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Estimating gas permeability and permselectivity of microporous polymers

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ABSTRACT

Experimental and computational investigations have shown that seemingly minor changes in the chemical structure can have a profound effect on the gas adsorption and separation properties of a polymeric membrane. However, the vast number of possible polymer functionalities makes the evaluation of candidate structures a daunting challenge. This study presents the first systematic screening for multiple series of amorphous porous polymers and elucidates several design principles, which will be useful in the design of new intrinsically microporous polymeric membranes for gas separation applications. Specifically, an efficient method for estimating the gas permeability and permselectivity of a polymeric sample by means of free volume theory, grand canonical Monte Carlo simulations, and the solution diffusion model is presented. This method for calculating permeability is orders of magnitude faster than other techniques involving molecular dynamics simulations and is shown to accurately calculate permeability and permselectivity values when compared to available experimental values. As an example, the method is applied to screen four series of polymers of intrinsic microporosity (PIMs) for CO₂, CH₄, and N₂ permeability and CO₂/CH₄, and CO₂/N₂ permselectivity. Outstandingly, the gas separation performance of these PIMs was shown not to move parallel to the upper bound for each gas pair. Several porous polymers with high permeabilities and high solubilities were identified, which highlights the fact that permeable polymers with high solubilities coefficients are feasible and a promising route toward achieving industrially applicable gas separation materials.

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1. Introduction

Using polymeric membrane materials to selectively separate the constituents of a gaseous mixture has attracted much attention due to the potential energy savings and growing industrial demand [1–3]. For example, these materials could be instrumental in removing CO₂, either from the exhaust of flue gas in post-combustion carbon capture or from rich sources of natural gas. According to the International Panel on Climate Change, CO₂ emissions must be controlled to achieve atmospheric stabilization, where flue gas (70% N₂ and 15% CO₂) from fossil-fuel based power generation plants accounts for up to 40% of greenhouse gas emissions [4]. Alternatively, CH₄-based energy sources are a promising route to satisfy the tremendous energy demands, which may be obtained from natural gas (80–95% CH₄ and 5–10% CO₂) or industrial landfill gas (40–60% CO₂), where CO₂ must be removed to meet US pipeline specifications (less than 2 vol%), as CO₂ is corrosive and lowers the overall natural gas energy density [5,6].

Thus, developing advanced polymeric membrane materials which are tailored toward effective CO₂/CH₄ and CO₂/N₂ gas separation technologies is vital for industrial efficiency.

The permeability coefficient of a polymer–gas combination is routinely measured as the essential characteristic in determining the quality of any polymeric gas separation membrane. During permeation, the gas is first adsorbed onto the surface at a specific pressure followed by diffusion through the polymer as a result of the trans-membrane partial pressure difference. The permeation of a gas (e.g., CO₂) in glassy polymers has been well described using the solution-diffusion model,

$$P_{\text{CO}_2} = D_{\text{CO}_2} \times S_{\text{CO}_2} \quad (1)$$

which equates the permeability coefficient (P) to the product of the polymer–gas solubility (S) and diffusivity coefficients (D). For improved gas separation performance, polymeric membranes need to be designed with ultra-high permeabilities [7]. Unfortunately, as the polymer permeability increases, a decrease in gas selectivity is traditionally observed [8,9], where ideal gas selectivity is the ratio of the gas permeability coefficients (i.e., P_i/P_j). Thus, selectivity and permeability are often competing factors, and it is fundamentally important to discover conditions at which the

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improvement of one factor is not compromised by a decline in the other to develop new polymeric materials with improved gas separation performance.

There are several classes of polymeric materials which exhibit large gas permeabilities such as polyacetylenes [10,11], polyimides [12], thermally rearranged polymers [13], and polymers of intrinsic microporosity [14,15]. Recently, specifically polymers of intrinsic microporosity (PIMs) have shown great promise for the future of gas separation technologies as several PIMs are performing above the Robeson Upper Bound (UB) for certain gas pairs [16–18]. PIMs are a class of glassy polymers that create free volume as a result of the inefficient packing of adjacent polymer chains, yielding a significant amount of porosity below 2 nm (i.e., microporosity). This inefficient packing is a result of two key structural components of the polymer chemical structure: (1) a series of conjugated aromatic rings, the *backbone* and (2) a shape-persistent site of contortion, the *spirocenter*. For the purpose of this work, PIM-like materials are defined as porous ladder polymers which contain rigid spirocenters separated by backbone units. These two key structural guidelines can be incorporated into more highly-functionalized polymeric structures, and thus superior permeability performance can be obtained.

