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Effect of methanol treatment on gas sorption and transport behavior of intrinsically microporous polyimide membranes incorporating Tröger's base

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ABSTRACT

The gas sorption behavior of polyimides (PIs) incorporating Tröger's base (TB) units was investigated for five representative small gases (H_2, N_2, O_2, CH_4, and CO_2) by barometric pressure decay methods at 35 °C. Methanol treatment of the PI-TB membranes increased the sorption, diffusion, and permeation of the small gas molecules because of increased interactions between the polymer and gas molecules as well as an increase of the *FFV* due to dilation of the polymers. Two different solubility determination methods, pressure-decay based and time-lag based methods, were introduced and compared. The gas solubilities of relatively condensable gases such as CO_2 and CH_4 showed good agreement between the two solubility measurements. Two different dianhydrides (6FDA and BTDA) in the PI-TBs were also introduced to determine their structural contributions to the gas sorption and transport properties. The two PI-TBs showed similar behavior in Henry's mode sorption. However, their Langmuir mode sorption demonstrated distinctive behavior, resulting in different gas transport phenomena. Methanol-treated PI-TB membranes exhibited plasticization resistance for CO_2 permeation under high CO_2 content feed in CO_2/CH_4 mixture. Incorporating TB units in the PI backbones achieved comparable microporosity and gas permeability results especially for CO_2 separation in highly permeable polymer membranes.

1. Introduction

Recently, membrane technology has received much attention as a means to achieve process intensification [1]. Membrane-based gas separation processes are particularly appealing due to their low energy usage because they avoid phase changes encountered in traditional cryogenic distillation processes. In addition, membrane systems have a small footprint, which reduces operation site requirements [2]. Established membrane gas separation processes include N_2 production from air [3], hydrogen recovery from ammonia production [4], and natural gas purification [5]. Emerging separation processes under investigation include CO_2 capture from flue gas emissions during power generation [6]. Polymers have been the prime materials considered for commercial membrane separation processes over the past three decades due to their easy processability and economics [7]. However, the properties of polymeric membranes such as their gas permeability and selectivity are relatively low compared to inorganic membranes [1]. Commercial membranes utilize relatively few polymers, typically those with modest gas permeabilities and high selectivities, which increase process costs because of the requirement of large membrane areas. Highly permeable polymer membranes, on the other hand, typically have low selectivities because they suffer from the well-known trade-off relationship between gas permeability and selectivity [8,9]. The microporous polymer poly(trimethylsilyl-1-propyne) (PTMSP) has been considered potentially useful for industrial applications because of its extraordinarily high gas permeability, which is very advantageous to reduce the membrane area [10]. However, it suffers from very low selectivity and rapid aging. Subsequent studies of PTMSP membranes have explored ways to improve their performance through strategies such as multilayer composites [11], nanoparticle composites [12], and mixed matrix membranes [13]. More recent research has been focused on the development of highly permeable microporous membrane materials with improved selectivity [14–17].

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A polymer of intrinsic microporosity (PIM) is a term coined by Budd and McKeown to represent a class of soluble microporous polymers having rigid ladder-like chains containing sites of contortion, which have characteristically high surface areas, very high gas permeabilities, and modest to good selectivities [18]. Since PIMs were first reported in 2002 [18] and the archetypal PIM-1 structure was developed in 2004 [19,20], a variety of related structures have been explored that gave a range of gas transport properties. However, the structural diversity of PIMs has been somewhat limited for several reasons including monomer availability, insufficient solubility, or the formation of insoluble polymer network products. New avenues which have been explored to improve processability include PIMs incorporating polyimide (PI) structures [21,22]. PIs are well-known and commonly used in various industrial applications due to their excellent physical properties such as thermal and chemical stabilities, and good gas permeability [23,24]. PIM-PI membranes exhibit outstanding gas permeabilities compared to other polyimide membranes due to the PIM structural segment.

Recently, Carta et al. reported a new class of extremely rigid PIMs containing bridged non-planar bicyclic ring systems formed by a Tröger's base (TB) polymerization reaction [14,25–30]. The higher chain rigidity derived from the ethanoanthracene (EA) ring system combined with the TB unit led to membranes with high gas permeability and selectivity due to the larger interchain spacing and high fractional free volume (*FFV*) [15]. The more rigid EA or TB units in the PIM-EA-TB restrict minor chain flexing, which occurs to a small extent in conventional PIM-1 in both the fused-ring dibenzodioxane and contorted spiro-center structural units. Thus, we and others have incorporated TB units into soluble polyimides to investigate intrinsically microporous polyimides in order to integrate the advantages of the high performance derived from the TB units along with the excellent physical properties of PIs [31–33]. The resulting PI-TB polymers possess good mechanical properties as well as high *FFV* values and very good gas transport properties compared to conventional PIs.

