Microporous polyimide VOC-rejective membrane for the separation of nitrogen/VOC mixture

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ABSTRACT

The treatment of VOCs (volatile organic compounds) in waste streams is very important. Herein, we propose to use a network microporous polyimide (PI) membrane for the molecular sieving of nitrogen over VOC molecules to control their emission. 2,6,14-triaminotriptycene (Trip) was reacted with aromatic dianhydride monomers, such as 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), to synthesize ultramicroporous polyimides, which readily form composite membranes via solution coating. The properties of the PIs were characterized by X-ray photoelectron spectroscopy (XPS), Brunner-Emmet-Teller (BET) analysis, etc., which validated the formation of a network structure and ultramicroporosity in these polyimides. Therefore, the outstanding separation performance for the separation of nitrogen over VOCs, such as cyclohexane, by molecular sieving was obtained by using these membranes; a rejection higher than 99 % was realized with a permeability of approximately 2000~2600 Barrer under a temperature of 25 °C and feed concentration of 30,000 ± 2000 ppm. Finally, the stability of the Trip-BTDA-PI membrane over time was studied.

1. Introduction

Microporous polymers such as polymers of intrinsic microporosity (PIMs) (Budd et al., 2004a, b), thermally rearranged (TR) polymers (Meckler et al., 2018), etc. have recently been widely studied because of their unique microstructure and excellent performance for gas separation (Guiver and Lee, 2013; Park et al., 2007). Many monomers have been synthesized or used for tuning the microstructure of microporous polymers to improve membrane performance (Sanaeepur et al., 2019; Low et al., 2018; Zhou et al., 2017). Triptycene is one of the most studied monomers because of its unique 3-dimensional, rigid framework, which strongly resists deformation. Voids (named internal free volume) in the clefts between aromatics rings will thus be formed, resulting in a higher free volume for the synthesized polymers owing to the existence of rigid triptycene and inefficient packing of triptycene-based polymer chains (Cho and Park, 2011a; Swaidan et al., 2015; Ghanem et al., 2014). Many different kinds of triptycene-based polymers (polyamides, polyimides (PI), polybenzoxazole, etc.) have thus been synthesized for the preparation of membranes (Zhou et al., 2017; Cho and Park, 2011a; Luo et al., 2018). Among these polymers, polyimide polymer seems to be promising for membrane fabrication due to its superior permeability/selectivity trade-off (Sanaeepur et al., 2019; Swaidan et al., 2015; Ghanem et al., 2014; Yong et al., 2014; Cho and Park, 2011b; Carta et al., 2014). For example, Ingo’s group synthesized two triptycene-based polyimides (KAUST-PI-1 and KAUST-PI-2), which showed excellent selectivity and permeability, and exceeded the 2008 upper bound limit for the separation of different gas pairs and defined the 2015 upper bound limit for O₂/N₂ separation (Swaidan et al., 2015; Ghanem et al., 2014).

Nevertheless, previous triptycene-based polyimides used for membrane fabrication often possess a linear structure and high solubility in common organic solvents (Cho and Park, 2011a; Zhou and Jin, 2019). For those polyimides with a network structure (Yan et al., 2018; Zhang et al., 2014), the stone-like solubility in common organic solvents relatively restricts membrane applications. However, it is anticipated that (Zhang et al., 2014; Ghanem et al., 2010) microporous polymers with network structures prepared using similar monomers and polymerization chemistry will have greater microporosity, and higher separation performance can be expected. As an example, membranes composed of network polymers show higher permeance compared to membranes composed of linear polymers under the same selectivity, especially when the thickness is lower than 100 nm (Karan et al., 2015). Additionally,
previous reports employing polyimide membranes for gas separation have all focused on O$_2$/N$_2$ separation, CO$_2$/N$_2$ separation, and the like. No previous reports have been published for the separation, especially, molecular sieving of gas/vapor mixture, such as nitrogen/VOC (volatile organic compound) mixture using polyimide membranes.

