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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 N_2 . 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 orthopositioned 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 CO₂/CH₄ and O₂/N₂ 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 N₂ 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 N₂ and air atmospheres. The systems considered are 6FAP-6FDA-API and 6FAP-6FDA-API aprecursors, 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 Nmethylpyrrolidone (NMP, \geq 98%), trimethylsilylchloride (TMSC, \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 twostep 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, DMSOd₆)): 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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Comparison of 6FAP-6FDA-API TR route and 6FAP-6FC-PHA cyclodehydration.

	API-TR route	PHA cyclodehydration route
Thermal conversion reaction	\cdot \downarrow	$\cdot \underbrace{+}_{HO} \underbrace{+}_{CF_3} \underbrace{+}_{OH} \underbrace{+}_{OH} \underbrace{+}_{CF_3} \underbrace{+}_{CF_3} \underbrace{+}_{CF_3} \underbrace{+}_{Heat} \underbrace{+}_{Heat} \underbrace{+}_{Heat} \underbrace{+}_{CF_3} \underbrace{+}_{CF$
	$\downarrow -2CO_2$ $CF_3 \qquad N \qquad CF_3 \qquad CF_3 \qquad \cdots$	$-2H_2O$ $-2H_2O$ $-2H_2O$ $-2H_2O$
	Red arrows indicate possible reactive sites	
Similarity	Both are soluble precursors that form PBOs upon thermal treatment in	the solid state
Conversion temperature	>400 °C for full conversion	<350 °C for full conversion
Conversion atmosphere	Strict inert atmosphere or vacuum	Feasible in both air and inert atmosphere
Weight loss	11.4% (release of 2 CO ₂ per repeat unit)	5% (release of 2H ₂ O per repeat unit)
PBO Structure	Mixed PBO structures with meta-, para-linkage and cross-linked	Most likely well-defined linear PBO structure determined by the PHA
	structures	linkage
Mechanical properties	Very brittle and fragile at full PBO conversion due to possible thermal	More robust due to lower temperature treatment
	degradation	
Transport properties	API-TR polymers are highly permeable and selective	Less permeable and selective than API-TR polymers

product was vacuum dried at 65 °C overnight (yield = 83%). ¹H NMR (500 MHz, DMSO- d_6): δ 7.47–7.48 (d, J = 8.30 Hz, 4H), 8.04–8.06 (d, J = 8.55 Hz, 4H).

2.3.2. Synthesis of 6FAP-6FC PHA precursor

The 6FAP-6FC PHA precursor was synthesized by the silylation method (Scheme 1). The silylation route was used because it has been shown to give a better yield and high molecular weight of the PHA [20,21]. In a typical synthesis, the 6FAP diamine (2.5035 g, 6.8 mmol) was first dissolved in 17 mL anhydrous NMP in a flame dried round-bottom flask equipped with nitrogen purge and a mechanical stirrer. After the complete dissolution of diamine, TMSC (3.5 mL, 27.6 mmol) was added to the solution to form silylated diamine (silylated-6FAP). After about 10 min, pyridine (2.4 mL, 29.7 mmol) was added to the solution to neutralize the released acid. The solution was stirred at room temperature for 2 h to ensure



Scheme 1. Polycondensation between silylated-6FAP and 6FC to produce 6FAP-6FC-PHA.

complete silvlation. The silvlated-6FAP solution was then icecooled to 0 °C before diacid chloride (6FC) (2.9333 g, 6.8 mmol) was added all at once, followed by the washing of solid 6FC with 4.8 mL anhydrous NMP, giving a solid concentration of \sim 25% (w/v) and adding pyridine (1.2 mL, 14.8 mmol) to neutralize the acid produced in the polycondensation reaction. The reaction was stirred and maintained at 0 °C for about 2 h before the bath gradually warmed to room temperature. The solution was stirred overnight at room temperature until a viscous solution of silylated polyamide was formed. The pale-yellow silylated polymer solution was precipitated in fibrous form using 800 mL of stirring 1:1 (v/v)water-methanol solvent, and washed repeatedly with pure methanol to convert the silylated groups into hydroxyl groups producing 6FAP-6FC-PHA. The PHA polymer collected via vacuum filtration was dried under vacuum at 165 °C overnight. ¹H NMR (500 MHz, DMSO- d_6): δ 7.00 (s, 4H), 7.49–7.50 (d, J = 7.8 Hz, 2H), 7.87 (s, 4H), 8.05–8.07 (d, J = 8.55 Hz, 4H), 9.72 (s, 2H), 10.33 (s, 2H).

2.4. Thermal conversion of the precursor films

2.4.1. Fabrication of precursor films

The API and PHA precursor films were solution cast by dissolving the polymers in NMP to make a 6–7% w/v solution (12–14 mL). The resulting solution was filtered using a 0.45 μ m syringe filter to remove any impurities and dust. The filtered solution was evenly spread on a leveled dry glass plate of 120 mm × 120 mm to completely cover the plate. The solution was first dried under an infrared lamp to remove most of the solvent and form a film (roughly 70 °C for 15–20 h). To remove residual solvent, the film was further dried under vacuum at 195 °C overnight. The film thickness was about 20–40 μ m, which can be adjusted by varying the solution concentration. Thermogravimetric analysis was used to confirm complete solvent removal.

2.4.2. Controlled thermal conversion of the precursor films

The poly(hydroxyimide) precursor (API) was converted via the known TR process [9,22]. The poly(hydroxyamide) precursor (PHA) was converted via thermal cyclodehydration. The precursor-to-PBO conversion in both cases was controlled by treating the films at different temperatures and/or for different amounts of time.

The precursor films (cut into small pieces in about 60 mm \times 60 mm size) were sandwiched between two porous ceramic plates and thermally treated in a preheated Thermo-Scientific muffle furnace at a desired temperature for a

predetermined amount of time in either nitrogen or air. After thermal treatment, the films were quenched at room temperature. For the inert atmosphere conversion, the furnace was purged with nitrogen gas for at least 15 min before the heat treatment started. High flow rate N₂ purging was maintained throughout the heating process to ensure an inert environment. For air atmosphere, no gas was passed through the furnace, but a small circular opening (about 25 mm) was left open at the top of the furnace.

