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Thermal rearranged poly(benzoxazole-co-imide) membranes for CO₂ separation

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ABSTRACT

The thermal rearrangement of α -hydroxyl-polyimide membranes improves gas permselectivity properties compared to the polyimide precursor. By introducing segments within the polymer that do not undergo thermal rearrangement, the gas separation properties of the thermally rearranged membrane can be modified. In particular, polyimides are a class of polymer that have wide gas separation performance, which can be incorporated into thermal rearranged membranes through random copolymers and enable tailoring of the gas separation properties of the resulting membrane, without the need to alter the thermal rearranged moieties. A range of polyimide copolymers based on 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA) and diamines 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) with 2,3,5,6-tetramethyl-1,4-phenylenediamine (4MPD) or 9,9'-bis(4-aminophenyl) fluorene (FDA) were synthesised, and thermally rearranged into poly(benzoxazole-co-imide) membranes. The diamine moiety HAB undergoes thermal rearrangement to form the benzoxazole segments of the copolymer, while 4MPD or FDA based segments remain as imide segments in the copolymer. These copolymers, in both polyimide and poly(benzoxazole-co-imide) form, were tested as gas separation membranes for CO₂ separation from N₂ and CH₄. Thermal rearrangement of the homo-polymer HAB-6FDA resulted in increased gas permeability compared to the polyimide precursor. With the addition of the 4MPD moiety in the copolymer, it was discovered that the gas permeability, solubility and selectivity of membrane were similar to the homo-polymer HAB-6FDA. This result was attributed to the 4MPD-6FDA segments having similar gas separation properties as the benzoxazole segments. The presence of FDA in the copolymer resulted in a reduction in gas permeability as the FDA to PBO segmental ratio increased. However, the gas selectivity of this poly(benzoxazole-co-imide) was independent of FDA amount. Hence, through the addition of diamine moieties in poly(benzoxazole-co-imide), the gas separation properties of the thermal rearranged membrane can be varied.

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1. Introduction

The solid state high temperature thermal rearrangement (TR) of α -hydroxyl-polyimides results in increased fractional free volume as well as the formation of a bimodal distribution of cavity sizes, compared to their polyimide precursor [1–4]. This transformation is of particular interest in gas separation, as TR polymeric based membranes achieve exceptional gas separation properties, with the permselectivity for CO₂/CH₄ and O₂/N₂ often surpassing other polymeric membrane types [1]. This is believed to be the result of high temperature conversion of the polyimide (PI) precursor into poly(benzoxazole) (PBO). This transforms the interior morphology by altering the polymer chain conformation

and the spatial location of rigid moieties [3]. Furthermore, PBOs are a class of polymers that are thermally and chemically resistant, making them attractive for membrane separation. However, there remains some controversy over the exact nature of the TR conversion [5–7]. As a result of improved gas separation performances, TR-PBO membranes have been studied from PI precursors [2], and found to often operate at or above the current Robeson's upper bound for a number of gas pairs.

Copolymers of TR-PBO with PI segments that are unable to undergo TR are of particular interest, because PI membranes have been an active research field for over 20 years, and it is well known that fractional free volume (FFV) and gas separation properties can be controlled through choice of anhydride and diamine [8–10]. Hence, the inclusion of PI segments that do not undergo TR within the PBO in the form of poly(benzoxazole-co-imide) random copolymers provide additional benefits in gas separation membranes by altering their fractional free volume and modifying their gas separation

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ability. Jung et al. [11] have studied copolymers based on 3,3',4,4'-biphenyltetracarboxylic dianhydride with 2,2'-bis(3-amino-4-hydroxyl-phenyl) hexafluoropropane and 4,4'-oxydianiline (BPDA-bisAPAF-ODA), of different PBO to PI segment ratios. They found improved gas separation properties of the TR copolymer compared to the PI precursor polymer. Importantly, they were able to achieve fractional free volume control through the ratio of PBO to PI segments, with the gas separation performance linearly dependent on that ratio. Choi et al. [12] synthesised PBO-pyrrolone copolymers for gas separation, and found that the permselectivity of the PBO could be tuned through copolymerisation with polypyrrolone at different ratios. Similarly, Burns and Koros [13] have converted, via heat treatment, amine-containing PI copolymers into polypyrrolone-PI copolymers. These polymers were found to provide decreasing permeability and increasing selectivity as the polypyrrolone content increased. Hence, the gas separation properties of polymers that undergo thermally induced structural changes can be tuned through the inclusion of non-thermally rearranged imide segments in the form of a random copolymer.

Here, the gas separation properties of PBO-PI copolymer membranes are investigated, where the PBO segment is achieved through high temperature TR in the solid state. The purpose is to take advantage of the high gas permselectivity properties of the PBO, while introducing the PI segment to modify the fractional free volume and improve separation performance. By varying the relative ratios of PI and PBO segments within the TR copolymer it becomes possible to control the gas separation properties of the polymeric membrane. This enables TR based membranes gas permeability and selectivity to be tuned through the addition of PI segments that do not undergo TR. In particular, the copolymer precursor is derived from 4,4'-hexafluoroisopropylidene dipthalic anhydride (6FDA) and 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB), which undergoes TR conversion because of the α -hydroxyl group(s), while the non-TR PI segment consists of either 2,3,5,6-tetramethyl-1,4-phenylenediamine (4MPD) or 9,9'-bis(4-aminophenyl) fluorene (FDA). These moieties were chosen because membranes based on 4MPD-6FDA polyimide have CO₂ separation performance on a par with reported TR membranes [14–16], while the diamine FDA is a bulky moiety that induces a high degree of free volume within a membrane structure. This differs from previously reported gas separation membranes based on the TR of HAB-6FDA [17,18], in that the non-TR PI segment is used to alter gas separation properties rather than varying the diamine or anhydride of the TR polymer. A series of poly(benzoxazole-co-imide) copolymers originating from the precursors HAB-4MPD/6FDA and HAB-FDA-6FDA, for different PBO:PI ratios, are reported here for their gas solubility and gas permeability properties for CO₂, N₂ and CH₄ separation.