VOCs emitted as gases from chemical industries have negative consequences on human health, such as genetic modification, and on the environment, such as the formation of tropospheric ozone (Della Pina et al., 2018; Salar-García et al., 2017; Zeng et al., 2020a, b; Yang et al., 2010, 2018a), if they are not adequately treated. Many strict laws and legislations have thus been issued in many countries to force industrial companies to manage such emissions (Salar-García et al., 2017; Yang et al., 2010, 2018a; Cheng et al., 2020). Many methods, such as catalytic combustion, biofiltration, bionticking filters, membrane separation, etc., have been proposed to fulfill VOC emission requirements (Salar-García et al., 2017; Yang et al., 2010, 2018a; Cheng et al., 2020; Yang et al., 2018b; Petrusová et al., 2019; Zhang et al., 2021). Among them, membrane technology is regarded as one of the most prospect methods due to its advantages of non-destruction, energy-efficiency, and smooth operation and integration (Petrusová et al., 2019; Yeom et al., 2002). Two kinds of membranes (VOC-rejective membrane (Zhou et al., 2017) and VOC-selective membrane (Yang et al., 2018b; Liu et al., 2009; Şahin et al., 2020) have been developed for the treatment of VOCs emitted from different emission sources. VOC-selective membrane is a membrane where VOC can preferentially transport over nitrogen for separating the VOC/nitrogen mixture.

VOC-rejective membrane refers to a membrane that lets smaller molecules, such as nitrogen, to permeate-selectively transport through the membrane over larger VOC molecules such as cyclohexane molecule for the separation of a nitrogen/cyclohexane mixture, which is very suitable for economical and effective treatment of unorganized VOC emission. The source control for VOC emissions can, thus, be ensured. In addition, such a membrane employs feed pressure instead of a traditional high vacuum at the downstream to provide the driving force (Yang et al., 2018b; Şahin et al., 2020), which is more energy-efficient. Furthermore, our previous work (Zhou et al., 2017) has already reported using trip-tylene and alkyl acyl chloride to synthesize polyimides for the fabrication of a VOC-rejective membrane, which showed excellent rejection. However, the relatively moderate flux obtained affects its potentially industrial feasibility.

In this work, aromatic polyimides with a network structure were synthesized using triaminotriptycene and aromatic dianhydride as monomers. Aromatic dianhydride monomers are used because such rigid molecular linkers can “lock in” permanently interconnected microporosity into polymers (Cooper, 2009), resulting in higher permeability. Four different aromatic dianhydride monomers were, thus, used for the synthesis. Different characterizations such as Fourier Transform infrared spectrometer (FTIR), X-ray photoelectron spectroscopy (XPS), and so on were used to determine the polymer properties. Then, these polyimides were fabricated into microporous membranes by using XPS (Thermo ESCALAB 250, USA) with monochromatized Al K$\alpha$ radiation. The N$_2$ and CO$_2$ adsorption behavior for the polyimides were purified under vacuum at 120 °C before use. Dimethylacetamide (DMAc) and tetrahydrofuran (THF) were purchased from Aladdin Reagent Co. Ltd., China and dried using NaA molecular sieves. Concentrated HNO$_3$, acetic anhydride, and pyridine were purchased from Sinopharm Co. Ltd., China and used directly without further treatment. A 0.22 μm Nylon-6 MF substrate membrane was purchased from Shanghai Xinya Purification Equipment Co., Ltd, China.

2.2. Synthesis of polyimides

Scheme 1 shows a schematic diagram for the synthesis of the four polyimides studied in this work. First, 3 mmol 2,6,14-triaminotriptycene was dissolved in 50 mL DMAc solution. Then, after stirring for 15 min, 4.5 mmol anhydride 3 wt/v% DMAc solution was added drop by drop to the solution under an ice bath (0–5 °C) with a constant pressure titration funnel. The mixture was continuously maintained under the protection of nitrogen. Next, 10 ml pyridine and acetic anhydride were added to the reaction solution after 6 h, followed by stirring for a further 24 h. The solution was then precipitated in methanol and filtrated under vacuum, which was repeated for more than three times. Finally, the solid was dried under vacuum at 100 °C for 24 h to obtain the polyimides. The molecular weight for the polyimides was measured to show a Mn of approximately 50,000 g/mol and Mw of approximately 80,000 g/mol, and a PDI ranging between 1.2 and 1.5.

