

Interfacially Polymerized Layers for Oxygen Enrichment: A Method to Overcome Robeson's Upper-Bound Limit

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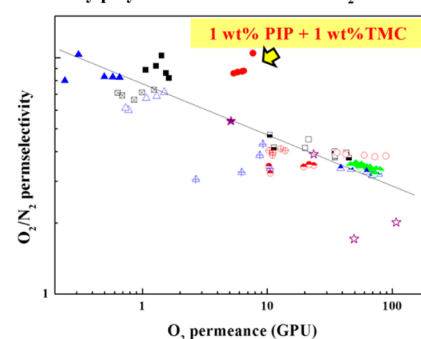
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ABSTRACT: Interfacial polymerization of four aqueous phase monomers, diethylenetriamine (DETA), m-phenylenediamine (mPD), melamine (Mela), and piperazine (PIP), and two organic phase monomers, trimethyl chloride (TMC) and cyanuric chloride (CC), produce a thin-film composite membrane of polymerized polyamide layer capable of O₂/N₂ separation. To achieve maximum efficiency in gas permeance and O₂/N₂ permselectivity, the concentrations of monomers, time of interfacial polymerization, number of reactive groups in monomers, and the structure of monomers need to be optimized. By controlling the aqueous/organic monomer ratio between 1.9 and 2.7, we were able to obtain a uniformly interfacial polymerized layer. To achieve a highly cross-linked layer, three reactive groups in both the aqueous and organic phase monomers are required; however, if the monomers were arranged in a planar structure, the likelihood of structural defects also increased. On the contrary, linear polymers are less likely to result in structural defects, and can also produce polymer layers with moderate O₂/N₂ selectivity. To minimize structural defects while maximizing O₂/N₂ selectivity, the planar monomer, TMC, containing 3 reactive groups, was reacted with the semirigid monomer, PIP, containing 2 reactive groups to produce a membrane with an adequate gas permeance of $7.72 \times 10^{-6} \text{ cm}^3 \text{ (STP) s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$ and a high O₂/N₂ selectivity of 10.43, allowing us to exceed the upper-bound limit of conventional thin-film composite membranes.

KEYWORDS: interfacial polymerization, gas separation membrane, permeability, oxygen enrichment membrane, oxygen and nitrogen permselectivity, polyamide layer structure

Interfacially polymerized membrane for O₂ enrichment



INTRODUCTION

Membrane gas separation allows for an easy to operate, energy-efficient, and compact system, which is now regarded as the most competitive method for industrial gas separation. A successful gas separation system requires a membrane with high permeability and selectivity; however, a high selectivity membrane often suffers from low permeation fluxes while a high flux membrane usually lacks selectivity. The trade-off relationship between selectivity and permeability of conventionally prepared polymeric membrane is well documented, where Robeson defined the trade-off between selectivity and permeability as the upper bound for membrane performance by drawing the inverse correlation between the O₂/N₂ selectivity and oxygen permeability of most polymeric gas separation membranes,^{1–3} and we hardly ever observe a polymeric material that is capable of exceeding this upper bound.^{1,4} Tremendous efforts have been devoted to developing a high flux, high selectivity gas separation membrane to overcome this upper bound.^{5–8} Because the permeability and selectivity are closely related to the polymer free volume, polymers can be synthesized with rigid backbone and bulky side chain to maximize the size of polymer free volume.^{9–13} However, not much success has been obtained in overcoming the upper-bound limit in the past 30 years. On the contrary, some inorganic membranes, such as molecular sieving zeolites or

carbon membranes, show superior performance compare to the polymer membrane.^{14,15} The performance of molecular sieving membranes was supposedly contributed to their narrow pore size distribution; however, these molecular sieving membranes are fragile and difficult to process making them less economically feasible.^{16–19}

Interfacial polymerization, a technique often used in reverse osmosis and nanofiltration membrane fabrication, can produce uniform and rigid micropores in the highly cross-linked layer as thin as 100 nm with narrow pore size distribution ranging from 3 to 5 Å.²⁰ An interfacial layer of uniformly packed structure may serve as a good candidate of high flux and high selectivity gas separation membrane. Thus, the thin-film composite (TFC) membrane by interfacial polymerization may help bring the performance of polymeric membranes over the upper bound.

