Impact of Tuning CO₂-Philicity in Polydimethylsiloxane-based Membranes for Carbon Dioxide Separation

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Abstract

Amidoxime-functionalized polydimethylsiloxane (AO-PDMSPNB) membranes with various amidoxime compositions were synthesized via ring-opening metathesis polymerization followed by post-polymerization modification. Compared to other previously reported PDMS-based membranes, the amidoxime-functionalized membranes show enhanced CO₂ permeability and CO₂/N₂ selectivity. The overall gas separation performance (CO₂ permeability 6800 Barrer; CO₂/N₂ selectivity 19) of the highest performing membranes exceeds the Robeson upper bound line, and the excellent permeability of the copolymer itself provides great potential for real world applications where huge volumes of gases are separated. This paper details how tuning the CO₂-philicity within rubbery polymer matrices influences gas transport properties. Key parameters for tuning gas transport properties are discussed, and the experimental results show good consistency with theoretical calculations. This study provides a roadmap to enhancing gas separation performance in rubbery polymers by tuning gas solubility selectivity.

Introduction

Excessive greenhouse gas emissions, such as carbon dioxide (CO₂), is one of the most significant environmental challenges we face today.[1-3] Although numerous technologies have been proposed as effective means to reduce these emissions, membrane-based separations have attracted significant attention due to their passive nature and reduced energy costs relative to other gas separation technologies.[4] Membrane performance is typically evaluated via two parameters: 1) gas permeability (P_A), which is determined by the product of the gas solubility (S_A) and diffusivity (D_A) ($P_A = S_A \times D_A$), and 2) selectivity (α_{AB}) which is defined as the ratio of the permeability of any two gases. Furthermore, selectivity may also be separated into solubility selectivity and diffusivity selectivity by the following equation: $\alpha_{AB} = \frac{P_A}{P_B} = \frac{S_A}{S_B} \times \frac{D_A}{D_B}$. These two parameters are traditionally evaluated using a log-log plot of selectivity versus permeability, which is often referred to as a "Robeson Plot." From this plot, the inherent trade-off relationship between permeability and selectivity of polymeric membranes can be observed in which polymers exhibiting higher permeability often show lower selectivity, and vice versa.[5-7] Moreover, membrane performance is compared to an empirically derived "upper bound", which is graphically represented by a straight line passing through data points corresponding to the best permeabilities and selectivities observed.

Unfortunately, the gas transport properties of most membranes fall significantly below this upper bound and do not meet the target performance for practical flue gas separations. Thus, the development of higher performing membranes for CO₂ separation is required for the successful implementation of this technology. Due to the extremely large volume of flue gas emissions, membranes with high CO₂ permeability and moderate selectivity offer more

significant cost reductions than membranes with high selectivity but moderate permeability. According to the cost analysis study of Merkel *et al.*, [8] separation costs do not decrease when CO₂/N₂ selectivities higher than ~30 are achieved, due to the limited pressure difference encountered in flue gas treatment. Because high permeability membranes require less area to treat an equal volume of gases, as compared to lower flux membranes, high flux membranes could reduce the carbon capture cost more effectively. Therefore, the development of high permeability membranes should be targeted and the optimum values of the permeability and selectivity need to be investigated.

In recent years, a large number of high-performing membranes with excellent permeability/permeance have been developed, some of which were shown to surpass the upper bound.[9] The majority of those membranes are mixed matrix membranes, while only a very small portion were purely polymeric membranes. Unlike purely polymeric membranes, mixed matrix membranes typically consist of a polymer matrix as the bulk phase and inorganic fillers, e.g. zeolite, carbon molecular sieves, or nano-size particles, as the dispersed phase.[9, 10] While the development of mixed matrix membranes could help overcome the permeability/selectivity trade-off, the advancement of purely polymeric membranes, which serve as a selective layer, is also crucial for fundamentally cultivating the material potential. Thus, in this work, we target purely polymeric membranes with high permeability and good selectivity.

Among highly permeable polymers, the majority of the studies have been performed on glassy membranes, such as polymers of intrinsic microporosity (PIMs), [11-13] thermally rearranged (TR) polymers, [14-16] etc., while less studies have been performed on highly permeable rubbery polymers. In rubbery polymers, polydimethylsiloxane (PDMS) exhibits excellent CO₂ permeability and offers the advantages of no aging issues, high thermal stability

and good ductile mechanical properties.[17-21] However, a major drawback of PDMS-based membranes are their relatively low CO₂/N₂ selectivity.[22, 23] If the gas selectivity of these PDMS-based membranes could be further improved, they will readily meet the required performance for practical deployment.