2.3. Preparation of composite membranes

Polyimide powder (0.4 g) was added in DMF solution (10 mL) to obtain the membranes solution, which was stirred for 48 h to disperse the polyimide polymer. The membrane solution was vacuum-degassed and then coated on the surface of the Nylon-6 substrate to form a composite membrane with a coating knife. Thickness of the selective layer was tuned by varying the height of the casting knife. A homogenous PI membrane was obtained by pouring a certain amount of membrane solution into a PTFE dish. Then, the nascent membrane was dried in a vacuum oven at 80 °C for 48 h.

2.4. Characterisation of the polyimides and membranes

FTIR spectra of the polyimides were measured using a spectrophotometer (Thermo Nicolet 8700) using KBr pellets between 4000 cm$^{-1}$ and 500 cm$^{-1}$. Field-emission scanning electron microscopy (FE-SEM, Hitachi-4800, Japan) was used to analyze the morphology of the composite membranes. X-ray diffraction (XRD) was carried out to characterize the polyimide crystal structure using Cu K$_\alpha$ radiation, in the range of 5–80° at increments of 0.02° at room temperature with a wavelength (λCu = 1.542 Å), in the range of 2θ from 5° to 60°. A thermal analyzer (Netzsch STA 449 F) was used to analyze the membrane thermal properties in the temperature range from 30 °C to 800 °C with a nitrogen flow rate of 25 mL/min and a temperature rate of 10 °C/min. The thermal stability of the polyimides was analyzed by using a thermal analyzer (Netzsch STA 449 F) at a heating rate of 10 °C/min for temperatures ranging between 30°C and 800°C under the flow of nitrogen. Analysis of the elemental composition in the polyimides was performed by using XPS (Thermo ESCALAB 250, USA) with monochromatized Al K$\alpha$ radiation. The N$_2$ and CO$_2$ adsorption behavior for the polyimides was measured through adsorption experiments at 77 K and 0 K, respectively (ASAP 2046, ASAP 2020, Micromeritics, USA). Static water contact angles were measured by using a contact-angle meter (Drop-Meter™ A-100, USA).

2.5. Measurement of membrane performance

The membrane separation performance for the separation of nitrogen and VOCs was conducted according to the method reported in our previous work (Zhou et al., 2017) and a schematic diagram is shown in
The permeation flux ($J_i$, $L/(m^2 \cdot h)$) for the composite membrane was measured using a soap bubble flowmeter and calculated using the following formula:

$$J_i = \frac{V_i}{S t} \quad (1)$$

The permeability ($P_i$) of component i was calculated by the following formula:

$$P_i = \frac{l \times J_i \times 273.15 \times P_0}{T \times \Delta p} \times \frac{76}{15} \quad (2)$$

Where $V_i$ is the volume, $S$ is the effective membrane area, $t$ is the time, $P_i$ is the gas permeability in Barrer ($1 \text{ Barrer} = 10^{-10} \text{ cm}^3/\text{(STP):cm/}(\text{cm}^2\cdot\text{s}\cdot\text{cmHg})$), $l$ is the thickness of the selective-layer of the composite membrane, which was obtained by measuring the cross-sectional thickness of the selective layer in an SEM image, $\Delta p$ is the trans-membrane pressure drop, $T$ is the temperature and $P_0$ is the upper stream pressure.

The rejection ($R$) was used as previously reported (Zhou et al., 2017) and calculated by the following formula:

$$R = \left( \frac{C_F}{C_P} \right) \times 100\% \quad (3)$$

Where $C_F$ is the feed VOC concentration, and $C_P$ is the permeate VOC concentration, which was analyzed by gas chromatography (SCION456-GC-SQ, China), equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Two columns (BR-5 MS capillary column (15 m x 0.25 mm, ID 2.5 μm) and MS-13 x 80/100 pack column) were used. The temperatures for the injector, oven, TDC detector, and FID detector were 250 °C, 70 °C, 120 °C, and 300 °C, respectively.

3. Result and discussion

3.1. Characterization of the polyimides

The structural properties of polymers have a significant influence on membrane performance, and different characterizations were thus carried out to reveal these properties. Fig. 1 illustrates the FTIR spectra of the four polyimides.