The heating temperature and thermal treatment times were carefully chosen to prevent or minimize thermal degradation of the films. Specifically, the API films were treated at either 300 °C, 350 °C or 400 °C for 2 h, or 450 °C for 30 min, all under N₂ atmosphere, to obtain TR films with varying PBO conversions. The resulting TR films are referred to as API-TR-300, API-TR-350, API-TR-400 and API-TR-450, respectively. Correspondingly, the PHA films were treated at 250 °C, 300 °C or 350 °C for 2 h in N₂ atmosphere to produce PHA-PBO-250-N, PHA-PBO-300-N, and PHA-PBO-350-N. The PHA precursor films were also treated following the same temperature/time protocols in air giving a second series of PHA-PBO-250-A, PHA-PBO-300-A, and PHA-PBO-350-A.

The weight loss of each film during the thermal conversion was monitored and used to estimate the degree of conversion towards the final TR polymers or PBOs by the following expression:

Degree of conversion
$$= \frac{\text{Observed weight loss}}{\text{Theoretical weight loss}}$$
 (1)

where the 'Observed weight loss' is calculated by taking the difference between the film weight before and after thermal treatment, and the 'Theoretical weight loss' is the weight loss expected if the precursor film is fully converted to its corresponding TR polymer or PBO. For 6FAP-6FDA-API precursor, the theoretical weight loss is 11.4% (2 molecules of CO₂ for each repeat unit); for 6FAP-6FC-PHA precursor, the theoretical weight loss is 5.0% (2 molecules of H₂O for each repeat unit). If the observed fractional weight loss was higher than the ideal fractional weight loss, 100% conversion was assumed, and excess weight loss was attributed to thermal degradation.

2.5. Characterization

Proton nuclear magnetic resonance (¹H NMR) spectroscopy tests were conducted on a 500 MHz Bruker NMR spectrometer with deuterated dimethylsulfoxide (DMSO- d_6) as the solvent.

Fourier transform infrared spectroscopy (FTIR) tests were performed on polymer thin films using a JASCO FTIR-6300 spectrometer with ATR (attenuated total reflection) attachment in the range of 650–4000 cm⁻¹ wavenumber with a resolution of 2 cm⁻¹.

Thermogravimetric analysis (TGA) was performed on a TA Q500 (TA instruments) system. The film samples were analyzed for a temperature range of 25–750 °C at a heating rate of 10 °C/min in nitrogen and/or air atmospheres, with 40 mL/min flow rate of the corresponding gases.

Differential scanning calorimetry (DSC) measurements were performed on a DSC Q2000 (TA Instruments) for the temperature range of 25–400 °C with a heating rate of 10 °C/min. All the polymer samples were examined in film state, which were freshly dried in vacuum oven at 180 °C just before the DSC measurements to ensure the same thermal history and solvent free status. The first heating cycle was reported.

Densities of all film samples were determined from Archimedes' principle at room temperature using a Mettler Toledo analytical balance (ML204) with a density measurement kit (ML-DNY-43). Water was used as the buoyant liquid because all samples in this study exhibited negligible water uptake over the time scale of the experiment. Density for each film was measured at least three times, and the average value is reported.

Fractional free volume (FFV) for all the polymer films was estimated using a group contribution method [23]. The specific occupied volume of a polymer, V_{o} , is estimated from the following formula using Bondi's group contribution method:

$$V_0 = 1.3 \sum V_k \tag{2}$$

where V_k is the van der Waals volume of the individual groups in polymer backbone structure taken from Park and Paul's work [24]. The final FFV was estimated as follows:

$$FFV = \frac{V - V_o}{V} \tag{3}$$

where *V* is the specific volume of the polymer film determined from density measurements.

For partially converted polymers where both the precursor and PBO are present, the effective occupied volume was calculated by taking the partial sum of the occupied volumes of the precursor and PBO. Thus, for conversion, x, of a polymer precursor with characteristic occupied volume, $V_{o,p}$, and PBO-based polymer with characteristic occupied volume, $V_{o,t}$, the effective occupied volume was estimated as follows:

$$V_{o} = xV_{o,t} + (1 - x)V_{o,p}$$
(4)

For the samples where the actual weight losses observed were higher than theoretical values, the conversion was taken as 100% for calculating effective occupied volume.

Wide-angle X-ray diffraction (WAXD) measurements were performed in reflection mode using a Bruker D8 Advance Davinci diffractometer to determine *d*-spacing values for all samples. The WAXD measurements were performed at room temperature for the range $2\theta = 5-45^{\circ}$. The scan speed and step size were 5 s per step and 0.02° per step, respectively. The average *d*-spacing was calculated using Bragg's equation:

$$d = \frac{\lambda}{2\sin\theta} \tag{5}$$

where λ is the wavelength of the X-ray used (1.5418 Å, Cu K α radiation source).

