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6 **Effect of Polymer Structure on Gas Transport Properties of**
7 **Selected Aromatic Polyimides, Polyamides and TR Polymers**
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GRAPHICAL ABSTRACT

ABSTRACT

Thermally rearranged (TR) polymers are formed through a thermally induced solid-state reaction of polyimides or polyamides that contain nucleophilic reactive groups ortho-positioned to their diamine. Naturally, the transport properties of TR polymers are intimately related to the chemical structure and reactivity of their precursors. Herein, we report characterization and transport properties for three poly(hydroxyimide) precursors prepared via thermal imidization in solution and for their corresponding TR polymers. Structural modifications to the polymer backbone can be used to control thermal rearrangement reaction kinetics. In regards to TR polymer formation, samples prepared from diamines with biphenyl functionality reacted more efficiently than those prepared from diamines with hexafluoroisopropylidene-linked aromatic units. However, hexafluoroisopropylidene functional units provided the highest combinations of permeability and selectivity for separations involving H₂, N₂, O₂, CH₄, and CO₂. Differences in permeability between samples correlated well with changes in free volume, and 3 poly(hydroxyimide)s showed unusually high selectivities for their given free volume. The effect of synthesis route was also investigated for a specific TR polymer derived from 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). Poly(hydroxyimide) precursors prepared via thermal imidization in solution and thermal imidization in the solid-state showed nearly identical permeabilities and selectivities regardless of synthesis route. However, after thermal rearrangement, the TR polymers prepared from polyimides synthesized via solid-state imidization have higher gas permeabilities than their solution-imidized analogs. In addition to light gas permeabilities, plasticization effects were investigated with CO₂ hysteresis loops for all samples, and pure-gas olefin/paraffin permeabilities were determined for a TR polymer derived from 2,2-bis (3-amino-4-

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7 hydroxyphenyl)-hexafluoropropane (APAF) and 6FDA. With the exception of HAB-
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9 6FDA polyimides, pure-gas CO₂ feed pressures up to approximately 50 bar do not reveal
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11 a plasticization pressure point, but conditioning effects are observed for most samples.
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13 APAF-6FDA TR polymers have pure-gas permeabilities and selectivities beyond the
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15 propylene/propane upper bound.
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21 **Keywords:** Thermally rearranged polymers; Polybenzoxazoles; CO₂ separations;
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23 Olefin/paraffin separations; Plasticization
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INTRODUCTION

Polymer membranes are currently deployed for applications such as natural gas sweetening, nitrogen enrichment, and syngas ratio adjustment.¹ To improve separation performance, new materials are sought with higher gas throughput, improved selectivity, and chemical/thermal resistance to aggressive feed conditions. Polybenzoxazoles (PBOs) and related structures have recently attracted significant interest from the membrane community, and these polymers are of interest for this work.

In 2007, Park *et al.* reported a method for synthesizing polymer films of PBO, polybenzothiazole, and polybenzimidazole structures.² These polymer films were formed from a solid-state reaction of polyimide precursors containing nucleophilic functional groups ortho-position to their diamine monomer. Although the technical nomenclature for this type of reaction is a 'condensation reaction', whereby 2 molecules of CO₂ are evolved per repeat unit,³ due to the thermal processing requirements needed to form these polymers, they are referred to as so-called 'thermally rearranged', or TR polymers.

Several synthetic design parameters can be used to modify the transport properties of these polymers. Han *et al.* investigated differences in the transport properties of TR polymers based on the synthesis route of their polyimide precursors.⁴ Calle *et al.* and Guo *et al.* demonstrated that the onset temperature for thermal rearrangement correlates with the glass transition temperature of the polyimide.⁵⁻⁷ Guo *et al.* and Sanders *et al.* demonstrated that transport properties could further be tuned by modifying the size of the ortho-functional leaving group, which, in addition to CO₂, is also evolved during thermal rearrangement.⁸⁻¹⁰

