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PII: S0032-3861(15)30105-1

DOI: 10.1016/j.polymer.2015.07.024

Reference: JPOL 17984

To appear in: *Polymer*

Received Date: 8 May 2015

Revised Date: 14 July 2015

Accepted Date: 15 July 2015

Please cite this article as: Borjigin H, Liu Q, Zhang W, Gaines K, Riffle JS, Paul DR, Freeman BD, McGrath JE, Synthesis and Characterization of Thermally Rearranged (TR) Polybenzoxazoles: Influence of isomeric structure on gas transport properties, *Polymer* (2015), doi: 10.1016/j.polymer.2015.07.024.

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1 Abstract

Isomeric polyhydroxyimides based on 3,3'-diamino-4,4'-dihydroxybiphenyl (m-HAB) or 3,3'-2 3 dihydroxy-4,4'-diaminobiphenyl (p-HAB) with 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane 4 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 5 6 chains. These ortho-functional polyimides were used as precursors for thermal rearrangement (TR) to polybenzoxazoles for gas separation membranes. The permeability coefficients of TR 7 polymers significantly improved as the ortho-functional polyimides converted to 8 polybenzoxazoles. The influence of meta and para isomeric monomers on the gas transport 9 properties of the resulting TR polybenzoxazoles were studied. In addition, gas permeation 10 properties show a dependency on the size of the *ortho*-functionality of the polyimide precursors. 11

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1 Introduction

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

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

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

Recently, Comesaña-Gándara et al. reported a study on isomer effects of TR polymers 15 and precursors and showed that the *meta*-linked linear polyhydroxyimide had a higher 16 permeability than the para-linked linear polyhydroxyimide.[19] After TR conversion, the 17 polybenzoxazole derived from the *meta*-linked linear polyhydroxyimide also had significantly 18 higher permeability than the TR polymer from the *para*-linked polyhydroxyimide. This result is 19 interestingly different from previously-reported gas transport properties on isomeric meta/para-20 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 reactions that occur during thermal rearrangement together with the added isomeric complexity 23

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

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

14

15 Experimental

16 Materials

4,4'-Biphenol, palladium on carbon, triethylamine, pyridine, acetic anhydride, calcium
hydride (CaH₂), anhydrous *o*-dichlorobenzene and hydrazine hydrate were purchased from
Sigma-Aldrich and used as received. Nitric acid, acetone, isopropanol, methanol and ethanol
were purchased from Spectrum Chemicals and used as received. Dimethylacetamide (DMAc)
and *N*-methyl-2-pyrrolidone (NMP) were purchased from Fisher. NMP used as a reaction solvent
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.

5 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'-dihydroxyybiphenyl. 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.

White crystals were filtered and washed with water. The product was dried in *vacuo* at 100 °C
 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 mechanical stirrer, N2 inlet, thermometer, reverse Dean-Stark trap and reflux condenser. Then, 6 50 mL of absolute ethanol (856 mmol) and 3 mL of triethylamine (21.5 mmol) were introduced, 7 and the Dean-Stark trap was filled with ethanol. A stirring, thermocouple-regulated, oil bath was 8 used to heat the reaction to 90 °C. The mixture was refluxed with stirring for 1 h. Once a clear 9 solution was obtained, the trap was drained. When distillation of ethanol ceased, the trap was 10 again drained and refilled with o-dichlorobenzene. m-HAB (3.4268 g, 15.9 mmol) was 11 introduced followed by 35 mL of NMP and 9 mL of o-dichlorobenzene (~4/1, v/v) to produce a 12 solids content of ~30% wt/v. The mixture was heated at 180 °C for 10 h, allowed to cool, and 13 then precipitated in methanol. The polyhydroxyimide was dried in vacuo at 180 °C overnight. 14 15 Yield 98%.

Synthesis of p-HAB-6FDA polyhydroxyimides via an ester acid monomer. The p-HAB6FDA polyhydroxyimide was synthesized in the exact manner as the *m*-HAB-6FDA polymer,
except *p*-HAB was used instead of *m*-HAB.

