



Preparation and characterization of polyimide membranes modified by a task-specific ionic liquid based on Schiff base for CO₂/N₂ separation

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Abstract

In order to increase CO₂/N₂ selectivity of polyimide (PI) dense membranes, task-specific ionic liquid (TSIL), 1-aminoethyl-3-buthylimidazolium hexafluorophosphate ([NH₂ebim][PF₆]), has been grafted to polymer chains as large side groups by forming the structure of Schiff base for the first time. The modified membranes were characterized by Fourier transform infrared spectroscopy (FT-IR), elemental analysis, thermogravimetric analysis (TGA), X-ray diffraction (XRD), dynamic thermomechanical analysis (DMA), and stress-strain testing. The results showed that TSIL had been successfully linked to PI chains by forming “C=N.” The modified membranes had more free volume, which was favorable to the improvement of CO₂ permeability. The reduction of spin degree of freedom means the rigidity increment of polymer chains, which indicated that the selectivity of CO₂/N₂ can be enhanced. As a result, CO₂ permeability of the modified membrane (TSIL-0.8 wt%) was increased from 5.28 to 10.2 Barrer, and CO₂/N₂ selectivity was increased from 21.9 to 92.8 at 30 °C and 0.1 MPa. Meanwhile, the effects of different feed pressures (0.1–0.6 MPa) and different operating temperatures (30–60 °C) on CO₂/N₂ transport properties were also investigated, and it was found that the separation performances of the modified membranes had already exceeded Robeson’s upper bound.

Keywords Polyimide · Schiff base · [NH₂ebim][PF₆] · Rigidity · Selectivity

Introduction

With the advance of human society, industrialization process has been accelerated dramatically. Massive emission of greenhouse gases, especially carbon dioxide (CO₂), has exerted an adverse impact on the global environment (Julien and Heldebrant 2018). But at the same time, increasing importance has been attached to CO₂ utilization such as manufacturing soda industry (Gajda et al. 2016), preparation for foaming agent in plastics industry (Tsivintzelis et al. 2016), shielding gas in welding process (Valensi et al. 2018), and supercritical

extraction technology (Fujii et al. 2018). Therefore, the recovery and utilization of CO₂ play important roles in contemporary age.

Gas separation membrane is progressively becoming a representative technology in separating CO₂ from mixed gas. Lower energy consumption, lower investment costs, smaller footprint, and friendly environment offer numerous advantages for the application of membrane separation (Bian et al. 2017; Jhaveri and Murthy 2016). Nevertheless, the trade-off between permeability and selectivity proposed by Robeson is a knotty problem in a course of industrialization. Namely, there is an inherent trade-off effect that membrane with high permeability exhibits low selectivity and vice versa (Robeson 1991, 2008). How to break through Robeson’s upper-bound limit has become a common target in the field of gas separation. Polyimide (PI) membranes have excellent comprehensive performance and high gas selectivity, which have been considered as an appropriate choice for gas separation (Luo and Shen 2013). Polyimide is an aromatic heterocyclic compound with imide rings (–CO–N–CO–). Matrimid® 5218 is one of the outstanding PI that is usually used as gas separation

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membrane because of its good mechanical properties, thermal stability, and so on (Castromuñoz et al. 2017; Moghadam et al. 2011).

There are many ways to improve the performance of gas permeability and selectivity, including the design of molecular (Ma et al. 2016b), inorganic incorporation (Dinari and Ahmadizadegan 2014; Li et al. 2015), chemical cross-linking (Eguchi et al. 2015), and organic species blending (Tao et al. 2014). Ionic liquids (ILs) not only are regarded as “green solvents” but also can make use of the feature of high CO₂ affinity effectively to ameliorate CO₂ gas separation transportation process (Akhmetshina et al. 2015; Mallakpour and Dinari 2011; Kumar et al. 2002). Furthermore, task-specific ionic liquids (TSIL) have aroused many scholars’ attention because their specific functional groups can be tailored onto cation or anion (Shahrom et al. 2016). One of the most extensively studied TSIL is amine-functionalized ionic liquid (Saravanamurugan et al. 2014; Shahrom et al. 2016). Bates et al. (2002) synthesized amine-based task-specific ionic liquids [apbm][BF₄] which enhanced absorption effect of CO₂ significantly by the chemical reaction between TSIL and CO₂. Ma et al. (2016a) fabricated MMMs through loading TSIL ([C₃NH₂bim][Tf₂N]) into a metal-organic framework (MOF, NH₂-MIL-101(Cr)). They found that CO₂ permeability values has been improved significantly, which reaches up to 2979 Barrer, and the CO₂/N₂ selectivity further increases up to 37. He et al. (2016) synthesized NH₂-functionalized ILs and three ether-functionalized ILs for CO₂ absorption. The results showed that the absorption performance of NH₂-functionalized ILs was higher than that of ether-functionalized ILs. Meanwhile, they also prepared supported ionic liquid membranes (SILMs) using these functionalized ILs for CO₂/N₂ and CO₂/CH₄ separation. These results proved that SILMs with NH₂-functionalized ILs had higher permeability but lower slightly selectivity than ether-functionalized ILs. Therefore, the emergence of TSIL further provides a new choice for the process of CO₂-targeted capture.

In addition, the framework of Schiff base is an important field of various research such as biomedical (Raj et al. 2017), fluorescent detection (Kao et al. 2015), and catalytic (Rather and Siddiqui 2018), and some novel Schiff base complex based on polyamides have been synthesized (Aghaei et al. 2019, 2020). It must be emphasized that the interaction between Schiff bases and CO₂ is always used in the catalysis field. Liu et al. (2017) took advantage of Schiff-base-modified gold catalysts to produce formic acid using the weak interaction between nitrogen center of the Schiff base and CO₂. Their finding offers a new way for activation of CO₂ at low temperature. However, the interaction between Schiff base and CO₂, as yet, has not been applied in the field of gas separation membrane. As known to us, Schiff base was synthesized with primary amine and carbonyl compound by taking place

condensation reaction (Pan et al. 2017). Thus, NH₂-functionalized IL can be grafted to PI chains via the formation of a Schiff base. This will not only ensure the stability of TSIL in membranes without losing TSIL, but also modify the structure of PI chains. Combining the advantages of both IL and PI chains’ change, CO₂ permeability and CO₂/N₂ selectivity can be improved in theory.

Here, 1-aminoethyl-3-buthylimidazolium hexafluorophosphate ([NH₂ebim][PF₆]) was synthesized and blended with PI (Matrimid® 5218) in casting solution to fabricate modified CO₂/N₂ separation membrane based on the structure of Schiff base. The modified membranes were prepared by the method of solvent evaporation. Meanwhile, the characterizations of the modified membranes were investigated by Fourier transform infrared spectroscopy (FT-IR), elemental analysis, thermogravimetric analysis (TGA), X-ray diffractometry (XRD), dynamic thermomechanical analysis (DMA), and stress-strain testing. Finally, the modified membranes were applied for the separation of CO₂/N₂ at different trans-membrane pressures and different operating temperatures.

Experimental

Materials

In this experiment, Matrimid® 5218 powder was purchased from Changzhou Furun special plastic new Materials Co., Ltd., China, which was made from 3,3',4,4'-benzophenone tetracarboxylic and diaminophenylindane (Mw ~ 55,000). The chemical structure of Matrimid® 5218 is depicted in Fig. 1. N-Methyl pyrrolidone (NMP) was provided by Tianjin Guangfu Fine Chemical Research Institute, China. 1-aminoethyl-3-buthylimidazolium hexafluorophosphate [NH₂ebim][PF₆] was made by us in our laboratory.

Synthesis of task-special ionic liquid

The synthesis process of [NH₂ebim][PF₆] refers to the report from Bate’s paper (Bates et al. 2002). But the purification procedure differs from this literature. The synthesis process and purification procedure are as follows: Firstly, 1-butylimidazole is mixed with 2-bromoethylamine hydrobromide in ethanol. After 24 h under reflux, ethanol is removed under vacuum, and viscous intermediate product, [NH₂ebim][Br], is obtained. The viscous residue is dissolved in a small quantity of ethanol for crystallization at 10 °C. The resultant pale yellow crystals are recrystallized. Subsequently, ion exchanges with KPF₆ in ethanol/water. The remaining process is the same as the depiction in Bate’s paper.