The thrust of this paper is to extend the current understanding of gas separations with TR polymers by investigating several polymer backbone chemistries. In this regard, we have investigated three poly(hydroxyimide) precursors synthesized via thermal

imidization in solution and their corresponding TR polymers. These polymers were selected due to their relevance in the field of polymer membrane research. 6FDA-based polyimides have been of interest for gas separations for years,¹¹⁻¹³ and analogous structures have been pursued for TR polymers.^{2,3,14-16} Ether-linkages, such as those found in polysulfones and polyamides, show a higher degree of rotational freedom,^{17,18} so the effect of these linkages on the thermal rearrangement reaction and transport properties were also investigated. In addition to light gas and CO₂ permeability measurements,² ether functionalities have also been investigated in TR polymers with dynamic mechanical analysis¹⁹ and for aromatic/aliphatic separations.²⁰ HAB and APAF-based TR polymers have shown promising transport properties for separating light gases and CO₂,^{2,3,15,16,21} and related structures have been fabricated into hollow-fibers and tested as thin films in physical aging studies.²²⁻²⁴

For separations involving CO₂ and other condensable penetrants, such as propylene and propane, plasticization can affect membrane performance.^{25,26} Polyimides are often susceptible to plasticization effects, and crosslinking strategies have been suggested to increase plasticization resistance.²⁷⁻²⁹ These strategies often result in polymers with higher selectivities but lower permeabilities.^{30,31} Conversely, for TR polymers, thermal treatment of polyimides typically results in higher permeabilities and lower selectivities.² Similar to crosslinking, however, TR polymers show improved plasticization resistance.^{2,32} This study investigates resistance to CO₂ plasticization through hysteresis pressurization-depressurization loops for a series of polyimides, polyamides, and TR polymers.

Olefin/paraffin separations have been identified as an emerging application for membrane-based separations,¹ and some of the best performing polymers are 6FDA-based polyimides.^{26,33,34} To investigate the performance of TR polymers with related

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7 structures, this study evaluates pure-gas permeability of C₂H₄, C₂H₆, C₃H₆, and C₃H₈ for
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9 one TR polymer, based on APAF-6FDA, and results show C₃H₆/C₃H₈ performance that is
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11 beyond the polymer upper bound.
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15 MATERIALS AND METHODS

16 17 18 Polyimide and polyamide synthesis

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20 Several polyimides and a polyamide were synthesized for this study. Diamines
21 included 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2-bis (3-amino-4-
22 hydroxyphenyl)-hexafluoropropane (APAF); dianhydrides included 2,2'-bis-(3,4-
23 dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 4,4'-oxydiphthalic
24 anhydride (ODPA); the diacid chloride was 2,2'-bis(4-chlorocarbonyl phenyl)
25 hexafluoropropane (6FCl). The chemically imidized polyimide, HAB-6FDA-C, was
26 synthesized according to a method described previously.^{16,35} HAB was supplied by
27 Wakayama Seiko Kogyo Co., Ltd. (CAS # 2373-98-0), 6FDA was purchased from Sigma
28 Aldrich (CAS # 1107-00-2), and APAF (CAS # 83558-87-6) and ODPA (CAS # 1823-
29 59-2) were purchased from Chriskev and Tokyo Chemical Industry (TCI), respectively.
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31 The thermally imidized APAF-6FDA polyimide and APAF-6FCl polyamide were
32 synthesized as described previously.³⁶ In addition to these samples, two additional
33 polyimides were thermally imidized in solution (i.e., HAB-6FDA and APAF-ODPA),
34 and one polyimide was synthesized via thermal imidization in the solid-state (i.e., HAB-
35 6FDA-SS). Unless otherwise noted, all concentration percentages for polymer solutions
36 are reported as the total mass of monomer in g per total volume of solvent in mL.
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Thermal imidization in solution for HAB-6FDA and APAF-ODPA

Standard solution thermal imidization techniques were used to prepare HAB-6FDA and APAF-ODPA.^{37,38} To prepare the monomers for synthesis, HAB and APAF were placed in a vacuum oven, which was shielded from light, and dried under full vacuum for 12 h at 60°C and 120°C, respectively. The dianhydrides were prepared using a two-step process. First, 6FDA and ODPA were held at 200°C under -10 in Hg for 6 h to dry the monomers and to close any hydrolyzed rings in the dianhydrides. Second, the oven temperature was lowered to 120°C and held for 12 h under full vacuum.