It can be seen from Fig. 1 that the FTIR spectra characteristic peaks at 1722 cm\(^{-1}\) and 1785 cm\(^{-1}\) are ascribed to symmetric and asymmetric C=O stretching in the imide ring, and the peaks observed at 710 cm\(^{-1}\) are assigned to CO\(=\)O bending (Wiegand et al., 2014; Grubb et al., 1999). A spectral peak at 1370 cm\(^{-1}\) due to CN\(=\)stretching is also observed for polyimides made in-house (Cho and Park, 2011a; Wang et al., 2014). Simultaneously, peaks due to C-H stretching of alkyl groups at approximately 2975 cm\(^{-1}\), which originate from the hypomethyl group in the triptycene structure (Zhou et al., 2017; Wang et al., 2014), can also be observed in the spectra, indicating successful reaction between triaminotriptycene and acid anhydride monomers. In addition, the disappearance of the obvious characteristic sharp peaks for C\(=\)O in the amide and carboxyl (1660 cm\(^{-1}\) and 1710 cm\(^{-1}\)) groups in the

![Scheme 1](image1.png)

Scheme 1. Diagram of the synthesis of polyimides using different monomers.

![Scheme 2](image2.png)

Scheme 2. Schematic diagram for the measurement of the membrane performance.
polymides also suggests that the polymers are completely imidized (Grubb et al., 1999).

Fig. 2 shows the XRD patterns and the mean d-spacing obtained for the four kinds of polymides. It is shown in Fig. 2(a) that all of the triptycene-based polymides show no sharp diffraction peaks, indicating an amorphous structure that makes it possible to fabricate a membrane, as shown in Fig. 3. Free-standing membranes can easily be obtained, which show a yellow and transparent appearance, indicating their easy membrane-forming properties. SEM surface images of the four membranes all express dense and defect-free properties, as shown in Figs. 4 and S1. In addition, it can be seen from Fig. S2 that these four polyimide membranes are hydrophilic with a water contact angle of approximately 80° (Ma et al., 2007), because the imide rings are hydrophilic (Wu et al., 2016).

Fig. 2(b) shows the mean d-spacing for these polymides, and peaks around 16° (approximately 5.4 Å) can be observed, which are regarded as the average chain-chain distances (Tian et al., 2018). The spacing trends are Trip-BTDA-PI < Trip-ODPA-PI < Trip-BPADA-PI < Trip-6FDA-PI, which is the same as that found in the simulated XRD shown in Fig. S3. The highest d-spacing found in the Trip-6FDA-PI may be ascribed to its relatively large side groups (-CF), which hinder dense packing of the polyimide chains, leading to a higher d-spacing compared to Trip-ODPA-PI without side groups (Hellums et al., 1989). The lowest d-spacing in the Trip-BTDA-PI may be due to the partial filling of the C=O groups, where these groups are small and partially fill the interchain voids (Luo et al., 2016), resulting in a smaller mean inter-chain distance compared to Trip-ODPA-PI. While for the Trip-BPADA-PI polymer, the backbone with phenyl rings and methyl groups is, theoretically, supposed to show a higher d-spacing. However, the higher mobility of the chains because of a longer repeat chain makes them pack more efficiently, which compensates for the effects of the side groups on the d-spacing, leading to a d-spacing ranging between that for Trip-BTDA-PI and Trip-6FDA-PI.

Fig. 5 shows the surface areas and pore sizes of the triptycene-based polymides. It is shown in Fig. 5(a) and Table S1 that surface area was determined to range from 71.5 m²/g to 103.8 m²/g by probing molecular nitrogen. However, their adsorption isotherms are not typical type I isotherms due to the usage of a relatively large probing molecular nitrogen, which means some micropores may not be accessible to the probing molecular nitrogen, leading to an underestimate of the polymer surface area, as reported previously (Jimenez-Solomon et al., 2016). However, the polymides still have pore sizes that all below 20 Å, as shown in Fig. 5(b), and all polymides are found to contain ultramicropores less than 7 Å in size; this is because of the rigid aromatic used, which forms a rigid intrachain that can “lock in” permanently interconnected microporosity into polymers (Cooper, 2009), consequently producing ultramicroporosity (<0.7 nm) in these four polymides (Swaidan et al., 2015). The Trip-BTDA-PI even shows ultramicropores that are less than 6 Å in size due to the “partial filling” mechanism (Luo et al., 2016). Therefore, smaller probing carbon dioxide was used to measure the polyimide surface area, as shown in Fig. 5(c) and Table S1, which showed surface areas that were higher than that obtained by using nitrogen as a probing molecular, confirming the microporous properties of the synthesized polymers (Jimenez-Solomon et al., 2016).

