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Gas sorption and transport in thermally rearranged polybenzoxazole membranes derived from polyhydroxylamides

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ABSTRACT

The sub-nano-sized microcavities in microporous thermally rearranged (TR) polymers can be tuned by varying the conditions of thermal rearrangement. Relatively small cavities were formed by thermal rearrangement of poly(*o*-hydroxylamide) (PHA) precursors compared to the cavities formed by that of polyimide precursors. TR polymers derived from PHAs, so-called TR- β -polymers, are known to exhibit a well-tuned cavity structure that can be used for H₂/CO₂ separation. According to a solution-diffusion model, both the permeability and selectivity for H₂/CO₂ separation were improved at elevated temperatures due to a significant increase in H₂ diffusion and a decrease in CO₂ sorption. In this study, gas solubility and permeability of five representative small gas molecules (H₂, N₂, O₂, CH₄, and CO₂) through TR- β -polymer membranes were characterized between 20 °C and 65 °C for gas solubility measurement and between 35 °C and 300 °C for gas permeability measurement. These measurements allowed for the calculation of thermodynamic factors such as the activation energy and heat of sorption.

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1. Introduction

Microporous materials have been investigated for gas storage, separation, and catalysis due to their high porosity and surface area. The utilization of microporous polymers as gas separation membrane materials has occurred in various applications such as ammonia purge gas recovery, natural gas stripping, and CO₂ capture [1–4]. Recently reported microporous polymers with high free volumes are distinguished from conventional polymers, which typically have a well-packed and non-porous structure. Rigid and contorted chain structures in microporous polymers result in higher free volume elements with effective size sieving properties that can be used as gas separation membranes. There has been recent progress in new types of polymers such as polymers of intrinsic microporosity (PIMs) and thermally rearranged (TR) polymers [5–14]. These have demonstrated extraordinary gas permeability with relevant selectivity. Moreover, easy scale-up and fabrication of highly permeable polymers are important for large-scale industrial processes, especially for CO₂ separation in carbon capture and sequestration (CCS) for post-combustion and pre-combustion to battle global warming issues, as well as natural gas sweetening applications [8].

The major emission sources of CO₂ are coal-fired power plants as a result of fuel combustion (post-combustion, CO₂/N₂ separation) and the water gas shift (WGS) reaction in the integrated

gasification combined cycle (IGCC) process (pre-combustion, H₂/CO₂ separation). Pre-combustion CO₂ separation processes are usually operated at high pressure (> 10 bar) and high temperature (150–900 °C) [15–17]. The pressure-driven gas separation membrane process has the benefit of high flux during the high pressure pre-combustion CO₂ separation process. However, the use of membrane materials is quite limited because the operation conditions are harsh and include high temperatures and pressures; commercially available membranes utilize polymers with low thermal stability [18–20]. Depending on the operation conditions of the WGS reaction, the feed gas is usually at a temperature higher than 300 °C, where common polymeric materials cannot be used because they undergo rapid degradation. As a result, various palladium-based metals and ceramics have been studied for pre-combustion CO₂ separation membranes; however, these are difficult to apply to large-scale operations due to problems in membrane module fabrication [16,17]. A heterocyclic polybenzimidazole (PBI), as a high-temperature polymer, has been investigated for use in pre-combustion CO₂ separation membranes because of its excellent thermal, chemical, and mechanical resistances [21–23]. Polyimides (PI) and poly(ether ether ketone) (PEEK) have also been investigated due to their high thermal stability, but the operation conditions of pre-combustion CO₂ separation are still too harsh for these materials. A cooling step is necessary in order to utilize commercial PI and PEEK membranes for pre-combustion CO₂ separation [24–26]. Alternatively, thermally rearranged (TR) polymer membranes are a good candidate for high temperature CO₂ separation due to their high thermal stability and rigid polymer structures [27].

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Thermal rearrangement is a suitable method to produce polymer membranes with high gas permeability and selectivity. One of the advantages of TR polymers is that the cavity sizes and distributions can be controlled by adopting specific polymer structures or thermal conversion routes and/or conditions [6]. To improve H₂/CO₂ selectivity, TR polymers obtained from poly(*o*-hydroxylamide)s (PHAs), so-called TR-β-polymers, were investigated because they present relatively smaller cavity sizes that can be tuned for H₂/CO₂ separation [27]. TR-β-polymers are compared with TR polybenzoxazole (TR-PBO) from hydroxyl polyimide, so-called TR-α-polymer for their distinguished physical properties such as free volume or gas transport properties. TR-β-polymers exhibit lower thermal conversion temperatures around 350 °C with the evolution of H₂O molecules, which is advantageous for economic membrane preparation [27]. The high thermal stability (stable above 300 °C) allows TR polymers to be applied to pre-combustion CO₂ separation processes in order to produce H₂ and generate power [27].