There are limitless combinations of potential polymeric membrane structures when considering the next functionalized gas adsorption material. As a result, computational methods are an attractive alternative for the screening of large arrays of frameworks, which have aided the ordered microporous gas adsorption community [19–21]. However, characterizing amorphous microporous gas adsorption materials is challenging, both experimentally and computationally, because the lack of a defined molecular structure [22]. While useful insights into adsorption phenomena of amorphous materials can be gained by continuum-based models [23], we aim to develop structure–property relationships through an explicit modeling of the polymer's microporosity, and as such, atomistic molecular simulations are required. However, there are two significant hurdles to the efficient computational screening for gas separation of microporous polymers: (1) predictively generating a physically accurate model of the amorphous structure without experimental data and (2) efficiently calculating permeability coefficients. The difficulties associated with generating an accurate atomistic model of a porous ladder polymer have been addressed by the development of a simulated polymerization algorithm, termed *Polymatic* [24], which is effective for virtually synthesizing sterically hindered polymers with complex bonding structures. On the other hand, calculating permeability coefficients from these atomistic models presents a unique challenge as a result of orders of magnitude difference between the timescales of experimental permeability and the timescales accessible to atomistic simulations. Thus, brute-force molecular dynamics simulations have difficulties in calculating permeability and diffusivity coefficients. This is overcome in this work by calculating the gas diffusivity using free volume theory with empirical models of experimental data, and the solubility using Monte Carlo molecular simulations, from which the permeability is calculated according to the solution-diffusion model (Eq. (1)). As a result, this work presents the first study of efficiently screening multiple series of porous polymers for gas permeability and permselectivity. Through this work we are able to conclude several important design principles to improve the gas separation performance of amorphous, linear, porous polymers, and highlight potential avenues of future experimental efforts.

The study is presented as follows: after a description of the hypothetical high-free volume polymers is presented, the predictive virtual synthesis and the method of estimating gas permeability coefficients are discussed. Then, presented are the results of estimating gas permeability coefficients for screening CO₂/CH₄ and

CO₂/N₂ gas separation performance of both PIM-1 and hypothetical structures. Finally, several design principles on the effects of the chemical structure on free volume and permselectivity are described. The limitations of the presented method for estimating gas permeability and permselectivity are covered in supplemental information. In short, through the systematic analysis performed here, the structure–property relationships between monomeric structure and gas separation performance are elucidated, from which new porous polymer structures may be designed which capitalize on these principles.

2. Hypothetical polymers

Herein, we analyze four different series of PIMs, each of which systematically alters one characteristic of the PIM structure: *spirocenter size*, *backbone functionality*, *sulfur-containing PIMs* and *backbone length*. The chemical structures of all PIMs analyzed in this study are shown in Fig. 1. The steric hindrance at the site of contortion has been shown to have an effect on how close adjacent polymers may be able to arrange [25], and thus a systematic analysis of the spirocenter size was performed, which varied the group from small hydrogen atoms (PIM-1h) to bulky trimethylsilyl groups (PIM-1tms). Also, the effect of the electronegativity distribution along the backbone of the polymer is expected to have an effect on the Coulombic repulsion of adjacent rigid segments, analyzed here through a backbone functionality series, which span from electro-neutral (PIM-1ch) to electronegative (PIM-1f2, PIM-1n2). Lastly, it is hypothesized that an optimum backbone segment length exists which allows for the greatest hindrance of efficient packing, and thus backbone segment lengths were designed ranging from 10 Å (PIM-0) to 29 Å (PIM-1r9). Even though all structures shown here are meant as theoretical test-cases to understand different structure–property relationships, several may be synthetically feasible. For example, sPIM-1 or PIM-1h may be synthesized by modification of the spirocenter unit to 5,5',6,6'-tetrathiol-3,3',3'-tetramethyl-1,1'-spirobisindane or 5,5',6,6'-tetrahydroxy-1,1'-spirobisindane, respectively, which can be reacted with 2,3,5,6-tetrafluoroterephthalonitrile to synthesize the corresponding polymer sample. In addition, Ref. [14] highlights the possible functional diversity of monomer units available to synthesize intrinsically microporous polymers. The essential point is that the design principles gained from this study are expected to aid in the development of future intrinsically microporous gas separation membrane materials.

3. Simulation methods

3.1. Structure generation

The method for estimating the permeability of a high free volume polymer utilized an atomistic definition of the polymer to explicitly model the microporosity, which was simulated here using transferable [27–33] and generalized force fields [34]. The hypothetical polymers were constructed using the available open-source simulated polymerization algorithm, *Polymatic* [35], in conjunction with the 21-step molecular dynamics compression and relaxation scheme [24,36], each of which has been utilized in predictively simulating amorphous materials in recent works [24–26,36–45]. More information in the implementation and use of *Polymatic* may be found in Ref. [24], with a thorough description of the parameters used for this work provided in electronic supplemental information (ESI). In all cases studied here, five independently generated samples were used to calculate the average value of interest for each polymer.

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