The highest surface area was obtained for Trip-6FDA-PI and followed by Trip-BTDA-PI, Trip-ODPA-PI, and Trip-BPADA-PI, which is also the same trend observed for the simulation results illustrated in Fig. 5(d). These results can be ascribed to their fractional free volume (FFV) or fractional accessible volume (FAV), as shown in Fig. S4, which expresses the same trends as that observed for the surface area: Trip-6FDA-PI > Trip-BTDA-PI > Trip-ODPA-PI > Trip-BPADA-PI. Higher FAV or FFV means a higher volume can be available for the adsorption of probing molecular, and higher surface area can be thus achieved.

As previously reported (Zhou et al., 2017; Wang et al., 2020), a monomer with three active groups is capable of forming a network structure, which will favor the formation of interchain covalent bonds and enhance the interchain rigidity. Therefore, XPS was used to estimate the carbon, oxygen, and nitrogen content in the polymides, because the degree of network crosslinking can be calculated from the relative values of nitrogen and oxygen (Zhou et al., 2017; Karan et al., 2015). Deconvolution of the F1s peak in the measured spectra because of the existence of trifluoromethyl groups (-CF₃). The highest O/N ratio in the polyimide was due to the linear cross-linked polymer, which has only one dianhydride side group linked to one amine on the 2,6,14-triaminotriptycene so that more oxygen exists in the polyimides, leading to a higher O/N ratio. As shown in Table 1, both a network structure and linear structure exists in the four polyimides, which is similar to that report previously (Zhou et al., 2017). Trip-BTDA-PI shows the highest degree of network cross-linking (98.09 %) and followed by Trip-ODPA-PI (90.62 %), Trip-BPADA-PI (97.93 %), and Trip-6FDA-PI (44.00 %). The reason for this is that a two-step method via poly (amic acid) was used to synthesize the polyimides. The mechanism for poly(amic acid) (polyimide precursor) formation involves a nucleophilic substitution reaction, whose reaction rate is thus primarily controlled by the nucleophilicity of the amino nitrogen atom of the diamine and the electrophilicity of the carbonyl groups of the polymides.
dianhydride (Ghosh, 1996). Here, the electron affinity for the four dia-
nhydrides follows the order of BTDA (1.55 eV) > 6FDA (1.48 eV) > ODPA
(1.30 eV) > BPADA (1.12 eV) (Ghosh, 1996; Svetlichnyi et al., 1977),
which shows almost the same trend to that found for the degree of
network crosslinking except for 6FDA. As reported previously (Ardash-
nikov et al., 1971), the reaction rate also depends on the structure of the
initial reactants. The 6FDA reactant possesses two large trifluoromethyl
groups, which may impede the nucleophilic substitution reaction with
triaminotriptycene owing to a steric effect, leading to a reduction in the
degree of network crosslinking. Simultaneously, the degree of network
cross-linking may also be the characteristic representative of the degree
of cross-linking, which endows these polyimides with excellent thermal
stability, as shown in Fig. S9; all polyimides have a decomposition
temperature above 500 °C.

Fig. 3. Digital pictures of the four homogeneous polyimide membranes (a: Trip-6FDA-PI; b: Trip-BTDA-PI; c: Trip-ODPA-PI; d: Trip-BPADA-PI).

Fig. 4. SEM cross-sectional images of the four composite membranes (a: Trip-6FDA-PI; b: Trip-BTDA-PI; c: Trip-ODPA-PI; d: Trip-BPADA-PI).
3.2. Membrane performances

In membrane research, the ultimate goal is to increase the membrane performance. Therefore, these novel polyimide membranes were carried out for the separation of a nitrogen/cyclohexane binary mixture, and results are shown in Fig. 7.

