFMB, 98%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Acetic acid (AcOH, 99.5%), acetic anhydride (Ac₂O, 99.5%), and toluene (99.5%) were purchased from Shanghai Macklin Biochemical Co., Ltd. All the reagents were used as received. Triptycene-2,3,6,7-tetracarboxylic acid was prepared according to a reported procedure [28]. The diazonium was synthesized by the decarboxylation process shown in Scheme S1 in the Supplementary Information, and its characterization is shown in Figs. S1 and S2. H₂, N₂, CO₂, and CH₄ (99.999%) were purchased from Nanjing Chuangda Special Gas Co. Ltd.

2.2. Polymer synthesis

The triptycene-based polyimides (PI-Trip-TFMB) were prepared by the reaction of triptycene-2,3,6,7-tetracarboxylic dianhydride with 2,2′-bis(trifluoromethyl)benzidine in m-cresol in the presence of toluene and isoquinoline at 190 °C, as illustrated in Scheme 1. In a 50 mL flask, triptycene-2,3,6,7-tetracarboxylic dianhydride (0.39 g, 1 mmol), equimolar amine, m-cresol (8 mL), toluene (3 mL) and a few drops of isoquinoline were added. The mixture was stirred at room temperature for 1 h, then the temperature was raised gradually to 190 °C for 4 h under a nitrogen atmosphere. The mixture was then poured into methanol (300 mL) with constant stirring and allowed to precipitate. The polymer was filtered, washed with water and methanol several times, and dried at 120 °C in a vacuum oven for 24 h to produce a yield of 97%. Analysis by GPC (THF): Mn = 135,115, Mw = 211,412, Mw/Mn = 1.56. The NMR and FT-IR spectra shown in Fig. S3 confirm the synthesis of PI-Trip-TFMB. The TGA curve shown in Fig. S4 exhibits good thermal stability. The adsorption isotherms of N₂ and pore size distribution analysis are shown in Fig. S5, which shows that the polymer possesses ultramicroporosity and a BET surface area of 406 m²/g. Detailed characterization is provided in the Supplementary Information.

2.3. Membrane preparation

Solutions (2.5 wt/vol%) of PI-Trip-TFMB in solvents were filtered through 0.45 μm polypropylene filters, and a homogeneous membrane was obtained by slow evaporation of the solvents at room temperature or 80 °C from a level glass Petri dish. To remove any traces of residual solvent, the dry membrane was soaked in methanol for 24 h, air-dried overnight, and then transferred into a vacuum oven for 24 h at 120 °C. The resulting membranes were used for gas permeation measurements. The membrane thickness for the gas permeation measurements was determined using a digital micrometer, and the average effective area was 12.56 cm².

2.4. Gas permeation measurements

Gas transport properties in polymeric membranes typically follow the solution-diffusion model as shown in equation (1):

\[ P = D \cdot S \]  

(1)

where \( P \) is the permeability (Barrer), \( D \) is the diffusion coefficient (cm²/s⁻¹), and \( S \) is the solubility coefficient (cm³(STP) cm⁻³ cmHg⁻¹), which can be calculated using Equation (2):

\[ S = \frac{Q \cdot p}{P} \]  

(2)

where \( Q \) is the quantity adsorbed (cm³(STP)/g), \( p \) is the density (g/cm³), and \( p \) is the pressure (cmHg).

The permeability and ideal selectivity for pure gas and the permeability of the gas mixtures were measured using a constant-pressure permeation system. Data points were obtained using multiple independent tests. A CO₂/CH₄ (50/50 vol%) mixture was used as the feed gas, and the stage cut was controlled to less than 1% to avoid the influence of feed concentration change on the separation performance. The concentrations of CO₂ and CH₄ on the permeate side were detected using a gas chromatograph (Agilent 7890 GC) equipped with a thermal conductivity detector. The gas permeability of component \( i \) (\( P_i \)) can be calculated using Equation (3):

\[ P_i = \frac{I \times 273.15}{A \times T} \times \frac{p}{76} \times \frac{V}{t} \times \frac{1}{2P_f} \]  