2.6. Pure gas permeation measurement

The pure gas permeabilities (P) of five gases (H₂, CH₄, N₂, O₂ and CO₂) were measured via constant volume, variable pressure method [22,25,26] at 35 °C with upstream pressure ranging from 3 to 17 atm. All measurements were made using UHP grade of gases from Airgas (Radnor, PA, USA) and are listed above in the order of testing. The polymers were loaded into the permeation cell and evacuated in situ for at least 24 h to degas the films prior to testing. A test gas was then introduced to the upstream side of the film, and the pressure rise into a known downstream volume was measured as a function of time. The downstream pressure was kept below 10 Torr. The linear slope of the pressure rise versus time, after steady-state was established, provides the permeation rates of permeating gases, which were used to calculate gas permeability coefficients [25]. The ideal selectivity (α) for a certain gas pair was determined by taking the ratio of the two permeabilities. For example, the ideal selectivity of CO_2 over CH_4 is taken as: $\alpha(CO_2)$ $CH_4) = P(CO_2)/P(CH_4).$

3. Results and discussions

3.1. Synthesis and characterization of API and PHA precursors

For comparison, a poly(hydroxyimide) (6FAP-6FDA-API) and a polv(hvdroxvamide) (6FAP-6FC-PHA) were considered for this work (cf., Table 1). The same *ortho*-functional dihydroxy diamine. 6FAP, was used for the synthesis of both precursors, enabling the thermal conversion of the precursors to corresponding PBOs via the API TR process or PHA cyclodehydration. The dianhydride (6FDA) and the diacid chloride (6FC) used for the synthesis of the respective precursors share the same $-C(CF_3)_2$ bridge structure. Essentially, these two precursors differ only in the imide or amide linkage, which upon thermal conversion, are expected to produce similar PBO structures. However, the two reactions, although following similar nucleophilic attack mechanism, involve completely different intermediate structures resulting in different conversion kinetics. The comparable precursor structures allow studying the influence of different PBO conversion mechanisms on the thermal conversion process and on the resulting PBO properties.

The -OH containing 6FAP-6FDA-API precursor was synthesized using conventional two-step solution imidization, and the 6FAP-6FC-PHA precursor was synthesized using the silvlation method described in the Experimental section. The fully imidized structure of 6FAP-6FDA polyimide was confirmed via the absence of poly(amic acid) characteristic bands in the FTIR spectrum (Fig. S1) and the integration of the peaks in ¹H NMR spectrum (Fig. S2). A similar structural analysis was done for 6FAP-6FC-PHA formed via the silvlation method. The complete deprotection of the silvlated polyamide to poly(hydroxyamide) was confirmed by observing the presence of an -OH group band and the absence of the trimethylsilane bands in both ATR-FTIR (Fig. S3) and ¹H NMR spectra (Fig. S4). Therefore, the protocol of methanol precipitation and washing of the silvlated polyamide was efficient in converting the silylated group to the desired -OH group. Tough and ductile films were solution cast from both precursors, indicating high molecular weight polymers were produced.

As demonstrated in previous studies [12,17,27,28], PHAs undergo cyclodehydration (release of two H₂O molecules per repeat unit) upon thermal treatment, leading to a linear PBO structure. This cyclodehydration process manifests itself as a two-stage weight loss during a TGA temperature ramp, similar to that observed in the TR process (i.e., decarboxylation) of hydroxyl-containing polyimides [9,10,29–34]. A TGA temperature ramp was conducted to assess the process of thermal cyclodehydration of the 6FAP-6FC-PHA precursor and the profile is compared with the



Scheme 2. Intermediates formed in (a) PHA cyclodehydration and (b) API-TR processes [8] (high energy ring structures are highlighted in red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

6FAP-6FDA-API precursor in Fig. 2. The purpose is: (i) to estimate the thermal conversion temperature range of the 6FAP-6FC-PHA precursor, and (ii) to investigate if the cyclodehydration of PHA precursor can occur in an air atmosphere.

As mentioned previously, the ortho-hydroxyl API precursors cannot thermally rearrange to PBOs in air, most likely because free radicals generated during the TR process may be inhibited by O₂ in the air, thereby preventing the conversion of such APIs to PBOs [9]. This finding was verified in this study on the 6FAP-6FDA-API precursor by conducting TGA scans in air and inert (N₂) atmosphere, as shown in Fig. 2(a). The thermogram for the TGA scan in nitrogen shows the expected two-stage weight loss profile with the first stage of weight loss (from ~350 °C to 450 °C) signifying the thermal rearrangement and the second stage (~500 °C) ascribed to primary thermal degradation of PBOs formed during the TR reaction. However, when thermally treated in air, only a single weight loss, due to thermal degradation, was observed for the 6FAP-6FDA-API precursor, confirming that the imide-to-benzoxazole TR conversion only occurs under inert atmosphere, as reported previously [22]. In contrast, 6FAP-6FC-PHA precursors (Fig. 2(b)) treated in air and an inert atmosphere show very similar TGA profiles, featuring two stages of weight loss, suggesting that the cyclodehydration of hydroxyamide to benzoxazole occurs efficiently in both inert and air atmospheres.

Conversion of PHA to PBO in both N_2 and air atmospheres can occur due to the nucleophilic attack mechanism of cyclodehydration, whereby a meta-stable planar ring intermediate is formed (Scheme 2a). This meta-stable intermediate is likely not



Fig. 2. TGA weight loss and weight loss derivative curves for (a) 6FAP-6FDA-API in air (dashed lines) and in N₂ (solid lines) and (b) 6FAP-6FC-PHA in air (dashed lines) and in N₂ (solid lines). The dotted horizontal lines labeled as "Theoretical" indicate the weight loss expected after full conversion of the precursor to the corresponding PBO. The weight loss derivatives of the samples are shown (air – dashed lines, N₂ – solid lines) to highlight the PBO conversion and thermal degradation regions.



Fig. 3. DSC curve of 6FAP-6FC-PHA demonstrating the endothermic cyclodehydration.

sensitive to the attack by oxygen. The API-TR process involves a highly unstable, contorted non-planar intermediate structure [8], which might prevent the PBO conversion of API in air atmosphere (Scheme 2b). The observed first stage weight loss in both atmospheres closely matches the expected weight loss for PHA thermal cyclodehydration (release of two H₂O molecules per repeat unit). Additionally, the second stage weight loss, due to degradation, starts at about 500 °C for both runs, suggesting that the same PBO product was likely formed under both reaction atmospheres. This atmosphere effect stimulates further comparisons between PBOs formed under different atmosphere from the PHA precursor, which are discussed in detail in Section 3.3. Regarding the thermal conversion temperature, it is evident that the PHA-to-PBO conversion via cyclodehydration starts at a temperature of about 250 °C and finishes at approximately 350 °C. Compared to the thermal conversion temperature for the API-TR process, the temperatures required for PHA cyclodehydration are significantly lower by approximately 100 °C for both N₂ and air atmospheres.