Up till now, few reports discuss the gas separation properties of TFC membranes. While there are few emerging reports in the recent year about using TFC membranes for CO₂/CH₄ and CO₂/N₂ separation, most of those reports focus mainly on increasing membrane polarity in order to enhance CO₂

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solubility and very few discuss the effect of thin layer structures have on gas separation, particularly on O₂/N₂ separation.^{21–25}

Here, we tried to compare the gas separation properties of the interfacially polymerized layers by using four aqueous phase monomers, diethylenetriamine (DETA), m-phenylenediamine (mPD), melamine (Mela), and piperazine (PIP), and two organic phase monomers, trimethyl chloride (TMC) and cyanuric chloride (CC). TMC and CC are both planar in structure and have three functional groups. Two of the three functional groups found on CC are able to react with amines at 60 °C. Mela and DETA have three reacting amines, but PIP and mPD have only two. Mela and DETA have three reacting amines, but PIP and mPD have only two. Mela and DETA are planar in structure where, PIP has a boat or chair structure, and DETA has a flexible, linear structure. By carefully controlling the concentration and the polymerization time of the selected monomers, we can construct membranes with different structures and physical properties. For instance, although DETA reacted with planar CC may result in a flexible net structure, the planar aqueous phase monomer (Mela) reacted with planar TMC may form a rigid planar structure in the interfacial layers. Furthermore, by selecting different monomer combination, we can also vary the nitrogen contents in the interfacial layers. Therefore, we intended to study how the structures of monomers, the number of functional groups, the nitrogen content of monomers, as well as the effect of interfacial polymerization time and monomer concentrations may affect the membrane performance.

MATERIALS AND METHODS

Chemical Components. The water-soluble monomers used in this study were diethylenetriamine, m-phenylenediamine, melamine, or piperazine; oil-soluble monomers were trimesoyl chloride or cyanuric chloride. The above monomers were purchased from Sigma/Aldrich and the structures were plotted in Figure 1. The solvents, including N-methyl-2-pyrrolidone (NMP), toluene, and polymers polyacrylonitrile (PAN) and polyvinylpyrrolidone (PVP), were also purchased from Sigma/Aldrich.

Preparation of Microporous PAN/PVP Support Membrane. The PAN/PVP casting solution was prepared by dissolving 13 wt % PAN and 7 wt % PVP in NMP. The resultant polymer solution was cast on a polyester nonwoven substrate with the thickness of ca. 150 μm and membranes were formed by wet phase inversion method in a

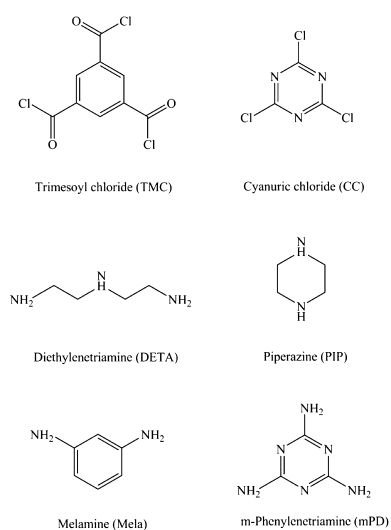


Figure 1. Chemical structures and abbreviations of the used organic and aqueous phase monomers in this study.

water bath. The casting temperature and relative humidity was 25–30 °C and 70–80%, respectively. The resulting PAN/PVP membranes were washed thoroughly with deionized water to remove all NMP. Before interfacial polymerization the membranes were immersed in a 1 N NaOH solution for 1 h. The final resulting PAN/PVP membranes were filtrated with water, and the water flux was roughly 700 ± 100 kg.