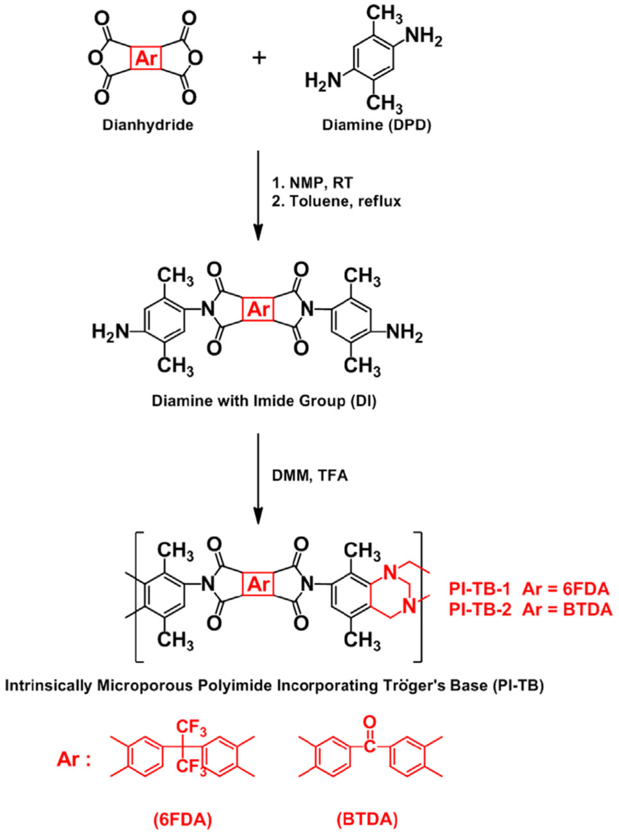

Fig. 1. Preparation of diamines with imide groups (DIs) and intrinsically microporous polyimides incorporating Tröger's base (PI-TBs).

In our previous work [31], preliminary evaluation of the gas transport behavior of PI-TB polymers compared to PIs having PIM-like structures or PIs prepared from the same dianhydride monomers was carried out. In the present work, we investigated the effect of methanol treatment on the gas sorption and transport properties of the PI-TB polymers, since it is known that glassy polymers with a high *FFV* such as PTMSP or PIMs are prone to physical aging and methanol or ethanol treatment removes residual solvents [10,25,34]. However, there have been very few studies conducted to analyze the effect of alcohol treatment on the change of gas solubility. Previously, the solubility coefficient was calculated from permeability and diffusivity data measured by time-lag analysis [34]. In addition, the effect of residual solvent on the change of gas separation behavior was investigated by atomistic simulation [35]. In the present study, we evaluated the gas permeability, diffusivity, and solubility of PI-TB membranes for small gas molecules in order to improve the understanding of gas transport properties by applying a solution-diffusion model. Different from other studies [36,37], the gas solubility was determined by the barometric pressure decay method and thereafter, the role of methanol treatment was elucidated based on the derived solubility coefficients. We also investigated the effect of methanol treatment on the membrane plasticization phenomena by monitoring the change in CO_2 permeability at elevated pressures in feed gas mixture.

2. Experimental

2.1. Polymer preparation

Polyimides with Tröger's base in the backbones were polymerized from diamines with imide groups (DIs) and dimethoxymethane (DMM), as reported in our previous study [31]. In the first step, DI monomers were prepared by a condensation reaction with a 3:1 M ratio of the diamines and a dianhydride, as shown in Fig. 1. In this study, two kinds of dianhydrides were incorporated into the DIs: 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA). 60 mmol of high purity 2,5-dimethyl-1,4-phenylenediamine (DPD) and 20 mmol of dianhydride were sequentially dissolved in *N*-methyl-2-pyrrolidinone (NMP) and reacted at 180 °C to form the DI monomers. After 12 h, 50 mL of toluene was added and the mixture was refluxed for more than 9 h at 180 °C under a nitrogen atmosphere to remove water from the condensation reaction by azeotroping using a Dean-Stark trap.

The PI-TBs were prepared from the TB-forming polymerization reaction of the resulting DI monomers and DMM in trifluoroacetic acid (TFA) [31]. 4 mmol of DI was dissolved in 22.4 mmol of DMM and then, 30 mL of TFA was added dropwise over 10 min for the TB formation. PI-TB polymers were formed after 48 h with vigorous stirring of the solution at room temperature under a nitrogen atmosphere. The resulting PI-TB solutions were alkalized by a 2.5% aqueous ammonium hydroxide solution and then washed three times with water and methanol, respectively. The polymers were purified by precipitation of a chloroform solution into methanol and the resulting PI-TB powder was dried in a vacuum oven 120 °C for 24 h. 6FDA, BTDA, DMM (99.0%), and the NMP (> 99.0%), and toluene (99.8%) solvents used in the experiment were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI, USA).

DPD, TFA (> 99.0%), and chloroform (> 99.0%) were obtained from Tokyo Chemical Industry (Tokyo, Japan). Other reagents such