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

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

8 Acetylation of p-HAB-6FDA polyhydroxyimide to form a p-polyacetylimide (p-HAB9 6FDA-Ac). Acetylation of p-HAB-6FDA was conducted in the exact manner as the m-HAB10 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

The polyhydroxyimide and polyacetylimide films were converted to their corresponding polyimide-polybenzoxazole TR polymer films via thermal rearrangement using a Carbolite tube 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.

4 Structural Characterization

¹H- NMR analysis was performed on a Varian Inova spectrometer operating at 400 MHz. 5 All spectra were obtained from 15% (w/v) 1-mL solutions in DMSO-d₆. Fourier Transform 6 Infrared Spectroscopy with attenuated total reflectance (FTIR-ATR) was performed to observe 7 acetylation of the polyhydroxyimides and to measure the conversion of thermal rearrangement to 8 form polyimide-polybenzoxazoles. The FTIR-ATR spectra were recorded on an FTIR 9 spectrometer (Bruker Tensor 27) equipped with an ATR attachment with a horizontal diamond 10 crystal. The resolutions of the spectra were 4 cm^{-1} and 32 background scans were performed. A 11 small amount of polymer film was placed on the diamond crystal and the FTIR spectrum was 12 measured with 32 scans. All measurements were performed at ambient temperature. Intrinsic 13 viscosities of the polymers were measured with a Cannon-Ubbelohde viscometer using 1.0, 0.67, 14 0.50 and 0.40 g/dL polymer solutions in NMP at 35 °C. 15

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

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

11 Thermal Analysis

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

18 Single Gas Transport Measurements

The single gas permeabilities of H₂, CH₄, N₂, O₂, and CO₂ through the polymers were measured using a constant-volume/variable-pressure method at 35 °C with feed pressures up to around 17 atm.[9] In this method, the polymeric membrane was enclosed inside a stainless steel 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:

$$P_A = \frac{Vl}{P_0 RTA} \left(\frac{dp}{dt}\right) \tag{1}$$

5

6 where V is the downstream volume, *l* is film thickness, P_0 is the upstream pressure, R is the gas 7 constant, T is absolute temperature, A is film area, and dp/dt is the rate of pressure change as the 8 gas permeated into the closed downstream volume.

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

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

- The ideal selectivity (pure-gas selectivity), α, was determined by taking the ratio between the
 single gas permeabilities of the gas pair under study:
- 12 $\alpha_{A/B} = P_A/P_B \quad (3)$
- 13 **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).



8

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

9 Synthesis and characterization of isomeric polyhydroxyimide TR precursors

10 The isomeric *meta-* and *para-*HAB-6FDA polyhydroxyimides were synthesized via a 11 diester-diacid monomer in a manner similar to previously described procedures.[13,15] In the 12 diester-diacid method (Scheme 1), the hydrolytically unstable dianhydride monomer was first 13 reacted with an alcohol at low temperature to form a hydrolytically-stable diester-diacid 14 monomer. Then, the aminophenol monomer was introduced and the temperature was elevated to

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

	m-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
$M_n(\times 10^{-3} g/mol)$	-	-	44	41





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



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

6

diacid monomer





- 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.

4 Thermal properties of isomeric polyhydroxyimide and polyacetylimide TR precursors

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5 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 6 7 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 8 precursors had earlier and more weight loss in the lower temperature region than the 9 polyhydroxyimides, and this is in agreement with previous reports.[13] Theoretical mass losses 10 for a 100% TR polybenzoxazole converted from the HAB-6FDA polyhydroxyimide and for a 11 fully converted HAB-6FDA-Ac are 14.1 and 24.0% respectively. Figure 5 shows the weight 12 losses observed upon heating those precursors in the TGA to be slightly lower than the 13

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.



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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.

8 Structures of TR precursors and TR polybenzoxazoles

9 Structural changes that occurred upon conversion of the polyhydroxyimides to 10 polyacetylimides and from the *ortho*-functional polyimide precursors to polybenzoxazoles 11 during the thermal treatments were examined by ATR-FTIR. Figure 6 shows ATR-FTIR 12 transmission spectra of *m*-HAB-6FDA, *m*-HAB-6FDA-Ac, *p*-HAB-6FDA and *p*-HAB-6FDA-

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



TR-m-HAB-6FDA

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

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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

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

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.

