**Synthesis and Characterization of Thermally Rearranged (TR) Polybenzoxazoles:
Influence of isomeric structure on gas transport properties**

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Abstract

Isomeric polyhydroxyimides based on 3,3'-diamino-4,4'-dihydroxybiphenyl (*m*-HAB) or 3,3'-dihydroxy-4,4'-diaminobiphenyl (*p*-HAB) with 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) were prepared via an ester-acid monomer. The polyhydroxyimides were then acetylated using acetic anhydride to change the *ortho*-functional groups on the polymer chains. These *ortho*-functional polyimides were used as precursors for thermal rearrangement (TR) to polybenzoxazoles for gas separation membranes. The permeability coefficients of TR polymers significantly improved as the *ortho*-functional polyimides converted to polybenzoxazoles. The influence of *meta* and *para* isomeric monomers on the gas transport properties of the resulting TR polybenzoxazoles were studied. In addition, gas permeation properties show a dependency on the size of the *ortho*-functionality of the polyimide precursors.

1 Introduction

2 Natural gas processing is by far the largest industrial gas separation application.[1]
3 Separation of CO₂ from natural gas is one of the treatments required to meet pipeline
4 specifications.[1,2] Membrane gas separation as a refinery technology has become crucial for
5 natural gas refinery processes.[1,3] In comparison to conventional separation technology,
6 membrane gas separation has several advantages including lower energy consumption, smaller
7 capital investment, and enhanced ease of operation.[4–6] However, to maximize the productivity
8 and efficiency of membrane separation technology, it still must overcome several challenges.
9 These include the trade-off relationship between permeability and selectivity of polymeric
10 membranes that limit the productivity of membrane gas separation.[2] In addition, CO₂-induced
11 plasticization is encountered with most of the commercial membrane gas separation
12 processes.[2] Plasticization, in general, will decrease the selectivities of polymeric
13 membranes.[7,8] Designing a polymeric membrane that has both high permeability and high
14 selectivity is one of the challenges for membrane gas separation.

15 Recently, a novel family of gas separation membranes known as thermally rearranged
16 (TR) polymers has attracted both academic and industrial attention.[9–12] TR polymers are
17 derived from polyimides with *ortho*-positioned functional groups that are treated at high
18 temperatures (350–450 °C) in an inert atmosphere. During the thermal rearrangement process,
19 polyimides with *ortho*-positioned functional groups undergo decarboxylation and rearrange
20 inter- and intra-molecularly to form crosslinked polybenzoxazoles. These TR polymer
21 membranes possess a combination of high permeability and high selectivity and have good
22 resistance to CO₂-induced plasticization due to their crosslinked structures.[9,13] Sanders *et al.*
23 reported that TR polymers with higher gas permeabilities can be prepared from polyimides with

1 various *ortho*-positioned functionalities including acetate or pivalate groups.[14] Guo *et al.*
2 demonstrated that the reaction temperature required for thermal rearrangement is related to the
3 glass transition temperatures of the TR precursor polyimides.[15] However, relationships
4 between the isomeric structures of the TR polymers and gas transport properties have not been
5 extensively studied. For linear polymer membranes, gas separation properties can often be
6 significantly manipulated by incorporating different isomeric structures.[16–18] For example,
7 *meta*-linked polysulfone exhibited higher selectivity and correspondingly lower permeability
8 than *para*-linked polysulfone.[16] The same phenomenon has also been found for polyimide
9 membranes. For example, Coleman *et al.* compared *meta* and *para*-linked fluorinated polyimides
10 and found that their permeability was greatly decreased when the *para*-connected diamine was
11 replaced by a *meta* isomer.[17] Both studies concluded that the decreased permeability was
12 attributed to the higher chain packing efficiency in the *meta*-linked polymer than in the *para*-
13 linked analog. As a result, a higher chain packing efficiency led to a *meta*-linked polymer with a
14 lower fractional free volume and therefore a lower permeability.

15 Recently, Comesaña-Gándara *et al.* reported a study on isomer effects of TR polymers
16 and precursors and showed that the *meta*-linked linear polyhydroxyimide had a higher
17 permeability than the *para*-linked linear polyhydroxyimide.[19] After TR conversion, the
18 polybenzoxazole derived from the *meta*-linked linear polyhydroxyimide also had significantly
19 higher permeability than the TR polymer from the *para*-linked polyhydroxyimide. This result is
20 interestingly different from previously-reported gas transport properties on isomeric *meta/para*-
21 linked linear polymers.[17,20] Nevertheless, the isomeric *meta/para* effects on gas transport
22 properties may not hold true for TR polybenzoxazoles due to the inter- and intra-molecular
23 reactions that occur during thermal rearrangement together with the added isomeric complexity

1 due to the anhydride monomer in the repeat unit as it converts to the polybenzoxazole (can
2 convert to either *meta* or *para*). As more of the benzoxazole structure forms, the TR polymers
3 may lose their structural identity related to *meta*- and *para*- linkages that existed in the
4 precursors. Moreover, the crosslinking that occurs during thermal rearrangement makes the
5 isomeric *meta/para* effects on gas transport properties less predictable.