Fabrication and Characterization of Thin-Film Composite Membrane. The separating layer was synthesized interfacially on the macroporous polyacrylonitrile (PAN) support. The supporting membrane was first immersed in a solution containing of 1 or 2 wt % aqueous phase monomer and then moved into a toluene solution containing of 1 or 2 wt % organic phase monomer. The reaction times of interfacial polymerization were controlled by 1, 2, 3, 5, and 30 min. The membrane was washed using toluene, ethanol and then distilled water. Finally, the membrane was stored in distilled water solution. The cross-section morphology of the membranes was obtained under JEOL JSM-5410 scanning electron microscopy (SEM) operating at an accelerating voltage of 3 keV. The membranes were mounted on the sample stages by means of double-sided adhesive tape and were sputter-coated with gold. The surface chemical element composition of the membranes was also characterized by X-ray photoelectron spectroscopy (XPS) using a PHI Quantera SXM/Auger spectrometer with a monochromated Al KR X-ray source (1486.6 eV photons).

Permeance and Selectivity Measurement. A gas permeation analyzer (Yanaco GTR10) was employed to perform the pure gas permeation experiment of O₂ and N₂. The rate of transmission of air was obtained by gas chromatography, from which the air permeability was calculated. The experiments were carried out under isothermal conditions at 35 °C (± 0.5 °C). The permeance tests were conducted by 1 atm. Permeance is expressed as gas permeation unit (1 × 10⁻⁶ cm³(STP)/ cm² s cmHg). The permeability was defined by Barrer (1 × 10⁻¹⁰ cm³(STP) cm/cm² s cmHg). The permselectivity (α) was calculated based on the ratio of the permeance of pure oxygen and nitrogen.

RESULTS AND DISCUSSIONS

Effect of Interfacial Polymerization Reaction Time on Gas Permeance. In this study, we conduct interfacial polymerization at monomer concentration of 1 and 2 wt %. Figure 2 showed the dependence of N₂ permeance on the interfacial polymerization time of all the synthesized membranes. As the interfacial polymerization concentrations of the aqueous and organic monomers were 1 and 2 wt %, respectively, they were abbreviated as “aqueous phase monomer1”+“organic phase monomer2” (e.g., DE-

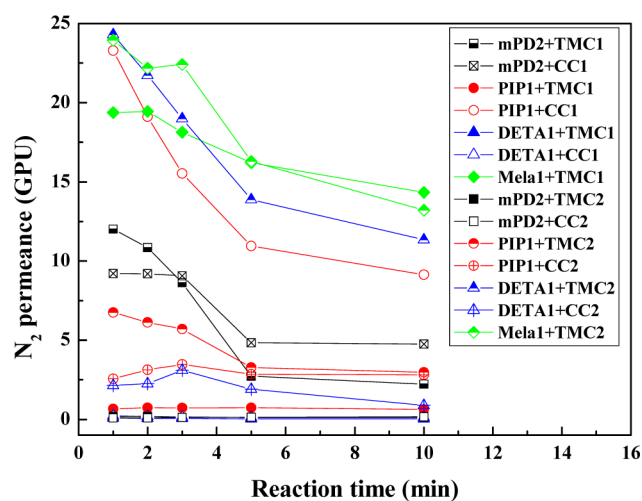


Figure 2. Nitrogen permeance of interfacially polymerized polyamide membranes along with the reaction time.

TA1+TMC2). The results revealed that the N_2 permeance of these membranes decreases with the increasing polymerization time up to 5 min, and beyond which the N_2 permeance remains constant approximately. Water permeability shows similar tendency to that of N_2 permeance with all membrane composition reaching a stable flux at 5 min polymerization time (data not shown). These results indicated that 5 min of interfacial polymerization reaction time may result in most densely cross-linked membrane skin layer.

The TFC polymerized membrane with appropriate concentration of TMC with another monomer unit, such as DETA1+TMC1, mPD2+TMC2, PIP1+TMC1, yields a membrane of high O_2/N_2 permselectivity approaching 8.00 to 10.43 (see Figure 3). However, the O_2/N_2 permselectivity of all