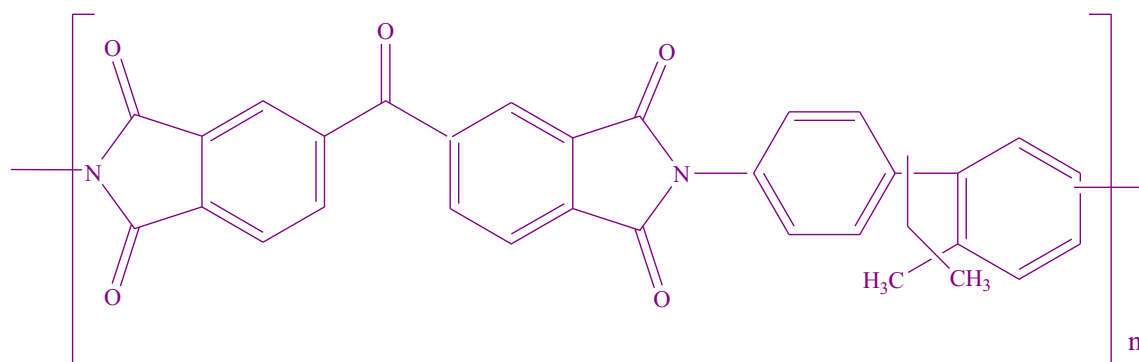


Fig. 1 Chemical structure of Matrimid® 5218

Membranes preparation

First, Matrimid® 5218 powder and TSIL were dried in ovens at 60 °C for 24 h to remove moisture. Second, Matrimid® 5218 powder was added into NMP solvent and stirred for 8 h at 60 °C to form the casting solution. After that, TSIL of different masses was added into the casting solution and blended with Matrimid® 5218 for another 12 h. Third, the homogenous casting solution should be stood for 12 h at room temperature to de-bubbling. Finally, after deaeration, the casting solution was cast on a clean glass plate. The fabricated membrane that is on the glass plate was quickly put in a vacuum oven at 60 °C for 72 h to remove residual solvent and solidify the membrane structure. The thickness of the dry membranes was controlled at $25 \pm 4 \mu\text{m}$. The compositions of all membranes with different TSIL concentrations are listed in Table 1.

Membrane characterization

Fourier transform infrared spectroscopy analysis

Fourier transform infrared spectroscopy (FT-IR) (Thermo Nicolet Corporation NEXUS-470, USA) was used to investigate the functional group of neat and the modified membranes with a wave number range from 400 to 4000 cm^{-1} .

Elemental analysis

CHN elemental composition of neat and modified membranes was determined using an elemental analyzer (Elementar Analysensysteme GmbH, Vario EL cube, Germany).

Thermo-gravimetric analysis

Thermo-gravimetric analysis (TGA Q50, TA, USA) was used to confirm the thermal properties of membranes. The heating rate of TGA is $10 \text{ }^\circ\text{C}/\text{min}$ under N_2 atmosphere and the range of temperature is from 25 to $800 \text{ }^\circ\text{C}$.

X-ray diffraction

The crystalline structures of neat and modified membranes were explored by a Rigaku RINT2000 X-ray diffraction analyzer (copper target) at an operation condition of 40 kV and 100 mA with a scanning angle ranging from 10° to 60° and a scanning velocity of $5^\circ/\text{min}$.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA 242E Artemis, Netzsch, Germany) was used to obtain glass transition temperature (T_g) of neat and modified membranes. The samples were cut into a rectangle shape with $6 \times 5.1 \times 0.3 \text{ mm}$, and the range of

Table 1 Compositions of the modified membranes with different TSIL concentrations

Membrane (wt%)	Matrimid® 5218 (wt%)	$[\text{NH}_2\text{ebim}][\text{PF}_6]$ (wt%)	NMP (wt%)
TSIL-0.0	10	0.0	90.0
TSIL-0.2	10	0.2	89.8
TSIL-0.4	10	0.4	89.6
TSIL-0.6	10	0.6	89.4
TSIL-0.8	10	0.8	89.2
TSIL-1.0	10	1.0	89.0
TSIL-1.3	10	1.3	88.7
TSIL-1.8	10	1.8	88.2

heating temperature is from 25 to 400 °C with the amplitude of 4 µm and the frequency of 1 Hz.

Mechanical properties analysis

Mechanical properties of neat and modified membranes were investigated using a tensile testing system (SHIMADZU Corporation, model AGS-X) operating at crosshead speed of 0.2 mm/s.

Viscosity measurement of casting solution with different TSIL concentrations

Viscosity measurement was carried out using NDJ-7 (INESA Analytical Instrument Co., Ltd., China). The casting solution that had been deaerated was first poured into the testing tin. The suitable spindle needles was selected and attached to the testing tin. The suitable spindle needle was needed to immerse into casting solution and rotated for 5–10 min until the value of measuring instrument remained constant. Five measurements were performed and the average value was taken.

Solubility measurements

It is of great importance to study the polymer solubility in common solvents. Only high solubility in solvents can guarantee the formation of membranes. So, NMP, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) were applied to verify the change of solubility after adding different masses TSIL in the casting solution.

Gas permeability experiments

Single gas permeability experiments with CO₂ (purity > 99.99%) and N₂ (purity > 99.99%) were tested by the traditional variable pressure, constant volume method. Gas permeability condition was measured at feed pressure of 0.1–0.6 MPa and operating temperature of 30–60 °C. It should be noted that before all experiments, membranes needed to be pre-pressed or pre-heated for about 1 h. The gas permeability (P) is calculated based on the following Eq. (1) (Ahmadizadegan 2017):

$$P_i = \frac{Q_i \cdot l}{\Delta P \cdot A} \quad (1)$$

where P_i is the permeability of the tested gas (Barrer); Q_i is the flow rate of the permeate gas passing through the membrane and measured by a bubble flow meter (cm³/s); l is the effective membrane thickness (cm); A is the effective membrane area (cm²); ΔP is the trans-membrane pressure (MPa). In general, gas permeability is expressed by Barrer unit.

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

The ideal gas selectivity of CO₂ and N₂ can be determined by Eq. (2):

$$\alpha = \frac{P_{\text{CO}_2}}{P_{\text{N}_2}} \quad (2)$$

Results and discussion

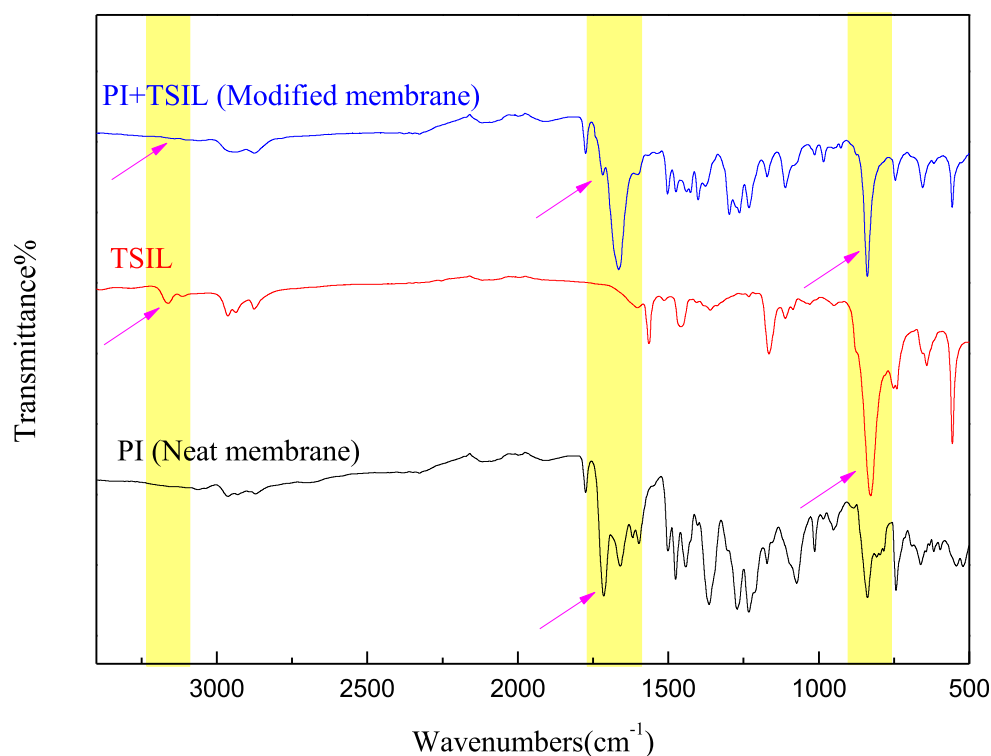
FT-IR analysis

In order to explore the chemical reaction between PI and TSIL, FT-IR analysis was carried out. The infrared spectra of PI, TSIL, and PI+TSIL are shown in Fig. 2.