6 In this paper, two isomeric thermally rearrangeable polyimides (*meta*- and *para*-linked
7 TR precursors) based on 4,4'-dihydroxy-3,3'-diaminobiphenyl (*m*-HAB) and 3,3'-dihydroxy-
8 4,4'-diaminobiphenyl (*p*-HAB) with 2,2'-bis-(3,4-dicarboxyphenyl)hexafluoropropane
9 dianhydride (6FDA) and with different *ortho*-functional groups (hydroxyl and acetate) and their
10 corresponding TR polymers are described. Synthesis, characterization, film preparation, and
11 single gas permeability/selectivity of the *meta/para* linked TR polyimide precursors and TR
12 polybenzoxazoles are reported. Relationships of structure to gas transport properties of the
13 isomeric *meta/para* linkages and *ortho*-functional groups of the TR polymers are discussed.

15 **Experimental**

16 **Materials**

17 4,4'-Biphenol, palladium on carbon, triethylamine, pyridine, acetic anhydride, calcium
18 hydride (CaH₂), anhydrous *o*-dichlorobenzene and hydrazine hydrate were purchased from
19 Sigma-Aldrich and used as received. Nitric acid, acetone, isopropanol, methanol and ethanol
20 were purchased from Spectrum Chemicals and used as received. Dimethylacetamide (DMAc)
21 and *N*-methyl-2-pyrrolidone (NMP) were purchased from Fisher. NMP used as a reaction solvent
22 was dried over CaH₂, distilled under reduced pressure and stored with 3Å molecular sieves

before use. 3,3'-Dihydroxy-4,4'-diaminobiphenyl (*p*-HAB) was purchased from TCI, recrystallized from a mixture of DMAc and methanol, and dried in *vacuo* at 80 °C before use. 2,2'-Bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was kindly provided by Air Products and dried in *vacuo* at 160 °C before use.

Synthesis

Synthesis of 3,3'-diamino-4,4'-dihydroxybiphenyl (m-HAB) monomer. 3,3'-Diamino-4,4'-dihydroxybiphenyl, hereafter referred to as *m*-HAB, was prepared according to a modified literature method.[21]

Synthesis of 3,3'-dinitro-4,4'-dihydroxybiphenyl. Excess 4,4'-biphenol (12.2 g, 65.5 mmol) and 250 mL of acetone were added to a 500-mL three-necked flask equipped with a condenser, mechanical stirrer and addition funnel. The reaction mixture was stirred at 60 °C until the 4,4'-biphenol completely dissolved. Nitric acid (11.9 g of 69.3% nitric acid, 131.0 mmol) was added dropwise via the addition funnel. Upon completion of addition, the solution was stirred for 6 h at 60 °C. The final heterogeneous mixture containing a yellow precipitant was washed with copious acetone. The product was filtered and dried in *vacuo* at 80 °C. Yield 87%.

Synthesis of 3,3'-diamino-4,4'-dihydroxybiphenyl. 3,3'-Dinitro-4,4'-dihydroxybiphenyl (11.6 g, 42.0 mmol), 1.1 g of Pd/C and 200 mL of NMP were added to a 500-mL three-necked flask equipped with a condenser, mechanical stirrer and addition funnel. The reaction mixture was heated in a thermocouple-regulated oil bath to 100 °C and stirred. Hydrazine hydrate (24 mL, 290 mmol) was added dropwise. After complete addition, the solution was stirred and refluxed for 12 h at 100 °C. The reaction mixture was hot-filtered through Celite. Methanol (200 mL) was slowly added into the filtered solution. The product started to crystallize upon cooling.

1 White crystals were filtered and washed with water. The product was dried in *vacuo* at 100 °C
2 overnight. Yield 81%. The monomer degrades before melting.

3 *Synthesis of m-HAB-6FDA polyhydroxyimide via an ester acid monomer.* The *m*-HAB-
4 6FDA polyimide was synthesized via an ester-acid method according to a modified literature
5 process.[22] 6FDA (7.0407 g, 15.9 mmol) was introduced into a 3-necked flask equipped with a
6 mechanical stirrer, N₂ inlet, thermometer, reverse Dean-Stark trap and reflux condenser. Then,
7 50 mL of absolute ethanol (856 mmol) and 3 mL of triethylamine (21.5 mmol) were introduced,
8 and the Dean-Stark trap was filled with ethanol. A stirring, thermocouple-regulated, oil bath was
9 used to heat the reaction to 90 °C. The mixture was refluxed with stirring for 1 h. Once a clear
10 solution was obtained, the trap was drained. When distillation of ethanol ceased, the trap was
11 again drained and refilled with *o*-dichlorobenzene. *m*-HAB (3.4268 g, 15.9 mmol) was
12 introduced followed by 35 mL of NMP and 9 mL of *o*-dichlorobenzene (~4/1, v/v) to produce a
13 solids content of ~30% wt/v. The mixture was heated at 180 °C for 10 h, allowed to cool, and
14 then precipitated in methanol. The polyhydroxyimide was dried in *vacuo* at 180 °C overnight.
15 Yield 98%.