Fig. 7 shows the rejection achieved for the four membranes for the separation of a nitrogen/cyclohexane mixture at different permeate fluxes. The data show that when the permeate flux is 60 L/(m$^2$·h), all membranes have a rejection higher than 99 %, suggesting excellent molecular sieving performance (or called VOC-rejective property) owing to their interconnected ultramicropores, which are believed to offer high selectivity (here, rejection) (Swaidan et al., 2015). When the permeate flux is increased further to 120 L/(m$^2$·h) and 180 L/(m$^2$·h), the Trip-BTDA-PI membrane can maintain the highest rejection, followed by the Trip-ODPA-PI membrane, Trip-6FDA-PI membrane, and Trip-BPADA-PI membrane. The reason for this is that many factors, such as d-spacing (Du et al., 2012), degree of crosslinking (interchain rigidity) (Swaidan et al., 2014), and intrachain rigidity (Swaidan et al., 2015; Du et al., 2012; Freeman, 1999), can affect the membrane selectivity. The Trip-BTDA-PI and the Trip-ODPA-PI have a lower d-spacing and higher degree of network crosslinking, resulting in greater movement

![Fig. 5.](image_url) (a) N$_2$ adsorption and desorption isotherms for the triptycene-based polyimide powders at 77 K; (b) Micropore distributions for the triptycene-based polyimide powders calculated by the HK method (slit-pore geometry, carbon-graphite model); (c) CO$_2$ adsorption isotherms for the triptycene-based polyimide powders at 273 K; (d) simulated CO$_2$ adsorption amount for the triptycene-based polyimide powders at 273 K.

![Fig. 6. XPS survey spectra for the four polyimides.](image_url)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C(%)</th>
<th>N(%)</th>
<th>O(%)</th>
<th>F(%)</th>
<th>O/N</th>
<th>Formula</th>
<th>Degree of network crosslinking (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trip-6FDA-PI</td>
<td>68.33</td>
<td>4.50</td>
<td>11.52</td>
<td>15.65</td>
<td>2.56</td>
<td>$9Y + 3X - O$</td>
<td>44.00</td>
</tr>
<tr>
<td>Trip-BTDA-PI</td>
<td>79.50</td>
<td>5.82</td>
<td>14.68</td>
<td>0</td>
<td>2.52</td>
<td>$11Y + 7X - N$</td>
<td>98.09</td>
</tr>
<tr>
<td>Trip-ODPA-PI</td>
<td>79.39</td>
<td>5.71</td>
<td>14.90</td>
<td>0</td>
<td>2.61</td>
<td>$11Y + 7X - O$</td>
<td>90.62</td>
</tr>
<tr>
<td>Trip-BPADA-PI</td>
<td>82.96</td>
<td>3.63</td>
<td>13.41</td>
<td>0</td>
<td>3.69</td>
<td>$13Y + 9X - O$</td>
<td>47.93</td>
</tr>
</tbody>
</table>
limitation and lower swelling of the polymer chains. This phenomenon is also supported by the adsorption results, as illustrated in Fig. S10; the adsorbed amount in the four polyimide membranes is low because of their hydrophilic properties. Furthermore, both experimental and simulated data show that the amount of cyclohexane adsorbed in the Trip-BTDA-PI and the Trip-ODPA-PI membranes is far less than that in the other two membranes. This is because that cyclohexane hardly diffuses into the polymers owing to the smaller pore size and stronger interchain rigidity in the Trip-BTDA-PI membrane and the Trip-ODPA-PI membrane. Higher rejection can, thus, be achieved with a higher permeate flux. Further comparison between the Trip-ODPA-PI membrane and the Trip-BPADA-PI membrane with similar d-spacing also shows the same result. These results confirm that covalent-bonded network polymer chains, called interchain rigidity, are paramount to the intrachain rigidity in keeping the membrane selectivity (rejection here) under an aggressive nitrogen/cyclohexane mixture (Swaidan et al., 2014). Furthermore, the Trip-BTDA-PI membrane also possesses pore sizes of less than 6 Å and a lower d-spacing than the Trip-ODPA-PI membrane does, resulting in a higher rejection under the same conditions.