For PI+TSIL, it can be noted that the characteristic peak at 3191 cm⁻¹ which is assigned to the primary amine (-NH₂) of TSIL has disappeared (Cao et al. 2018). The characteristic peaks at 1730 cm⁻¹ and 1660 cm⁻¹ are corresponded to C=O stretching bands in Fig. 2, which are respectively attributed to the ketonic group and the imide group of PI (Cataldo and Angelini 2006; Dorosti et al. 2015). It can be seen that there is a clear distinction from 1660 to 1730 cm⁻¹ between PI+TSIL and PI. Compared with the neat membrane, the peak at 1730 cm⁻¹ (ketonic group) almost disappeared and the peak at about 1650 cm⁻¹ gets stronger after modification. Due to an overlap of the C=O group (imide group) and C=N group around 1640–1670 cm⁻¹ (Makhneva et al. 2016), it is hard to distinguish these two groups. But we know that there is no C=O group in our TSIL and it is impossible that PI can produce new C=O group during our experimental process. So, the increment of intensity from 1640 to 1670 cm⁻¹ can be attributed to the formation of C=N because the ketonic group (C=O) of PI has been already reacted with primary amine (-NH₂) of TSIL to produce the C=N band. Thus, we propose the possible grafting mechanism of Matrimid® 5218 by [NH₂ebim][PF₆] which is illustrated in Fig. 3. The reaction process is as follows: First, nitrogen atom with lone electron pairs in the amino group of TSIL attacked carbon atom with positive charge in the ketonic group of PI to complete nucleophilic addition reaction. Second, hydrogen ion was exchanged between the amino group and the ketonic group, and then hydroxylamine compounds can be formed. Finally, the “C=N” of Schiff base was synthesized by the condensation reaction of hydroxylamine. Therefore, in this way, ionic liquid can be better immobilized on polymer chains.

In addition, the peak at 841.7 cm⁻¹ is a typical stretching vibration peak of P-F (TSIL) shown in modified membrane (Li et al. 2010), which further proves that TSIL can be successfully remained among PI chains.

Fig. 2 FT-IR spectra of PI (neat membrane), TSIL ($[\text{NH}_2\text{ebim}][\text{PF}_6]$), and PI+TSIL (modified membrane)



Above all, through these changes of characteristic peaks shown in Fig. 2, the effectiveness reaction between PI and TSIL can be confirmed. So, we can conclude that TSIL is successfully grafted to PI chains by the formation of C=N Schiff base.

Elemental analysis

The neat membrane and the modified membrane (TSIL-0.8 wt%) were characterized by elemental analysis techniques, and the results are shown in Table 2. Theoretically, if TSIL

is successfully grafted to the PI chains, C element can decrease from 74.51 to 72.75%, H element can increase from 4.678 to 4.726%, and N element can increase from 5.061 to 5.672%. As can be seen from Table 2, the results of element contents for the neat and the modified membranes by elemental analysis are almost the same as those of theoretical prediction. Thus, it can be preliminarily judged that TSIL has already existed in PI chains. Furthermore, combined with the disappearance of primary amine and the formation of C=N from FT-IR analysis, it can be inferred that TSIL is successfully grafted to PI chains by the formation of C=N.

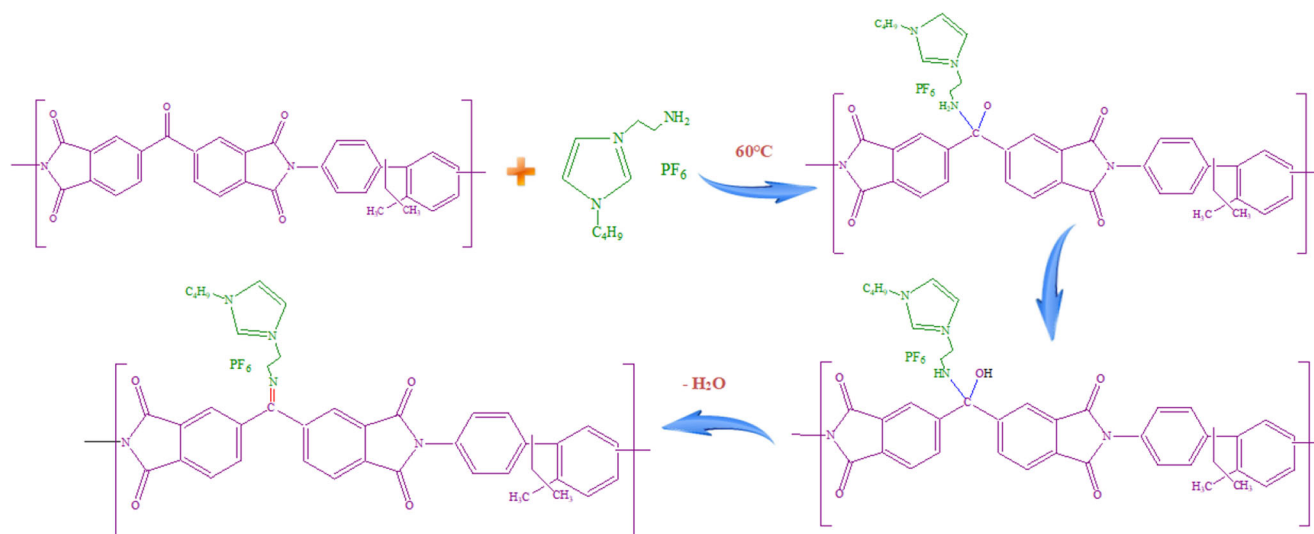


Fig. 3 Proposed grafting mechanism for PI and $[\text{NH}_2\text{ebim}][\text{PF}_6]$

Table 2 Elemental analysis of the neat membrane and the modified membrane (TSIL-0.8 wt%)

Polymer	C (%)	H (%)	N (%)
Neat membrane	74.51	4.678	5.061
Modified membrane (theoretical value)	72.75	4.726	5.672
Modified membrane (testing value)	72.27	4.754	5.770

TGA analysis

The thermal properties of neat membrane, TSIL, and modified membranes at different temperatures are very significant in gas separation application, and thermal properties can be characterized by TGA as shown in Fig. 4. A two-step decomposition process of neat membrane can be observed. Neat membrane has first loss from 25 to 510 °C (about 5% weight loss, T_5) because of moisture and solvent evaporation. Besides, 10% weight loss (T_{10}) temperature of neat membrane is observed at about 530 °C. The char yields of neat membrane is about 60% at 800 °C (about 40% weight loss), which is attributed to the polymer main chain decomposition. TGA curve of TSIL also has a two-step decomposition process. The first weight loss is due to the departure of water in TSIL from 25 to 270 °C (about 5% weight loss). And the subsequent weight loss is due to the decomposition of TSIL structure from 270 to 400 °C (about 98% weight loss). TGA curve of the modified membrane exhibits three-step thermal transformation. The first weight loss of modified membrane is also attributed to moisture and solvent evaporation from 25 to 300 °C (about

5% weight loss, T_5). The second weight loss from 300 to 500 °C corresponds to the decomposition of grafted TSIL decomposition (about 10% weight loss, T_{10}). The third weight loss is attributed to the decomposition of polymer main chains from 500 to 800 °C and left 38% char yields. Though the thermal property of the modified membrane is a little lower than other PI membranes because of the TSIL decomposition (Dinari and Ahmadizadegan 2015b; Dinari and Asadi 2015; Dinari et al. 2015b), it can still be used for gas separation membrane normally.