16 *Synthesis of p-HAB-6FDA polyhydroxyimides via an ester acid monomer.* The *p*-HAB-
17 6FDA polyhydroxyimide was synthesized in the exact manner as the *m*-HAB-6FDA polymer,
18 except *p*-HAB was used instead of *m*-HAB.

19 *Acetylation of m-HAB-6FDA polyhydroxyimide to form a m-polyacetylimide.* Acetylation
20 of the *m*-HAB-6FDA polyhydroxyimide was conducted according to a modified literature
21 method.[13] The acetylated *m*-HAB-6FDA polyacetylimide is hereafter referred to as *m*-HAB-
22 6FDA-Ac. The *m*-HAB-6FDA polyhydroxyimide (4.00 g, 6.4 hydroxyl eq) and 20 mL of NMP

1 were introduced into a 3-necked flask equipped with a mechanical stirrer, N₂ inlet, and a
2 condenser. Once the polymer was fully dissolved, acetic anhydride (38.4 mmol, 3.63 mL) and
3 pyridine (37.2 mmol, 3 mL) were added to the solution. The mixture was heated to 50 °C, and
4 maintained at that temperature for 24 h with continuous stirring and a N₂ purge. The resulting
5 viscous solution was cooled to room temperature, and precipitated by slowly dripping the
6 solution into stirring methanol (1 L). The *m*-polyacetylimide (*m*-HAB-6FDA-Ac) was dried in
7 *vacuo* at 180 °C overnight. Yield 99%.

8 *Acetylation of p-HAB-6FDA polyhydroxyimide to form a p-polyacetylimide (p-HAB-*
9 *6FDA-Ac).* Acetylation of *p*-HAB-6FDA was conducted in the exact manner as the *m*-HAB-
10 6FDA-Ac, except *p*-HAB-6FDA was used instead of *m*-HAB-6FDA.

11 **Film preparation**

12 The polyhydroxyimide was dissolved in DMAc or NMP (~7%, w/v) and filtered through
13 a 0.45-μm Teflon syringe filter to remove any dust and particulates. The filtered solution was
14 sonicated for 15 min to degas the solution, then it was cast onto a level, dry glass plate (cleaned
15 with acetone) and dried initially with an infrared lamp at approximately 60 °C for 24 h to remove
16 most of the solvent and form a film. The film was soaked in deionized water for 24 h to remove
17 residual solvent, then dried in *vacuo* at 180 °C for at least 24 h.

18 **Thermal rearrangement of *ortho*-functional polyimide films to form polyimide-** 19 **polybenzoxazoles**

20 The polyhydroxyimide and polyacetylimide films were converted to their corresponding
21 polyimide-polybenzoxazole TR polymer films via thermal rearrangement using a Carbolite tube
22 furnace (Model# HZS 12/600) under a N₂ atmosphere with a purge rate of 900 mL/min. In this

study, the polyhydroxyimide films were first heated at 5 °C/min to 300 °C and held at that temperature for 1 h under N₂, and then heated to a desired TR temperature (350 or 400 °C) at 5 °C/min and held at that temperature for either 30 or 60 min.

Structural Characterization

¹H- NMR analysis was performed on a Varian Inova spectrometer operating at 400 MHz. All spectra were obtained from 15% (w/v) 1-mL solutions in DMSO-d₆. Fourier Transform Infrared Spectroscopy with attenuated total reflectance (FTIR-ATR) was performed to observe acetylation of the polyhydroxyimides and to measure the conversion of thermal rearrangement to form polyimide-polybenzoxazoles. The FTIR-ATR spectra were recorded on an FTIR spectrometer (Bruker Tensor 27) equipped with an ATR attachment with a horizontal diamond crystal. The resolutions of the spectra were 4 cm⁻¹ and 32 background scans were performed. A small amount of polymer film was placed on the diamond crystal and the FTIR spectrum was measured with 32 scans. All measurements were performed at ambient temperature. Intrinsic viscosities of the polymers were measured with a Cannon-Ubbelohde viscometer using 1.0, 0.67, 0.50 and 0.40 g/dL polymer solutions in NMP at 35 °C.