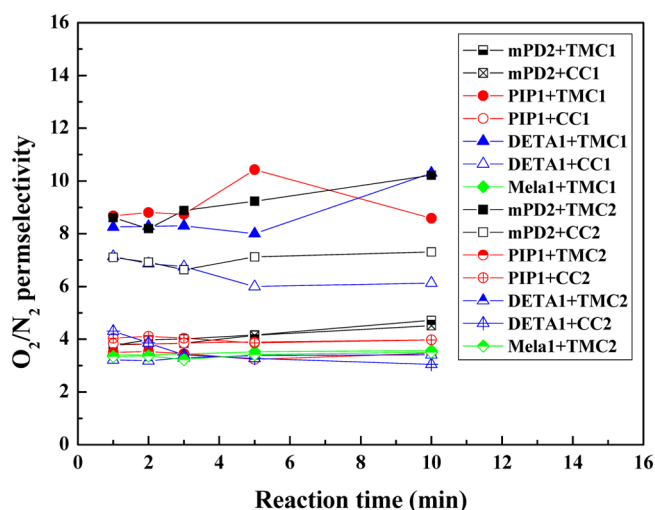


Figure 3. Oxygen/Nitrogen Permselectivity of Interfacially Polymerized Polyamide Membranes along with Reaction Time.

membranes tested showed no significant changes with respect to interfacial polymerization reaction time, indicating O_2/N_2 permselectivity are more likely to be effected by monomer composition rather than of interfacial polymerization time. For the TFC membranes with CC instead of TMC as their organic phase monomer, for instance mPD2+CC2 and DETA1+CC1,

the O_2/N_2 permselectivity was observed decrease slightly to around 7. Membranes of other monomer composition showed lower O_2/N_2 permselectivity than those with TMC or CC organic phase discussed above with O_2/N_2 permselectivities around 3–4.5. The SEM images of membranes containing TMC and CC with polymerization time of 5 min are shown in Figure 4, showing the interfacial polymerization membrane layers to have thickness ranging from ~ 127 nm to ~ 536 nm. Our data also suggests the lack of direct correlation between the O_2/N_2 permselectivity and the thickness of the membrane layers. Therefore, the monomer ratio between aqueous and organic phase, nitrogen content within the membrane skin layer, and the number of reactive group in the monomers may be crucial factors for TFC membranes' performance.

Effect of Aqueous to Organic Phase Monomer Ratio.

In this study, we also investigated how the ratio between aqueous and organic phase monomer affects interfacial polymerization reaction and membrane selectivity. Aqueous to organic phase monomer ratio ranged from 1.1 to 5.3 were investigated for their gas separation efficiency as summarized in Table 1. To obtain a membrane with maximum O_2 selectivity, we observed the optimal aqueous to organic phase monomer molar ratio range to be between 2.6 and 2.7. The membrane selectivity was also observed to decrease with either an increase or decrease in monomer molar ratio. The separating layer made of mPD and TMC has an O_2 selectivity of 9.23 when the aqueous to organic phase monomer molar ratio was 2.7. However, the O_2 selectivity was decreased to 4.16 as the monomer molar ratio was increased to 5.3. On the other hand, the separating layer made from PIP and TMC at monomer molar ratio of 2.7 yields O_2 selectivity as high as 10.43, but as we decrease the monomer molar ratio to 1.3, the O_2 selectivity decreased to 3.24.

In PIP1+TMC2 system, the diffusion rate of PIP into organic phase was relatively low because of the low PIP concentration. As a result, the PIP monomers were fast to react with TMC forming TMC-PIP-TMC complexes. In contrast to PIP, TMC diffuses much faster making an uniformly interconnected network rather difficult. However, the slow initial diffusion rate of PIP also results in a loosely linked separating layers resulting in low O_2 selectivity. To address these issues, we increased the aqueous to organic phase monomer ratio to 2.7.