X-ray diffraction

XRD was applied to identify the crystalline phase changes of the modified membrane, and the patterns are shown in Fig. 5. A diffuse characteristic diffraction peak at around $2\theta = 15.0^\circ \sim 20.0^\circ$ is observed for the neat membrane and the modified membranes, which is attributed to its amorphous structure (Dinari and Ahmadizadegan 2015a). However, the diffraction peak of the modified membranes gradually becomes weaker with the increase of TSIL concentrations, which confirms that polymer crystalline has been decreased due to the introduction of TSIL. In addition, the improvement of solubility can also be attributed to the reduction of crystallinity for the modified PI as described in the section of solubility properties of the modified PI, which is consistent with the rule that the solubility increases with decreasing crystallinity (Dinari and Ahmadizadegan 2015a; Dinari et al. 2015a).

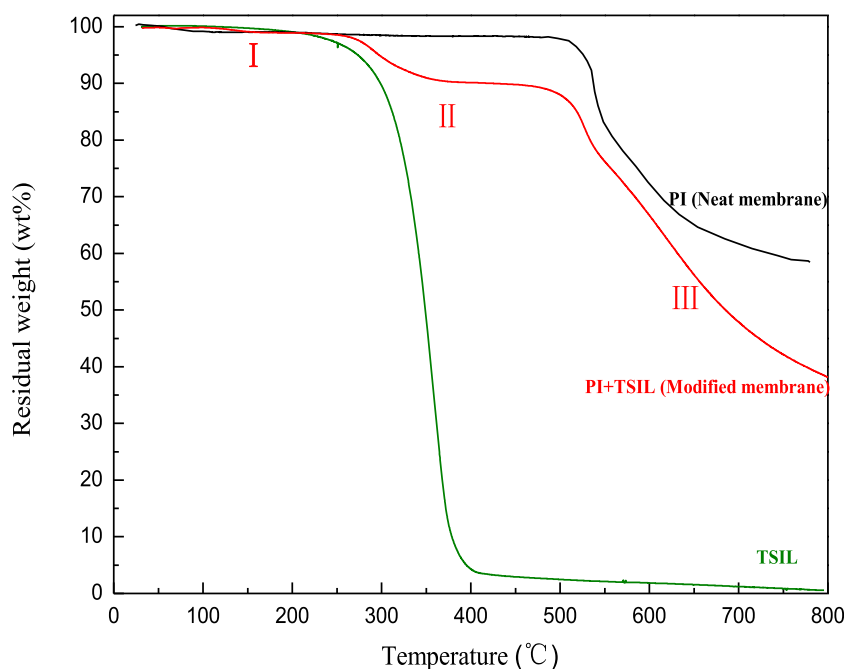
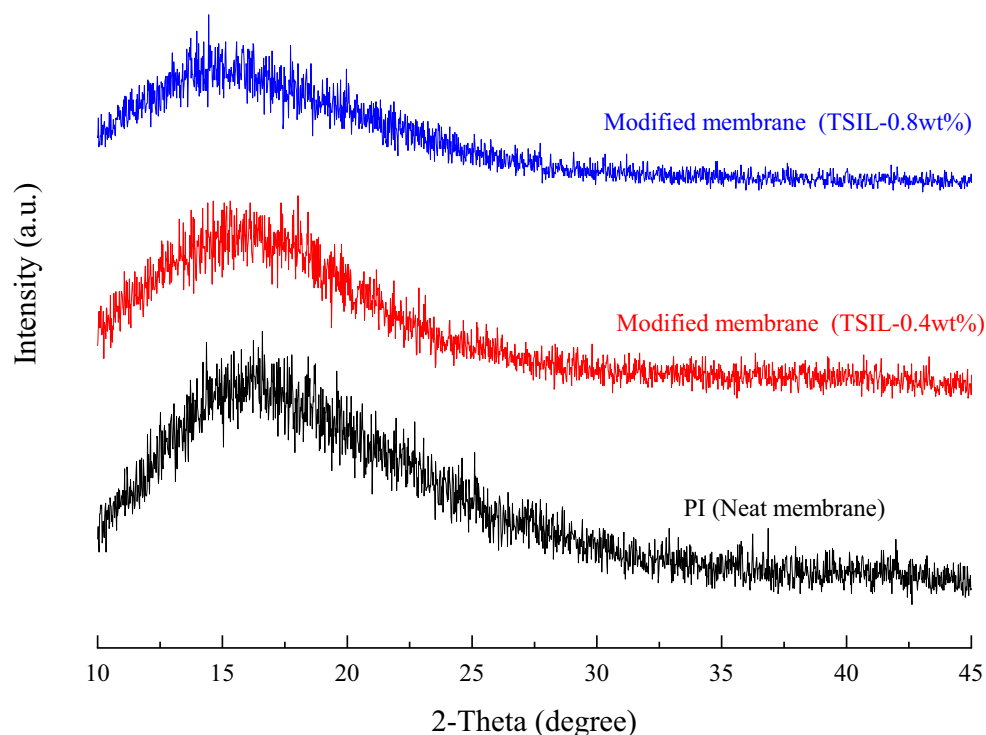
Fig. 4 TGA curves of PI (neat membrane), TSIL ($[\text{NH}_2\text{ebim}][\text{PF}_6]$), and PI+TSIL (modified membrane)

Fig. 5 XRD patterns of the neat membrane and the modified membrane (TSIL-0.4 wt% and TSIL-0.8 wt%)



Glass transition temperature analysis

Glass transition temperature (T_g) tested by DMA can be used to explore the flexibility of polymer chains. The maximum of $\tan\delta$ is corresponded to the T_g value of the modified membrane as shown in Fig. 6, and the T_g value is also listed in Table 4.

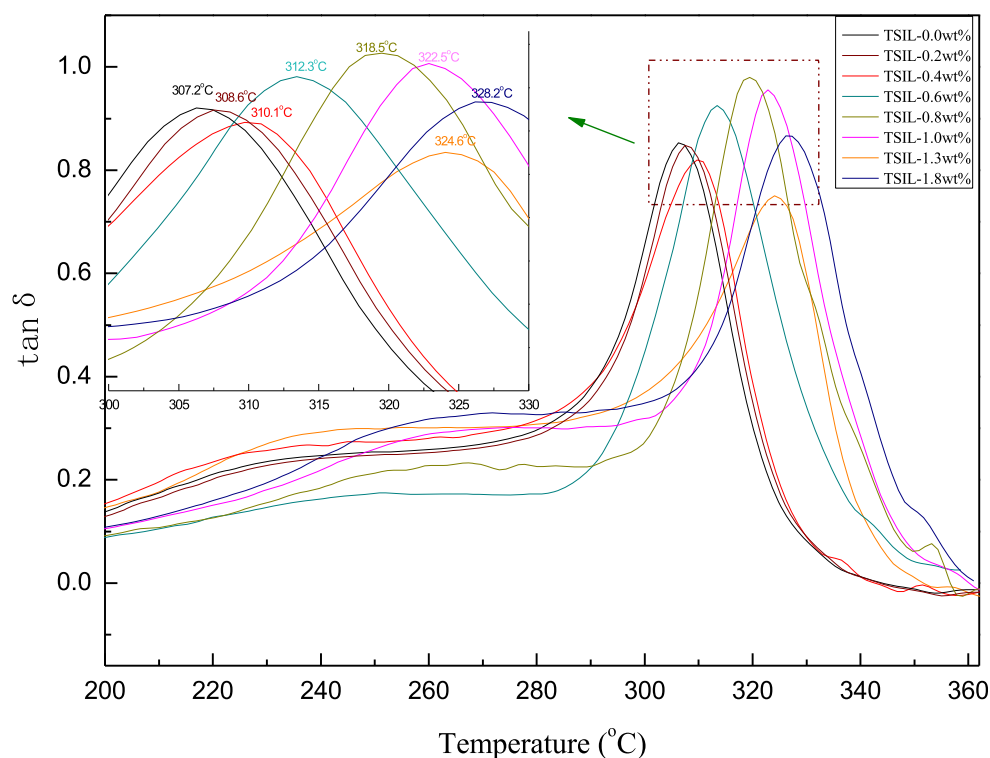
It can be seen that T_g of the neat membrane is about 307.2 °C as shown in Fig. 6, which is lower than those of all modified members. T_g of the modified members increases from 308.6 (TSIL-0.2 wt%) to 328.2 °C (TSIL-1.8 wt%). The modified membranes have an increased T_g because the polymer chains' mobility has been decreased. Polymer chains' mobility is relevant to the spin degree of freedom (Alastalo et al. 2004). In our experiments, TSIL is grafted to PI chains as large side groups. This structure can increase the resistance among polymer chains and result in the reduction of spin degree of freedom. So, T_g of the modified membranes gradually increases with the increase of TSIL concentrations. The introduction of large side groups by TSIL plays an important role in improving the rigidity of modified membrane. Normally, the enhancement of rigidity is favorable for improving gas selectivity. Thus, it can be predicted that the CO_2/N_2 selectivity of the modified membranes could be improved in a gas membrane separation process.