Size exclusion chromatography (SEC) was conducted on the HAB-6FDA-Ac polyacetylimides to measure molecular weight distributions. The solvent was DMAc that was distilled from CaH₂ and that contained dry LiCl (0.1 M). The column set consisted of 3 Agilent PLgel 10-μm Mixed B-LS columns 300x7.5 mm (polystyrene/divinylbenzene) connected in series with a guard column having the same stationary phase. The column set was maintained at 50 °C. An isocratic pump (Agilent 1260 infinity, Agilent Technologies) with an online degasser (Agilent 1260), autosampler and column oven was used for mobile phase delivery and sample

1 injection. A system of multiple detectors connected in series was used for the analyses. A multi-
2 angle laser light scattering (MALLS) detector (DAWN-HELEOS II, Wyatt Technology Corp.),
3 operating at a wavelength of 658 nm, a viscometer detector (Viscostar, Wyatt Technology
4 Corp.), and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX,
5 Wyatt Technology Corp.) provided online results. The system was corrected for interdetector
6 delay and band broadening. Data acquisition and analysis were conducted using Astra 6 software
7 from Wyatt Technology Corp. Validation of the system was performed by monitoring the molar
8 mass of a known molecular weight polystyrene sample by light scattering. The accepted variance
9 of the 21,000 g/mole polystyrene standard was defined as 2 standard deviations (11.5% for M_n
10 and 9% for M_w) from a set of 34 runs.

11 **Thermal Analysis**

12 The polyimide films were characterized by thermogravimetric analysis (TGA) and
13 differential scanning calorimetry (DSC). TGA scans were conducted using a TA Instruments
14 Q500 thermogravimetric analyzer under an air atmosphere. A heating rate of 10 °C min⁻¹ was
15 employed to 700 °C. Differential scanning calorimetry was performed using a Perkin-Elmer
16 DSC6000. The glass transition temperatures of the polyimide samples were heated from 25 to
17 300 °C with a heating rate of 10 °C min⁻¹ under a N₂ atmosphere.

18 **Single Gas Transport Measurements**

19 The single gas permeabilities of H₂, CH₄, N₂, O₂, and CO₂ through the polymers were
20 measured using a constant-volume/variable-pressure method at 35 °C with feed pressures up to
21 around 17 atm.[9] In this method, the polymeric membrane was enclosed inside a stainless steel
22 Millipore filter holder (Millipore, Billerica, MA, USA) and the test gas was allowed to permeate

through the membrane into a known downstream volume. The pressure increase of the collected permeate gas in the downstream volume was monitored using a pressure transducer. The linear slope of the pressure rise versus time provided the permeation rates of penetrating gases. Hence the gas permeabilities were calculated by equation 1:

$$P_A = \frac{Vl}{P_0RTA} \left(\frac{dp}{dt} \right) \quad (1)$$

where V is the downstream volume, l is film thickness, P_0 is the upstream pressure, R is the gas constant, T is absolute temperature, A is film area, and dp/dt is the rate of pressure change as the gas permeated into the closed downstream volume.

Permeabilities are commonly reported in units of Barrer, defined by equation 2:

$$1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3(\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \quad (2)$$

The ideal selectivity (pure-gas selectivity), α , was determined by taking the ratio between the single gas permeabilities of the gas pair under study:

$$\alpha_{A/B} = P_A/P_B \quad (3)$$

Results and Discussion

Synthesis and characterization of the 3,3'-diamino-4,4'-dihydroxybiphenyl (*m*-HAB) monomer

Synthesis of 3,3'-diamino-4,4'-dihydroxybiphenyl was conducted in two steps starting from 4,4'-biphenol, which is a commonly used monomer for various commercial polymers such

as polysulfone, poly(arylene ether ketone) and polycarbonate.[23] 4,4'-Biphenol was nitrated in an aromatic electrophilic substitution reaction to form 3,3'-dinitro-4,4'-biphenol, and this was followed by reduction of the nitro groups with hydrazine hydrate in the presence of Pd/C as the catalyst. The product was recrystallized in a mixture of NMP and methanol to give the monomer with a high yield. The structure of the final product, 3,3'-diamino-4,4'-dihydroxybiphenyl, was confirmed by ^1H NMR (Figure 1).

Figure 1. ^1H NMR spectrum confirms the structure of the *m*-HAB monomer.

Synthesis and characterization of isomeric polyhydroxyimide TR precursors

The isomeric *meta*- and *para*-HAB-6FDA polyhydroxyimides were synthesized via a diester-diacid monomer in a manner similar to previously described procedures.[13,15] In the diester-diacid method (Scheme 1), the hydrolytically unstable dianhydride monomer was first reacted with an alcohol at low temperature to form a hydrolytically-stable diester-diacid monomer. Then, the aminophenol monomer was introduced and the temperature was elevated to