All monomers were allowed to cool to room temperature under full vacuum before beginning synthesis. Reactions were performed in a three-neck flask with an overhead mechanical stirrer. Synthesis glassware and Teflon[®] stirring blades were kept in a drying oven at approximately 115°C for 24 h before use. Ultra-high purity nitrogen gas (Airgas, 99.999%) was flowed through a Drierite column (W.A. Hammond Drierite Co., Ltd., Xenia, OH) to minimize the presence of water vapor in the reaction vessel.

In a typical synthesis batch, 25 mmol of diamine was added to the reaction flask. The diamines were dissolved in anhydrous N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, P/N 328634). HAB was dissolved in approximately 55 mL of NMP, and APAF was dissolved in approximately 51 mL of NMP. The diamines were allowed to dissolve for approximately 1 h, and an ice bath was used to cool the reaction solution before adding the dianhydrides. To the reaction flask containing HAB, 25 mmol of 6FDA were slowly added before adding an additional 55 mL of NMP. For the reaction flask containing APAF, 25 mmol of ODPA were slowly added before adding an additional 51 mL of NMP. Therefore, the solids concentration in the HAB-6FDA solution was 15%, and that in the APAF-ODPA solution was 20%. The reaction proceeded for approximately 18 h.

To begin thermal imidization, additional anhydrous NMP and an azeotropic agent, 1,2-dichlorobenzene (Sigma Aldrich, P/N 240664), were added to the reaction flask. To the HAB-6FDA poly(amic acid), approximately 55 mL of NMP and 41 mL of 1,2-dichlorobenzene were added to make an 8% solution, where a 1:4 volumetric ratio was maintained for 1,2-dichlorobenzene to NMP. A 10% solution was used for APAF-ODPA. A Dean Stark trap and condenser was attached to the nitrogen outlet of the reaction flasks, and the poly(amic acid)s were imidized at 180°C for 24 h.

Following imidization, the polymer solutions were cooled, further diluted with NMP to decrease solution viscosity, and precipitated in a non-solvent. HAB-6FDA was diluted to a 5% solution, and APAF-ODPA was diluted to an 8% solution. For HAB-6FDA, the non-solvent was methanol (VWR, P/N BDH-1135), and for APAF-ODPA, the non-solvent was an 85:15 mixture of methanol:deionized water. Approximately 10 mL of polymer solution was precipitated in approximately 400 mL aliquots of non-solvent, which were left stirring on low speeds in a blender. The polymer fibers were filtered from the solution using a Büchner funnel and washed with the non-solvent mixture.

Reaction solvent was initially removed by solvent extraction. HAB-6FDA was left stirring in approximately 1.5 L of methanol, and APAF-ODPA was left stirring in 1.5 L of a 20:80 mixture of methanol:deionized water for approximately 24 h. The polymers were then dried by filtration, rinsed thoroughly with their extraction solvent, and placed in fresh batches of extraction solvent. After waiting an additional 24 h, the polymers were again filtered and rinsed and placed in evaporation dishes before being transferred to a vacuum oven. Samples were dried in the vacuum oven at 80°C for 24 h, 120°C for 24 h, and 200°C for 48 h. Complete removal of solvent was confirmed by thermogravimetric analysis (TGA).

Thermal imidization in the solid-state for HAB-6FDA

HAB-6FDA was also prepared via thermal imidization in the solid state. The label, -SS, will be used to designate this type of imidization. For this synthesis method, the HAB-6FDA poly(amic acid) was prepared identically to the method described in the preceding section. However, instead of imidizing the poly(amic acid) in solution, the poly(amic acid) solution was diluted to 10% with NMP and poured onto flat glass plates. The glass plates were placed in a vacuum oven and heated under a light vacuum of approximately -10 in Hg at 60°C, 100°C, and 150°C for 1 h, 1.5 h, and 1.5 h, respectively. Next, the temperature was increased to 200°C for 1.5 h and 250°C for 1.5 h while applying full vacuum. Residual solvent was removed from the HAB-6FDA-SS films by heating at approximately 270°C for 12 h under full vacuum. Solvent removal was confirmed by TGA.