A common approach to improve gas selectivity, especially for glassy polymer membranes, is to enhance diffusivity selectivity by tuning the pore size, thereby increasing the membrane's size-sieving capability.[14, 16, 24, 25] However, this method is not sufficient for CO₂/N₂ separations due to the similar kinetic diameters of CO₂ and N₂ (CO₂~3.30 Å, N₂~ 3.64 Å). Another approach, to which less attention has been paid, is to enhance solubility selectivity.[26, 27] For instance, a number of studies on Pebax membranes, which exhibits high CO₂ solubility due to the strong affinity of the polar ether linkages in the structure, have demonstrated the potential of enhancing CO₂ solubility in order to improve the CO₂ separation performance.[28-32] Thus, our strategy focuses on the incorporation of CO₂-philic groups into the PDMS matrix, thereby tuning the CO₂/N₂ solubility selectivity. Among the various CO₂-philic groups that have been reported,[33-42] we chose to evaluate the incorporation of amidoximes (AO) within our cross-linked PDMS matrices for CO₂ separation.[38] Herein, we demonstrate that PDMS-based membranes bearing AO groups display enhanced CO₂ separation performance and exceed the Robeson upper bound. We also show that the observed enhancement in CO₂ separation performance correlates well with our calculated CO₂-AO complex binding energies.

Experimental section

Materials

(Bicycloheptenyl)ethyl terminated polydimethylsiloxanes (PDMSNB) with weight-average molecular weights ranging from 12,000-16,000 g/mol were purchased from Gelest Inc. Grubbs catalyst, 2nd generation (Grubbs-II), dicyclopentadiene, fumaronitrile, hydroxylamine solution (50 wt. % aqueous solution) and anhydrous dichloromethane (DCM) were purchased from Sigma-Aldrich. Nitrogen and carbon dioxide gases (99.99% purity) were obtained from Air Liquide. All chemicals were used as received. All ^1H and ^{13}C NMR spectra were collected using a Bruker ADVANCE III spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C . Chemical shifts are reported in ppm downfield from tetramethylsilane. CDCl_3 was used as the solvent for all NMR samples. Elemental analyses were performed by Galbraith Laboratories, Inc.

Synthesis of bicyclo[2.2.1]hept-5-ene-2,3-dicarbonitrile(dicyanonorbornene, diCyNb)

Dicyclopentadiene (7.2 g, 54.4 mmol) and fumaronitrile (9.3 g, 108.8 mmol, 2.2 equiv.) were added to a 300 mL round bottom flask with stir bar. The mixture was heated at 190 °C under an inert atmosphere. After 48 h, the product-diCyNb (5.30 g, 72% approx. yield) was isolated from the product mixture by distillation. ^1H NMR (400 MHz, CDCl_3): δ = 6.18 (m, 2H, $-\text{CH}=\text{CH}-$); 3.23-3.20 (m, 2H, $-\text{CH}-\text{CN}$); 3.07(t, 1H, $^3J_{23} = 7.9$, $=\text{CH}-\text{CH}<$); 2.38 (m, 1H, $=\text{CH}-\text{CH}<$); 1.44-1.54 (m, 2H, $>\text{CH}_2$). ^{13}C NMR (100 MHz, CDCl_3): δ =136.55 ($-\text{CH}=\text{CH}-$); 134.70 ($-\text{CH}=\text{CH}-$); 119.45 ($-\text{CH}-\text{CN}$); 119.07 ($-\text{CH}-\text{CN}$); 47.44 ($=\text{CH}-\text{CH}<$); 46.30($=\text{CH}-\text{CH}<$); 45.46($>\text{CH}_2$); 33.64 ($-\text{CH}-\text{CN}$); 33.41 ($-\text{CH}-\text{CN}$).

Precursor Membrane Synthesis and Post-modification

The precursor membranes were synthesized via the *in-situ* ring-opening metathesis polymerization (ROMP) of PDMSNB and dicyanonorbornene (diCyNb) (Scheme 1). In a typical process, PDMSNB (375 mg, 2.68×10^{-5} mol) and diCyNb (125 mg, 8.68×10^{-4} mol) were dissolved in DCM (6 mL). In a separate vial, Grubbs-II catalyst (10 mg, 1.18×10^{-5} mol) was dissolved in DCM (2 mL). Then 1 mL of the Grubbs-II catalyst stock solution was added to the monomer solution and shaken for 60 s before being poured into a 100 mL PTFE dish (with a diameter of 10 cm). The PTFE dish was covered with aluminum foil for 72 h in which the *in-situ* cross-linked membrane was formed. A mixture of ethyl vinyl ether (2 mL) in DCM (6 mL) was added to the film to terminate the metathesis reaction. The membrane was dried under argon atmosphere overnight and moved to a vacuum oven for 3 days to remove residual solvent. Finally, the cross-linked free-standing polymer membrane was detached from the PTFE dish and cut into pieces for further functionalization or testing.

The PDMSPNB-*co*-PdiCyNb membranes were synthesized with varying feed compositions of diCyNb ranging from 10 to 30 wt%. No uniform membranes with diCyNb feed contents higher than 30 wt% were successfully made due to the heterogeneity between two components in PDMSPNB-*co*-PdiCyNb. From elemental analysis results, the ratio of diCyNb:PDMSNB incorporated in the copolymer membrane was lower than the feed ratio. For example, at 25 wt% feed content only produced about 17 wt% composition.