1 produce the polyhydroxyimide in a one-step process. The diester-diacid monomer is less reactive
2 than the corresponding dianhydride. Our objective was to avoid any reaction of the *ortho*-
3 hydroxyl group with the very reactive dianhydride during imide formation. The structural
4 differences between the two isomeric polyhydroxyimides, *meta*- and *para*-HAB-6FDA, were
5 confirmed by ¹H NMR (Figure 2). Previous studies have demonstrated that the pendent
6 functional groups affect the transport properties of TR polymers.[13] For example, TR polymers
7 that were prepared from *ortho*-acetate functional polyimides had significantly higher
8 permeabilities than the TR polymers that were prepared from *ortho*-hydroxyl functional
9 polyimides. In order to compare the isomer effect and the bulky pendent group effect on the TR
10 polymers, the two isomeric polyhydroxyimides were post-acetylated using acetic anhydride and
11 a weak base as the catalyst to form the corresponding isomeric polyacetylimides, *meta*- and
12 *para*-HAB-6FDA-Ac (Scheme 2). Since the *meta*- and *para*-HAB-6FDA-Ac polyacetylimides
13 were chemically modified from the initial polyhydroxyimides (*meta*- and *para*-HAB-6FDA), any
14 effects of different molecular weights or possible isoimide structures resulting from different
15 synthetic methods were avoided. Acetylation of the isomeric polyhydroxyimides was confirmed
16 by ¹H NMR and FT-IR (Figures 3 and 5). Molecular weights of these polyimides were estimated
17 by intrinsic viscosities and SEC (Table 1). Lower intrinsic viscosities were observed for the
18 acetylated polyimides as compared to the polyhydroxyimides due to lack of hydrogen bonding
19 interactions. SEC of the polyacetylimides quantitatively substantiated high molecular weight,
20 and these results are shown in Figure 2 and Table 1.

	<i>m</i> -HAB-6FDA	<i>p</i> -HAB-6FDA	<i>m</i> -HAB-6FDA-Ac	<i>p</i> -HAB-6FDA-Ac
[η]	1.33	1.58	0.93	1.04
M _n (×10 ⁻³ g/mol)	-	-	44	41

$M_w (\times 10^{-3} \text{ g/mol})$	-	-	112	92
PDI	-	-	2.6	2.2

Table 1. Molecular weights of *meta* and *para*-HAB-6FDA *ortho*-functional polyimides

Figure 2. Light scattering SEC chromatograms of *para* and *meta*-HAB-6FDA-Ac

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5 **Scheme 1. Synthesis of *para*- (left) and *meta*-HAB-6FDA (right) polyhydroxyimides via the diester-**
6 **diacid monomer**

Figure 3. ^1H NMR spectra confirm the structures of *meta*- (top) and *para*-HAB-6FDA (bottom) polyhydroxyimides.

- 1
- 2 **Scheme 2. Acetylation of *meta*- and *para*-HAB-6FDA polyhydroxyimides to form polyacetylimides**

Figure 4. ^1H NMR spectra confirm the structures of *meta*- (top) and *para*-HAB-6FDA-Ac (bottom) polyacetylimides.

Thermal properties of isomeric polyhydroxyimide and polyacetylimide TR precursors

TGA profiles (Figure 5) show similar two-step weight loss stages for the two isomeric polyhydroxyimides and their acetylated analogs in a nitrogen atmosphere. As reported previously,[14] the first weight loss corresponds to the thermal rearrangement process with loss of the by-products and the second depicts degradation of the polymers. The polyacetylimide precursors had earlier and more weight loss in the lower temperature region than the polyhydroxyimides, and this is in agreement with previous reports.[13] Theoretical mass losses for a 100% TR polybenzoxazole converted from the HAB-6FDA polyhydroxyimide and for a fully converted HAB-6FDA-Ac are 14.1 and 24.0% respectively. Figure 5 shows the weight losses observed upon heating those precursors in the TGA to be slightly lower than the

theoretical values for full conversion. This may at least be partially attributable to the heating rates being too fast (10 °C/min) to allow the precursors to achieve full TR conversion before they underwent degradation as the temperature was elevated.

Figure 5. TGA profiles of meta/para HAB-6FDA polyhydroxyimides and polyacetylimides: Samples were heated at 10°C/min from 25 to 700°C under a N₂ atmosphere.

Structures of TR precursors and TR polybenzoxazoles

Structural changes that occurred upon conversion of the polyhydroxyimides to polyacetylimides and from the *ortho*-functional polyimide precursors to polybenzoxazoles during the thermal treatments were examined by ATR-FTIR. Figure 6 shows ATR-FTIR transmission spectra of *m*-HAB-6FDA, *m*-HAB-6FDA-Ac, *p*-HAB-6FDA and *p*-HAB-6FDA-