For the Trip-6FDA-PI membrane and the Trip-BPADA-PI membrane with almost the same degree of network crosslinking, the existence of two ether bonds and relatively longer repeat chains in the Trip-BPADA-PI membrane weakens the intrachain rigidity despite the smaller d-spacing. Therefore, the movement and swelling of the polymer chains is stronger (Swaidan et al., 2015; Freeman, 1999); lower rejection can, thus, be observed for the Trip-BPADA-PI membrane. Fig. S11 shows the permeabilities of the four composite membranes. It shows that the higher the FFV, the higher the permeability, because a higher FFV implies that the membrane possesses more channels or interspaces to enable gas transport (Liao et al., 2016).

Given the above results, the Trip-BTDA-PI membrane was used for the following experiments. Furthermore, it can be observed that the results obtained above (flux 60 L/(m²·h)) are higher than our previous results (flux of 20 L/(m²·h)) (Zhou et al., 2017), which indicates less membrane area is needed for application using the same volume membrane. Excellent industrial feasibility for the polyimide VOC-rejective membrane can, thus, be expected.

Fig. 8 shows the effect of the thickness on rejection, which shows a constant rejection value with different thickness. As described by Fick’s law, if membranes are defect-free, selectivity (here rejection) should be independent of the selective layer thickness (Koops et al., 1994), which also suggests an excellent membrane-filming property for the synthesized polyimide. Furthermore, Fig. 8 shows that a thicker membrane leads to higher transportation resistance as expected, and higher feed pressure is needed to reach the fixed flux. If the feed pressure is too high, membrane performance will deteriorate, as shown in Fig. S12. Higher feed pressure leads to lower rejection because more cyclohexane molecules are pushed into transport channels in the membrane with a higher partial pressure difference, which occupy the channels and block the transportation of nitrogen molecules through the membrane. Finally, cyclohexane permeability increases and nitrogen permeability decreases, leading to lower rejection with increased feed pressure. These results also imply that membranes with a network structure can enhance interchain rigid owing to the covalent bonds formed between chains, which may restrict polymer chain motion, leading to depressed membrane swelling (Swaidan et al., 2014). Therefore, even though more cyclohexane molecules are adsorbed into the membrane, the depressed membrane swelling does not favor the permeation of nitrogen. Furthermore, the feed pressure was found to be less than 10 kPa when the membrane thickness is lower than 4 μm. This is because the introduction of rigid 3D contorted triptycene with built-in free volume prevents efficient packing of the polymer network and forms interconnected network pores, leading to a low feed operating pressure, which further suggests an economical operating cost and good commercial feasibility (Zhou et al., 2017).

As shown by the above data, the Trip-BTDA-PI membrane fabricated in house expresses a molecular sieving property, where large cyclohexane molecules are rejected and small nitrogen molecules are allowed to pass through the membrane. To further confirm this mechanism, the Trip-BTDA-PI membrane was studied for the molecular sieving of nitrogen over VOCs with different molecular dimensions (Table S2), and the results are shown in Fig. 9. The highest rejection was observed for cyclohexane because of the highest molecular dimension, followed by toluene, hexane, and acetone, which corresponds to the order of their molecular dimensions (Webster et al., 1998). This further confirms the molecular sieving mechanism in this membrane. Furthermore, although the kinetic diameter of acetone is higher than that of hexane (Table S2), its rejection is still lower than that of hexane, because, except for the effect of size selectivity, shape selectivity may be more important in this molecular sieving separation process (Zhou et al., 2017).

Feed pressure and VOC properties can affect the membrane separation performance, and other operating parameters such as temperature, feed VOC concentration will also affect the membrane performance, as shown in Figs. S13 and S14. Fig. S13 shows that constant rejection with increasing temperature is observed because of the network structure and
the 3D rigid structure of triptycene, which restricts thermal movement of the polymer chains (Cho and Park, 2011a; Swaidan et al., 2014), leading to constant rejection. Fig. S14 shows that higher feed cyclohexane concentration results in higher rejection. The reason for this is that the covalent crosslinking network structure and the limited movement of polymer chains (Zhou et al., 2017) restricts the membrane swelling induced by the adsorption of cyclohexane in the membrane. Therefore, the resistance in the membrane leads to an increase in the permeation flux that is less than the increase in the feed cyclohexane concentration. The cyclohexane permeability displays a decreasing trend, and a higher rejection can be observed for higher feed cyclohexane concentration.

