



Bromination/debromination-induced thermal crosslinking of 6FDA-Durene for aggressive gas separations



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ABSTRACT

A new method for enhancing condensable gas-induced plasticization resistance of aromatic polyimides (PIs) as well as increasing the flux of gas penetrants with negligible selectivity loss was demonstrated via a so-called bromination/debromination-induced thermal crosslinking. Our newly developed crosslinking approach essentially loosened the polymeric chain packing of 6FDA-Durene PIs by forming ethylene crosslinking bonds, while retaining its rigid PI backbone. As the degree of crosslinking increased, the permeability increased with trivial selectivity loss. Notably, the 75% bromination/debromination-induced crosslinked PI membranes drastically improved CO₂ and C₃H₆ permeabilities by as much as 157% and 172%, respectively, compared to those of the pristine-PI analogs due to the debromination-induced free volume enhancement, while maintaining good selectivity due to the crosslinked ethylene bridges. As a result, outstanding separation performances for CO₂/N₂, CO₂/CH₄ and C₃H₆/C₃H₈ gas pairs have been obtained, and most importantly, a high tolerance to CO₂- or C₃H₆-induced plasticization was observed up to CO₂ or C₃H₆ pressure of 24 and 10 atm, respectively. Our current crosslinking approach can be extended to industrially attractive hollow fiber forms of various aromatic PIs for high plasticization resistance as well as high flux.

1. Introduction

Membrane-based separation technology has been promoted as an energy-efficient and small footprint technology in the industrial scale of gas separation processes. Polymeric materials are attractive membrane source due to their good cost efficiency as well as facile processability [1]. Polyimides (PIs), especially 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)-bearing PIs tend to exhibit high selectivity due to their rigid and contorted polymeric backbones [2]. Highly sorbing penetrants such as heavy hydrocarbons or carbon dioxide, however, tend to disrupt chain packing and accelerate inter-segmental mobility at high feed pressure, a phenomenon known as plasticization, substantially degrading separation performance [3,4]. Also, a strong inherent trade-off between permeability and selectivity invariably affects PI membranes, limiting their gas separation performance [5,6]. With those in mind, improving separation performance of polymeric membranes in aggressive feeds is of great interest for condensable gas-

involved aggressive gas separations such as natural gas sweetening, olefin/paraffin separations or aromatic/aliphatic separations [7–10].

Crosslinking is one of the most widely accepted approaches to suppress plasticization and therefore has been extensively investigated over the past two decades [11]. A wide variety of crosslinking strategies have been developed for PI membranes including chemically- or thermally-induced crosslinking. Typically, chemical crosslinking of PI membranes is executed by using either diamine-crosslinkers [12–14] or diol-crosslinkers [15–17]. The diamine-involved crosslinking proceeds through the imide ring opening of PI caused by the amines, creating intermolecular amide bonds, while the diol-involved analog progresses through a reaction between hydroxyl groups of the diol and carboxyl groups of some specially functionalized PIs, resulting in crosslinked ester bonds. While both strategies have shown to substantially improve CO₂-induced plasticization resistance, the diamine-based crosslinking leads to substantial reduction in permeability [12–14] and the amide linkages can be reversed to imides at high temperatures [18]. The ester

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linkages can also be cleaved possibly due to hydrolysis in aggressive acid gas streams [19].

Kratochvil and Koros [19] introduced a decarboxylation-induced thermal crosslinking by using carboxylic acid containing 6FDA-based co-PIs, demonstrating substantial improvement in resistance against CO₂-induced plasticization. Furthermore, Qiu et al. [20] demonstrated that the thermal cross-linking of 6FDA-DAM:DABA (3:2) where 6FDA stands for 4,4'-(hexafluoroisopropylidene) diphthalic anhydride, DAM represents 2,4,6-trimethyl-1,3-diaminobenzene and DABA means 3,5-diaminobenzoic acid can be executed at relatively moderate temperatures below the glass transition temperature with excellent CO₂-induced plasticization resistance. Chen et al. [21] extended it to industrially attractive forms by fabricating defect-free 6FDA-DAM:DABA (3:2) hollow fiber membranes and successfully verified their excellent plasticization resistance under high CO₂ feed pressures up to a CO₂ partial pressure of 400 psia. Chung et al. [22–25] developed a new approach of enhancing permeability as well as securing high plasticization resistance by incorporating thermal labile molecules with large dimensions into cross-linkable polyimides. The decomposition of beta-cyclodextrins generated microcavities for high permeability, while decarboxylation-induced crosslinking improved plasticization resistance [22].

In the current work, preparation of crosslinked 6FDA-Durene by a free radical-induced thermal crosslinking, so-called bromination/debromination-induced thermal crosslinking is reported. Polymers with aromatic functionality can be regioselectively brominated by either electrophilic substitution on the aromatic ring [26,27] or free radical substitution on the benzylic side chain [28,29], depending on the reagents and reaction conditions. Guiver et al. [30] investigated a strong correlative study of bromine functionalization of Matrimid® 5218 polyimides (PIs), as well as the gas permeability of the resultant membranes using the electrophilic bromination on aromatic groups. The direct attachment of bromine atoms onto the aromatic ring of Matrimid® 5218 increased chain rigidity and free volume in the polymer matrix due to the presence of bulky bromine groups, increasing gas permeability. In the present work, we are exclusively aiming to explore a method of free-radical induced crosslinking with controlled -CH₂CH₂- ethylene crosslinked bridges, which can only be achieved from brominated polymeric backbones. While pendant benzyl bromine atoms may cause chain densification, the subsequent debromination creates an ethylene crosslink bridge between polymeric backbones of 6FDA-Durene during thermal treatment, achieving high plasticization resistance through crosslinking and also, leading to high permeability through perturbed chain packing with negligible selectivity loss. Different degrees of bromination are expected to generate varying degrees of crosslinking as well as different free volume elements during thermal treatment. The effect of different degrees of debromination on both separation performance and plasticization resistance was investigated by using condensable gas-based (e.g., CO₂ and C₃H₆) feed streams.

