

Preparation and properties of polybenzoxazole-based gas separation membranes: A comparative study between thermal rearrangement (TR) of poly(hydroxyimide) and thermal cyclodehydration of poly(hydroxyamide)



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ABSTRACT

This comparative study focuses on the cyclodehydration reaction of poly(hydroxyamide)s (PHAs) and the thermal rearrangement (TR) reaction of aromatic poly(hydroxyimide)s (APIs) to produce polybenzoxazoles (PBOs) for application as gas separation membranes. Systematic comparisons between the two routes showed that PHA cyclodehydration can produce fully converted PBO membranes at a temperature more than 100 °C lower than the API-TR route. Gas separation performance of PHA–PBOs is comparable to API-TR polymers, and PHA–PBOs are considerably more mechanically robust. More importantly, PBO films can be produced equally well in both air and inert atmospheres via the PHA cyclodehydration route. The PHA–PBOs formed in air have statistically the same physical and transport properties as those formed in N₂. The present study provides fundamental information regarding the PHA-to-PBO cyclodehydration process.

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1. Introduction

Use of polymer membranes for gas separations, as opposed to the existing cryogenic distillation or solvent absorption processes, have a number of potential advantages [1–3], such as lower production cost, lower energy consumption [1,4], simple operation, and compact setup with small footprints [3,5]. However, despite these advantages over conventional separation technologies, many commercial polymer membranes suffer from insufficient separation efficiency and/or productivity as well as other issues, such as plasticization and stability to aggressive feed conditions [6]. The development of mechanically and chemically robust polymer membranes that surpass the permeability-selectivity tradeoff has been a key research focus in membrane materials research.

Among the many new polymeric materials considered for gas separation membranes, some thermally rearranged (TR) polymer membranes have favorable permeability and selectivity

combinations, as well as excellent resistance to plasticization [1,7,8]. As the name suggests, TR polymers, which have complicated polybenzoxazole (PBO) structures, are typically formed via thermal treatment of aromatic polyimide precursors (APIs) with *ortho*-positioned hydroxyl groups, as shown in Fig. 1(a). Despite the interesting separation performance of TR polymers, two significant challenges associated with the API-TR route may complicate implementation of TR membranes in practical application. First, full conversion to high performance TR polymers can only be achieved at very high temperatures, typically >400 °C [1,9,10]. The best performing TR polymers reported in the literature were all prepared at 450 °C [11,12], which often adversely affects mechanical properties, and this observation has stimulated research into modifying rigid polyimide-based structures with more flexible units on the polymer backbone [13]. However, TR polymers achieve high separation performance due to diffusivity selectivity [14], so more flexible backbones may work against high diffusion selectivity. Another approach to improve mechanical properties has been to form PBOs from poly(hydroxyamide) (PHA) precursors, which undergo cyclodehydration reactions at lower temperatures

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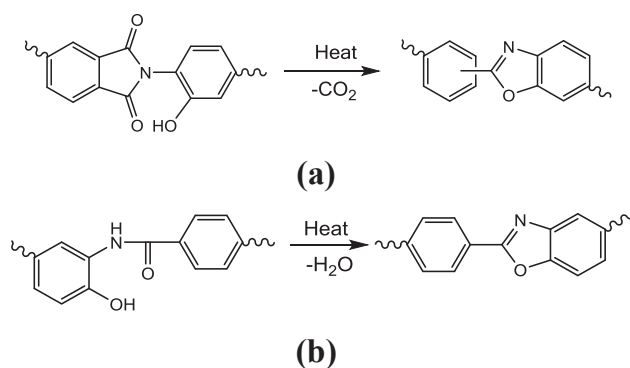


Fig. 1. (a) API-TR route; (b) PHA cyclodehydration route to form PBOs.

to form PBOs by releasing two H_2O molecules per repeat unit, as shown in Fig. 1(b) [11,12]. The second major challenge associated with the API-TR route is the thermo-oxidative stability of precursors when exposed to high TR temperatures, which requires strict inert atmosphere for successful TR process. It was proposed that the presence of oxygen generates free radicals for polyimides at elevated temperatures, and this type of chemistry can substantially degrade mechanical properties and the efficiency of the TR conversion [15]. Interestingly, cyclodehydration of PHAs appears to have good oxidative stability that does not require inert atmosphere [15]. As such, formation of PBO membranes via PHA cyclodehydration seems to be a very promising route to address the challenges faced by the API-TR route, which also defines the research scope of this paper.