DSC measurements were conducted on the 6FAP-6FC-PHA precursor to track the glass transition temperature and the cyclodehydration reaction, as shown in Fig. 3. The broad peak between 250 and 350 °C corresponds to the endothermic cyclodehydration of PHA, which is in agreement with TGA observations. There is no perceivable glass transition temperature (T_g) observed for the 6FAP-6FC-PHA precursor, which most likely overlaps with the broad endothermic cyclodehydration peak. In other words, the thermal cyclodehydration of PHA can occur at a temperature below its T_g , which is in remarkable contrast to API-TR route, where the efficient TR temperature was shown to be strongly dependent on the T_g of the API precursor, and TR-PBO conversion is unlikely to occur below the T_g of the API precursor considering it is a solid-state reaction [9,10]. This significant difference may be ascribed to a much lower activation energy for hydroxyamide-to-benzoxazole conversion than that for hydroxyimide-to-benzoxazole conversion, which is likely related to the energy barrier associated with the stability of the ring intermediates formed during the conversion reaction as shown in Scheme 2.

3.2. Comparison of PHA cyclodehydration (N_2) route and API-TR route to PBOs

3.2.1. Feasibility and efficiency of PHA route compared to API route

Thermal treatment of PHA and API precursors results in solidstate conversion to form PBOs as the final product (cf., Table 1). The API-TR reaction starts with the *o*-hydroxy group attacking one of the two imide carbonyl groups to form a five member ring intermediate, and subsequent decarboxylation produces the final benzoxazole structure. Since the API structure has two probable reaction sites, the final TR polymers are expected to be a mixture of para- and meta-PBO isomers as well as cross-linked structures due to possible intermolecular reactions [17]. As a result, API-TR polymers have very complicated structures featuring highly non-linear rigid backbones, large inter-chain gaps, and chemical crosslinking, which leads to high fractional free volume and in turn, high gas permeabilities. On the other hand, the PHA precursor has only one site available for nucleophilic attack, so a completely para-PBO structure is obtained. The control of the resulting PBO structure is useful for fundamental structure-property studies and property tunability because the geometry of the benzoxazole link can be accurately controlled by the monomer structures in the PHA synthesis. For example, using either meta or para diacid chlorides will produce correspondingly meta or para linked PHAs, and consequently meta or para linked PBOs. In this sense, the chemical conformation of PBO obtained via the PHA-cyclodehydration route is more predictable than that obtained via the API-TR route, and if designed properly, may allow greater control of the final PBO structures.

ATR-FTIR measurements were performed on the thermally treated samples to follow the evolution of structural change during the thermal conversion, as shown in Fig. 4(a) and (b) for the API and



Fig. 4. FTIR spectra showing the structural changes during (a) TR process of 6FAP-6FDA-API and (b) cyclodehydration of 6FAP-6FC-PHA, both in a N₂ environment. The arrows marked on the spectra are used to indicate the decrease (downward arrows) or increase (upward arrows) in the strength of specific identifying bands corresponding to the different thermal treatments.

Table 2	
Degrees of PBO conversion for each precursor treated at different temperatures with a N_2 atmosphere	

	6FAP-6FDA-API			6FAP-6FC-PHA	6FAP-6FC-PHA		
	Weight loss	observed (%) Degree of conve	ersion (%) ^a Degree of degr	radation (%) ^b Weight loss of	oserved (%) Degree of conv	ersion (%) ^a Degree of degradation (%) ^b	
250 °C	_	_	_	3.5	69	_	
300 °C	3	27	_	7.5	100 ^c	2.5	
350 °C	8.4	74	_	9.1	100 ^c	4.1	
400 °C	9.1	80	_	_	_	_	
450 °C	20	100 ^c	8.6	_	_	_	

^a Degree of conversion for API was calculated based on 11.4% theoretical weight loss; degree of conversion for PHA was calculated based on 5.0% theoretical weight loss.

⁹ Degree of degradation is estimated by the difference between the observed weight loss and the theoretical weight loss.

^c The degree of conversion is assumed to be 100% for calculation simplicity, since the observed weight loss was more than theoretical weight loss.

PHA series, respectively. The cyclodehydration temperatures chosen for the PHA were 250, 300, and 350 °C. The API samples were treated at 300, 350, 400, and 450 $^\circ$ C. In both cases, N₂ was used as the reaction atmosphere. For each sample, the precursor-to-PBO conversion was confirmed by the disappearance of characteristic bands in the precursor spectrum and appearance of the PBO characteristic bands. For the API series shown in Fig. 4(a), even at temperatures as high as 400 °C, the characteristic polyimide precursor bands [3398 cm⁻¹ (-OH), 1784 cm⁻¹ (sym -C=O), 1720 cm^{-1} (asym -C=0) and 1380 cm^{-1} (-C-N)] were still present, indicating incomplete PBO conversion even at 400 °C. On the other hand, for PHA cyclodehydration shown in Fig. 4(b), unambiguous PBO characteristic bands [1554 cm⁻¹ (–C=N), 1479 cm⁻¹ (-C=N) and 1057 cm⁻¹ (-C-O)] are observed even at a treatment temperature of 250 °C, thereby supporting the assertion that the PHA conversion route is more favorable and efficient than the API-TR route. In addition, a very negligible difference in the spectra for the PHA-PBO-300 and PHA-PBO-350 suggests almost complete PHA-to-PBO conversion at 300 °C, which is achieved at much lower temperatures than those required in the API-TR route.