In this study, the gas sorption, diffusion, and permeation properties of TR-β-polymer membranes were investigated in order to characterize their gas transport behaviors. Gas permeability and solubility values of five representative small gas molecules including H₂, N₂, O₂, CH₄, and CO₂ were characterized for TR-β-polymer membranes. Gaining information about gas solubility can allow for the study of the individual contributions of gas permeability, diffusivity, and solubility of TR-β-polymer membranes according to the solution–diffusion model [28–30]. We also investigated the effect of operation temperature on gas permeability and solubility. It was our aim to investigate the thermodynamic aspects of gas permeation and sorption measurements at elevated temperatures, including the activation energies and heat of sorption [17,31,32].

2. Background

Gas transport through a polymer membrane is explained by a solution–diffusion model where the gas permeability coefficient (P) is a product of the diffusion coefficient (D) and the sorption coefficient (S), as described in the following equation [31,33]:

$$P = D \cdot S \quad (1)$$

The selectivity (α) is related to the separation properties of the membranes and is calculated as the ratio between the permeabilities of penetrants, as described in the following equation:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{D_i \cdot S_i}{D_j \cdot S_j} \quad (2)$$

Sorption, as a thermodynamic factor related to the affinity between a polymer matrix and gas molecules, occurs when a gas molecule in the bulk state adsorbs physically onto a membrane surface based on the concentration difference. Diffusion, a kinetic factor, explains how fast a gas molecule passes through the membrane and is related to the size of the gas molecule and the free volume in the polymer [33–35]. Sorption and diffusion are activated energy processes and are strongly affected by temperature; thus, D , S , and P are expressed as a function of temperature

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad (3)$$

$$S = S_0 \exp\left(\frac{-\Delta H_S}{RT}\right) \quad (4)$$

$$P = P_0 \exp\left(\frac{-E_P}{RT}\right) \quad (5)$$

where E_D is the activation energy of diffusion, ΔH_S is the heat of sorption, and E_P ($E_P = E_D + \Delta H_S$) is the activation energy of

permeation over the entire temperature range. Eqs. (3)–(5) can be translated into the following equations in order to determine E_D , ΔH_S , and E_P [8]:

$$\ln D = \frac{1}{T} \cdot \frac{-E_D}{R} + \ln D_0 \quad (6)$$

$$\ln S = \frac{1}{T} \cdot \frac{-\Delta H_S}{R} + \ln S_0 \quad (7)$$

$$\ln P = \frac{1}{T} \cdot \frac{-E_P}{R} + \ln P_0 \quad (8)$$

Since gas diffusion through polymers and sorption on polymers are affected by the type of polymer being used, the gas permeability is determined by the gas–polymer affinity. Therefore, both thermodynamic and kinetic factors are important to achieve high permeation and separation performances. Moreover, studying the temperature dependence of the gas permeability, diffusivity, and solubility of the polymer membranes allows us to suggest a practical approach for process design.

3. Experimental

3.1. Polymer preparation

Two rigid aromatic acid chlorides of *meta*-phenylene and *para*-phenylene, i.e., isophthaloyl dichloride (IPCl) and tetrachloro dichloride (TPCl) were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA), and 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (bisAPAF) as a bisaminophenol was obtained from Central Glass Co., Ltd. (Tokyo, Japan). *N*-methyl-2-pyrrolidinone (NMP), dimethylformamide (DMF), *n*-hexane, and toluene were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA) and used as solvents without further purification.

The different PHA precursors were prepared using the same protocol but with different dichloride monomers in each case. The polycondensation reaction of bisAPAF and dichloride (IPCl or TPCl) was performed in NMP for 4 h in an ice bath, and the resulting polymer solution was a viscous, yellowish solution. After terminating the reaction, the solution was precipitated in deionized water and washed overnight. PHA powders were dried at 100 °C under vacuum. PHA membranes were cast onto glass plates from a PHA solution in NMP at 15 wt% using a doctor blade, kept at 80 °C overnight, and then gradually heated to 100, 150, 200, and 250 °C in a vacuum oven. PHA membranes with a thickness of 30–40 μm were treated to 350 °C at a heating rate of 5 °C min⁻¹ in a muffled furnace (Lenton, London, UK) to complete thermal rearrangement into a PBO structure [27]. The chemical structures of the PHA precursors and their resulting TR polymers are described in Fig. 1.

3.2. Gas permeation measurement

The gas permeability of the PHA precursors and the resulting TR-PBO membranes were measured using a high-vacuum time-lag apparatus with a calibrated downstream volume of 30 cm³. The pressures at the upstream and downstream were measured using Baratron 626A pressure transducers (MKS Instruments Corp., MA, USA) with a full-scale of 10,000 Torr and 10 Torr, respectively. All pure gas permeation measurements, with different kinetic diameters, in order of H₂ (2.89 Å), N₂ (3.64 Å), O₂ (3.46 Å), CH₄ (3.8 Å), and CO₂ (3.3 Å) were performed at 35 °C considering a gas condensability [36]. The membrane film, masked with aluminum tape and sealed with epoxy, was mounted in a 47 mm HP Filter Holder (Millipore, MA, USA). The effective area of the membrane was 4.00 cm², and the pressure difference between the upstream

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