Mechanical properties analysis

Stress-strain curves could be used to evaluate the effects of TSIL on the mechanical properties of the modified

membranes, and the results are shown in Fig. 7 and Table 3. Figure 7 shows the stress-strain curves of the neat and modified membranes. As can be seen, the modified membranes with the increment of TSIL have higher tensile strength, higher tensile modulus, but lower elongation at break compared with the neat membrane. Table 3 shows the mechanical properties of the neat membrane and the modified membranes, including the tensile strength, tensile modulus, and elongation at break. It can be seen that the tensile strength and modulus of the modified membrane (TSIL-0.8 wt%) is increased to 100.9 MPa and 2514.4 MPa, which is 30.78% and 29.76% higher than the neat membrane, respectively. Generally, the tensile strength of polymer can be improved by increasing the polarity and forming hydrogen bonds. The polarity of the modified PI has been increased due to the introduction of TSIL as polar groups. Moreover, the strong electronegativity of fluorine atoms contained in TSIL can form hydrogen bonds with the hydrogen atoms of PI. So, the tensile properties of the modified membranes exhibit reinforcement effect. Furthermore, the elongation at break of the modified membranes (TSIL-0.4 wt%, TSIL-0.8 wt%) are decreased to 13.45% and 11.48%, which is 11.48% and 22.9% lower than the neat membrane, respectively. It could be attributed to the rigidity increment of the modified PI. Therefore, according to the above results, we can deduce that the selectivity of the modified membranes can be increased.

Fig. 6 T_g of the neat membrane and the modified membranes with different TSIL concentrations



Casting solution viscosity

Table 4 lists casting solution viscosities of the modified PI with different TSIL concentrations. It clearly illustrates a drastic decrease in viscosity with TSIL concentration increasing, and their viscosities decrease from 1750 (TSIL-0.0 wt%) to 66 cp (TSIL-1.8 wt%). The reason is that the distances of polymer chains had been increased because TSIL was grafted to the polymer main chains as large side groups, so the interaction forces among polymer chains had been reduced. Meanwhile, the introduction of large side group can also reduce the physical cross-link of modified PI. Increasing the distance of polymer chains implies the increment of CO₂ permeability.

Solubility properties of modified PI

The applications of PI in many fields have been limited due to the low solubility in many common organic solvents (Lee et al. 2006; Yu et al. 2006). So, the solubility of the modified

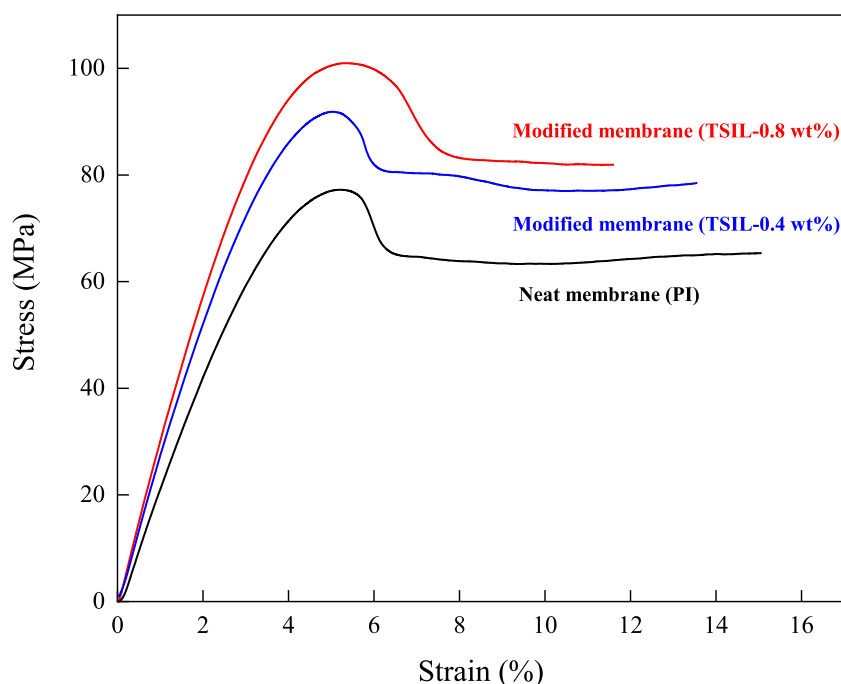
polyimide in NMP, DMF, DMAc, DMSO, and THF has been explored, and the results are summarized in Table 5. It is observed that PI powder can be dissolved in NMP. But it is insoluble in DMF, DMAc, DMSO, and THF. Fortunately, PI showed increasing solubility when TSIL was added into the solvent as shown in Table 5.

High solubility depends on the structural similarity and polar similarity between polymers and solvents (Jian et al. 2010). According to molecular structures, the reason for dissolution of PI in NMP is that they have similar structure. As for other solvents, their chemical structural formula differs considerably. So, PI has low solubility in these solvents. For PI+TSIL system, TSIL has been grafted to PI main chains as polar pendant groups. This not only increases the distance between polymer chains but also increases the polarity of PI. The increment of polarity is predominant, which results in high solubility of the modified PI in DMF, DMAc, DMSO, and THF. Furthermore, the improvement of solubility can also be attributed to the reduction of crystallinity for the modified PI. Thus, the PI modified by TSIL exhibits better solubility in

Table 3 Mechanical characterizations of the neat and the modified membranes

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
Neat membrane	77.2	14.90	1937.7
Modified membrane (TSIL-0.4 wt%)	91.8	13.45	2309.7
Modified membrane (TSIL-0.8 wt%)	100.9	11.49	2514.4

Fig. 7 Tensile stress-strain curves of the neat membrane and the modified membranes with different TSIL concentrations



common organic solvents, which is beneficial to the further application of gas membrane separation such as the preparation of membrane with lower cost and easy processing.

Gas permeation

It should be noted that the modified membrane is fissile because of relatively large rigidity when the TSIL concentration is beyond 1.8 wt%. Therefore, we only study the modified membranes containing TSIL, whose concentrations ranged from 0.2 to 1.3 wt%.

Effect of TSIL concentration on gas separation performance

In order to seek appropriate TSIL concentration added in PI for CO₂/N₂ separation, modified membranes with different TSIL concentrations (0.2–1.3 wt%) were investigated at 30 °C and 0.1 MPa. The results of permeability and selectivity were illustrated in Fig. 8.