Quantitative estimation of PBO conversion was conducted based on the weight loss observed for each film upon thermal treatment. The degree of conversion for each process can be calculated by taking the ratio of the observed weight loss and the theoretical weight loss as described in the Section 2.4 (Eq. (1)). A comparison of these degrees of precursor-to-PBO conversion in inert medium is shown in Table 2. Based on weight loss measurements, the API precursor did not reach full conversion until 450 °C treatment, while complete PBO conversion was readily obtained for the PHA precursor treated at 300 °C. This trend is consistent with the cyclodehydration of the PHA being more efficient than the API TR route in terms of PBO formation, possibly due to a much lower



Fig. 5. DSC thermograms for the PHA precursor and corresponding PBOs obtained at different temperatures in N_2 .

activation energy of the conversion.

DSC thermograms for all PHA-PBO-N samples are shown in Fig. 5 and compared with that of the PHA precursor. Upon 250 °C treatment, the endothermic cyclodehydration peak became smaller and the peak maximum shifted to a higher temperature, indicating partial conversion of the PHA precursor to more rigid PBO structure. The PHA precursor treated at 300 °C shows an almost negligible peak corresponding to the cyclodehydration reaction, indicating an almost complete conversion of PHA to PBO. The fully converted sample (i.e., PHA-PBO-350-N) shows a T_g of ~330 °C, consistent with high chain rigidity of the resulting PBO. TGA measurements also confirmed that 300 °C treatment of the PHA precursor resulted in almost complete PBO conversion since only one major weight loss stage was observed for PHA-PBO-300-N (Fig. S5 in Supporting information).

3.2.2. Comparison of physical properties of PBO films from the API-TR route and the PHA cyclodehydration route

In the API-TR route, high performance TR polymers are obtained after very high temperature treatment (400–450 °C), which can be fairly close to or even overlap the thermal degradation temperature of the API precursors. As a result, TR polymers are often brittle or mechanically fragile [22,35,36]. In the PHA-to-PBO route, cyclodehydration occurs at a temperature that is significantly lower than the degradation temperature of PHA precursors. Therefore, PBOs formed from the PHA route may have improved mechanical strength. Fig. 6 provides a simple visual comparison of the physical appearance and mechanical robustness between PBO films obtained from these two different routes. As shown, API-TR-450-N is very dark in color, brittle, and fragile, suggesting thermal degradation of the polymer, while the PHA-PBO-350-N film retains not only qualitatively comparable levels of flexibility and ductility as those of the PHA precursor, but also similar color and transparency. Additionally, the converted PHA-PBO films are not soluble in common organic solvents, suggesting comparable levels of chemical resistance as in API-TR polymers. The solubility of the PHA precursor and the converted PHA-PBO films is listed in Table S1 in Supporting information.

As the result of precursor-to-PBO conversion via both the API-TR and PHA cyclodehydration routes, significant configurational and conformational changes are likely induced as benzoxazole heterocyclic rings form during thermal conversion. Depending on the degree of PBO conversion and the precursor structure, these changes alter chain packing, leading to an increase in fractional free volume (FFV) in the polymer film, which increases gas permeability. Table 3 summarizes film density and FFV changes as a function of treatment temperature for the PHA route in comparison with the API TR route. As a general trend for both routes, the overall FFV of the polymer films gradually increases with increasing treatment temperature, and the films become less dense with



API Precursor

API-TR-450

Fig. 6. Comparison of the physical appearance and mechanical robustness of PBO films formed by the cyclodehydration of PHA (PHA-PBO-350-N) and thermal rearrangement of API precursor (API-TR-450).

Table 3

Density and fractional free volume (FFV) comparison for the two polymer precursors and corresponding PBOs obtained at different temperatures.

	6FAP-6FDA-API			6FAP-6FC-PHA		
	Conversion (%)	Density (g/cm ³)	FFV (%)	Conversion (%)	Density (g/cm ³)	FFV (%)
Precursor	0	1.543	14.5	0	1.469	19.7
PBO250	_	_	_	69	1.446	20.2
TR/PBO300	27	1.531	15.1	100 ^a	1.428	20.9
TR/PBO350	74	1.524	15.6	100 ^a	1.402	22.3
TR400	80	1.514	16.1	_	_	_
TR450	100 ^a	1.434	20.6	_	_	_

^a The degree of conversion is assumed to be 100% for calculation simplicity, since the observed weight loss was more than theoretical weight loss.

increasing conversion. These observations are consistent with the formation of TR polymers or PBOs increasing the size and/or quantity of free volume elements. Comparing the two routes, the PHA precursor yields a PBO sample with a higher FFV than that of the API precursor, possibly because of denser polymer chain packing in the polyimide induced by charge transfer complex (CTC) interchain interactions in addition to strong hydrogen bonding. However, after being fully converted to PBO films, the relative increase in FFV in the case of the API-TR route (14.5%–20.6%) is much greater than that in the case of the PHA route (19.7%–22.3%), i.e., a 42% increase in FFV for API route and only a 13% increase for PHA route. The larger increment in free volume for API route may be rationalized by: 1) reconstruction of imide rings into benzoxazole rings induces greater change in the torsional angle than that in the

case of cyclizing hydroxyamide into benzoxazole rings, leading to a more contorted backbone structure and, in turn, less efficient chain packing; and 2) the API-TR route produces both *para*-linked and *meta*-linked PBOs due to the two reactive carbonyl groups in the API precursor structure, while the PHA cyclodehydration produces only *para*-linked PBOs. A more disrupted chain packing is thus expected in the API-TR polymers.

Wide angle X-ray diffraction (WAXD) measurements can provide information on the average inter-chain spacing (i.e., *d*-spacing) in the polymer films, which is, in some cases, closely related to the average size of the free volume elements. X-ray diffraction patterns and the calculated *d*-spacing values for both the precursors and fully converted films are shown in Fig. 7. The broad peaks present in all X-ray diffraction patterns indicate that both the precursors and



Fig. 7. WAXD diffraction patterns of (a) API precursor and API-TR-450 film and (b) PHA precursor and PHA-PBO-350-N film.

converted PBO-based films are completely amorphous. Comparing the two routes, the *d*-spacing for the PHA precursor (5.55 Å) is higher than that for the API (5.13 Å), which correlates well with the higher total fractional free volume of PHA precursor, as previously discussed. As expected, thermal treatment in both routes increases the *d*-spacing. Moreover, the relative increase in *d*-spacing is lower in case of the PHA route (0.49 Å) than in the API route (1.01 Å), suggesting less significant change in chain packing in the former case. This observation is reasonable since the API-TR-450 is a complex mixture of *meta*- and *para*-linked PBOs with a possibly crosslinked structure, while PHA-PBO-350-N only contains linear *para*-linked PBO.