A few recent reports from several research groups have investigated the physical and transport properties of PBO membranes prepared via the PHA cyclodehydration route using various PHA precursors [11,12,15–17]. Studies by Calle et al. [11] demonstrated that PHA thermally treated in argon had essentially the same PBO structure as those prepared from polyhydroxyimide (API) precursors. Han et al. [12] reported a series of PHA–PBO systems showing excellent separation properties and ascribed the performance to the optimized cavity size distribution in the thermally converted films. In this study, the PHA-to-PBO conversion temperature reportedly began at 230–250 °C, which is significantly lower than the temperature needed for the API analogs. More recently, Smith et al. reported solid-state NMR studies that clearly confirmed the formation of PBOs via cyclodehydration of PHAs [17]. Although comparable systems were reported in these studies, they did not focus on thermo-oxidative stability (atmosphere effect) or transport properties for CO_2/CH_4 and O_2/N_2 for partially converted PHA–PBO membranes. Studies by Wang and Chung [16] revealed that PHA membranes treated in the range of 300–425 °C had similar PBO conversion, but enhanced separation performance was only obtained for higher temperature treatments. The same group later reported that nearly identical PBO structure and gas permeabilities were obtained for PHA films converted at 300 °C and 425 °C, regardless of air or N_2 environment [15]. However, their work investigated API and PHA precursors with different chemical compositions (e.g., a biphenyl diamine for the API series versus a hexafluoroisopropylidene-based diamine for the PHA series). The nucleophilicity of the hydroxyl group within the PHA or API has been shown to strongly effect thermal reactivity for these systems [18], so modification of the diamine makes direct structure/property comparisons difficult. Moreover, the final TR polymer structures are different, not only from the standpoint of meta/para backbone connectivity [17], but also from the difference in the oxazole heterocycle location in the polymer backbone. Therefore,

systematic comparative studies between the PHA–PBO and API-TR routes have yet to be done on comparable API and PHA precursor structures to explore the potential of PHA cyclodehydration as an alternative energy-efficient route to produce high performance PBO-based gas separation membranes. Moreover, systematic studies investigating the influence of the composition of the contiguous atmosphere on the PHA cyclodehydration process may provide insights into the practicality of this approach.

In this work, we compare API thermal rearrangement and PHA cyclodehydration with an emphasis on elucidating the chemical changes that occur during thermal treatment. Additionally, morphological changes are evaluated by comparing transport properties in the PHA cyclodehydration route in both N_2 and air atmospheres. The systems considered are 6FAP-6FDA-API and 6FAP-6FC-PHA precursors, since the TR polymers derived from 6FAP-6FDA-API showed the most promising separation performance [7]. Moreover, these two precursors are very comparable in their chemical structures, which should produce nearly identical PBO structures upon thermal treatment. A general comparison of these two routes is shown in Table 1.

2. Experimental

2.1. Materials

Aromatic diamine 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FAP, $\geq 98.5\%$) and aromatic dianhydride 2,2'-bis(3,4-dicarboxy-phenyl) hexafluoropropane dianhydride (6FDA, $\geq 99\%$), purchased from Akron Polymer Systems, were dried under vacuum overnight at 65 °C and 170 °C, respectively. Aromatic diacid 2,2'-bis(4-carboxyphenyl)hexafluoropropane (6FAC, $\geq 98\%$) was purchased from TCI Chemicals and used as received. Anhydrous N-methylpyrrolidone (NMP, $\geq 98\%$), trimethylsilylchloride (TMSCl, $\geq 98\%$), thionyl chloride ($\geq 99\%$), pyridine (anhydrous, $\geq 99.8\%$) and *o*-dichlorobenzene (*o*-DCB, $\geq 99\%$) were purchased from Sigma Aldrich and used as received. Methanol and hexanes were purchased from BDH (VWR) and EMD Chemicals, respectively.

2.2. Synthesis of 6FAP-6FDA API precursor

API precursor was synthesized from the 6FAP diamine and 6FDA dianhydride via polycondensation, following the conventional two-step solution imidization. Since 6FAP-6FDA polyimide synthesis is known in the literature, the synthesis details are provided in the Supporting information (Scheme S1). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 7.04–7.06 (d, $J = 8.30$ Hz, 2H), 7.18–7.19 (d, $J = 6.60$ Hz, 2H), 7.47 (s, 2H), 7.71 (s, 2H), 7.91–7.92 (d, $J = 5.10$ Hz, 2H), 8.10–8.11 (d, $J = 7.55$ Hz, 2H), 10.39 (s, 2H). ATR-FTIR (membrane, ν , cm^{-1}): 3393 (hydroxy –OH str), 1788 (imide sym C=O str), 1720 (imide asym C=O str), 1300 (imide –C–N), 724 (imide ring deformation).

2.3. Synthesis of 6FAP-6FC-PHA precursor

2.3.1. Monomer 2,2'-bis(4-carboxyphenyl)hexafluoropropane (6FC) synthesis

The diacid chloride monomer, 6FC, used for the synthesis of the poly(hydroxy-amide) precursor was synthesized by the chlorination of diacid 2,2'-bis(4-carboxyphenyl)hexafluoropropane (6FAC) with thionyl chloride, following a previously reported procedure [19]. 6FAC was treated in 35% w/v solution in thionyl chloride for 14 h at 90 °C in a single neck round bottom flask equipped with a magnetic stirrer and reflux condenser. The pale-yellow product obtained was dried by evaporating the thionyl chloride in a rotovap, followed by vacuum drying at about 65 °C for 6 h. The dry product was purified by recrystallization using hexanes. The final 6FC

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