The gas permeability of PDMSPNB-*co*-PdiCyNb membranes were tested and the CO₂/N₂ selectivity was calculated. Due to the optimum balance of CO₂ permeability and CO₂/N₂ selectivity obtained in the permeation data of PDMSPNB-*co*-PdiCyNb membranes, the precursor with 25 wt% feed of diCyNb was selected for use in further experiments.

Each batch of amidoxime-PDMSPNB membranes were functionalized from one specific PDMSPNB-*co*-PdiCyNb membrane, which was cut into small pieces and treated for amidoximation. In a typical amidoximation experiment, 0.1g of cross-linked PDMSPNB-*co*-PdiCyNb membrane was added to methanol (10 mL), followed by the addition of hydroxylamine solution (0.12g, 1.82 mmol, 3 equiv). The mixture was placed in a 56 °C oil bath. A control experiment using only methanol but without hydroxylamine was also performed and the results showed no CN group conversion and extended cross-link density (Figure S1 and Table S1). By varying the amidoximation time from 6 h to 48 h, membranes with varying degrees of amidoximation were obtained. The membranes were then washed with methanol and DI water several times and dried in a vacuum oven for another 3 days at room temperature. All membranes were homogeneous in nature. The thickness of the membranes ranged from 100-130 μm . The density of all the membranes were obtained from density-gradient column measurements (0.9780-0.9840 g/cm^3) and the estimated fractional free volume using Bondi's method[43] ranged from 0.190-0.195, which is comparable with previously reported data.[44] The resulting membranes were cut into approximately 2 cm $\times$ 2 cm squares for permeation measurement. The as-prepared membranes were labeled as "AO-amidoxime time (h)." For example, AO-12 is the membrane with 12 h amidoximation. The compositions of the membranes were determined by elemental analysis.

Scheme 1. ROMP reaction of the diCyNb-PDMSPNB membrane and post functionalization.

Membrane Characterizations

Fourier transform infrared spectroscopy (FTIR) of the polymer membranes was conducted in transmission mode using a Perkin-Elmer Frontier mid-infrared FT-IR instrument. A minimum of 16 scans were signal-averaged with a resolution of 4 cm^{-1} to obtain the final spectrum. An open air measurement was used for the background.

Differential scanning calorimetry (DSC) measurements were performed under argon atmosphere using a TA Instruments Q1000 with standard aluminum pans. Temperature-modulated DSC (TMDSC) measurements were performed using the following procedure: sample

was equilibrated at 100 °C, isothermal for 5 min to erase the thermal history, and then cooled to −160 °C at 3 °C/min with a modulation of ± 1 °C/min, and then heated to 100 °C. The glass transition temperature (T_g) value was taken as the midpoint of the transition step in the heating process of the reversible heat flow signals. Representative curves of AO-PDMSPNB membranes are presented in Figure 1, in which the inset shows the derivative curves of the heat flow change. The glass transition temperature (T_g) can be estimated from both the transition process in reversible heat flow curves and the peak position in the derivative curves. In all AO-PDMSPNB membranes, only one T_g for PDMS and crystallization at higher temperature (not shown) are observed. The data reveal no changes in T_g (T_g of all samples are -125°C) for AO-PDMSPNB membranes with different amounts of AO groups.

Figure 1. DSC curves for AO-PDMSPNB membranes illustrating the glass transition step. Inset is the derivative of reversible heat flow change. All curves have been shifted vertically to illustrate the systematic change of the peak shape and position.

Gas permeability measurements

The permeation measurements were performed at room temperature (25 ± 1 °C) with single gas tests using a custom test chamber following the constant-volume variable-pressure method under 38 kPa.[45, 46] Before loading, the membrane sample was mounted using a 47 mm non-porous aluminum tape disc with a hole (10 mm diameter) cut in the center and sealed with epoxy (Devcon). The mounted membrane sample was then placed on a highly porous stainless steel support, which was for mechanical stability and shows negligible resistance to gases, and the entire assembly was installed into the test chamber. The chamber was evacuated with a mechanical pump to a base pressure of 20 mTorr. The membrane was allowed to remain in the test chamber overnight to fully degas the solvent residue and reach a steady base pressure.

Calculation of binding energies

CO₂ affinities were estimated by calculated binding energies (BE) between CO₂ and polymer units. Structures of complexes and monomers were optimized at the RI-MP2/def2-TZVPP level with the Turbomole 6.5 software package.[47] We have shown that weak interactions between CO₂ and dipolar molecules can be reproduced accurately at this level.[48] Basis set superposition error (BSSE) was further corrected for reported BEs with counterpoise correction.

Results

Determination of membrane compositions

The compositions of the PDMSPNB-*co*-PdiCyNb and AO-PDMSPNB membranes were determined using a combination of FTIR spectroscopy and elemental analysis. The IR spectra of

AO-PDMSPNB series membranes are shown in Figure 2. It can be noticed that the band associated with the $\text{C}\equiv\text{N}$ group at 2250 cm^{-1} disappears with the conversion to AO groups. The broad bands in the region of $3000\text{--}3500\text{ cm}^{-1}$ represent the N-H and O-H stretching vibration while the band at 1660 cm^{-1} represents the $\text{C}=\text{N}$ stretch vibration.[49, 50] These peaks confirm the conversion from CN groups to AO groups. The band at 1260 cm^{-1} is related to the Si-CH_3 symmetric deformation[51, 52] in the PDMS matrix, which remains constant during the amidoximation.