3.2.3. Comparison of transport properties of PBO films from the API TR route and the PHA route

Free volume architecture (i.e., size and size distribution) plays a key role in polymer membrane gas separation processes [37,38]. As discussed before, formation of polybenzoxazoles via both routes induces reconstruction of the "microcavities" in the polymer films, naturally leading to differences in gas transport properties for these films. Pure gas permeability coefficients, *P*, of H₂, N₂, O₂, CH₄, and CO₂ were determined at 35 °C using the constant volume, variable pressure method [22,25,26]. To examine the effect of feed pressure on the performance, the permeability was measured at feed (i.e., upstream) pressures ranging from 3 to 17 atm, and the full plots are shown in Fig. S6 in the Supporting information. For all samples, standard dual-mode behavior was observed over the tested feed pressure range. Preliminary tests on the plasticization resistance of the PHA–PBO films were done over a CO₂ pressure range of

Table 4

Pure gas permeabilities of the precursors and films treated in N_2 (35 $^\circ\text{C},$ 10 atm).

Table 5

Pure gas ideal selectivities of the precursors and films treated in $N_2\,(35\ ^\circ C,\,10\ atm).$

Sample	Ideal selectivities					
	CO ₂ /CH ₄	O_2/N_2	CO_2/N_2	H_2/N_2	H ₂ /CH ₄	
6FAP-6FDA-API system						
API	62 ± 13	6.2 ± 1	19 ± 3	93 ± 16	300 ± 70	
API-TR-300	80 ± 11	6.4 ± 0.8	20 ± 3	98 ± 13	390 ± 60	
API-TR-350	65 ± 6	5.9 ± 0.4	19 ± 1	67 ± 13	224 ± 50	
API-TR-450	21 ± 2	3.5 ± 0.5	13 ± 2	14.9 ± 2.0	24 ± 3	
6FAP-6FC-PHA system						
PHA	47 ± 4	5.4 ± 0.6	18 ± 2	47 ± 6	125 ± 15	
PHA-PBO-250-N	48 ± 5	5.2 ± 0.3	19 ± 4	52 ± 10	133 ± 30	
PHA-PBO-300-N	32 ± 3	4.7 ± 0.5	19 ± 2	41 ± 3	67 ± 5	
PHA-PBO-350-N	27 ± 5	4.2 ± 0.8	16 ± 3	26 ± 5	45 ± 8	
Matrimid [®] [39] ^{,a}	36	6.6	31	56	64	
Cellulose acetate [40]	32	5.5	32	80	80	

^a Values reported at 4.1 bar.

3–36 atm as shown in Fig. S7. The CO₂ permeabilities for all PHA–PBO samples showed no significant change with gas fugacity as high as 36 atm, indicating a strong plasticization resistance of PHA–PBO series [18].

Tables 4 and 5 compare pure gas permeation properties (35 °C, 10 atm) of the precursors and thermally treated films for both routes. The PHA precursor is more permeable than the API precursor, which is consistent with the finding that PHA has a higher fractional free volume. However, the API permeabilities reported here are approximately a factor of 2 lower than previously reported values [17]. These differences are most likely due to the use of both

Sample	Gas permeabilities (Barrer) ^a						
	CO ₂	CH ₄	H ₂	N ₂	02		
6FAP-6FDA-API system							
API	5.0 ± 0.4	0.08 ± 0.01	24 ± 2	0.26 ± 0.02	1.6 ± 0.1		
API-TR-300	9.6 ± 0.6	0.12 ± 0.01	47 ± 3	0.48 ± 0.03	3.1 ± 0.2		
API-TR-350	27 ± 1	0.42 ± 0.02	94 ± 10	1.40 ± 0.05	8.3 ± 0.3		
API-TR-450	780 ± 60	37 ± 2	880 ± 60	59 ± 4	210 ± 10		
6FAP-6FC-PHA system							
PHA	15 ± 1	0.32 ± 0.02	40 ± 4	0.85 ± 0.06	4.6 ± 0.4		
PHA-PBO-250-N	22 ± 2	0.46 ± 0.02	61 ± 5	1.18 ± 0.07	6.1 ± 0.4		
PHA-PBO-300-N	73 ± 6	2.3 ± 0.1	155 ± 10	3.8 ± 0.3	18 ± 1		
PHA-PBO-350-N	140 ± 10	5.2 ± 0.4	233 ± 20	9.0 ± 0.8	38 ± 4		
Matrimid [®] [39] ^{,b}	10	0.28	18	0.32	2.1		
Cellulose acetate [40]	4.8	0.15	12	0.15	0.82		

 $^a~1~Barrer = 10^{-10}~cm^3$ (STP) cm cm $^{-2}$ s cm Hg = 3.35 $\times~10^{-16}~mol~m/m^2$ s Pa.

^b Values reported at 4.1 bar.

different synthesis approaches and differences in film drying protocols. Both of these variables are known to influence the gas permeation properties of such materials.