1 Ac. Figures 7-8 show ATR-FTIR transmission spectra of the *m*-HAB-6FDA and *m*-HAB-6FDA-
2 Ac polyimides and their corresponding TR polymers. Peak a (3500 cm^{-1}) represents the H-O
3 stretch. Peaks b (1780 cm^{-1}) and c (1720 cm^{-1}) represent the symmetric and asymmetric imide
4 carbonyl stretches, and peak d (1380 cm^{-1}) represents the imide C-N stretch. Peaks e (1560 cm^{-1}),
5 f (1480 cm^{-1}) and g (1050 cm^{-1}) represent the benzoxazole ring stretches. As the
6 polyhydroxyimides were converted to polyacetylimides, the peak associated with the hydroxyl
7 functional groups (peaks a, Figure 6) disappeared, which is a sign of complete acetylation. In
8 Figure 7, as the polyhydroxyimides were exposed to different thermal treatments, the hydroxyl
9 peak (a) and peaks associated with the polyimide structures (b, c and d) declined in intensity.
10 Figure 8 shows the FTIR spectra of the polyacetylimides treated under different conditions. For
11 the *m*-HAB-6FDA-Ac-TR350 polymer, a broad peak associated with the hydroxyl functionality
12 was observed (peak a). The presence of the hydroxyl peak is a result of the loss of the acetate
13 functional group and the formation of a hydroxyl group on the polyimide prior to the thermal
14 rearrangement to form the polybenzoxazole. For *m*-HAB-6FDA-Ac-TR400 polymers, peaks (e, f,
15 and g) began to develop that may be evidence of benzoxazole formation, but these peaks were
16 very weak. Nevertheless, ATR-FTIR was a critical technique for monitoring the thermal
17 rearrangement process from polyimides to polybenzoxazoles.

Scheme 3. Thermal rearrangement of acetylated and non-acetylated *m*-HAB-6FDA polyimides

As polyimides undergo the TR process, their masses decrease. Therefore, conversion of the polyimides to TR polymers was quantified by weight loss using the following equation:¹²

$$\text{Conversion (\%)} = \frac{\text{Actual Mass Loss}}{\text{Theoretical Mass Loss}} \times 100$$

Table 2 shows the theoretical weight losses for the TR precursor polyimides, the measured losses due to thermal rearrangement after being heated at 400 °C for 60 min, and the percent conversion from the *ortho*-functional polyimides to the TR polymers. Thus, it appears that while the polyhydroxyimides convert almost quantitatively to polybenzoxazoles under these conditions, the efficiency of conversion of the acetylated polymers is rather low, even after treatment at 400 °C for 60 minutes.

1

Precursors	Theoretical weight loss (wt%)	Measured weight loss	Conversion
		(wt%)	(%)
		TR400-60 min	
<i>m</i> -HAB-6FDA	14.1	13.0	92
<i>p</i> -HAB-6FDA	14.1	12.4	88
<i>m</i> -HAB-6FDA-Ac	24.3	11.3	47
<i>p</i> -HAB-6FDA-Ac	24.3	13.0	54

2

3

Table 2. Weight losses of meta/para *ortho*-functional polyimides during the TR processes

Figure 6. FT-IR spectra of *meta*- and *para*-HAB-6FDA *ortho*-functional polyimides

Figure 7. FT-IR spectra of *m*-HAB-6FDA and its corresponding TR polymers

Figure 8. FT-IR spectra of *m*-HAB-6FDA-Ac and its corresponding TR polymers.

Gas transport

Pure-gas permeation properties of H₂, O₂, N₂, CO₂, and CH₄ of the four *ortho*-functional polyimide precursors and their corresponding TR polymers were measured at 35 °C with an upstream pressure of 10 atm. Tables 3-4 show the gas permeation properties of the isomeric precursors with different *ortho*-functionalities and their corresponding TR polymers that were thermally treated at 400 °C for 60 minutes. The gas permeability coefficients of HAB-6FDA polyimides from this study are lower than those reported by Comesaña-Gándara et al. The permeability coefficients of all five gases for *p*-HAB-6FDA polyhydroxyimide were higher than those of *m*-HAB-6FDA. For example, permeability of CO₂ was 5.9 Barrer for *m*-HAB-6FDA and 8.3 Barrer for *p*-HAB-6FDA. Because *para*-connected polymers are believed to have greater sub-translational rotational mobility around the phenylene groups than do *meta*-connected polymers, *para*-linked isomers typically have higher fractional free volume (FFV), and thus, higher gas permeability coefficients, than *meta*-linked analogs. However, the differences in permeability of these polyimide precursors are not as substantial as some of the traditional aromatic polyimides reported in previous studies.[17,20,24] For example, *para*-linked polyimide derived from 6F-dianhydride and 6F-*p*-diamine (6FDA-6FpDA) had a CO₂ permeability of 63.9 Barrer while the polyimide derived from the 6F-dianhydride and 6F-*m*-diamine (6FDA-6FmDA) only had a CO₂ permeability of 5.1 Barrer. *Para*-oriented aromatic polymers usually pack less efficiently and have less inter-segmental mobility than *meta*-oriented aromatic polymers.[20] Thus, higher fractional free volumes and higher permeabilities for *para*-oriented aromatic polymers are often observed. However, these TR precursors that contain highly polar functional groups along the backbone likely complicate such effects. Typically, the presence of polar groups decreases fractional free volume, resulting in a lower gas permeability.[25,26] For

1 example, gas permeability coefficients for polysulfone decrease dramatically with degree of
2 nitration.[26] For the polyhydroxyimides, much closer gas permeabilities are observed between
3 *meta*- and *para*-oriented polymers than the traditional polyimides. Therefore, we hypothesize
4 that in addition to the *para/meta*-configuration difference, the presence of polar functionalities in
5 the *ortho*-position also influences gas transport properties. As a result, the difference in gas
6 transport properties of these polyhydroxyimides is not as drastic as traditional polyimides
7 reported in previous studies.

