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# Liberation of small molecules in polyimide membrane formation: An effect on gas separation properties

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A B S T R A C T

The ultra-micropores in polymeric membranes play a key role on the separation performance. This work demonstrates that liberation of small molecules in the membrane formation process is an effective approach to create ultra-micropores in a narrow size distribution in polymeric membranes. A crosslinkable Meldrum's acid derivative is used as the effective agent that liberates $CO_2$ and acetone molecules in the polyimide (PI) membrane formation process and to chemically crosslink the PI-based membranes. Compared to the neat PI membrane, the modified membrane shows small ultra-micropores in a narrow size distribution measured with a positron annihilation lifetime spectroscopy. Consequently, the modified PI membranes become highly-selective toward $H_2$ gas. With a small reduction of permeability (from 23.1 to 15.5 barrer), the ideal selectivity for $H_2/N_2$ (155) and $H_2/CO_2$ (5.3) of the modified PI membrane are about 3-fold of the values recorded with the neat PI membrane. In a binary mixed gas test at 20 atm, the modified PI membrane shows a high $H_2$ permeability of 24.5 barrer and a high $H_2/CO_2$ selectivity 14.1. The results demonstrate an effective and simple method to enhance the gas separation performance of polymeric membranes with modulation of the cavity sizes and size distribution of the membranes.

## 1. Introduction

Gas separation mediated with polymeric membranes is attractive for relatively low cost, low energy consumption, and flexibility of raw materials in membrane fabrication [1,2]. Gas molecules dissolve into the membranes and then transport through the membranes by means of diffusion in the free-volume pores [3]. As the thermally-induced chain motion, the cavity sizes of free volume in the polymeric membranes are not fixed, polymers with high chain rigidity are more attractive for gas separation as to minimize the chain flexibility and the corresponding dynamic changes in the free volume cavity [1]. One example of the rigid polymer for gas separation is polyimide [4–11]. Nevertheless, polyimides usually have small free volume sizes [12] so as to show high selectivity and low permeability in gas separation. Consequently, rigid polymers possessing large free volume pores have been reported to demonstrate high permeability. Some important examples include polymers with intrinsic microporosity (PIM) [13–20], thermally-rearranged polymers (TR polymers) [21–26], multiptycene-containing polymers [27,28], and polymers

possessing Tröger's base (TB) groups [29–31]. Compared to the conventional rigid polymers, for several gas pairs these polymers show high permeability and reasonable selectivity exceeding the Robeson upper bounds at the high permeability side.

The membrane formation mechanism for TR polymers is interesting [21]. The polyimide precursor shows small cavity sizes and a wide cavity-size distribution, just like conventional polyimides. After thermal treatment at about 450 °C, the obtained membranes possess larger cavities with a very narrow size distribution. Both chemical reaction-induced chain rearrangement and repacking and liberation of $CO_2$ molecules occur in the thermal process. Lee et al. [21] firstly attributed the cavity formation of the TR membranes mainly to the chain rearrangement and repacking behavior, and said that $CO_2$ evolution is not a decisive factor for cavity formation. The inference was based on a model study employing a carboxylic acid containing PI which evolves $CO_2$ molecules with the thermally-induced decarboxylation reaction. The decarboxylated and the pristine PIs exhibited similar gas permeability. Similar results were reported for thermal decarboxylation-induced crosslinked PIM membranes [32]. The carboxylic acid-containing PIM precursor was thermally heated at 375 °C. Liberation of $CO_2$ occurred with the decarboxylation reaction in the thermal treatment process of the membrane. The effect of $CO_2$ liberation on the membrane gas separation performance was not obvious. Nevertheless, in the later papers [22,26]

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Lee's group attributed the high free volume and permeability of the TR polymer-based membranes to both $CO_2$ releases and chain conformation changes.

Based on the above discussion, the effect of liberation of small molecules on the ultra-micropore formation and the gas separation performance attracts the research interests. Chung's group [33–35] has demonstrated the concept with uses of cyclodextrin molecules as thermally labile groups, which were grafted to polyimide chains and then thermally removed. The space of the cyclodextrin molecules transformed into microvoids so as to significantly increase the gas permeability of the PI membranes. In this work, a Meldrum's acid (MA) derivative is used as an additive to introduce the liberation of small molecules in membrane formation of polyimides. PI has been used as the membrane material based on its good thermal stability and high gas permeability [33–36] compared to other polymers like polyamides, although Albo et al. [37,38] recently reported the improvements on gas transport properties of interfacially polymerized polyamide composite membranes with different pre-treatment and temperatures. PI membranes possessing the MA derivative are prepared and applied to thermal treatment. Thermal decomposition of the MA group of the added agent liberates one molecule of acetone and one molecule of $CO_2$ to form a highly reactive ketene group for further chemical reactions [39,40]. Hence, liberation of acetone and $CO_2$ molecules carries out in the PI-based membrane formation process. The effect of the modification on the microporosity and gas separation performance of the PI-based membranes is studied. It is noteworthy that the modified PI membranes show a significant change in the membrane cavity sizes and size distribution. The gas permeability of the modified membranes, especially for the gas molecules (such as $CO_2$ and $N_2$) in relatively large kinetic diameters, is significantly depressed. As a result, with the modification the membrane selectivity increases from 55 to 155 for $H_2/N_2$ gas pair and from 1.8 to 5.3 for $H_2/CO_2$ gas pair with a $H_2$ permeability decrease from about 23.1 to 15.5 barrer. A simple and effective approach to create ultra-micropores of narrow size distribution in polymeric gas separation membrane has been demonstrated.