For all five gases, the permeabilities of the PHA precursor are two to four times of those of API precursor. After thermal treatment in a N₂ atmosphere to convert the precursors to PBOs, the permeabilities of converted films prepared via both routes increase significantly, reflecting the substantial increase in free volume induced by the formation of benzoxazole rings via chain rearrangement. Comparing the two routes, the increase in gas permeability with PBO conversion degree is more significant in the API series than in the PHA series. For example, at the same full conversion to PBOs, the API-TR-450 film shows two orders of magnitude increase in the permeability from the API precursor while the PHA-PBO-350-N shows only one order of magnitude increase from the PHA precursor, despite the fact that the PHA-PBO-350-N film has higher total fractional free volume. Thus, structural changes during cyclodehydration of the PHA into PBOs likely generate a large concentration of free volume elements that may be very small in size. These small free volume elements contribute to the increase in overall fractional free volume but do not contribute effectively towards improving gas permeability since they may be too small and lack connectivity to construct diffusion pathways for gas molecules. This trend is consistent with the *d*-spacing data in XRD measurements, where the API-TR-450 film shows a larger dspacing than that of the PHA-PBO-350-N film, perhaps reflecting a larger average "cavity" size. However, comparing the films treated at the same temperature, the PHA route is much more effective in providing high gas permeability. For example, the permeabilities of both PHA-PBO-300-N and PHA-PBO-350-N are an order of magnitude higher than those of the analogous API-TR samples treated at the same temperature.

To compare gas separation performance of the PBO samples prepared via two different routes, the permeability-selectivity relationship for CO₂/CH₄ separation is plotted on the Robeson Upper Bound plot in Fig. 8 with representative commercially available polymers included for comparison. Generally, in both API and PHA routes, thermal conversion of precursors to PBOs shifts the membrane separation performance towards or beyond the 1991 upper bound, indicating that a more favorable combination of permeability and selectivity is achieved at higher PBO conversions. This trend suggests that free volume elements created from chain rearrangement in these PBO films were well-tuned in both size and size distribution. Compared to the API-TR route, the PHA route shows less significant enhancement in terms of overcoming the permeability-selectivity tradeoff. For example, the PHA-PBO-350-N sample, even at 100% conversion, resides below the upper bound while the fully converted API-TR-450-N film surpasses the



Fig. 9. ATR-FTIR spectra comparing PHA–PBO films obtained after treatment at $350 \degree C$ in air (top) and in N₂ (bottom).

1991 Upper Bound, though it is below the 2008 Upper Bound. However, the significant improvement in separation performance of the API-TR-450 film is at the expense of a loss in mechanical integrity. The PHA-PBO-350-N film still possesses excellent qualitative flexibility and ductility as demonstrated previously in Fig. 6. Considering gas separation performance, mechanical integrity, and the advantage of lower temperature conversion, the PHA cyclodehydration has some distinct advantages for the formation of PBO separation membranes. Further studies in fine tuning of the PHA precursor structures would be of great interest to boost the separation performance.

3.3. Effect of thermal treatment atmosphere on PHA cyclodehydration

As described before, the API conversion route requires inert atmosphere to produce high performance TR polymer films. This requirement adds some complexity to the preparation of TR polymers. To investigate the effect of the thermal treatment environment on the PHA conversion route, the cyclodehydration of PHA was also performed in air, and the properties of the air-treated samples were compared side by side with those of the N₂-treated samples.

3.3.1. Feasibility of PHA-to-PBO conversion in air

As already shown in Fig. 2(b), the TGA thermographs for the PHA sample treated in air and nitrogen are very similar, since both of them feature a profile of two-stage weight loss. Additionally, the weight loss occurs over similar temperature ranges, suggesting the



Fig. 8. Transport property comparison of PBOs formed via API-TR (open squares) and PHA cyclodehydration (triangles) routes for: (a) CO₂/CH₄ and (b) O₂/N₂ separation.



Fig. 10. Weight loss comparison of PHA precursor thermally treated in air and N_2 at different temperatures.

occurrence of a cyclodehydration reaction in a nitrogen environment as well as in air. To confirm if the same benzoxazole structure was obtained under different atmospheres, FTIR spectra of the PHA-PBO films converted in air and N2 at 350 °C are compared in Fig. 9. The two spectra show the same characteristic PBO bands and the complete disappearance of characteristic precursor amide functionality, suggesting the formation of identical PBO structures as final products. This evidence validates the feasibility of producing PBO films via PHA cyclodehydration route in air, which is not possible for the API-TR conversion route. The ability for cyclodehydration to occur for the PHA under an inert medium as well as in air is supported by Wang et al., albeit for a different PHA precursor [15]. Additionally, the PHA-PBO-350 film obtained via air treatment shows the same level of transparency and gualitative mechanical flexibility and ductility as that obtained in N₂, suggesting no significant oxidative degradation due to air treatment.

3.3.2. Comparison of physical properties of PHA–PBO films obtained in N_2 and air

Although the final chemical structure obtained from thermal treatment in air is the same as that in N₂, it is still unknown if the treatment in air has the same efficiency in constructing the desirable free volume architecture as that in inert atmosphere. As described before, the amount of weight loss during the thermal treatment can be directly related to the degree of conversion towards PBO. Fig. 10 shows a comparison of weight loss as a function of treatment temperature between the two series of PBOs obtained in air and inert atmospheres. This figure depicts that the weight loss



Fig. 12. Comparison of WAXD patterns for PHA precursor and PHA–PBO films obtained in N₂ (PHA-PBO-350-N) and in air (PHA-PBO-350-A).

of the films treated in air is very close to that of those treated in N_2 for all three temperatures, suggesting similar efficiency in converting PHA precursor to PBOs in these two atmospheres. For the fully converted samples, the PBO-350-A film obtained in air shows almost the same weight loss as PBO-350-N film obtained in N_2 .

Comparisons of film density and fractional free volume between PBO films converted in N_2 and in air are presented in Fig. 11. As shown in Fig. 11(a), the difference in densities of the PBO films obtained by conversion in air and N_2 is very small and diminishes as treatment temperature increases. A similar trend is observed for the free volume of the films, as shown in Fig. 11(b). There is little difference between the two series at all three treatment temperatures, which, combined with FTIR observation and density data, suggests that the PBOs formed in air and in N_2 have the same chemical structure and very similar free volume architecture given the same temperature treatment.