8 After acetylation of the polyhydroxyimides, both of the polyacetylimides have increased
9 permeability as the *ortho*-hydroxyl groups are changed to acetate groups. This phenomenon has
10 been reported in previous literatures. Interestingly, the permeability coefficients of *para/meta*
11 linked the polyacetylimide contradict from the permeability coefficients of traditional *meta/para*
12 linked polyimides. For all five gases, shown in Table 3 and 4, *meta* linked *m*-HAB-6FDA-Ac has
13 higher permeability coefficients than that of *para* linked *p*-HAB-6FDA-Ac. However, the
14 *meta/para* linked polyimides that previous reported for gas transport studies, do not have any
15 bulky groups at the *ortho*-position to the imide ring. Therefore we hypothesize that the presence
16 of bulky groups at the *ortho*-position, in this case the acetate groups, can cause steric hindrance
17 and inhibit the phenylene “ring flip” effect of the *para* isomer. Consequently, the acetate groups
18 diminish the *para/meta* isomer effect and appears to disrupt polymer chain packing to a greater
19 extent for *m*-HAB-6FDA-Ac than for *p*-HAB-6FDA-Ac. Thus, greater permeability coefficients
20 of *meta* linked polyacetylimide are observed than that of *para* linked polyacetylimide.

21 Like other TR polymers, conversion of *ortho*-functional polyimides to polybenzoxazole TR
22 polymers significantly improved the permeability coefficients of both *m*-HAB-6FDA and *p*-
23 HAB-6FDA TR polymers.[27,28] The permeabilities of five common gases through the TR

precursors and TR polymers are compared for *m*-HAB-6FDA and *p*-HAB-6FDA based structures (Tables 3 and 4). Upon thermal rearrangement at 400 °C for 60 minutes, all of the gas permeabilities increased. For example, permeability of O₂ for TR-*m*-HAB-6FDA-Ac and TR-*p*-HAB-6FDA-Ac increased by 400 and 936%, respectively, compared with those of their corresponding TR precursor polyimides. Additionally, the TR polymers derived from the polyacetylimide precursors had much higher gas permeabilities than the TR polymers derived from polyhydroxyimide precursors. For example, the permeability of CO₂ through the TR-*m*-HAB-6FDA-Ac was 75 Barrer whereas the permeability of CO₂ for TR-*m*-HAB-6FDA was only 57 Barrer. This phenomenon agrees with previous literature.[13,14,29]

Moreover, the TR polymers derived from *meta*- and *para*-oriented precursors also exhibited small differences in gas permeability. For example, the CH₄ gas permeability through TR400-*m*-HAB-6FDA-Ac was 2.0 Barrer and that of TR400-*p*-HAB-6FDA-Ac was 3.0 Barrer. There are two reasons for the small difference in gas permeability between the two isomers. First, the precursors have small differences in gas permeabilities between the *meta* and *para* isomers. These TR polymers could have two components depending on the percentage of conversion: unconverted polyimide with *ortho*-functional groups and rearranged polybenzoxazole. It was found that the permeability coefficients of the *meta* and *para* oriented polyhydroxyimides were not significantly different. Thus, the unconverted polyimide component may only contribute a small difference in gas permeabilities between the two isomeric TR polymers derived from the polyacetylimides. Second, unlike more conventional *meta*- or *para*-linked polymers, the benzoxazole structures in the isomeric TR polymers may not have significant differences in inter-segmental mobility (Scheme 4). As a result, the TR polymer component derived from *meta* and *para* isomeric precursors also may only contribute small

differences in gas permeability. So the simplicity of the *m*-HAB monomer synthetic route makes *meta*-oriented TR polymers an economically better option.

Table 3. Single-gas permeabilities for *meta/para* HAB-6FDA *ortho*-functional polyimides and their corresponding TR polymers measured at 10 atm feed pressure and 35 °C.

Samples	Single Gas Permeabilities (Barrer)					
	H ₂		N ₂		O ₂	
	polyimide	TR400-	polyimide	TR400-	polyimide	TR400-
	precursor	60 min	precursor	60 min	precursor	60 min
<i>m</i> -HAB-6FDA	33 ± 1	124 ± 4	0.23 ± 0.01	3.1 ± 0.1	1.7 ± 0.06	15 ± 0.5
<i>p</i> -HAB-6FDA	36 ± 2	147 ± 6	0.3 ± 0.02	3.7 ± 0.1	2.1 ± 0.1	18 ± 0.7
<i>m</i> -HAB-6FDA-Ac	43 ± 1	165 ± 7	0.7 ± 0.02	4.0 ± 0.2	4.0 ± 0.1	20 ± 0.8
<i>p</i> -HAB-6FDA-Ac	37 ± 2	237 ± 9	0.47 ± 0.02	6.0 ± 0.2	2.8 ± 0.1	29 ± 1

Table 4. Single-gas permeabilities of CO₂ and CH₄ and ideal selectivity of CO₂/CH₄ for *meta/para* HAB-6FDA *ortho*-functional polyimides and their corresponding TR polymers measured at 10 atm feed pressure and 35 °C.