Film Casting

For the chemically imidized polyimide (i.e., HAB-6FDA-C), films were cast according to a procedure described previously.¹⁶ All solution thermally-imidized/amidized films (i.e., HAB-6FDA, APAF-6FDA, APAF-6FCl, and APAF-ODPA) were cast as described previously.³⁶ APAF-6FDA, APAF-6FCl, and APAF-ODPA were cast from 2% solutions of N,N-dimethylacetimide (DMAc, Sigma Aldrich, P/N D137510), and HAB-6FDA, which was more difficult to filter, was cast from a 1% solution. HAB-6FDA-SS was prepared as a film according to the method described in the previous section. All samples were approximately 30 - 40 μm in thickness except for the APAF-ODPA sample, which was approximately 20 μm . APAF-ODPA had the lowest permeability of all of the samples, and a thinner film was needed to more accurately determine permeability.

TR Polymer Formation

TR polymers were formed via a solid-state reaction of polyimide and polyamide films. All thermally imidized samples (i.e., HAB-6FDA, HAB-6FDA-SS, APAF-6FDA, and APAF-ODPA) were treated according to the following heating protocol. Polymer films were placed onto a flat ceramic boat and were covered by a ceramic plate. To allow for nitrogen to flow across the sample but to prevent the samples from curling during thermal treatment, the plate was separated from the boat by approximately 1 mm thick metal spacers. The sample was placed into a Carbolite three zone hinged tube furnace (Model HZS 12/–/600, Watertown, Wisconsin, USA), and a nitrogen (Airgas, 99.999%) flowrate of 900 mL/min was applied across the furnace tube. The samples were heated to 300°C at a rate of 5°C/min, held for 1 h, and then heated to 450°C at a rate of 5°C/min and held for 30 min. Next, the samples were cooled at a rate not to exceed 10°C/min. For the TR polymer formed from the polyamide (i.e., APAF-6FCI), the sample was heated at 5°C/min from ambient temperature to 350°C and held for 1 h, followed by cooling at a rate not to exceed 10°C/min.

Characterization

Thermogravimetric analysis (TGA) was used to study the thermal reactivity and thermal stability of polyimide and polyamide films using a TA Instruments Q500 TGA (TA Instruments, New Castle, DE, USA). Samples were heated under ultra-high purity N₂ (Airgas, 99.999%) with a balance flowrate of 40 mL/min and a sample flowrate of 60 mL/min. TGA thermograms were used to analyze the relative thermal reactivity and stability of films by heating at 5°C/min from ambient temperature to 800°C and monitoring the total mass loss and the derivative mass loss. The experimental mass loss during thermal rearrangement was also determined with TGA by following the same thermal treatment protocol used in the tube furnace, but with one exception: the cooling

rate for the TGA, which could be more accurately controlled than the furnace, was maintained at exactly 10°C/min.

Gel fractions were determined using a Soxhlet extractor (Wilmad-LabGlass, LG-6900-100) with DMAc (Sigma Aldrich, P/N D137510) as a solvent. Samples were weighed, placed into the extractor, and then refluxed in DMAc for 3 days or until the sample was fully dissolved. Next, samples were dried for 12 h at 225°C to remove solvent and the remaining portion of sample was weighed again. Gel fraction is reported as the final mass of polymer after solvent exposure divided by the initial mass of polymer.

Molecular weight was determined using size exclusion chromatography (SEC). This system consisted of a differential refractometer detector (VE 3580 RI detector, Viscotek), a differential viscometer, and right angle light scattering (RALS) detector (Trisec Model 270, Dual Detector, Viscotek), as described previously.³⁶

Solution ¹H and ¹³C NMR was performed with a Varian Inova 500 MHz NMR. Samples were dissolved in DMSO (Cambridge Isotope, P/N DLM-10-10) at concentrations of approximately 3% by weight. Peak assignments were determined from the following 2-D NMR experiments: correlation spectroscopy (COSY), heteronuclear single quantum correlation (HSQC) spectroscopy, and heteronuclear multiple bond correlation (HMBC) spectroscopy, similar to a method described previously.³⁶