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	The sure that have in the large	Measured weight loss	Conversion
Precursors	(wt%)	(wt%)	(%)
	(wt/6)	TR400-	-60 min
m-HAB-6FDA	14.1	13.0	92
p-HAB-6FDA	14.1	12.4	88
m-HAB-6FDA-Ac	24.3	11.3	47
p-HAB-6FDA-Ac	24.3	13.0	54

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





1 Gas transport

Pure-gas permeation properties of H₂, O₂, N₂, CO₂, and CH₄ of the four *ortho*-functional 2 polyimide precursors and their corresponding TR polymers were measured at 35 °C with an 3 4 upstream pressure of 10 atm. Tables 3-4 show the gas permeation properties of the isomeric 5 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 6 polyimides from this study are lower than those reported by Comesaña-Gándara et al. The 7 permeability coefficients of all five gases for *p*-HAB-6FDA polyhydroxyimide were higher than 8 those of *m*-HAB-6FDA. For example, permeability of CO₂ was 5.9 Barrer for *m*-HAB-6FDA 9 and 8.3 Barrer for p-HAB-6FDA. Because para-connected polymers are believed to have 10 greater sub-transitional rotational mobility around the phenylene groups than do meta-connected 11 polymers, para-linked isomers typically have higher fractional free volume (FFV), and thus, 12 higher gas permeability coefficients, than meta-linked analogs. However, the differences in 13 permeability of these polyimide precursors are not as substantial as some of the traditional 14 aromatic polyimides reported in previous studies.[17,20,24] For example, *para*-linked polyimide 15 derived from 6F-dianhydride and 6F-p-diamine (6FDA-6FpDA) had a CO₂ permeability of 63.9 16 Barrer while the polyimide derived from the 6F-dianhydride and 6F-*m*-diamine (6FDA-6F*m*DA) 17 only had a CO₂ permeability of 5.1 Barrer. Para-oriented aromatic polymers usually pack less 18 efficiently and have less inter-segmental mobility than *meta*-oriented aromatic polymers.[20] 19 Thus, higher fractional free volumes and higher permeabilities for para-oriented aromatic 20 21 polymers are often observed. However, these TR precursors that contain highly polar functional 22 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 23

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

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

Like other TR polymers, conversion of *ortho*-functional polyimides to polybenzoxazole TR polymers significantly improved the permeability coefficients of both *m*-HAB-6FDA and *p*-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 1 structures (Tables 3 and 4). Upon thermal rearrangement at 400 °C for 60 minutes, all of the gas 2 permeabilities increased. For example, permeability of O₂ for TR-m-HAB-6FDA-Ac and TR-p-3 HAB-6FDA-Ac increased by 400 and 936%, respectively, compared with those of their 4 corresponding TR precursor polyimides. Additionally, the TR polymers derived from the 5 polyacetylimide precursors had much higher gas permeabilities than the TR polymers derived 6 7 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 8 57 Barrer. This phenomenon agrees with previous literature.[13,14,29] 9

Moreover, the TR polymers derived from meta- and para-oriented precursors also 10 exhibited small differences in gas permeability. For example, the CH₄ gas permeability through 11 TR400-*m*-HAB-6FDA-Ac was 2.0 Barrer and that of TR400-*p*-HAB-6FDA-Ac was 3.0 Barrer. 12 There are two reasons for the small difference in gas permeability between the two isomers. 13 First, the precursors have small differences in gas permeabilities between the meta and para 14 isomers. These TR polymers could have two components depending on the percentage of 15 conversion: unconverted polyimide with ortho-functional rearranged 16 groups and polybenzoxazole. It was found that the permeability coefficients of the meta and para oriented 17 polyhydroxyimides were not significantly different. Thus, the unconverted polyimide component 18 may only contribute a small difference in gas permeabilities between the two isomeric TR 19 polymers derived from the polyacetylimides. Second, unlike more conventional meta- or para-20 21 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 22 component derived from meta and para isomeric precursors also may only contribute small 23

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

corresponding TR polymers measured at 10 atm feed pressure and 35 °C.