The conversion percentage of the CN group is calculated from the change of the integrated area of the CN peak (2250 cm^{-1}) relative to the Si-CH_3 symmetric deformation peak (1260 cm^{-1}) and the representative results are shown in Figure 3 and Table 1. The conversion of the CN groups increases with increasing amidoximation time and reached a plateau after 24 h. Previous studies reported an amidoximation time around 20 h to reach the plateau[41, 42, 53], which is consistent with our results. The post-modification of the hydrophobic cross-linked membranes may limit diffusion and penetration of the hydroxylamine through the membrane matrix,[54] thus resulting in slightly less than 100% conversion. No further measurements of the 48 h sample were taken due to its similarity to the 24 h sample.

Figure 2. FTIR spectra of AO-PDMSPNB series membranes. Inset: change of CN peaks at 2250 cm^{-1} .

All spectra have been shifted vertically to illustrate the systematic changes of the peak.

Figure 3. Red circles represent the conversion of CN groups in AO-PDMSPNB series calculated from FTIR mode at 2250 cm^{-1} . Blue squares represent the increase of Nitrogen wt% calculated from elemental analysis.

Table 1. Summary elemental analysis and FTIR calculation results.

Sample code	Carbon wt%	Nitrogen wt%	Nitrogen/Carbon ratio %	Nitrogen wt% increase	CN group conversion %
AO-0	42.01 ± 0.07	3.27 ± 0.10	7.79 ± 0.23	0	0
AO-6	39.49 ± 0.65	3.42 ± 0.10	8.65 ± 0.10	11.2 ± 2.0	15.8 ± 1.0
AO-12	39.48 ± 0.61	3.96 ± 0.13	10.16 ± 0.31	30.5 ± 0.2	38.9 ± 2.8
AO-24	38.67 ± 0.04	4.10 ± 0.02	10.60 ± 0.04	36.3 ± 3.5	82.6 ± 5.4
AO-48	38.40	4.03	10.50	38.9	86.7

Gas transport properties of AO-PDMSPNB membranes

To study the effects of amidoximation on gas separation performance, each membrane was tested using the constant-volume variable-pressure gas flux method. All the membranes show much higher CO_2 permeability than that of N_2 . The results of the single-gas permeability and CO_2/N_2 selectivity values are summarized in Table 2 and Figure 4. As seen in Figure 4a and 4b, for AO-PDMSPNB membranes, the CO_2 and N_2 permeabilities show a monotonic decrease with increasing AO conversion. The CO_2/N_2 selectivity increases as a function of AO content, but reaches a maximum at ~39% conversion, and further increase in AO conversion results in decreased selectivity (Figure 4c). When these values are plotted on a 2008 Robeson plot (Figure 5), it can be seen that AO-PDMSPNB membranes achieve much better CO_2/N_2 separation

performance than most of the other polymer membranes. Furthermore, although the performance of our membranes was measured at 25 °C which is slightly different from 35 °C, the highest performing membrane, AO-12 has exceeded the Robeson upper bound, showing great enhancement as compared with the majority of the membranes.

Figure 4. a) CO₂ permeability, b) N₂ permeability, and c) CO₂/N₂ selectivity versus degree of CN group conversion (%) for the AO-PDMSPNB membranes.

Table 2. Summary of gas permeability and CO₂/N₂ selectivity for prepared samples.

Sample code	CN conversion	CO ₂ Permeability (Barrer)	N ₂ Permeability (Barrer)	CO ₂ /N ₂ Selectivity
AO-0	0	10500 ±2400	1540 ±110	6.8 ±1.2
AO-6	15.8 ±1.0	7600 ±1200	670 ±210	11.3 ±2.1
AO-12	38.9 ±2.8	6800 ±1200	360 ±90	18.8 ±2.2
AO-24	82.6 ±5.4	4800 ±1300	320 ±80	15.0 ±0.2
PDMSPNB[23]	-	6734	489	13.8

Figure 5. Summary of the AO series membranes (measured at 25 °C) as a function of amidoximation time in 2008 Robeson plot. The conventional PDMS[22], PDMSPNB[23] and AO-PIM-1[41] data are from references. The averaged permeability values are used and the error bar is not included.

Figure 6. Summary of the calculated structure and binding energy (BE) for CO_2 -CN and CO_2 -AO complexes.

BE calculations (Figure 6) show that the conversion of CN groups to AO groups (Figure 6a to Figure 6b, 6c) leads to an approximately 45% increase in the BE, which should lead to an increase in CO_2 solubility. Interestingly, the cyclo-AO structure (Figure 6d), which typically forms during the amidoximation reaction[55-57], shows weaker BE than AO groups (Figure 6b, 6c). Thus, the conversion from the AO structure to the cyclo-AO structure is expected to result in a slight decrease in CO_2 solubility due to the decrease of the BE from about -20 kJ/mol to -17 kJ/mol .