(3)

where \( A \) is the membrane area, \( I \) is the thickness, \( T \) is the temperature, \( p \) is the pressure, \( p_f \) is the feed pressure, \( P_f \) is the pressure of component \( i \) in the feed mixture, and \( V \) is the volume of gas produced.
is the atmospheric pressure, \( V / t \) is the volumetric displacement rate in the soap bubble flowmeter, \( \Delta P \) is the transmembrane pressure, \( p_0 \) and \( p_1 \) represent the pressure of the raw material side and permeate side, respectively, and \( x \) and \( y \) represent the volume fraction of the raw material side and permeate side of component \( i \), respectively. The ideal selectivity of the gas pair can be determined by the ratio of the permeability of the individual gases using Equation (4):

\[
\alpha_{ij} = \frac{P_i}{P_j}
\]

(4)

Here, \( i \) and \( j \) represent different components. The mix-gas selectivity was calculated using Equation (5):

\[
\alpha_{ij} = \frac{y_i}{y_j}
\]

(5)

where \( i \) and \( j \) represent different components and \( x \) and \( y \) represent the volume fractions of the raw material and permeate sides, respectively.

3. Results and discussion

3.1. Characteristics of membrane

In the membrane fabrication process, polymer processability is a key factor affecting polymer applications in the membrane field. Solubility in different solvents, such as dichloromethane, chloroform, THF, DMF, DMAc, and NMP, was investigated. The results showed that the synthesized PI-Trip-TFMB polymer was solubile only in THF, DMF, DMAc, and NMP to form membranes, and their membrane performance was characterized by gas permeability, as shown in Table 1. The membrane fabricated in THF shows the highest selectivity but the lowest permeability; in contrast, the membranes fabricated in DMF, DMAc, and NMP show similar separation performance but lower selectivity and higher permeability than those of the membrane fabricated in THF. To investigate the intrinsic mechanism, THF, DMAc, and a mixture of the two were selected to fabricate membranes, and their properties were characterized, as shown in Fig. 1 and 2.

From Fig. 1 (a), it can be seen that homogeneous membranes with high transparency and flexibility were obtained in all solvents with different DMAc/THF ratios. This is because the trifluoromethyl group has a strong electron-withdrawing ability and a large molecular volume, which can hinder electron flow, conjugation between molecular chains, and the probability of charge transfer complex (CTC) formation, thus improving transparency [29–31].

The surface and cross-sectional morphology of the membranes is shown in Fig. 1 (b). It can be seen that all the membrane surfaces are compact without visible surface defects, and there are no precipitated particles or delamination in the cross-sectional view, demonstrating that PI-Trip-TFMB can be dissolved in these solvents owing to the presence of trifluoromethyl groups in the polymer backbone, which favors the solubility of the polymer [29–31].

Fig. 2 (a) shows that the characteristic absorption bands of all membranes obtained using different solvents are observed at \( \sim 780, 1720, \) and \( 1357 \text{ cm}^{-1} \), assignable to the imide asymmetric and symmetric \( \text{C}=\text{O} \) stretching and \( \text{C}=\text{N} \) stretching, respectively. All membranes represent a consistent peak shift, indicating that solvation only affects the physical structure of the membrane and the separation performance [32], instead of a change in the degree of hydrolysis of the structure [24, 33].

Fig. 2 (b) shows \( \text{CO}_2 \) adsorption isotherms for four membranes measured at 273 K. \( \text{CO}_2 \) was used as a probe because of its smaller kinetic diameter than that of the \( \text{N}_2 \) molecule, so that more area can be accessed by \( \text{CO}_2 [34] \), leading to a higher surface area than that obtained by the \( \text{N}_2 \) molecule, as shown in Fig. S6. The specific surface area of the four membranes is approximately 280–310 \( \text{m}^2/\text{g} \), and the higher the proportion of DMAc, the larger the specific surface area; thus a higher adsorption capacity can be expected.