Table 3. Single-gas permeabilities for meta/para HAB-6FDA ortho-functional polyimides and their

		Sing	gle Gas Permea	abilities (Ba	rrer)	
Samples	H ₂	1	N ₂		0	2
-	polyimide	TR400-	polyimide	TR400-	polyimide	TR400-
	precursor	60 min	precursor	60 min	precursor	60 min
m-HAB-6FDA	33 ± 1	124 ± 4	0.23 ± 0.01	3.1 ± 0.1	1.7 ± 0.06	15 ± 0.5
p-HAB-6FDA	36 ± 2	147 ± 6	0.3 ± 0.02	3.7 ± 0.1	2.1 ± 0.1	18 ± 0.7
m-HAB-6FDA-Ac	43 ± 1	165 ± 7	0.7 ± 0.02	4.0 ± 0.2	4.0 ± 0.1	20 ± 0.8
p-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.

X	Sin	Single Gas Permeability (Barrer)				Selectivity	
	CC	2	СН	4	CO ₂ /C	CH ₄	
	polyimide	TR400-	polyimide	TR400-	polyimide	TR400-	
Samples	precursor	60 min	precursor	60 min	precursor	60 min	

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



5



TR-p-HAB-6FDA

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

polymers.

7



2

1

Figure 9. The upper bound plot of the CO_2/CH_4 gas pair.

3 Figure 9 illustrates a CO₂/CH₄ upper bound plot for *m*-HAB-6FDA, *p*-HAB-6FDA, *m*-HAB-4 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 5 lower CO₂ permeabilities than the polyacetylimides. The TR polymers derived from 6 polyacetylimide precursors showed even greater CO₂ gas permeability and more competitive 7 CO₂/CH₄ selectivity than the TR polymers derived from the polyhydroxyimide precursors. This 8 may also be influenced by the fact that conversions of the TR-polyacetylimides were incomplete 9 under the conditions imposed in this study, and thus, this aspect will require further investigation 10 11 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 12 13 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 1 should be done to understand the sensitivity of such materials, particularly to processing 2 conditions. There are some differences in the CO₂ gas permeability and the CO₂/CH₄ selectivity 3 between *meta* and *para* oriented TR precursors and their corresponding TR polymers, and a 4 detailed discussion of the differences in permeability between *meta* and *para* oriented TR 5 precursors and TR polymers will be reported in a separate publication.[30] To this end, the 6 7 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 8 demonstrate better CO₂/CH₄ gas separation properties than the TR polymers derived from the 9 10 polyhydroxyimides at high conversion.

11 Conclusions

12 Meta and para oriented high molecular weight aromatic polyimides containing orthopositioned hydroxyl groups were synthesized using a diester-diacid monomer to avoid possible 13 reactions of the ortho-hydroxyl groups with the more reactive dianhydride monomer. Those 14 polyhydroxyimides were post-modified to change the *ortho*-functional groups to acetates. Then 15 the isomeric ortho-functional polyimides were converted to polymers with benzoxazole 16 17 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 18 efficient for conversion of the polyhydroxyimides but was insufficient for the corresponding 19 polyacetylimides. 20

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

1	rearrangement. Unlike traditional linear polymer membranes, the TR precursors had similar gas
2	permeabilities between meta and para oriented isomers due to a possible dominating effect of the
3	polar functional groups over the meta/para isomer effect. The TR polymers derived from
4	meta/para oriented isomeric TR precursors also had similar gas separation properties, especially
5	for CO ₂ /CH ₄ separation, and it is hypothesized that this is due to a lack of intersegmental
6	mobility distinction between the two isomeric TR polymers. Finally, the TR polymers derived
7	from meta/para isomeric precursors had similar gas separation properties, but the TR polymers
8	derived from the same backbone structure but with different ortho-functional groups had
9	different gas separation properties.
10	Acknowledgments
11	The authors gratefully acknowledge the financial support of Air Products and Chemicals, Inc.
12	and the National Science Foundation (Award Numbers DMR-1126564 and IIP-1237857).
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Highlights

- Polyhydroxyimides with different meta vs para monomers and their rearranged polybenzoxazoles were synthesized
- The polyacetylimides were shown to have high molecular weights and narrow distributions by SEC
- Both *meta* and *para* oriented TR polymers (TR400-*m*-HAB-6FDA-Ac and TR400-*p*-HAB-6FDA-Ac) surpassed the 1991 CO₂/CH₄ upper bound

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