Discussion

Membrane characterization

As illustrated in Scheme 1, the CN group can be converted into three different AO structures within the polymer matrix. Thus, it is of high importance to determine the actual compositions of each structure. When one CN group is converted to an AO group, one extra nitrogen atom is gained, which should result in a 100% increase in nitrogen wt% for the film. However, the

elemental analysis results show a lower value than what was expected for 100% weight increase, which is attributed to the subsequent conversion of some di-AO groups to the cyclo-AO analogue.[50, 55, 56] The formation of a cyclo-AO group from two AO groups results in the loss of one equivalent nitrogen atom. In other words, if two CN groups are converted to one cyclo-AO group, only 50% extra nitrogen amount is gained. Therefore, by monitoring the nitrogen increase via elemental analysis (Table 1), the amount of the cyclo-AO structure present in the matrix can be estimated (Table S2). The full conversion of CN groups to cyclo-AO groups in AO-24 membranes should result in about 41% increase of nitrogen wt%, while the data showed a slightly lower value. Considering the experimental and fit errors, the value is within the range of uncertainty, and the majority of CN groups in AO-24 membranes should be converted to cyclo-AO groups.

As shown in Figure 1, the T_g values obtained from DSC do not show any changes, and are consistent with our previously reported XLPDMSPNB membranes[23]. Although the conversion from CN groups to AO groups introduces sterically bulky functional groups as well as H-bonding, the overall influence on the averaged segmental dynamics in the PDMS matrix is negligible, which we attribute to PDMS being the major component within the polymer matrix. Thus, the observed changes in gas permeability are not related to changes in polymer segmental dynamics.

Impact of amidoximation on gas permeability

Generally, with higher diCyNb content in the precursor, gas permeability increases, while the CO₂/N₂ selectivity showed a decreasing trend. The gas transport property data of membranes with 10, 25, and 30% diCyNb is summarized in Table S3. Due to the optimum balance of CO₂ permeability and CO₂/N₂ selectivity obtained in the permeation data of PDMSPNB-*co*-PdiCyNb

membranes, AO-25 was selected for use in further experiments. It is reported that with the formation of AO groups, the intermolecular hydrogen bonding can be stacked up between the structures.[38, 58] The H-bond rich structure can result in significant reduction of the gas diffusivity,[27, 59] which explains the monotonic decrease in gas permeability with the conversion from CN to AO groups (Figure 4a, 4b). Several reported studies on CO₂ separation and capture have achieved enhanced selectivity of CO₂ over other gas pairs with the addition of AO groups.[38-42] In this study, the increase of CO₂/N₂ selectivity from AO-0 to AO-12 (Figure 4c) agrees well with the enhanced performance by the addition of CO₂-philic AO groups. However, the observed maximum in CO₂/N₂ selectivity was not expected and requires a separate explanation.

The BE calculations of these complexes (Figure 6) can elucidate the different performance in gas transport properties of AO-PDMS membranes. The increase in BE upon the conversion of the CN groups to AO groups is likely the source of the observed increase in CO₂/N₂ selectivity (Figure 6a-c). When CN conversion is less than 39% (AO-12), the enhanced CO₂ solubility partly compensates the loss of gas diffusivity caused by H-bonding. This is the major reasons why the CO₂ permeability decreases less than that of N₂, although they have a similar kinetic size. When the CN conversion is higher than 39%, the cyclo-AO structures become dominant in the polymer matrix (Figure 6c to Figure 6d), which results in decreasing BE to -17 KJ/mol (~15%) and corresponding decrease in CO₂/N₂ selectivity from AO-12 to AO-24. Therefore, a decrease in CO₂-philicity with cyclization of AO groups is most likely a major reason for the decrease of selectivity at higher CN conversion. Thus, the CN conversion to various AOs structures should be carefully tuned in order to explore the optimum range.

Importance of tuning gas solubility

Our results clearly demonstrate that tuning the CO₂-philicity of PDMS-based membranes indeed improves CO₂/N₂ selectivity without sacrificing permeability. It is of great fundamental interest to understand the optimum range of CO₂ BE, in which a balance of increased selectivity with the decrease in diffusivity should be met. More specifically, if the BE is too low, the membrane could not offer high enough gas solubility, while if the BE is too high, the strong CO₂ affinity may cause capture of the CO₂ molecule within the membranes and a strong reduction in its diffusivity and overall efficiency of the CO₂ separation. It is of great importance to study the correlation between BE and CO₂ separation performance, while simultaneously investigating other factors such as polymer dynamics and H-bonding, in order to develop a roadmap to design and synthesize high performance CO₂ separation membranes in the future.