2. Experimental

2.1. Materials

4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 2,3,5,6-tetramethyl benzene-1,4-diamine (Durene) were purchased from Tokyo Chemical Industry (TCI) Co., Ltd. (Tokyo, Japan), and dried under vacuum at 60 °C for 24 h prior to polymerization. Triethylamine and acetic anhydride were obtained from Sigma Aldrich and used as obtained. Tetrachloroethane and N-bromosuccinimide (NBS) were obtained from Tokyo Chemical Industry (TCI) Co., Ltd. (Tokyo, Japan). All other chemicals, unless otherwise noted, were obtained from commercial sources and used as received.

2.2. Synthesis of 6FDA-Durene and brominated 6FDA-Durene

A general two-step polycondensation reaction such as polyamic acid formation followed by chemical imidization was performed for the synthesis of pristine 6FDA-Durene polyimide [31]. Both the monomers, 6FDA (18 g, 40.52 mmol) and durene (6.67 g, 40.52 mmol) were dissolved with DMAc (100 mL) in a 1000 mL two-necked round bottom flask equipped with a magnetic bar, nitrogen inlet, and a condenser. Then the reaction mixture was allowed to stir for 12 h at -5 °C (ice-bath) in order to form the corresponding high molecular weight polyamic acid. After this time, triethylamine (11.87 mL, 85.09 mmol) and acetic anhydride (8.04 mL, 85.09 mmol) were added to induce a complete imidization of polyamic acid to form polyimide at 110 °C under vigorous stirring for 3 h. Finally, the resultant viscous mixture was cooled to room temperature and diluted with some more DMAc (20 mL), followed by precipitated into methanol (400 mL). White polymer beads were collected by filtration and washed several times with deionized water, and dried at 80 °C under vacuum condition for 48 h to give the pristine 6FDA-Durene polyimide (23.5 g, 95%); δ_{H} (400 MHz, CDCl₃) 8.10–8.08 (2H, br signal, ArH), 8.00–7.95 (4H, br signal, ArH), and 2.13 (12H, s, CH₃); (ATR-FTIR)/cm⁻¹ 2925, 1780, 1710, 1350, 1260, 1187, 1112, 725 and 650; GPC (THF, RI)/Da M_n 124.59 kg/mol, M_w 164.46 kg/mol and M_w/M_n 1.32.

The obtained 6FDA-Durene PI (6 g, 10.5 mmol) and a catalytic amount of biphenyl peroxide (BPO) were dissolved with tetrachloroethane (30 mL) in a 250 mL two-necked flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser. This solution was heated to 80 °C for a complete dissolution before adding N-bromosuccinimide (12.6, 23.1 and 33.5 mmol respectively for 25%, 50% and 75% degree of bromination) and allowed to stir for 12 h at this temperature. The resultant red colored polymer solution was cooled to r.t. and precipitated into methanol (400 mL). The yellow-colored polymer beads were collected by filtration and washed several times with deionized water, and dried under vacuum at 80 °C for 48 h to give the brominated polyimides (93%); δ_{H} (400 MHz, CDCl₃) 8.15–7.98 (6H, br signal, ArH), 4.45 (2H, s, ArCH₂) and 2.35–2.26 (9H, br signal, CH₃); (ATR-FTIR)/cm⁻¹ 2927, 1790, 1714, 1355, 1269, 1191, 1100, 720, 660 and 650.

2.3. Membrane fabrication

All the 6FDA-Durene and brominated 6FDA-Durene membranes were prepared in a THF solution of corresponding polymers using the solution-casting method under a controlled THF vapor environment. The corresponding polymers (0.25 g) were dissolved in 5.0 cm³ of dry THF and stirred at room temperature overnight. The resultant solutions were filtered through a plug of cotton before pouring directly onto Teflon plates kept in a glove-bag saturated with THF vapor, and allowed to set at room temperature for 12 h. Finally, all the membranes were vacuum dried at 80 °C for 24 h in order to remove residual solvent. The thickness of the membranes was controlled to be 20–40 μm . The heat treatment of dense films was conducted by vertical heat treatment system (a detailed heating protocol was described in Supporting information, Fig. S1). Crosslinked 6FDA-Durene membranes were prepared by thermally treating three different degrees of brominated 6FDA-Durene membranes and the detailed temperature protocol will be discussed later.

2.4. Transport characterization

All gases used in this work were purchased from Shin Yang Oxygen Co. (Seoul, Korea). Single gas permeation measurements were performed using a high-vacuum time lag measurement unit based on constant-volume/variable-pressure method [32]. Before each measurement, all samples were thoroughly degassed at least 1 day to prevent overestimation induced by any residual gas trapped in them. All

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