Samples	Single Gas Permeability (Barrer)				Selectivity	
	CO ₂		CH ₄		CO ₂ /CH ₄	
	polyimide	TR400-	polyimide	TR400-	polyimide	TR400-
	precursor	60 min	precursor	60 min	precursor	60 min

<i>m</i> -HAB-6FDA	5.9 ± 0.2	56 ± 2	0.065 ± 0.003	1.8 ± 0.06	91	31
<i>p</i> -HAB-6FDA	8.3 ± 0.5	73 ± 3	0.09 ± 0.006	2.2 ± 0.1	92	33
<i>m</i> -HAB-6FDA-Ac	15 ± 0.5	75 ± 3	0.39 ± 0.01	2.0 ± 0.08	39	38
<i>p</i> -HAB-6FDA-Ac	9.6 ± 0.5	115 ± 4	0.23 ± 0.01	3.0 ± 0.1	42	38

Scheme 4. Comparison of *meta* and *para*-oriented HAB-6FDA polyimides and their corresponding TR polymers.

Figure 9. The upper bound plot of the CO₂/CH₄ gas pair.

Figure 9 illustrates a CO₂/CH₄ upper bound plot for *m*-HAB-6FDA, *p*-HAB-6FDA, *m*-HAB-6FDA-Ac, *p*-HAB-6FDA-Ac and their TR polymers. As a general observation, the polyhydroxyimides (*m*-HAB-6FDA and *p*-HAB-6FDA) have higher CO₂/CH₄ selectivities and lower CO₂ permeabilities than the polyacetylimides. The TR polymers derived from polyacetylimide precursors showed even greater CO₂ gas permeability and more competitive CO₂/CH₄ selectivity than the TR polymers derived from the polyhydroxyimide precursors. This may also be influenced by the fact that conversions of the TR-polyacetylimides were incomplete under the conditions imposed in this study, and thus, this aspect will require further investigation to fully understand. The gas transport properties of the polymers from this study differ from those reported by Comesaña-Gándara et al.[19] This could be attributed to differences in either the synthetic methods employed to prepare the precursor polymers, or more likely, to differences

in membrane casting and thermal conversion procedures. What this suggests is that further work should be done to understand the sensitivity of such materials, particularly to processing conditions. There are some differences in the CO₂ gas permeability and the CO₂/CH₄ selectivity between *meta* and *para* oriented TR precursors and their corresponding TR polymers, and a detailed discussion of the differences in permeability between *meta* and *para* oriented TR precursors and TR polymers will be reported in a separate publication.[30] To this end, the *meta/para* oriented TR polymers do not have a substantial advantage over one another in CO₂/CH₄ gas separation but TR polymers derived from the partially-rearranged polyacetylimides demonstrate better CO₂/CH₄ gas separation properties than the TR polymers derived from the polyhydroxyimides at high conversion.

Conclusions

Meta and *para* oriented high molecular weight aromatic polyimides containing *ortho*-positioned hydroxyl groups were synthesized using a diester-diacid monomer to avoid possible reactions of the *ortho*-hydroxyl groups with the more reactive dianhydride monomer. Those polyhydroxyimides were post-modified to change the *ortho*-functional groups to acetates. Then the isomeric *ortho*-functional polyimides were converted to polymers with benzoxazole structures via thermal rearrangement (TR). Mass measurements before and after conversion suggested strongly that thermally rearranging these polyimides at 400 °C for 60 minutes was efficient for conversion of the polyhydroxyimides but was insufficient for the corresponding polyacetylimides.

Gas transport measurements conducted on these isomeric polymer membranes confirmed the expected dramatic increases in permeabilities for all of these materials upon thermal

rearrangement. Unlike traditional linear polymer membranes, the TR precursors had similar gas permeabilities between *meta* and *para* oriented isomers due to a possible dominating effect of the polar functional groups over the *meta/para* isomer effect. The TR polymers derived from *meta/para* oriented isomeric TR precursors also had similar gas separation properties, especially for CO₂/CH₄ separation, and it is hypothesized that this is due to a lack of intersegmental mobility distinction between the two isomeric TR polymers. Finally, the TR polymers derived from *meta/para* isomeric precursors had similar gas separation properties, but the TR polymers derived from the same backbone structure but with different *ortho*-functional groups had different gas separation properties.

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