Table 4 μ and T_g of the modified membranes with different TSIL concentrations

Membrane	μ (cp)	T_g (°C)
TSIL-0.0 wt%	1750	307.2
TSIL-0.2 wt%	1510	308.6
TSIL-0.4 wt%	1253	310.1
TSIL-0.6 wt%	729	312.3
TSIL-0.8 wt%	524	318.5
TSIL-1.0 wt%	280	322.5
TSIL-1.3 wt%	110	324.6
TSIL-1.8 wt%	66	328.2

CO₂ permeabilities of all modified membranes are higher than these of the neat membranes. First, it has shown that TSIL is successfully grafted to PI chains from FT-IR analysis. The capture of CO₂ can be achieved through a weak interaction between nitrogen center of C=N and carbon of CO₂ (Liu et al. 2017). Second, TSIL can be immobilized to polymer chains through grafting modification, so TSIL exists more stably in modified membrane. For TSIL itself, the weak basic of imidazole can enhance CO₂ absorption (Mei et al. 2012). And TSIL containing fluorine which is the highest electronegative element can attract the lone-pair electrons in the oxygen atom of CO₂. The synergistic effect of TSIL can facilitate the solubility of CO₂ in modified membranes. Third, importantly, the distance among the modified PI chains has been increased

Table 5 Dissolution behavior of PI and PI+TSIL in different solvents.

Polymer	Solubility				
	NMP	DMF	DMAc	DMSO	THF
PI+TSIL 0.0 wt%	+	-	-	-	-
PI+TSIL 0.2 wt%	+	-	-	-	-
PI+TSIL 0.4 wt%	+	±	±	-	-
PI+TSIL 0.6 wt%	+	+	+	-	-
PI+TSIL 0.8 wt%	+	+	+	±	-
PI+TSIL 1.0 wt%	+	+	+	±	±
PI+TSIL 1.3 wt%	+	+	+	+	±
PI+TSIL 1.8 wt%	+	+	+	+	±

+, soluble on heating at 60 °C for 12 h; -, insoluble on heating at 60 °C for 12 h; ±, soluble on heating at 80 °C for 12 h

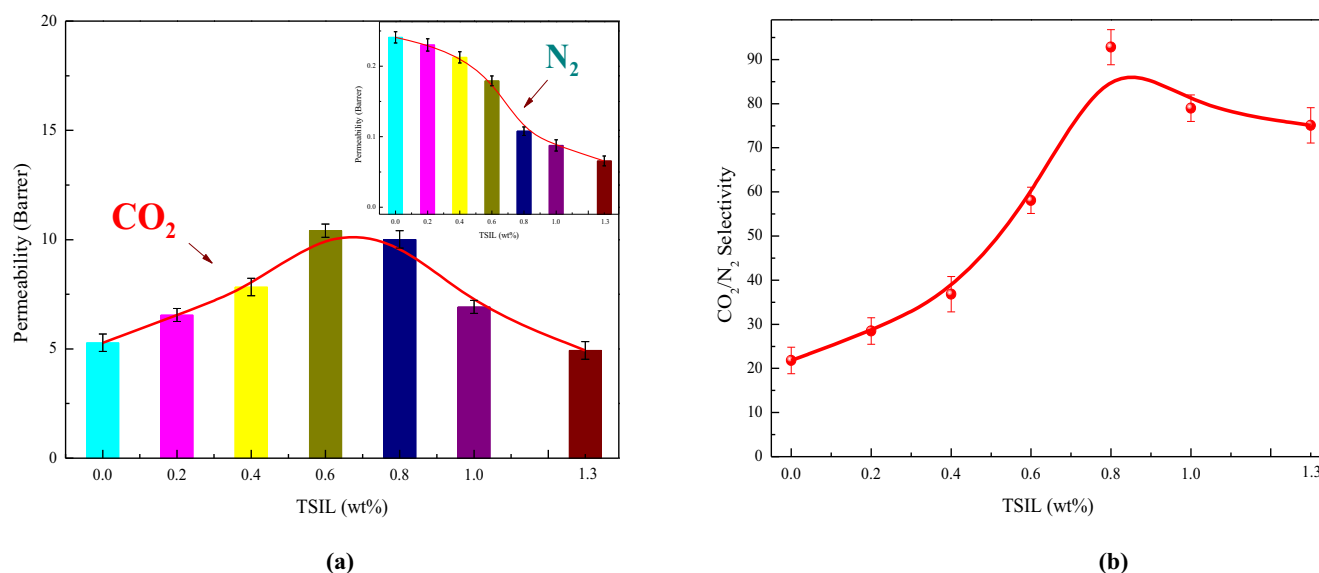


Fig. 8 Gas permeabilities and selectivities of the neat membrane and the modified membranes at 30 °C and 0.1 MPa

due to the introduction of TSIL as large side group, which increases polymer-free volume. Thus, CO₂ permeability has been increased because of these synergistic effects even though polymer chain gets rigid. But the CO₂ permeability started to decrease at TSIL-0.8 wt%. The entanglement of polymer chains has begun to develop due to the hydrogen bonding between F atoms of PF₆ and H atoms of PI chains. So, polymer chains' movement is restrained. The rigidity increase of the modified membranes plays a dominant role in the process of gas transport according to the solution-diffusion mechanism (Tomé and Marrucho 2016). So, the increment of CO₂ permeability is limited. N₂ permeability decreases gradually with TSIL concentration increasing. According to our above characterization, the rigidity of PI chains has been greatly enhanced and no functional group can help N₂ absorption. So, N₂ permeability would be decreased significantly.

Figure 8(b) reveals the changes of selectivity with the increase of TSIL concentration. Astonishingly, selectivity value reached up to 92.8 (TSIL-0.8 wt%), which is higher than that of the neat membrane.

Effect of feed pressure on gas separation performance

Figure 9 depicts the effect of feed pressure (0.1–0.6 MPa) on CO₂ permeability and CO₂/N₂ selectivity for both neat membrane and modified membranes at 30 °C. As can be seen from Fig. 9 (a), CO₂ permeability decreases slightly with the increased feed pressure when the TSIL content is up to 0.8 wt%. Furthermore, CO₂ permeability has a slightly increasing trend with increasing feed pressure when the TSIL content is up to 1.3 wt%. The reason is that increasing the feed pressure of membranes leads to the compactness of polymer chains, which decreases gases diffusion rate (Amooghini et al. 2015). However, the above analysis results indicate that the

rigidity of the modified membranes has been gradually improved with the increase of TSIL concentration. Consequently, the polymer chains are not easily to be compressed when feed pressure is increased, which can lead to the improvement of mass transfer and result in the enhancement of CO₂ permeability. Furthermore, the resistance to N₂ diffusion in membrane is greater than CO₂ as the pressure increases due to the larger kinetic diameter of N₂ (Iwase et al. 2004). Therefore, CO₂/N₂ selectivity increases significantly as shown in Fig. 9 (b).

Effect of temperature on gas separation performance

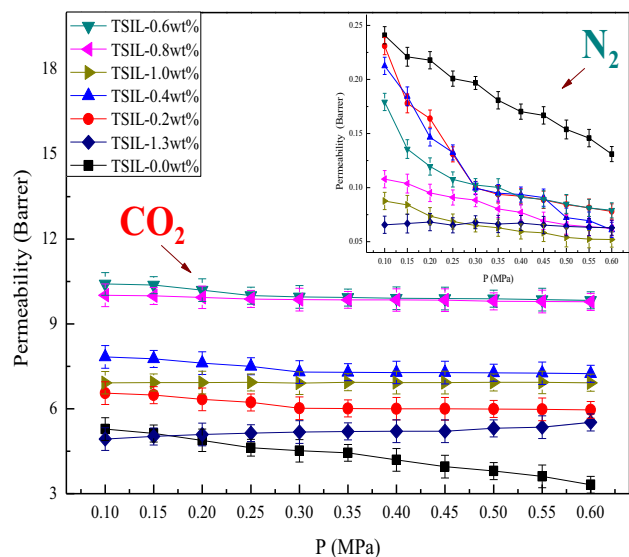
Figure 10 illustrates the effect of operating temperature ranged from 30 to 60 °C on gas permeation and selectivity of the neat membrane and the modified membrane (TSIL-0.8 wt %) at feed pressure 0.2 MPa.