Permeability was determined at 35°C using a constant volume variable pressure apparatus.^{39,40} Pure-gas permeability was calculated according to Equation (1):

$$P_i = \frac{V_D l}{p_2 A R T} \left[\left(\frac{dp_1}{dt} \right)_{ss} - \left(\frac{dp_1}{dt} \right)_{leak} \right] \quad (1)$$

where P_i is the permeability of component i , V_D is the calibrated volume downstream of the polymer film, l is the film thickness, p_2 is the upstream pressure, A is the area of the film accessible to gas permeation, R is the ideal gas constant, T is the absolute experimental temperature, $\left(\frac{dp_1}{dt}\right)_{ss}$ is the steady state rate of pressure-rise, and $\left(\frac{dp_1}{dt}\right)_{leak}$ is the system leak rate. For C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 , upstream fugacity values, f_2 , were used instead of upstream pressure values, p_2 , to calculate permeabilities. Fugacities were calculated using second and third virial coefficients from Dymond et al., and gas density data was taken from a NIST database, REFPROP.^{41,42} Third virial coefficients were estimated by fitting a polynomial to multiple data points around the temperature range of interest (e.g., 35°C) and taking the best fit value. Saturation fugacities were estimated by calculating fugacities at the saturation pressure. For supercritical gases, saturation pressures were determined by extrapolating vapor-pressure curves of $\ln p_{sat}$ versus $1/T$ to 35°C.⁴³ In certain cases where pressure-based permeabilities are reported, there are significant differences between the values of pressure and fugacity. For example, at the highest pressure considered (i.e., 50 bar), CO_2 has a fugacity of 39.2 bar, and CH_4 has a fugacity of 46.4 bar. While these differences do have an effect on permeability values calculated based on fugacity, there were no differences in the qualitative trends for our data, including CO_2 plasticization pressure curves. Pure-gas selectivity values were calculated as the ratio of the pure-gas permeabilities. The permeabilities used in the selectivity calculations were based on pressure for H_2 , N_2 , O_2 , CH_4 , and CO_2 , and they were based on fugacity for C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 .

For H_2 , N_2 , O_2 , CH_4 , and CO_2 , samples were tested at a pressure of approximately 1 bar, and then from 5 bar to 50 bar in increments of 5 bar. For the HAB-6FDA polyimide, the permeability of N_2 and CH_4 at 1 bar was close to the sample leak rate, and

these points were discarded. All gases were allowed to permeate for at least 6 times the time lag before recording the permeation data. For CO₂, the time lag was estimated at 1 bar, and each pressure step was run for 6 times the time lag at 1 bar. Because the initial pressurization step took several seconds to reach the set point at the upstream pressure, diffusion coefficients determined from these time-lag measurements showed significant test-to-test variability. Therefore, we cannot report diffusion coefficients for CO₂. The time-lag for the APAF-6FDA TR polymer was too fast to estimate, so this sample was held for 6 min at each pressure. Hysteresis loops for CO₂ were run using the aforementioned pressure steps, followed by decreasing the upstream pressure in increments of 5 bar down to a pressure of 5 bar. Following this hysteresis loop, the sample was then held under vacuum for approximately 25 time-lags, and a second pressurization step was performed using a protocol identical to that of the first pressurization step.

For C₂H₄, C₂H₆, C₃H₆, and C₃H₈, different pressurization steps were used according to the activity of the gases, where activity is defined as the ratio between the experimental upstream fugacity and the saturation fugacity (i.e., f / f_{sat}). The time-lag for these samples was determined at an activity of 0.05, and the sample was subsequently pressurized by incrementally increasing the upstream activities by 0.05. For C₂H₄, C₂H₆, C₃H₆, and C₃H₈, the maximum activities that could be reached with our systems were approximately 0.90, 0.95, 0.80, and 0.75, respectively. For samples that went through a plasticization pressure, comparisons of sample permeability and selectivity to the upper bound were only made up to the plasticization pressure except for olefin/paraffin datasets, where the entire pressure range is considered.

