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Polybenzoxazole (PBO)-based gas separation membranes thermally derived from blends of *Ortho*-functional polyimide and polyamide precursors

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ABSTRACT

This study investigates the physical properties and gas separation performance of a series of PBO-based membranes derived from thermal conversion of blends containing *ortho*-OH polyamide (PHA) and polyimide (API) precursors. Homogeneous films were obtained in varying PHA/API molar ratios before and after thermal conversion, indicating good compatibility between the two precursors and resulting PBOs. This study reveals that PBO conversion efficiency, fractional free volume and gas transport properties of the resulting PBO-based blend films show an unexpected non-linear dependence on the blend composition (i.e., PHA/API ratio), due to an interplay between API thermal rearrangement (TR) process and PHA cyclodehydration process. Particularly, the B11 blend membrane, containing API and PHA in 1:1 M ratio, showed an optimal combination of gas separation performance and mechanical robustness, while the B31 blend (PHA:API = 3:1) showed little degradation of separation performance relative to both constituent polymers. This is possibly because of the localization of the excess PHA fraction that discourages the formation of inter-connected diffusive transport pathways. In summary, physical blending of API and PHA precursors at an optimal composition is demonstrated to be a simple yet instrumental approach to mitigate the mechanical deterioration issue of API-TR process while greatly improving the separation performance of the PBOs derived from the PHA cyclodehydration process.

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1. Introduction

Polybenzoxazole (PBO)-based membranes obtained by a solid-state, high-temperature thermal rearrangement (TR) reaction of *o*-hydroxy aromatic polyimide (API) precursors are widely known for their superior gas separation performance and exceptional resistance to plasticization [1–9]. However, the TR process of API to PBO conversion requires high temperature (typically > 400 °C), which tends to cause collateral thermal degradation, leading to mechanical weakening of the resultant TR membranes. Moreover, the high treatment temperature limits the choice of membrane support materials when incorporating TR polymers into gas separation membrane modules such as hollow fibers. As such, a major research interest of advancing the practical implementation of TR membranes focuses on lowering the conversion temperature by using different precursors or using copolymer/blend approaches to improve the mechanical properties of the resulting TR membranes. For example, Jo et al. studied a copolymer with both TR-able and non-TRable units and reported improvements in the mechanical strength of resulting copolymer films [10]. Scholes et al. investigated the properties of blends of a TR polymer with a non-TR polymer and found a significant improvement in mechanical strength of the blends, with a slight drop in the permeation performance [11]. In particular, preparing PBO membranes via solid-state thermal cyclodehydration of poly(hydroxyamide) (PHA) precursors seems to be potentially useful for lowering the conversion temperature [8,9,12–14]. Multiple studies, including ours, showed that the temperature required for full PBO conversion from a PHA precursor is at least 100 °C lower than that of the TR process of a API counterpart [9,13,15]. However, PHA-derived PBO membranes exibited inferior gas separation performance compared to API-derived TR polymers, although they are more mechanically robust due to their relatively lower conversion temperatures [8,14–16]. These findings stimulated further research into viable approaches that are able to combine the advantages of API-TR process (i.e., superior gas separation performance) with PHA cyclodehydration (i.e., low conversion temperature)

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[10,11,17]. Wang et al. reported a copolymer containing thermally convertible API and PHA units which demonstrated the possibility of selective conversion by varying the conversion temperature to tailor the permeation properties [17]. However, there are no studies on how these two PBO-forming routes interplay when a physical blend of both thermally convertible precursors undergoes thermal conversion reaction under different conditions, which is the focus of the present study.

6F-based precursor systems, i.e., 6FAP-6FDA-API and 6FAP-6FC-PHA precursors (shown in Fig. 1), are considered for this work, since they are the most studied precursors for thermal conversion to PBO-based membranes [10,12,14,16,18]. Additionally, these two precursors have fairly similar structures. After thermal conversion reactions, the final PBO polymers are very comparable in their backbone structures. This structural similarity ensures homogeneous blends can be obtained before and after thermal conversion.