An excellent membrane should possess not only high rejection (selectivity) and permeability but should also show good stability, which is necessary for the implementation of a membrane (Bachman et al., 2016). Fig. 10 illustrates the change of separation performance with operating time. During the first 40 days, membrane performance showed a rejection that was maintained at over 99% with constant permeabilities. Rejection starts to decline for a further increase in time, which is accompanied by an increase in the permeability for nitrogen and cyclohexane. This may be related to a change in the membrane structure after 40 days. Three composite membranes: new membrane, membrane used for two weeks, and membrane used for three months, were, thus, selected for comparison by employing XPS (Figs. 11, and S15) and SEM analysis (Figs. 12 and S16).

Fig. 11 shows the C1s XPS spectra obtained at different ion etching depths for the three membranes. An obvious difference between the former two membranes and the membrane used for three months can be observed. The new membrane and the membrane used for two weeks express similar C1s spectra, suggesting no major structural changes in these two membranes. The O1s spectra shown in Fig. S15(a) and S15(b) also display similar spectra for these two membranes. Furthermore, Figs.12(a) and (b) also show a similar cross-sectional morphology, and no visible cracks can be observed. Constant separation performance can thus be observed for these two membranes. For the membrane used for three months, the C1s XPS spectrum from the 0 etch level is found to be similar to that obtained by the other two membranes. However, peaks observed at approximately 290 eV in the C1s spectra (Fig. 11(c)) and 538 eV in the O1s spectra (Fig. S15(c)) can be seen from the 1 etch layer, indicating formation of a shake-up satellite associated with π to π* transitions (Ghosh et al., 1997; Battirola et al., 2018). As the etch depth continues to increase, the peak shows a continuous to shift to the right, and then shifts left to the same site for the 0 etch layer. The corresponding O1s spectra in Fig. S15(c) also show similar trends for different etching depths, which indicates that some bonds may be broken or the microstructure inside the membrane may change to form non-selective voids with time, as shown in Fig. 12(c), where a loose morphology was obtained. These non-selective voids may be too large to achieve molecular sieving of nitrogen over cyclohexane, and lower rejection can thus be observed. Simultaneously, non-selective voids also mean bigger channels for the transportation of nitrogen and cyclohexane molecules; higher permeability can thus be obtained. However, a dense layer with a thickness of approximately 50–100 nm can be seen on the top of the cross-section in the membrane used for three months. This is the reason that the C1s XPS spectrum from the 0 etch level in the membrane used for three months is similar to that obtained by the other two membranes. In addition, Fig. S16 shows the SEM surface images of the three composite membranes, from which no visible difference can be observed. Therefore, a preliminary conclusion can be drawn here in that the structure inside the membrane varies after the membrane is used for three months, which leads to a decrease in rejection. More specific reasons for the observed stability are still under investigation in our group.

4. Conclusion

In this work, triptycene-based ultramicroporous polyimides with a network structure were successfully synthesized using 2,6,14-triaminotriptycene and aromatic dianhydrides, which were fabricated into the membranes for the molecular sieving of a nitrogen/cyclohexane mixture by solution coating. Rejections of above 99% were observed for all the polyimide membranes with a permeation flux as high as 60 L/(m²·h), indicating an excellent molecular sieving property due to the network structure and ultramicroporosity in these polyimides. The membrane with a higher degree of network crosslinking showed higher rejection at different permeate fluxes, suggesting the importance of interchain rigidity compared to intrachain rigidity under such aggressive separation. Different binary nitrogen/VOC mixtures were further investigated to
verify the molecular sieving mechanism for the in-house fabricated membrane. Finally, investigation of the membrane stability showed that rejection starts to decrease after 40 days due to a possible change in the structure inside the membrane.

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.

CRediT authorship contribution statement


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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2020.123817.