From Fig. 2 (c), it can be seen that these membranes possess many ultramicropores (at about 5.5 Å). This corresponds well with the \( d \)-spacing shown in Fig. S7. The pore size distributions of the membranes prepared with different DMAc/THF ratios are very similar, but their pore volumes are different. The pore volume increases with an increase in the DMAc ratio. An increase in pore volume indicates an increase in free volume, which is beneficial for the improvement of gas permeability [35].

To characterize the change in the free volume of the membranes, PALs was employed. Table 2 presents the PALs results of the two samples. The ortho positron lifetime (\( \tau \)), free volume (\( V \)), etc. of each sample are listed, and fall within the ranges reported in the literature [36–38]. The membrane prepared from pure THF possesses a smaller free volume than that prepared from pure DMAc, which is consistent with the results in Fig. 2 (b) and (c). This can be explained by the effect of the solvent on the degree of relaxation of the polymer chains during the membrane-forming process.

The degree of polymer chain relaxation at different ratios of solvents can be judged according to the coil sizes of the polymer chains in the DLS characterization, as shown in Fig. 3. It can be seen that the average coil sizes of the polymer prepared at DMAc/THF ratios of 0:10, 5:5, 9:1, and 10:0 were 15.67, 11.67, 7.53, and 7.53 nm, respectively, showing that coil size decreases with an increasing DMAc ratio. This may be due to solvation, which strongly affects the chemical environment of adjacent groups [21]. In the three groups of PI-Trip-TFMB shown in Fig. 4, \( \text{o-xylene (1) and phthalic anhydride (2) groups form a rigid part and the benzotrifluoride (3) group is a flexible part. The phthalic anhydride group has strong polarity, but the others are weakly polar or nonpolar. For solvents, the polarity of DMAc is much larger than that of THF because the dielectric constant of DMAc (37.8) is much larger than that of THF (7.58), and the dielectric constant is related to the dipole moment of the polymer molecule, which is the vector sum of all bond moments in the molecule. The dipole moment can be used to judge the

Table 1

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Gas permeability (Barrer)</th>
<th>Ideal Selectivity (( \alpha ))</th>
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<tbody>
<tr>
<td></td>
<td>( \text{H}_2 )</td>
<td>( \text{N}_2 )</td>
</tr>
<tr>
<td>THF</td>
<td>284</td>
<td>22</td>
</tr>
<tr>
<td>DMAc</td>
<td>1571</td>
<td>131</td>
</tr>
<tr>
<td>DMF</td>
<td>1346</td>
<td>166</td>
</tr>
<tr>
<td>NMP</td>
<td>1782</td>
<td>134</td>
</tr>
</tbody>
</table>
spatial configuration of molecules and to indicate the magnitude of polarity [39]. Generally, the larger the dipole moment, the larger the dielectric constant and polarity [40]. According to the principle of “like dissolves like” [41], molecules with more polar groups are more soluble in polar solvents. Therefore, in highly polar solvents such as DMAc, the phthalic anhydride group is close to the DMAc solvent, but the o-xylene
group is far from the DMAc solvent, and the flexible benzotrifluoride group will shrink more. The coil size of the sol is the smallest (7.53 nm) in DMAc solvent; thus, the number of solvent molecules entering the polymer chain is less, which leads to insufficient relaxation of the polymer chain and lower coil sizes of the polymer chains. When the solvent evaporates, tiny voids between these coils may exist, leading to more transportation channels and free volume, as shown in Table 2. In low polarity solvents, such as THF, the o-xylene group is close to the THF solvent, but the phthalic anhydride group is far from the THF solvent, and the flexible benzotrifluoride group stretches more, which indicates that the polymer chain relaxes more, and a larger coil size (15.67 nm) of polymer chains in the solvent is thus observed. Thus, the polymer chains interpenetrate each other tightly when THF is evaporated, resulting in a solvent, but the phthalic anhydride group is far from the THF solvent, low polarity solvents, such as THF, the o-xylene group is close to the THF group will shrink more. The coil size of the sol is the smallest (7.53 nm) in DMAc solvent; thus, the number of solvent molecules entering the polymer chain is less, which leads to insufficient relaxation of the polymer chain and lower coil sizes of the polymer chains. When the solvent evaporates, tiny voids between these coils may exist, leading to more transportation channels and free volume, as shown in Table 2. In low polarity solvents, such as THF, the o-xylene group is close to the THF solvent, but the phthalic anhydride group is far from the THF solvent, and the flexible benzotrifluoride group stretches more, which indicates that the polymer chain relaxes more, and a larger coil size (15.67 nm) of polymer chains in the solvent is thus observed. Thus, the polymer chains interpenetrate each other tightly when THF is evaporated, resulting in a smaller free volume and pore size, as shown in Table 2, and lower permeability and higher selectivity are observed.