2. Experimental

The anhydride precursor, 6FDA, and diamine precursors, HAB, 4MPD and FDA, were purchased from Chriskev Company Inc. (Lenexa, KS, USA). Both the anhydride and diamines were heated under vacuum to prepare them for polymerisation [19]. All solvents were obtained from Sigma Aldrich. Homo-polyimides and random copolymers were synthesised by a two-step polycondensation method with thermal imidization in solution, following standard procedures in *N*-methyl-2-pyrrolidone solvent [20]. The chemical structures of the two random copolymers are shown in Fig. 1.

The polyimides were characterised by ¹H NMR spectroscopy, ATR-FTIR spectroscopy, thermogravimetric analysis and density measurements. ¹H NMR spectra were recorded on a Varian INOVA-500 spectrometer operating at 500 MHz, with deuterated dimethyl sulfoxide or CDCl₃ as the solvent. Ratios of HAB to 4MPD or FDA in

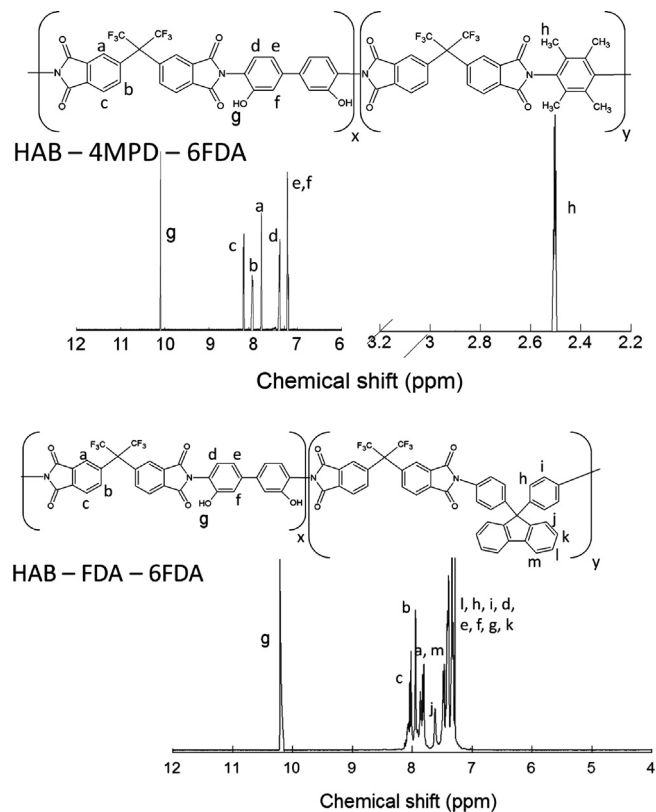


Fig. 1. ¹H NMR spectra of the polyimide copolymer HAB-4MPD-6FDA (1:1) and HAB-FDA-6FDA (1:1) precursors, with CDCl₃ and DMSO-d₆ as the solvent respectively.

the copolymers were determined by the resonance area ratio of hydroxyl group in HAB to the methyl groups in 4MPD or the ortho positioned proton in FDA. ATR-FTIR was performed on a Nexus 470 Fourier-Transform Infrared Spectrometer (Thermo Nicolet). Thermogravimetric analysis (TGA) was performed on a Q500 thermogravimetric analyser (TA Instruments), using a heating rate of 5 °C/min under nitrogen atmosphere. Density of polymer films was determined through standard procedures [21].

Dense polyimide films were prepared from solution by controlled solvent evaporation of a 2.5 wt% polymer in *N,N*-dimethylacetamide. The solvent was slowly evaporated for 4 h at 80 °C, overnight at 100 °C and for 150 °C under vacuum for 3 days. This protocol reflects a balance between heating the sample to a temperature high enough to remove the solvent in as short a period of time as possible, while maintaining the temperature below levels that would initiate the thermal rearrangement process. The final film thickness was on average 50 μm. Polybenzoxazole or poly(benzoxazole-co-imide) films were prepared from their polyimide precursor films by thermal treatment at the target temperature of 450 °C for 1 h under nitrogen atmosphere in a tubular furnace (Carbolite, Model HZS 12/600/301 or Ceramic Engineering Australia). Films of ~13 cm² in area were placed between two ceramic plates separated by a stainless steel washer. This enabled the films to contract during TR but not curl. The target temperature was reached at a heating rate of 5 °C/min. The films were allowed to cool back to ambient temperature overnight, at a cooling rate no greater than 10 °C/min. The loss of weight after thermal treatment indicated 80–85% conversion of the polyimide membrane films.

Gas sorption measurements of CO₂, CH₄ and N₂ in the copolyimide and poly(benzoxazole-co-imide) films were undertaken on a Gravimetric sorption analyser (VTI Instruments) operating at 35 °C and for gas pressures ranging from 0 to 20 bar, under standard

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