Apparent activation energy is a function of temperature, which could help us to analyze the effect of temperature on apparent activation energy as the following Eq. (3) (Clarizia et al. 2004):

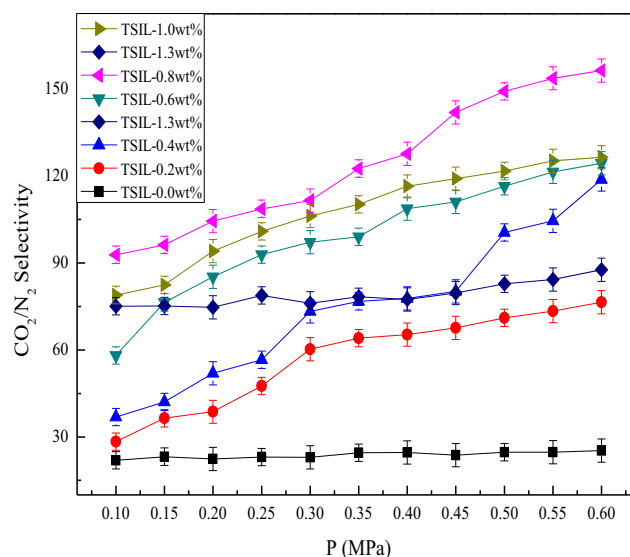
$$P = P_0 e^{-E_p/RT} \quad (3)$$

where P is the permeability of gases (Barrer), P_0 is as pre-exponential factor and independent of temperature (Barrer), E_p is activation energy (kJ/mol), R is the gas constant (8.314 J K⁻¹ mol⁻¹), and T is the absolute temperature (K). For convenience of calculation, the activation energy of CO₂ and N₂ can be determined using slope method of $\ln P$ vs $1/T$.

The calculative results show that apparent activation energy of CO₂ decreases from 13.54 for the neat membrane to 4.962 kJ/mol for the modified membrane as shown in Fig. 10. CO₂ permeability increases with increasing temperature



(a)



(b)

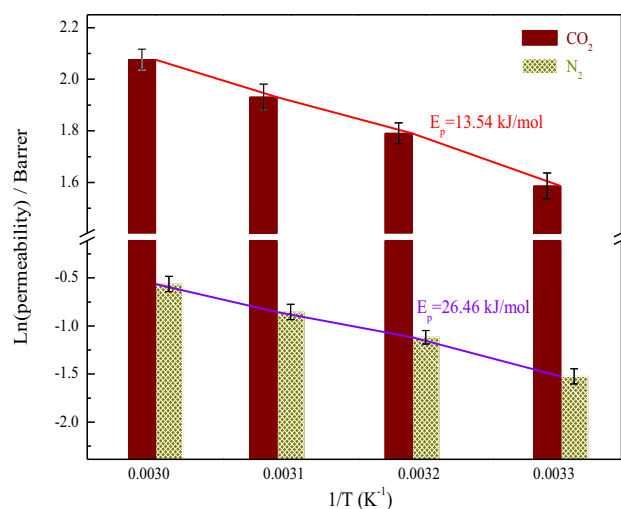
Fig. 9 Effect of feed pressure on (a) gas permeability and (b) selectivity

for both neat membrane and modified membranes from Fig. 10. The reason is that thermodynamic energy of CO_2 increases with increasing temperature. And polymer chains generally become more flexible as temperature increases higher, which results in the improvement of diffusivity (Basu et al. 2010; Shamsabadi et al. 2014). But CO_2 permeability of the modified membrane fluctuates within a narrow range because the enhancement of rigidity offsets the enhancement of flexibility of polymer chains. Besides, the solubility of CO_2 in IL which grafted to PI chains decreased with increasing temperature (Liang et al. 2014). Thus, the changing range of CO_2 permeability of the modified membranes is not obvious with the increase of operating temperature. Furthermore, N_2 has the

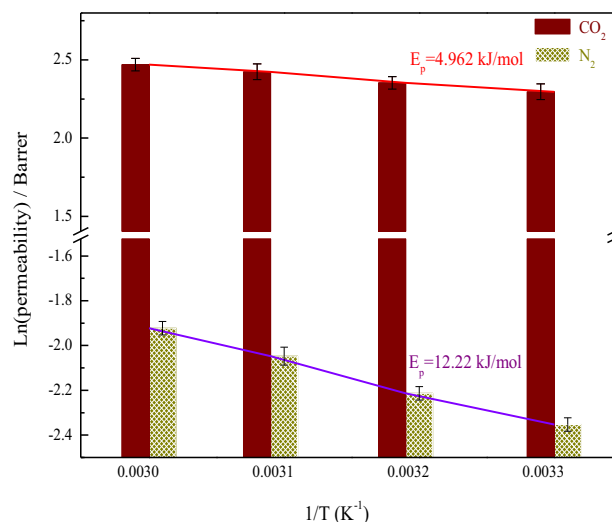
higher E_p than CO_2 from Fig. 10, which causes the decrease of selectivity. Investigation about the effect of temperature on gas separation performance indicates that the modified membranes have good separation property with temperature increment.

Fractional free volumes of neat and modified membranes

Estimation of fractional free volumes (FFVs) values of neat and modified membranes is a better evidence to investigate gas separation performance. Therefore, FFVs for the neat and the modified membranes with CO_2 and N_2 were estimated based on group contribution methods developed by previous



(a)



(b)

Fig. 10 Effect of temperature on (a) neat membrane and (b) modified membrane (TSIL-0.8 wt%) (representative Arrhenius plot $\ln P$ vs $1/T$)

Table 6 Fractional free volumes (FFVs) of the neat and the modified membranes

Polymer	(FFVs) _{CO₂} (%)	(FFVs) _{N₂} (%)
Neat membrane	11.88	10.06
Modified membrane	19.87	17.95

literatures (Lazzús 2010; Park and Paul 1997; Qiao et al. 2010; Yue et al. 2018; Zhang et al. 2017), and the results are shown in Table 6. It can be seen that the FFV of neat membrane is higher than that of modified membrane (TSIL-0.8 wt%) for both CO₂ and N₂. Polymer chains of the modified PI become looser with the reduction of crystallinity due to the grafting effect of TSIL, which is helpful for the improvement of gas separation performance.

Cavity size distribution of neat and modified membranes

Free volume is not the only factor to determine gas permeation (Lock et al. 2016). In order to further clarify the gas separation performance of the modified membrane, the cavity size distributions of membranes could help us explain this phenomenon. Cavity size distributions of gas separation membranes have been studied by previous papers (Golzar et al. 2014; Jiang et al. 2011). Thus, the cavity size distributions for the neat and the modified membranes (TSIL-0.8 wt%) in our work could be calculated according to their papers, and the results are demonstrated in Fig. 11.

It can be seen that the cavity diameter with the highest probability density for neat membrane is 4.0 Å, but that of modified membrane decreases to 3.6 Å. The possible reason may be the partial filling of molecular cavities among the

modified PI chains with free anions (PF₆) (Luo et al. 2015). The cavity diameter with the highest probability density for the modified membrane is just between the kinetic diameter of CO₂ (0.330 nm) and that of N₂ (0.364 nm). Although the FFVs have been increased, the decrease of the cavity diameter for modified membranes limits N₂ to transfer, which is beneficial for the improvement of selectivity. Therefore, the cavity size distributions of polymer membranes have been changed due to the grafted effect of TSIL, which facilitates the separation of CO₂ and N₂.