Conclusions

We have successfully incorporated CO₂-philic amidoxime groups into the PDMS matrix by using an *in-situ* ROMP technique, followed by a post-polymerization modification. The degree of amidoximation was found to significantly alter gas separation performance, which has been attributed to CO₂ binding affinity and H-bonding within the AO functionalities. Furthermore, these results demonstrate that by careful tuning of the CO₂-philicity of these PDMS-based rubbery membranes, it is possible to significantly increase CO₂/N₂ selectivity with a minimum loss in permeability. The highest performing membrane (AO-12) shows significantly enhanced performance relative to previously reported PDMS-based membranes. These significant gains allowed AO-12 to exceed the Robeson upper bound at very high permeability (6800 Barrer), which is critical for practical applications in treating the enormous amount of flue

gases generated by power plants. This systematic report provides strong evidence detailing how AO content influences gas transport properties in rubbery membranes. Furthermore, the versatility of the ROMP technique will allow us to incorporate various CO₂-philic groups into the PDMS matrix, providing tunable gas separation performance for future development. These findings provide a path to future CO₂ separation material development, as well as fostering fundamental understanding of the gas separation process using polymer membranes.

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References

[1] R.K. Pachauri, M. Allen, V. Barros, J. Broome, W. Cramer, R. Christ, J. Church, L. Clarke, Q. Dahe, P. Dasgupta, Climate Change 2014: Synthesis Report. Contribution of Working Groups

I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, 2014.

[2] B. Metz, O. Davidson, H. De Coninck, M. Loos, L. Meyer, IPCC, Cambridge University Press, Cambridge, 2005, p. 4.

[3] I. Capellán-Pérez, I. Arto, J.M. Polanco-Martínez, M. González-Eguino, M.B. Neumann, Likelihood of climate change pathways under uncertainty on fossil fuel resource availability, *Energy & Environmental Science*, 9 (2016) 2482-2496.

[4] Materials for Separation Technologies—Emissions and Energy Reduction Opportunities, 2005, United States Department of Energy, http://www1.eere.energy.gov/manufacturing/industries_technologies/imf/pdfs/separationsreport.pdf.

[5] L.M. Robeson, Correlation of Separation Factor Versus Permeability for Polymeric Membranes, *Journal of Membrane Science*, 62 (1991) 165-185.

[6] L.M. Robeson, The upper bound revisited, *Journal of Membrane Science*, 320 (2008) 390-400.

[7] B.D. Freeman, Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes, *Macromolecules*, 32 (1999) 375-380.

[8] T.C. Merkel, H. Lin, X. Wei, R. Baker, Power plant post-combustion carbon dioxide capture: an opportunity for membranes, *Journal of membrane science*, 359 (2010) 126-139.

[9] S. Wang, X. Li, H. Wu, Z. Tian, Q. Xin, G. He, D. Peng, S. Chen, Y. Yin, Z. Jiang, Advances in high permeability polymer-based membrane materials for CO₂ separations, *Energy & Environmental Science*, 9 (2016) 1863-1890.

[10] Y. Li, G. He, S. Wang, S. Yu, F. Pan, H. Wu, Z. Jiang, Recent advances in the fabrication of advanced composite membranes, *Journal of Materials Chemistry A*, 1 (2013) 10058-10077.

[11] P.M. Budd, K.J. Msayib, C.E. Tattershall, B.S. Ghanem, K.J. Reynolds, N.B. McKeown, D. Fritsch, Gas separation membranes from polymers of intrinsic microporosity, *Journal of Membrane Science*, 251 (2005) 263-269.

[12] B.S. Ghanem, N.B. McKeown, P.M. Budd, N.M. Al-Harbi, D. Fritsch, K. Heinrich, L. Starannikova, A. Tokarev, Y. Yampolskii, Synthesis, characterization, and gas permeation properties of a novel group of polymers with intrinsic microporosity: PIM-polyimides, *Macromolecules*, 42 (2009) 7881-7888.

- [13] N.B. McKeown, P.M. Budd, Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogen storage, *Chemical Society Reviews*, 35 (2006) 675-683.
- [14] H.B. Park, S.H. Han, C.H. Jung, Y.M. Lee, A.J. Hill, Thermally rearranged (TR) polymer membranes for CO₂ separation, *Journal of Membrane Science*, 359 (2010) 11-24.
- [15] J.I. Choi, C.H. Jung, S.H. Han, H.B. Park, Y.M. Lee, Thermally rearranged (TR) poly (benzoxazole-co-pyrrolone) membranes tuned for high gas permeability and selectivity, *Journal of Membrane Science*, 349 (2010) 358-368.
- [16] S.H. Han, J.E. Lee, K.-J. Lee, H.B. Park, Y.M. Lee, Highly gas permeable and microporous polybenzimidazole membrane by thermal rearrangement, *Journal of Membrane Science*, 357 (2010) 143-151.
- [17] M. McCaig, D. Paul, Effect of film thickness on the changes in gas permeability of a glassy polyarylate due to physical aging Part I. Experimental observations, *Polymer*, 41 (2000) 629-637.
- [18] J.W. Gilman, Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites, *Applied Clay Science*, 15 (1999) 31-49.
- [19] G. Camino, S. Lomakin, M. Lazzari, Polydimethylsiloxane thermal degradation Part 1. Kinetic aspects, *Polymer*, 42 (2001) 2395-2402.
- [20] K. Keshoju, L. Sun, Mechanical characterization of magnetic nanowire–polydimethylsiloxane composites, *Journal of Applied Physics*, 105 (2009) 023515.
- [21] P. Djemia, Y. Roussigné, G.F. Dirras, K.M. Jackson, Elastic properties of β -SiC films by Brillouin light scattering, *Journal of applied physics*, 95 (2004) 2324-2330.
- [22] T. Merkel, V. Bondar, K. Nagai, B. Freeman, I. Pinnau, Gas sorption, diffusion, and permeation in poly (dimethylsiloxane), *Journal of Polymer Science Part B: Polymer Physics*, 38 (2000) 415-434.
- [23] T. Hong, Z. Niu, X. Hu, K. Gmernicki, S. Cheng, F. Fan, J.C. Johnson, E. Hong, S. Mahurin, D.e. Jiang, Effect of Cross - Link Density on Carbon Dioxide Separation in Polydimethylsiloxane - Norbornene Membranes, *ChemSusChem*, 8 (2015) 3595-3604.
- [24] H.B. Park, C.H. Jung, Y.M. Lee, A.J. Hill, S.J. Pas, S.T. Mudie, E. Van Wagner, B.D. Freeman, D.J. Cookson, Polymers with cavities tuned for fast selective transport of small molecules and ions, *Science*, 318 (2007) 254-258.