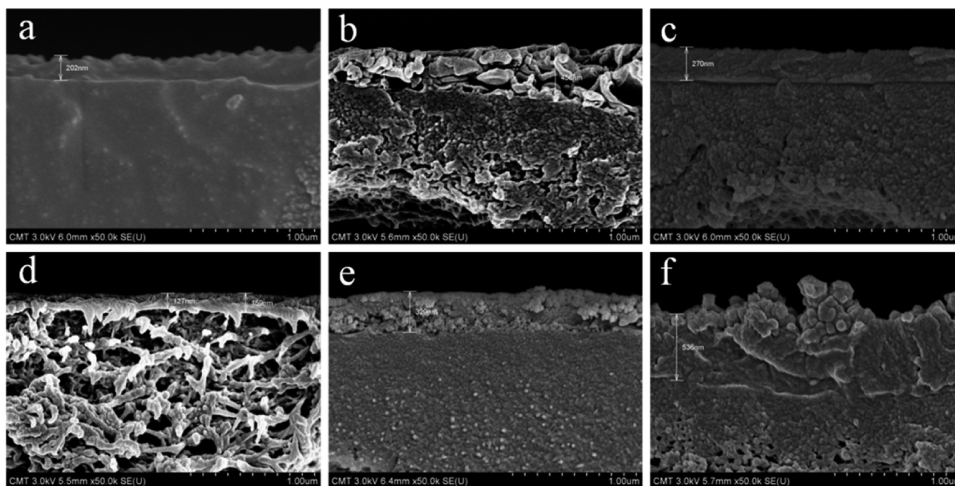


Figure 4. Cross-Section SEM Images of the TFC Membranes by Interfacial Polymerization for 5 min. (a) DETA1+TMC1; (b) mPD2+TMC2; (c) PIP1+TMC1; (d) Mela1+TMC1; (e) mPD2+CC2; (f) DETA1+CC1.

Table 1. Molar Ratio of Aqueous to Organic Phase Monomer and the Membrane Performance after 5 min of Polymerization

	molar ratio of aqueous/organic phase monomer	N ₂ permeance (GPU)	O ₂ permeance (GPU)	O ₂ /N ₂ selectivity	oxygen permeability coefficient (Barrer) ^a
mPD2+TMC1	5.3	2.73	11.36	4.16	N/A
mPD2+TMC2	2.7	0.14	1.29	9.23	0.59
PIP1+TMC1	2.7	0.74	7.72	10.43	2.08
PIP1+TMC2	1.3	3.28	10.63	3.24	6.03
DETA1+TMC1	2.6	0.03	0.24	8.00	0.05
DETA1+TMC2	1.3	13.88	46.91	3.38	26.41
Mela1+TMC1	2.1	16.20	57.02	3.52	7.24
Mela1+TMC2	1.1	16.29	55.71	3.42	8.30
mPD2+CC1	3.7	4.84	20.04	4.14	N/A
mPD2+CC2	1.9	0.14	1.00	7.12	0.33
PIP1+CC1	1.9	10.95	42.60	3.89	13.50
PIP1+CC2	1.0	2.86	11.04	3.86	N/A
DETA1+CC1	2.6	0.13	0.78	6.0	0.42
DETA1+CC2	1.3	1.91	6.25	3.27	1.91

^aN/A, not available.

By increasing the amount of aqueous phase monomers (e.g., PIP), the initial rate of diffusion maybe increased resulting in the continuous formation of a cross-linked structure resulting in higher O₂ selectivity.

In the mPD2+TMC1 system, on the other hand, the higher molar concentration of mPD relative to TMC allows the diffusion of mPD through the aqueous/organic boundary much easier allowing for higher rate of polymerization making the interface region mostly occupied by (mPD)₃-TMC subcomplexes. Then, as TMC slowly diffuse into the region rich with (mPD)₃-TMC subcomplexes, the (mPD)₃-TMC subcomplex may be further connected by TMC monomer units forming a loosely cross-linked structure.

Effect of Number of Reacting Groups. To test the effect of the number of reacting groups on the O₂/N₂ selectivity and oxygen permeability, we studied the polymerization of organic phase monomer, TMC and CC, with aqueous phase monomer, Mela, DETA, PIP, and mPD, in more detail. The organic phase monomers, TMC, have three active acyl chlorides groups, which can readily react with the amines of aqueous phase monomers. Similar to TMC, the CC organic phase monomers also have three cyanogen chloride functional groups; however, at the operating temperature of 60 °C, only two of the cyanogen chloride functional groups can readily react with the aqueous phase monomers. Among the selected aqueous phase monomer, Mela and DETA have three reacting amines, whereas PIP and mPD have only two. As a result, the interfacial polymerization layers were conducted at 3 × 3, 3 × 2, 2 × 3, and 2 × 2 monomer pairs.

