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Impact of tuning CO_2-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 CO_2 permeability and CO_2/N_2 selectivity. The overall gas separation performance (CO_2 permeability 6800 Barrer; CO_2/N_2 selectivity 19) of the highest performing membrane 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 CO_2-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.

1. Introduction

Excessive greenhouse gas emissions, such as carbon dioxide (CO_2), 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 CO_2 separation is required for the successful implementation of this technology. Due to the extremely large volume of flue gas emissions, membranes with high CO_2 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 CO_2/N_2 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,

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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 fewer studies have been performed on highly permeable rubbery polymers. In rubbery polymers, polydimethylsiloxane (PDMS) exhibits excellent CO_2 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 CO_2/N_2 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 CO_2/N_2 separations due to the similar kinetic diameters of CO_2 and N_2 (CO_2~3.30 Å, N_2~ 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 CO_2 solubility due to the strong affinity of the polar ether linkages in the structure, have demonstrated the potential of enhancing CO_2 solubility in order to improve the CO_2 separation performance [28–32]. Thus, our strategy focuses on the incorporation of CO_2-philic groups into the PDMS matrix, thereby tuning the CO_2/N_2 solubility selectivity. Among the various CO_2-philic groups that have been reported [33–42], we chose to evaluate the incorporation of amidoximes (AO) within our cross-linked PDMS matrices for CO_2 separation [38]. Herein, we demonstrate that PDMS-based membranes bearing AO groups display enhanced CO_2 separation performance and exceed the Robeson upper bound. We also show that the observed enhancement in CO_2 separation performance correlates well with our calculated CO_2-AO complex binding energies.

2. Experimental section

2.1. Materials

(Bicycloheptenyl)ethyl terminated polydimethylsiloxanes (PDMSNB) with 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.

2.2. 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 MH_Z, $CDCl_3$): δ=6.18 (m, 2 H, -C$\underline{H=CH}$-); 3.23-3.20 (m, 2 H, -C$\underline{H}$-CN); 3.07(t, 1 H, $^3J_{23}$ =7.9, =CH-C$\underline{H}$ <); 2.38 (m, 1 H, =CH-C$\underline{H}$ <); 1.44–1.54 (m, 2 H, > C$\underline{H}_2$). ^{13}C NMR (100 MH_Z, $CDCl_3$): δ=136.55 (-$\underline{C}$H=CH-); 134.70 (-CH=CH-); 119.45 (-CH-$\underline{C}$N); 119.07 (-CH-$\underline{C}$N); 47.44 (=CH-$\underline{C}$H <); 46.30(=CH-$\underline{C}$H <); 45.46(> $\underline{C}H_2$); 33.64 (-$\underline{C}$H-CN); 33.41 (-$\underline{C}$H-CN).

2.3. 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% diCyNb feed content only produced about 17 wt% composition.

The gas permeability of PDMSPNB-*co*-PdiCyNb membranes were tested and the CO_2/N_2 selectivity was calculated. Due to the optimum balance of CO_2 permeability and CO_2/N_2 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, 0.1 g of cross-linked PDMSPNB-*co*-PdiCyNb membrane was added to methanol (10 mL), followed by the addition of hydroxylamine solution (0.12 g, 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 no extended cross-link density (Fig. 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 to 130 µm. The