- [25] M. Calle, Y.M. Lee, Thermally rearranged (TR) poly (ether– benzoxazole) membranes for gas separation, *Macromolecules*, 44 (2011) 1156-1165.
- [26] B. Freeman, I. Pinnau, Separation of gases using solubility-selective polymers, *Trends in polymer science*, 5 (1997) 167-173.
- [27] H. Lin, B.D. Freeman, Materials selection guidelines for membranes that remove CO₂ from gas mixtures, *Journal of Molecular Structure*, 739 (2005) 57-74.
- [28] A. Car, C. Stropnik, W. Yave, K.-V. Peinemann, PEG modified poly (amide-b-ethylene oxide) membranes for CO₂ separation, *Journal of Membrane Science*, 307 (2008) 88-95.
- [29] Y. Li, T.-S. Chung, Molecular-level mixed matrix membranes comprising Pebax® and POSS for hydrogen purification via preferential CO₂ removal, *international journal of hydrogen energy*, 35 (2010) 10560-10568.
- [30] A. Car, C. Stropnik, W. Yave, K.-V. Peinemann, Pebax®/polyethylene glycol blend thin film composite membranes for CO₂ separation: performance with mixed gases, *Separation and Purification Technology*, 62 (2008) 110-117.
- [31] R.S. Murali, S. Sridhar, T. Sankarshana, Y. Ravikumar, Gas permeation behavior of Pebax-1657 nanocomposite membrane incorporated with multiwalled carbon nanotubes, *Industrial & Engineering Chemistry Research*, 49 (2010) 6530-6538.
- [32] B. Yu, H. Cong, Z. Li, J. Tang, X.S. Zhao, Pebax - 1657 nanocomposite membranes incorporated with nanoparticles/colloids/carbon nanotubes for CO₂/N₂ and CO₂/H₂ separation, *Journal of Applied Polymer Science*, 130 (2013) 2867-2876.
- [33] M.L. Jue, R.P. Lively, Targeted gas separations through polymer membrane functionalization, *Reactive and Functional Polymers*, 86 (2015) 88-110.
- [34] C.R. Mason, L. Maynard-Atem, K.W. Heard, B. Satilmis, P.M. Budd, K. Friess, M. Lanč, P. Bernardo, G. Clarizia, J.C. Jansen, Enhancement of CO₂ affinity in a polymer of intrinsic microporosity by amine modification, *Macromolecules*, 47 (2014) 1021-1029.
- [35] N. Du, G.P. Robertson, J. Song, I. Pinnau, M.D. Guiver, High-performance carboxylated polymers of intrinsic microporosity (PIMs) with tunable gas transport properties†, *Macromolecules*, 42 (2009) 6038-6043.
- [36] N. Du, H.B. Park, G.P. Robertson, M.M. Dal-Cin, T. Visser, L. Scoles, M.D. Guiver, Polymer nanosieve membranes for CO₂-capture applications, *Nature materials*, 10 (2011) 372-375.