Figure 5 shows the O₂/N₂ permselectivity of membranes obtained at the aqueous to organic phase monomer molar ratio ranging between 1.9 and 2.7. We first investigated the membranes formed by monomers with only two active groups (2 × 2), which produce only linear polymers and no cross-linked networks.

We hypothesized that the oxygen selectivity is dependent upon the packing of the synthesized polymers. Figure 5 showed that membrane layers formed by mPD2+CC2 had a relatively high selectivity of 7.1. The membrane layers made from PIP1+CC1 pair, on the other hand, had relatively low O₂/N₂ permselectivities of 4. The polymer synthesized by mPD and CC had planar benzene and triazine rings connected by rigid amide bonds allowing the polymer to pack well, resulting in the

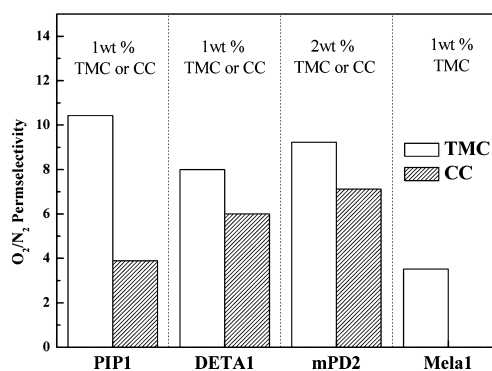


Figure 5. Oxygen/nitrogen permselectivity of interfacially polymerized polyamide membranes by the molar ratio of aqueous/organic monomer within 1.9–2.7.

low free volume in the separating layer. On the contrary, the layer made from PIP1+CC1 pair contained nonplanar monomers that cost the polymers to pack was loose against each other.

We further studied the membranes formed using the 3 × 3 monomer pairs, which we expect to produce highly cross-linked the selective layers that can effectively select for oxygen. The results shown in Figure 5, however, indicated that only the DETA1+TMC1 system resulted in a high O₂/N₂ permselectivity (greater than 8). The selecting layers formed using Mela1+TMC1 shown a low O₂/N₂ permselectivity of lower than 4. We were surprised by the result because both Mela and TMC were planar monomers and the synthesized polymer was relatively well packed. We believed the low O₂/N₂ permselectivity of Mela1+TMC1 selecting layer was due to small defects within the polymer structures formed from multiple linkages being formed on the same plane.

Interestingly, however, all the 2 × 3 and 3 × 2 pairs showed high O₂/N₂ permselectivity. The 2 × 3 pairs, PIP1+TMC1 and mPD2+TMC2, even had a higher permselectivity than that of the 3 × 2 pair, DETA1+CC1. Our data suggests that while the number of reacting groups and the number of reacting group pairs were not critical to interfacial polymerization, the cross-linking and polymer packing were essential factors affecting the process. Planar monomers were also demonstrated to be suitable choice for forming a well-packed polymer structure;

however, a 3×3 reaction pair with two planar monomers may result in uneven cross-linking during polymerization.

Effect of Nitrogen Content on O_2/N_2 Permselectivity.

High nitrogen contents in a polymeric gas separation membrane resulting in an increased polarity of the membrane and higher solubility of condensable gas which contributes to better oxygen selectivity. The N/C ratios of interfacially polymerized selecting layers were analyzed by XPS measurement, and the results were listed in Table 2. We observed that

Table 2. Nitrogen/Carbon Ratios of the Interfacially Polymerized Layers

	reaction time (min)	N/C	O_2/N_2 permselectivity
mPD2+TMC2	5	0.40	9.23
PIP1+TMC1	5	0.46	10.74
DETA1+TMC1	5	0.47	3.38
mPD2+CC2	1	0.52	7.10
PIP1+CC1	1	0.96	3.83
DETA1+CC1	1	1.00	4.31

the three TMC containing membranes, mPD2+TMC2, PIP1+TMC1, and DETA1+TMC2, had similar N/C ratio, but the O_2/N_2 permselectivity varied dramatically. From the three cyanuric chloride containing membrane samples, however, the O_2/N_2 permselectivity was found to decreased with increasing N/C ratio, suggesting the lack of a strong correlation between nitrogen content and oxygen selectivity.