Positron annihilation lifetime spectroscopy (PALS) was used to compare differences in free volume between samples. Similar to our previous study,³⁶ we fitted

the PALS data to three lifetimes, indicating the presence of a single free volume distribution. For the TR polymers in this study, bimodal distributions could also be fit using four lifetimes, but, despite adding an additional fitting parameter, similar parameter uncertainties were obtained when fitting data to three or four lifetimes (single or bimodal distributions). Initial lifetimes and intensities were fit using a computer program, LT9,⁴⁴ and these parameters were used as initial fitting parameters for determining free volume distributions with another computer program, PAScual.⁴⁵ Very low intensities were recorded for some of the polyimide samples and partially converted TR polymers, which potentially indicates ortho-positronium (*o*-Ps) inhibition due to carbonyl functionality in the imides considered in this study.^{36,46} Therefore, we do not report PALS intensities for our samples; instead, we compare free volume using a semiempirical model.⁴⁷⁻⁵⁰

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R_F}{R_F + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R_F}{R_F + \Delta R} \right) \right]^{-1} \quad (2)$$

where τ_3 is the *o*-Ps lifetime, R_F is the radius of the free volume element, and ΔR is the electron layer thickness (1.66 Å).^{48,51} The volume of a hypothetical, spherical free volume element, V_F , can then be estimated from R_F :⁵²

$$V_F = \frac{4}{3} \pi (R_F)^3 \quad (3)$$

RESULTS AND DISCUSSION

Overview of polyimides, polyamide, and TR polymers considered in this study relative to other materials reported in the literature

Chemical structures of the polymers considered in this study are presented in Table 1. These structures are drawn as linear polymers, but, in reality, these structures may contain some degree of crosslinking. Sanders *et al.* and Smith *et al.* studied the permeability, diffusivity, and solubility of the HAB-6FDA-C polyimide and its corresponding TR polymers and found that the process of thermal rearrangement more strongly increases diffusivity than solubility.^{15,16,35} Guo *et al.* and Sanders *et al.* studied acetate and hydroxyl functional HAB-6FDA polyimides and TR polymers, among others, and found that gas permeability is more strongly influenced by the size of the ortho-functional leaving group than by the method in which these polymers were synthesized.⁸⁻¹⁰ Park *et al.* reported H₂, N₂, O₂, CH₄ and CO₂ permeabilities for a number of solid-state imidized polyimides and their corresponding TR polymers.^{2,3} These samples include an APAF-6FDA-SS polyimide, several APAF-6FDA-SS TR polymers treated for 1 h at temperatures between 350°C and 450°C, and an APAF-ODPA-SS TR polymer treated for 1 h at 450°C.^{2,3} Han *et al.* extended this work by investigating the effect of synthesis route on transport properties for APAF-6FDA polyimides and their corresponding TR polymers.⁴ These experiments were performed for polyimides synthesized from thermal imidization in the solid-state, thermal imidization in solution, and two forms of chemical imidization: chemical imidization with silylation and chemical imidization without silylation.⁴ Additional work by Han *et al.* has shown H₂ and CO₂ permeation results over a range of temperatures for the APAF-6FCl polyamide and corresponding TR polymer.²¹

Permeation and characterization data for the HAB-6FDA-C polyimide and TR polymers converted at temperatures between 350°C and 450°C have been reported in our previous studies.¹⁵ Herein, an additional four polyimides (i.e., HAB-6FDA-SS, HAB-

6FDA, APAF-ODPA, APAF-6FDA), a polyamide (APAF-6FCl), and their corresponding TR polymers are considered.

HAB-6FDA-C	
HAB-6FDA-SS HAB-6FDA	
APAF-ODPA	
APAF-6FDA	
APAF-6FCI	

Table 1. List of polyimides, polyamide, and TR polymers considered. Reaction temperatures and reaction products are included in the table. HAB-6FDA-C was thermally treated at 350°C for 1 h, 400°C for 1 h, or 450°C for 30min according to our previous work.^{15,16} The HAB-6FDA-SS, HAB-6FDA, APAF-ODPA, and APAF-6FDA samples were treated at 450°C for 30min, and the APAF-6FCI sample was treated at 350°C for 1h.