- [37] N. Du, G.P. Robertson, M.M. Dal-Cin, L. Scoles, M.D. Guiver, Polymers of intrinsic microporosity (PIMs) substituted with methyl tetrazole, *Polymer*, 53 (2012) 4367-4372.
- [38] S. Zulfiqar, F. Karadas, J. Park, E. Deniz, G.D. Stucky, Y. Jung, M. Atilhan, C.T. Yavuz, Amidoximes: promising candidates for CO₂ capture, *Energy & Environmental Science*, 4 (2011) 4528-4531.
- [39] S. Zulfiqar, S. Awan, F. Karadas, M. Atilhan, C.T. Yavuz, M.I. Sarwar, Amidoxime porous polymers for CO₂ capture, *RSC Advances*, 3 (2013) 17203-17213.
- [40] S.M. Mahurin, J. Gorka, K.M. Nelson, R.T. Mayes, S. Dai, Enhanced CO₂/N₂ selectivity in amidoxime-modified porous carbon, *Carbon*, 67 (2014) 457-464.
- [41] R. Swaidan, B.S. Ghanem, E. Litwiller, I. Pinnau, Pure-and mixed-gas CO₂/CH₄ separation properties of PIM-1 and an amidoxime-functionalized PIM-1, *Journal of Membrane Science*, 457 (2014) 95-102.
- [42] H.A. Patel, C.T. Yavuz, Noninvasive functionalization of polymers of intrinsic microporosity for enhanced CO₂ capture, *Chemical Communications*, 48 (2012) 9989-9991.
- [43] A. Bondi, van der Waals volumes and radii, *The Journal of physical chemistry*, 68 (1964) 441-451.
- [44] U. Senthilkumar, B. Reddy, Polysiloxanes with pendent bulky groups having amino-hydroxy functionality: structure–permeability correlation, *Journal of membrane science*, 292 (2007) 72-79.
- [45] H. Czichos, T. Saito, L.E. Smith, *Springer handbook of metrology and testing*, Springer Science & Business Media, 2011.
- [46] S.M. Mahurin, J.S. Lee, G.A. Baker, H.M. Luo, S. Dai, Performance of nitrile-containing anions in task-specific ionic liquids for improved CO₂/N₂ separation, *Journal of Membrane Science*, 353 (2010) 177-183.
- [47] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Electronic structure calculations on workstation computers: The program system turbomole, *Chemical Physics Letters*, 162 (1989) 165-169.
- [48] Z. Tian, T. Saito, D.-e. Jiang, Ab Initio Screening of CO₂-philic Groups, *The Journal of Physical Chemistry A*, 119 (2015) 3848-3852.

- [49] H. Nizam El - Din, S. Badawy, A. Dessouki, Chelating polymer granules prepared by radiation - induced homopolymerization. I—Kinetic study of radiation polymerization process, *Journal of Applied Polymer Science*, 77 (2000) 1405-1412.
- [50] S. Brown, Y. Yue, L.-J. Kuo, N. Mehio, M. Li, G. Gill, C. Tsouris, R.T. Mayes, T. Saito, S. Dai, Uranium Adsorbent Fibers Prepared by Atom-Transfer Radical Polymerization (ATRP) from Poly (vinyl chloride)-co-chlorinated Poly (vinyl chloride)(PVC-co-CPVC) Fiber, *Industrial & Engineering Chemistry Research*, 55 (2016) 4139-4148.
- [51] X. Zhang, H. Ye, B. Xiao, L. Yan, H. Lv, B. Jiang, Sol– gel preparation of PDMS/Silica hybrid antireflective coatings with controlled thickness and durable antireflective performance, *The Journal of Physical Chemistry C*, 114 (2010) 19979-19983.
- [52] D. Bodas, C. Khan-Malek, Formation of more stable hydrophilic surfaces of PDMS by plasma and chemical treatments, *Microelectronic engineering*, 83 (2006) 1277-1279.
- [53] N. Şahiner, N. Pekel, O. Güven, Radiation synthesis, characterization and amidoximation of N-vinyl-2-pyrrolidone/acrylonitrile interpenetrating polymer networks, *Reactive and Functional Polymers*, 39 (1999) 139-146.
- [54] T. Kawai, K. Saito, K. Sugita, T. Kawakami, J.-i. Kanno, A. Katakai, N. Seko, T. Sugo, Preparation of hydrophilic amidoxime fibers by cograftering acrylonitrile and methacrylic acid from an optimized monomer composition, *Radiation Physics and Chemistry*, 59 (2000) 405-411.
- [55] S.O. Kang, S. Vukovic, R. Custelcean, B.P. Hay, Cyclic imide dioximes: Formation and hydrolytic stability, *Industrial & Engineering Chemistry Research*, 51 (2012) 6619-6624.
- [56] N. Seko, A. Katakai, M. Tamada, T. Sugo, F. Yoshii, Fine fibrous amidoxime adsorbent synthesized by grafting and uranium adsorption–elution cyclic test with seawater, *Separation science and technology*, 39 (2004) 3753-3767.
- [57] S. Brown, Y. Yue, L.-J. Kuo, N. Mehio, M. Li, G.A. Gill, C. Tsouris, R.T. Mayes, T. Saito, S. Dai, Uranium adsorbent fibers prepared by ATRP from PVC-co-CPVC fiber, *Industrial & Engineering Chemistry Research*, (2016).
- [58] E.A. Bruton, L. Brammer, F.C. Pigge, C.B. Aakeröy, D.S. Leinen, Hydrogen bond patterns in aromatic and aliphatic dioximes, *New journal of chemistry*, 27 (2003) 1084-1094.
- [59] W. Lee, Selection of barrier materials from molecular structure, *Polymer Engineering & Science*, 20 (1980) 65-69.