Overall Performance. During our study, we discovered three aqueous/organic monomer combination that produce interfacial polymerized membranes with O_2/N_2 permselectivity higher than 8.0 (Figure 5). However, as we compared the nitrogen permeance of these three membranes, was found that the DETA1+TMC1 membrane had a low nitrogen permeance (Figure 2) which may be cast by the highly cross-linked structure from a 3×3 monomer pair. The fact that the mPD2+TMC2 membrane, 2×3 cross-linked, had a higher nitrogen permeance than the DETA1+TMC1 membrane, 3×3 cross-linked, even though the monomers in both phases were planar further support our hypothesis that the lower nitrogen permeance of the DETA1+TMC1 membrane was the result of the highly cross-linked structure. The PIP1+TMC1 membrane was identified to have the highest N_2 permeance among the three. As we compared the semirigid PIP1+TMC1 structure, due to the chair or boat conformation of PIP, to the mPD2+TMC2 selecting membrane, the semirigid structure of PIP1+TMC1 led to a higher N_2 permeance while maintained a high O_2/N_2 permselectivity. Figure 6 showed O_2/N_2 permselectivity plotted against the O_2 permeance of all the tested membranes, and the results from Peinemann and Aminabhavi were also included.^{26,27} If connecting the data from Peinemann and Aminabhavi as the pseudoupperbound, we found that the membrane PIP1+TMC1 had the best performance. The results indicated that the moderate 2×3 cross-linking and semirigid structure were necessary for a high performance O_2/N_2 separation membrane. If we measure the thickness of separating layer from SEM images, the PIP1+TMC1 selecting membrane had a thickness of 270 nm, indicating that the PIP1+TMC1 selecting membrane had a permeability coefficient of 2.08 Barrer at O_2/N_2 selectivity of 10.43. The performance of PIP1+TMC1 is higher than the Robeson's upper bound.

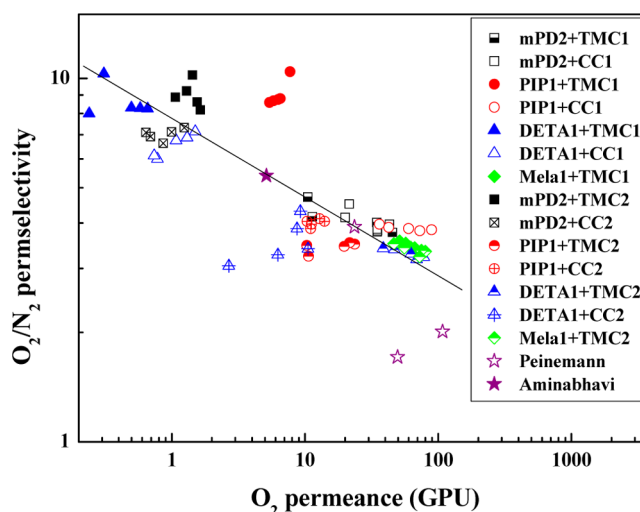


Figure 6. O_2/N_2 permselectivity versus O_2 permeance for all the synthesized membranes.

CONCLUSION

Two organic phase monomers: trimesoyl chloride and cyanuric chloride, and four aqueous phase monomers, diethylenetriamine, m-phenylenediamine, melamine, and piperazine, were used to synthesize the separating layers for oxygen enrichment. The effects of aqueous to organic phase monomer ratio, number of reacting groups in monomer, and nitrogen content on membrane performance were discussed. We have found that a monomer molar ratio from 1.9 to 2.7 was required for evenly interfacial polymerization at 60 °C, and the nitrogen content of membrane is irrelevant to membrane performance. We obtained the TFC membrane had an oxygen permeance of $7.72 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ s}^{-1} \text{ cm}^{-2} \text{ cmHg}^{-1}$ and a O_2/N_2 permselectivity of 10.43 using 1 wt % PIP and 1 wt %TMC on a polyacrylonitrile support. We found that the 2×3 or 3×2 reacting group pair and a semirigid cross-linked structure can be used to optimize the membrane performance. Consequently, overcoming the upper-bound limit could be approached by the thin-film composite membranes with interfacially polymerized polyamide layer, and the layer structure is crucial implication to gas separation performance.

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Notes

The authors declare no competing financial interest.

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