Diffusivity and solubility coefficients analysis of neat and modified membranes

To assess gas permeation results more accurately, gas diffusivity and solubility coefficients are better evidences. The diffusivity (D) and solubility (S) coefficients of the neat and the modified membranes were simulated by molecular simulation developed by previous paper due to the insufficient sensitivity of the equipment (Golzar et al. 2014), and the results are summarized in Table 7. Diffusivity and solubility selectivity coefficients are also tabulated in Table 7. As shown in Table 7, for CO₂, the diffusivity and solubility coefficients are both increased, and the solubility coefficient is improved significantly. The reason is that the TSILs grafted to PI chains have stronger interaction with CO₂, which can increase the solubility selectivity. Meanwhile, the increment of the diffusivity coefficient could be attributed to the increment of FFVs for the modified membranes. For N₂, its solubility coefficient is almost constant but its diffusivity coefficient decreases obviously. Although FFVs is increased, the cavity diameter with the highest probability density for the modified membrane is reduced to 3.6 Å, which makes the diffusion of N₂ more

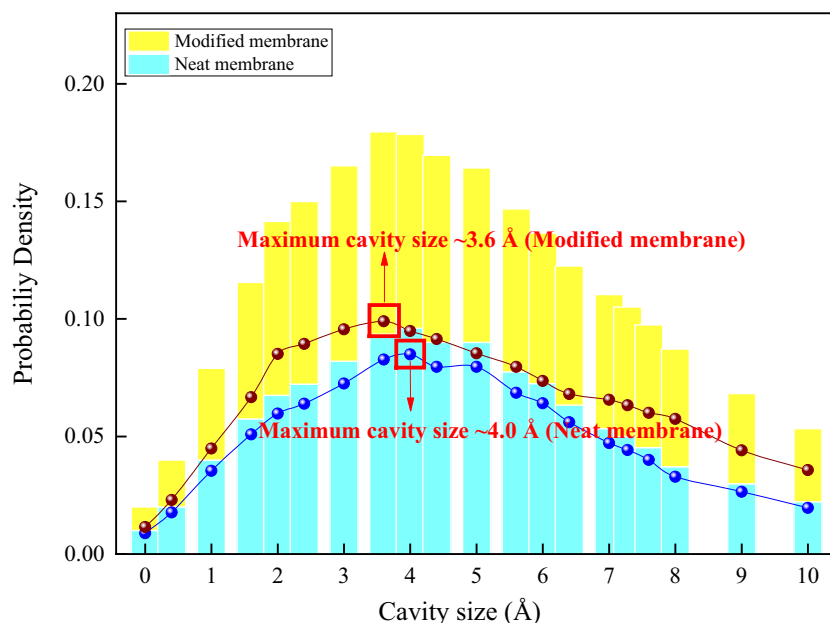
Fig. 11 Cavity size distributions of the neat and the modified membranes (TSIL-0.8 wt%)

Table 7 Gas diffusion coefficients (D) and solubility coefficients (S) of the neat and the modified membranes (TSIL-0.8 wt%) at 30 °C and 0.1 MPa for CO₂ and N₂

Polymer membrane	CO ₂		N ₂		CO ₂ /N ₂	
	D (10 ⁻⁸ cm ² /s)	S (10 ⁻² cm ³ (STP)/cm ³ cmHg)	D (10 ⁻⁸ cm ² /s)	S (10 ⁻² cm ³ (STP)/cm ³ cmHg)	α_D	α_S
Neat membrane	0.67	6.51	0.120	1.43	5.58	4.55
Modified membrane	1.02	8.38	0.073	1.42	13.97	5.90

α_D , diffusivity selectivity values (D_{CO_2}/D_{N_2}); α_S , solubility selectivity values (S_{CO_2}/S_{N_2})

difficult through the modified membranes. Furthermore, no functional group can help the absorption of N₂, leading to the unchanged solubility coefficient. Therefore, the modified membranes display a good synergy effect on both permeability and selectivity.

Robeson's upper bound for CO₂/N₂ separation of modified membranes

It is clear that the performance of the modified membranes in our experiments approaches and even surpasses Robeson upper bound as shown in Fig. 12. Above all, it is a pretty good outcome since our modified membranes not only have good resistance to pressure and temperature variation but also have excellent selectivity property.

Table 8 lists CO₂ permeabilities and CO₂/N₂ selectivities between this work and other literatures. It can be seen that the separation performance in this work is better than those reported by most early literature, especially in CO₂/N₂ selectivity. However, CO₂ permeability of the modified membranes in this work is relatively low compared with these references.

Therefore, current and future studies should be focused on some materials with flexible polymer chains to improve CO₂ permeability under the precondition of ensuring the CO₂/N₂ selectivity.

Conclusion

Herein, the preparation and characterization of polyimide membranes modified by [NH₂ebim][PF₆] based on Schiff base for CO₂/N₂ separation are presented. [NH₂ebim][PF₆] has been successfully grafted to polymer chains as large side groups by forming the structure of Schiff base. FT-IR and elemental analysis results confirm the formation of C=N. The polymer crystalline, casting solution viscosity, and thermal stability of modified membranes are decreased due to the grafting effect of ionic liquid on polyimide. The mechanical resistance, glass transition temperatures, and solubility in DMF, DMAc, DMSO, and THF of modified membranes are increased due to the improvement of rigidity and polarity. Gas separation properties of CO₂ and N₂ through these modified

Fig. 12 Robeson's plot from the CO₂/N₂ separation with the upper bound and the data for the membranes prepared in this work

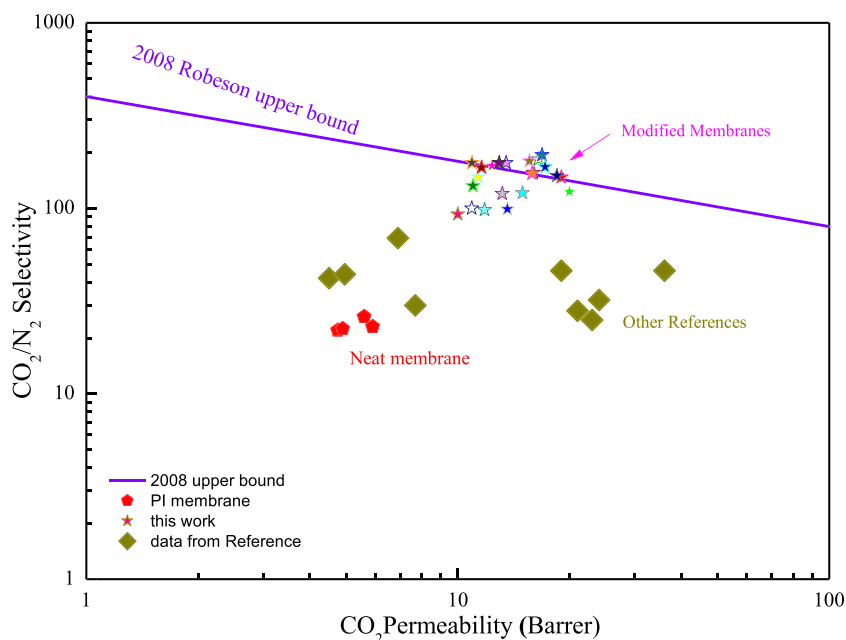


Table 8 Comparison of CO₂ separation performance between our modified membrane and other Matrimid® 5218 membranes

Membranes	Pco ₂ (Barrer)	α CO ₂ /N ₂	Test Condition	References
Matrimid® 5218/ZIF-8, 30 wt%	28.72	17.1	25 °C 0.4 Mpa	(Song et al. 2012)
Matrimid® 5218/ZIF-8, 10 wt%	13.67	21.6	25 °C 0.4 Mpa	(Song et al. 2012)
PTMSP/Matrimid® 5218	7.43	28.6	30 °C 0.13 MPa	(Peter and Peinemann 2009)
Matrimid®5218/[Emim][C(CN) ₃]/Mg-MOF-74	17.2	36.2	35 °C 0.2 Mpa	(Monteiro et al. 2017)
Matrimid® 5218/Silica	9.59	50.7	35 °C 0.2 Mpa	(Nezhadmoghadam et al. 2017)
ZSM-5/Matrimid® 5218	19.0	38	25 °C 0.2 MPa	(Chaidou et al. 2012)
13X/Matrimid® 5218	18.2	41	25 °C 0.2 MPa	(Chaidou et al. 2012)
CNTs/GO/Matrimid® 5218	38.07	81	25 °C 0.2 MPa	(Li et al. 2015)
Matrimid® 5218/TSIL	10.2	92.8	30 °C 0.1 MPa	This work

membranes were investigated. The results show that both CO₂ permeability and CO₂/N₂ selectivity have been increased. Meanwhile, modified membranes have better resistance to pressure and temperature due to the rigidity improvement of PI chains. As a result, the separation performance of modified membranes has already exceeded 2008 Robeson's upper bound. In this way, not only the interaction between ionic liquid and CO₂ can be better preserved, but also the structure of polymer chain can be changed. These excellent properties make the modified membranes become potential candidates for CO₂ separation, which can provide a promising direction of the improvement for gas separation membrane process.

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