For polymer blends, a linear relation between the logarithms of gas permeabilities *P* has been empirically established [19,20].

$$\ln P_{blend} = \phi_1 \ln P_1 + \phi_2 \ln P_2 \tag{1}$$

where ϕ_i and P_i are the volume fractions and permeabilities of each component, respectively. However, the properties of a polymer blend can deviate from Eq. (1) when strong interactions between the constituents exist in the blend. In the specific case of API and PHA precursor blends, there are polar hydroxyl, carbonyl and amide groups included in the polymer backbone, all of which have a strong tendency to form robust hydrogen bonds, introducing localized interactions, especially between amide and carbonyl groups. These interactions may cause deviations from Eq. (1) when the strong localized interactions are present in the precursor blends [21]. Additionally, the solid-state thermal conversion efficiency of API and PHA components to PBOs is expected to be affected by the interactions mentioned above, since the local chain dynamics are completely different from that in their pure states. Moreover, these inter-chain interactions are expected to be sensitive to the composition of the blends as these localized interactions are additive in nature. As such, this study focuses on investigating the interplay between the API-TR process and the PHA cyclodehydration process in a series of physical mixtures of API and PHA precursors with systematically varied composition. Specifically, structural changes during thermal conversion including chain packing, fractional free volume, and density are comprehensively evaluated for both the precursor blends and the films converted at different temperatures. The gas transport properties of the precursor blends and resulting converted films are correlated with these structural changes to provide insights into the effects of mixing.

2. Experimental

2.1. Chemical reagents and precursors synthesis

Monomer grade aromatic diamine 2,2-bis(3-amino-4-hydroxy phenyl)hexafluoropropane (6FAP, ≥98.5%) and aromatic dianhydride 2,2′-bis(3,4-dicarboxy-phenyl)hexafluoropropane dianhydride (6FDA, >99%) were purchased from Akron Polymer Systems. Both monomers were dried at 65 °C and 170 °C respectively under vacuum to remove any residual moisture before polymerization. Aromatic diacid 4,4′-(hexafluoropropane-2,2-diyl) dibenzoic acid (6FAC, ≥98%) was purchased from TCI Chemicals and used as received. 4,4′-(hexafluoropropane-2,2-diyl)dibenzoyl chloride (6FC) monomer was prepared by the chlorination of 6FAC using thionyl chloride, as described in the Section S1 in supporting information.

The solvent used for polymer synthesis was anhydrous N-methylpyrrolidone (NMP, ≥99.5%), which was purchased from Sigma-Aldrich and used as received. Anhydrous *o*-dichlorobenzene (*o*-DCB), used as the azeotroping reagent, was purchased from Sigma-Aldrich and used as received. Thionyl chloride was purchased from Sigma Aldrich. Anhydrous Pyridine (≥99.8%) and methanol were purchased from EMD Chemicals, and were used as received. Dimethyl formamide (DMF) was purchased from Alfa Aesar and used as received.

6FAP-6FDA-API polyimide precursor was synthesized by the conventional two-step solution imidization method [15], as described in the Section S2 in supporting information. 6FAP-6FC-PHA polyamide precursor was synthesized via silylation-assisted polycondensation reaction of 6FAP with 6FC prepared via chlorination of 6FAC, as described in our previous work [15] as well as in Section S3 in the supporting information.

2.2. Membrane fabrication and controlled thermal conversion

Thin films of blends were prepared via solution casting with varying composition. In a typical case, a mixture of API and PHA precursors in predetermined amounts was dissolved in NMP, making up 6–7% w/v solution. The solvent was slowly removed

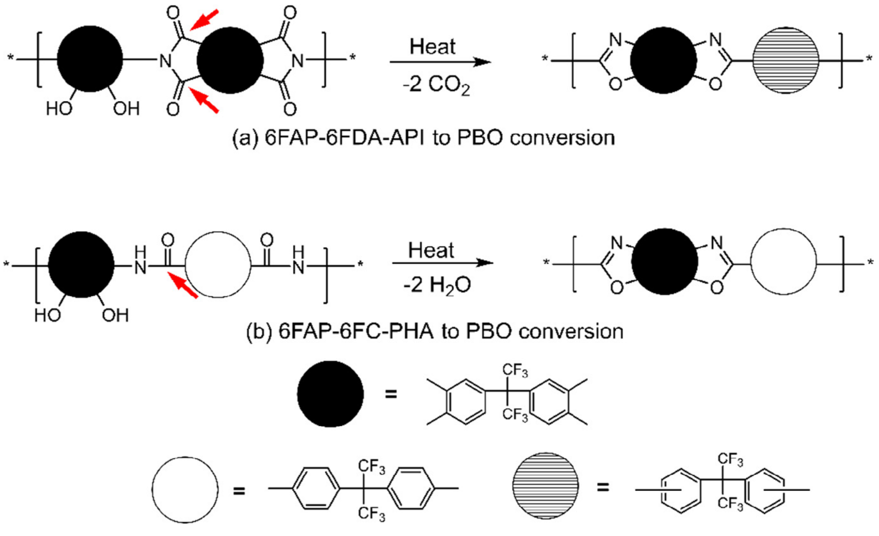

Fig. 1. Thermal conversion of (a) 6FAP-6FDA-API and (b) 6FAP-6FC-PHA precursors to corresponding PBOs.

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