### 3.2. Effect of different solvent ratios on pure-gas permeation

Table 3 shows the gas permeability and ideal selectivity of the polyimide membranes prepared using different solvent ratios. As expected after comparing Tables 1 and 3, the membrane prepared in pure DMAc shows higher gas permeability than that in pure THF, and the membrane properties prepared from mixed solvents are in between those of the pure solvents, whereas the ideal selectivity shows an opposite trend, as discussed above. Table 4 shows the trend of the gas diffusion coefficient of the polyimide membrane obtained at different solvent ratios, also confirming that membranes show a decrease in diffusion coefficient with an increase in the proportion of THF. However, the solvent ratio has little effect on the solubility coefficient, because the polymers used to prepare these membranes are the same. Furthermore, the diffusion selectivity in Table S1 shows a decreasing trend with an increasing proportion of DMAc in the mixture, because a higher proportion of DMAc in the mixed solution results in a looser membrane structure and a larger channel size and free volume available for gas transportation. The pure-gas permeation shows that solvation affects the membrane performance by changing the free volume and pore size owing to interactions between the solvents and groups in the polyimide backbone.

### 3.3. Physical aging of membrane for CO$_2$/CH$_4$ separation

Fig. 5(a) shows the separation performance of the membranes for CO$_2$/CH$_4$ separation, and only the membranes prepared using DMAc: THF = 9:1 and 10:0 exceed 2008 upper bound. A similar phenomenon is observed in the separation of other gas pairs (Fig. S8) owing to the higher number of transport channels available for membranes prepared with higher DMAc concentration in the membrane solution. This is because with an increase in the proportion of DMAc in the mixed solution, the pore sizes in the membranes change slightly (Table 1), whereas the pore volume in the membrane prepared with a solution of DMAc:THF = 9:1 is approximately 30% higher than that prepared with a solution of DMAc:THF = 0:10, and the BET area is also higher by approximately 10%. Furthermore, the membrane fabricated with DMAc: THF = 9:1 has a higher selectivity and permeability, similar to those of DMAc:THF = 10:0. Thus, the membrane fabricated in DMAc:THF = 9:1 was selected for further investigation.

Fig. 5(b) shows the stability of the membranes for CO$_2$/CH$_4$ separation; similar to many glassy polymer membranes, the permeability drops dramatically at the initial stage of aging and then decreases slowly. After aging for 354 days, the permeability of CO$_2$ decreased by more than 50% to only 1104 Barrer, which indicates that although solvation can indeed enhance membrane permeability, the solvent-induced enhancement of free volume or pore volume is not stable.