## 2. Experimental

### 2.1. Materials

Soluble thermoplastic Matrimid® polyimide (PI) is purchased from Alfa Aesar Co. MA, 4-chloromethylstyrene, and furfural were all purchased from Aldrich Chemical Co. and used as received as the raw materials for preparation of the MA derivative (MA-FS), which possesses one furan and one styrene groups. N-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), and N,N'-dimethylformamide (DMF) were purchased from Echo Chemical Co. and used as received.

### 2.2. Instrumental characterization

Fourier transform infrared (FTIR) analysis was conducted with a Perkin Elmer Spectrum Two FTIR. The obtained PI membranes were directly applied to the measurements with a transmission method. Thermogravimetric analysis (TGA) thermograms were recorded with a Thermal Analysis (TA) STD Q600 instrument at a heating rate of 10 °C min$^{-1}$ under a $N_2$ inlet flow of 100 mL min$^{-1}$. The glass transition temperatures of the PI based membranes were recorded with the temperatures of tan $\delta$ peak in the dynamic mechanical analysis thermograms (DMA, Perkin-Elmer Pyris Diamond DMA) at a heating rate of 5 °C min$^{-1}$. The mechanical property of the membranes was measured with stress–strain curves recorded with an instron instrument (Instron model 5543 analyzer) at room temperature. The elongation rate was 5 mm min$^{-1}$. Scanning electron microscopy (SEM) observation was conducted with a Hitachi SU8010 SEM. The free volume pore sizes and distribution of the PI membranes were measured with a lab-assembled instrument of positron annihilation lifetime spectroscopy (PALS) using $^{22}$Na as a positron source and $BaF_2$ as a lifetime detector. The collected PAL data was analyzed with a PATFIT program (purchased from Riso National Laboratory, Denmark) to determine the mean positron lifetime. An MELT software, which is based on a finite-term lifetime analysis using the maximum entropy method, is used to get the positron lifetime distribution.

### 2.3. Preparation of MA-FS

Preparation of MA-FS was carried out according to the reported method [40]. A solution of MA (2.88 g 20 mmol), furfural (1.92 g 20 mmol), piperidine (0.086 g, 1.0 mmol), and acetic acid (0.18 mg, 3.0 mmol) in 20 mL DMSO was prepared and reacted at 50 °C for 24 h. $NaBH_4$ (0.40 g, 10.6 mmol) was added to the solution slowly at 0 °C and then the solution was stirred at room temperature for 0.5 h. After being quenched with 5 mL of $H_2O$ and 10 mL of 10 wt% $HCl_{(aq)}$, the product was extracted with ethyl acetate for 3 times. The crude product (MA-F) was obtained from the collected organic solution and purified with a flash column. MA-F was furthered reacted with 4-chloromethylstyrene to give MA-FS. 4-Chloromethylstyrene (1.58 g, 10.4 mmol) was added to a DMF (10 mL) solution of MA-F (1.87 g, 8.3 mmol) and $K_2CO_3$ (1.65 g, 12 mmol). The solution was reacted at room temperature for 20 h, quenched with 10 mL 10 wt% $HCl_{(aq)}$, and extracted with chloroform. The collected organic solution was washed with water and dried with $MgSO_4$. The collected crude product was purified with a flash column to give the product of MA-FS (60%). Characterization data in detail was reported in the previous work [40].

### 2.4. Fabrication of MA compound-modified PI membranes

A certain amount of MA-FS was added to a 15 wt% PI solution of NMP. Four samples in which the MA-FS fractions in the solid contents were 0, 10, 20, and 30 wt%, respectively, were prepared. The solutions were ultrasonically treated for 1.5 h at room temperature, filtered with a cotton cloth, and then standing for 24 h for degassing. The solutions were then cast on a glass plate with a casting knife at a thickness of 300 μm. The samples were then heated at 120 °C for 24 h to slowly remove the solvent, at 180 °C for 1 h to further dry the membrane, and at 240 °C for 1 h to perform the MA-FS decomposition and polymerization. After being cool to room temperature, free-standing PI membranes were obtained with releasing them from the substrates in water and drying at 120 °C for 18 h. The samples were coded as PI/MA-FS-X, where X denotes to the weight fraction of MA-FS for preparation of the corresponding membrane.

### 2.5. Gas sorption and separation measurements

The physical sorption behavior of the PI –based membrane for individual gas is measured with a gravimetric method using a Cahn-D200 microbalance (Thermo Fisher Scientific Inc.) at 35 °C. The solubility ($S$, cm$^3$ (STP)/(cm$^3 \cdot$ cmHg)) of individual gas in the PI-based membrane was calculated from the time-dependent sorption data.

The gas permeability ($P$) of the PI-based membrane was measured with a Yanaco GTR-11MH gas permeation analyzer. The measurements were carried out at a feed gas pressure of 1 atm and at 35 °C. The experimental data was continuous recorded for