The WAXD patterns and corresponding inter-chain spacing values for the air-treated (i.e., PBO-350-A) and N₂-treated PBO films (i.e., PBO-350-N) are compared in Fig. 12. A broad amorphous halo was observed for both samples, proving the same amorphous nature of the two PBO films. In both cases, thermal cyclodehydration to PBOs results in a larger *d*-spacing than in the PHA precursor, consistent with a more open structure, which will contribute to higher permeability in the converted samples. Moreover, there is no observable difference in the diffraction patterns or the average inter-chain distance between films prepared in different atmospheres. This result again supports the above conclusion that the



Fig. 11. Comparison of: (a) densities and (b) fractional free volume (FFV) of the PBO samples obtained after thermal cyclodehydration of the PHA in air and N₂.

Table 6
Pure gas permeabilities of PBOs obtained from the PHA precursor in air and N2

Sample	Gas permeabilities (
	CO ₂	CH ₄ H ₂		N ₂	02
In nitrogen					
PHA-PBO-250-N	22 ± 2	0.46 ± 0.02	61 ± 5	1.18 ± 0.07	6.1 ± 0.4
PHA-PBO-300-N	73 ± 6	2.3 ± 0.1	155 ± 10	3.8 ± 0.3	18 ± 1
PHA-PBO-350-N	140 ± 10	5.2 ± 0.4	233 ± 20	9.0 ± 0.8	38 ± 4
In air					
PHA-PBO-250-A	21.0 ± 2.6	0.49 ± 0.06	61.1 ± 7.4	1.18 ± 0.14	6.14 ± 0.76
PHA-PBO-300-A	94.8 ± 5.0	3.36 ± 0.18	169 ± 9	6.06 ± 0.32	25.9 ± 1.4
РНА-РВО-350-А	171 ± 18	7.13 ± 0.73	262 ± 27	11.8 ± 1.2	46.6 ± 4.8

All the values are reported for ~10 atm upstream pressure and 35 °C.

Table 7

Pure gas selectivities of PBOs obtained from the PHA precursor in air and $N_{\rm 2}$

Sample	Ideal selectivities					
	CO ₂ /CH ₄	O_2/N_2	CO_2/N_2	H_2/N_2	H ₂ /CH ₄	
In nitrogen PHA-PBO-250-N PHA-PBO-300-N PHA-PBO-350-N In air	47 ± 5 32 ± 5 27 ± 4	5.2 ± 0.6 4.8 ± 0.7 4.2 ± 0.7	18 ± 2 19 ± 3 16 ± 3	52 ± 7 41 ± 5 26 ± 5	130 ± 20 69 ± 9 45 ± 7	
PBO-250-A PBO-300-A PBO-350-A	43 ± 10 28 ± 3 24 ± 5	$\begin{array}{c} 5.2 \pm 0.3 \\ 4.3 \pm 0.5 \\ 4.0 \pm 0.8 \end{array}$	18 ± 4 16 ± 2 15 ± 3	52 ± 10 28 ± 3 22 ± 5	$130 \pm 30 \\ 50 \pm 5 \\ 37 \pm 8$	

same PBO films were obtained when formed in air or in an inert atmosphere.

3.3.3. Comparison of transport properties of PHA–PBO films obtained in N_2 and air

Tables 6 and 7 show the comparisons of transport properties of the two series of PBOs obtained after thermal cyclodehydration in air and N₂. Comparing the permeabilities and ideal selectivities, the two PBO series are statistically similar to each other. The general trend also shows that PBOs formed in air at higher temperatures show a slightly higher permeability and lower selectivity, possibly due to the thermal-oxidation of low molecular weight chains present in the PHA or oxidative instability of other organic functionality not related to the cyclodehydration reaction.

The respective permeability–selectivity relationship of the two PHA–PBO series is compared by plotting the transport data against Robeson's upper bounds. Fig. 13 shows the plots for CO_2/CH_4 and O_2/N_2 gas pairs. The overall separation performance of the PBO films obtained from air treatment is statistically very close to those

obtained from inert gas treatment. Based on all of the above comparisons, the PHA precursor undergoes the thermal cyclodehydration reaction in air that produces PBO films having the same chemical structure, free volume and chain packing efficiency as those obtained in inert atmosphere. The technical significance of this finding lies in the fact that it eliminates the requirement of inert atmosphere for the PBO conversion, which may help advance the development of PBO-based membranes.

4. Conclusions

PBO films demonstrating good gas separation performance have been successfully synthesized using the PHA thermal cyclodehydration approach. Similar to the well-known API-TR route leading to high performance TR-PBO membranes, significant increases in gas permeabilities, accompanied with only moderate losses in ideal selectivities, were achieved after the PHA-to-PBO conversion. Full conversion to PBO via PHA cyclodehydration route could be achieved efficiently at temperatures between 300 and 350 °C, more than 100 °C lower than temperatures required for the API-TR route. The much lower conversion temperature required in the PHA route could allow for the production of more mechanically robust PBO membranes that are difficult to form through the API-TR route, which requires much higher temperatures and may lead to more thermal degradation.

Studies of the atmospheric effect on the PHA cyclodehydration process showed that the same PBO films were obtained in air atmosphere and in inert N_2 , as evidenced by the same chemical structure, free volume and physical properties exhibited by the two films. Accordingly, no significant differences were observed in the gas transport properties for the PHA–PBO films produced in nitrogen and in air. This finding suggests that a more oxidatively stable reaction intermediate exists for the PHA cyclodehydration



Fig. 13. Comparison of gas separation performance of PBO films obtained via thermal cyclodehydration of the PHA in air (triangles) and in nitrogen (squares) for (a) CO₂/CH₄ and (b) O₂/N₂.

reaction compared to that of the API decarboxylation reaction. On a more practical level, this finding eliminates the need for inert atmosphere to produce high performance PBO membranes, which may simplify PBO membrane formation in the gas separation field.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.09.045.

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