### Table 3

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Gas permeability (Barrer)</th>
<th>Ideal Selectivity (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$</td>
<td>N$_2$</td>
</tr>
<tr>
<td>DMAc:THF = 9:1</td>
<td>1505</td>
<td>120</td>
</tr>
<tr>
<td>DMAc:THF = 9:1</td>
<td>1505</td>
<td>120</td>
</tr>
<tr>
<td>DMAc:THF = 9:1</td>
<td>1505</td>
<td>120</td>
</tr>
<tr>
<td>DMAc:THF = 9:1</td>
<td>1505</td>
<td>120</td>
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</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Diffusion coefficient ($10^{-8}$ cm$^2$/s)</th>
<th>Solubility coefficient ($10^{-2}$ cm$^3$(STP)/(cm$^3$ cmHg))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>N$_2$</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>DMAc:THF = 9:1</td>
<td>87.6</td>
<td>3.0</td>
</tr>
<tr>
<td>DMAc:THF = 9:1</td>
<td>103.8</td>
<td>3.5</td>
</tr>
<tr>
<td>DMAc:THF = 9:1</td>
<td>434.5</td>
<td>12.0</td>
</tr>
<tr>
<td>DMAc:THF = 9:1</td>
<td>443.8</td>
<td>15.7</td>
</tr>
</tbody>
</table>
Crosslinking of the membrane after solvent treatment was conducted to enhance the anti-aging properties, and the results will be published in the future. However, Fig. 5(b) also shows that even when the permeability decreases by 50%, the membrane performance still exceeds the upper bound after aging for 354 days, suggesting good membrane performance with solvent induction.

Fig. 5(c) shows the mixed gas separation performance of the membrane, which was measured with a CO$_2$/CH$_4$ (50:50 M) mixture. It is shown that membrane permeability to CO$_2$ slowly decreases owing to membrane resistance, caused by the polar sorption effect of the amide group, which can interrupt, to a certain extent, the transportation of CO$_2$ through the membrane [27]. With an increase in feed pressure, CH$_4$ permeability decreases due to competition and hindrance between CO$_2$ and CH$_4$ molecules in the membrane, because the interaction between the polymer chains and CO$_2$ is stronger than that between the polymer chains and CH$_4$ [27,42]. More sorption sites become occupied by CO$_2$ with an increase in feed pressure, leading to lower CH$_4$ permeability. Finally, the selectivity has a minimum with an enhancement in feed pressure. Similar results were also observed in pure-gas separation (Fig. S9), which indicates good anti-plasticization of the membrane due to the presence of rigid 3D triptycene [43]. Almost constant selectivity can thus be preserved. Furthermore, the synthesized membrane shows a slight difference in selectivity between the pure-gas and mixed-gas separations, which also indicates that this polymer can resist the plasticization of CO$_2$ to a certain extent and keep the selectivity stable.

3.4. Comparison to the literature

In industrial applications, membrane performance is often evaluated using mixed-gas pairs. To compare the membrane performance with that of previously reported polymer membranes, the separation performance was measured with a 50:50 CO$_2$/CH$_4$ mixture, as shown in Fig. 6. The results showed that the separation performance of the synthesized membrane surpassed that of the 2018 mixed-gas CO$_2$/CH$_4$ upper bound with a CO$_2$ permeability of 2197 Barrer and a CO$_2$/CH$_4$ selectivity of 22.6, even after aging for 70 days, thereby making it a promising membrane material for CO$_2$ removal from natural gas or biogas applications.

4. Conclusions

In this work, a new PI-Trip-TFMB polyimide membrane with enhanced gas separation performance was obtained using various solvents such as DMAc and THF. DMAc enhances membrane permeability, whereas THF increases selectivity owing to different degrees of polymer chain relaxation in different ratios of solvents, because the different dielectric constants of DMAc and THF result in different interactions with PI-Trip-TFMB polyimide: polymer chains can stretch more in THF, resulting in more interpenetration of polymer chains and a smaller free volume, BET area, and pore size, lower permeability, and higher selectivity, which is opposite to that observed when DMAc is used. An analysis of diffusion and solubility coefficients also revealed an enhancement of the diffusion coefficient and an almost constant solubility coefficient with a higher proportion of DMAc in the coating solution. Therefore, a CO$_2$/CH$_4$ ratio of 22.6, and a CO$_2$ permeability of 2197 Barrer were obtained for the separation of 50:50 CO$_2$/CH$_4$ mixed gas when a 9:1 DMAc:THF solvent mixture was used for the preparation of the polyimide membrane, which breaks through the 2018 mixed-gas upper bound of CO$_2$/CH$_4$, even after aging for 70 days, indicating a good method of solvent mixtures to tune the membrane microstructure.

Author statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Data availability
No data was used for the research described in the article.

Acknowledgments
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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2022.121199.

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