1.1.1 Thermal reactivity of polyimides and the polyamide

Table 2 presents the glass transition temperatures (T_g), theoretical mass loss expected from stoichiometric conversion of the polyimide to its TR polymer, and actual mass loss of samples considered. All samples have near-quantitative or slightly above quantitative conversion to their TR polymer structure. The uncertainty in these experiments is approximately $\pm 0.1\%$. Thus, mass loss beyond that expected from stoichiometric conversion is likely associated with some thermal degradation.

For the thermally imidized poly(hydroxyimide)s, changes in T_g track with the difference between the actual mass loss and the theoretical mass loss. The glass transition temperature increases in the following order: APAF-ODPA < APAF-6FDA < HAB-6FDA. Correspondingly, the sample with the highest T_g (i.e., HAB-6FDA), loses 0.4% more mass than theoretically expected, and the sample with the lowest T_g (i.e., APAF-ODPA), loses 0.9% more mass than theoretically expected. Calle *et al.* and Guo *et al.* have correlated the onset of thermal rearrangement with T_g for a variety of polyimides,^{5,6} and our findings support this interpretation of the thermal rearrangement reaction occurring at lower temperatures for samples with lower T_g s.

Table 2 also presents data for HAB-6FDA/-C/-SS and the other samples in this study. HAB-6FDA and HAB-6FDA-SS TR polymers have similar, near-quantitative mass loss. Sanders *et al.* have shown that conversion and permeation properties are similar between samples of identical chemical structure but prepared through different synthesis routes.¹⁰ Our results support the same conclusion. However, for HAB-6FDA-C, which contains an acetate-functional group, samples converted under the same conditions as the hydroxyl-functional HAB-6FDA polymers (i.e., 450°C and 30 min), showed a lower mass loss, indicating lower thermal reactivity for acetate-functional

groups than hydroxyl-functional groups. Additionally, the polyamide (i.e., APAF-6FCl), which has a similar T_g to that of HAB-6FDA-C, undergoes nearly quantitative thermal rearrangement at a much lower temperature than HAB-6FDA-C, which suggests that the thermal rearrangement reaction is not merely a function of T_g , but also the reactivity of the ortho-functional group as well. We did not detect a T_g for HAB-6FDA-SS, similar to an earlier publication by Hirayama *et al.*⁵³

Sample	T_g (°C)	Rearrangement Temperature (°C)	Rearrangement Time (min)	Theoretical Mass Loss (%)	Actual Mass Loss (%) [†]	Theoretical Mass Loss Minus Actual Mass Loss (%)	Reference
HAB-6FDA-C	255 ¹⁶	350, 400, 450	60, 60, 30	24.3	9.5, 14.6, 18.5	NA	¹⁶
HAB-6FDA-SS	--	450	30	14.1	14.6	0.5	This Study
HAB-6FDA	314 ⁶	450	30	14.1	14.5	0.4	⁶
APAF-ODPA	266 ⁶	450	30	13.7	14.6	0.9	⁶
APAF-6FDA	303 ⁶	450	30	11.4	12.2	0.8	⁶
APAF-6FCl	258 ⁵⁴	350	60	5.0	5.3	0.3	⁵⁴

Table 2. Glass transition temperatures for polyimide and polyamide precursors, conversion conditions, theoretical mass loss, actual mass loss, and the difference between the theoretical and actual mass loss of samples upon thermal rearrangement. No T_g was detected for HAB-6FDA-SS. [†]The heating rate was set at 5°C/min for increasing temperatures and -10°C/min for decreasing temperatures. All samples except APAF-6FCl had isothermal holds at 300°C for 1 h.

Figure 1 presents TGA thermograms for samples considered in this study. Two distinct regions of mass loss are observed. Such results are common for TR polymers, where the first stage of mass loss is attributed to thermal rearrangement, and the second stage of mass loss is attributed to thermal degradation.^{2,5-8,16,21,24,54-61} By comparing these regions, the temperature range and intensity of thermal rearrangement and degradation

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7 can be identified. Derivative weight loss values, shown on the secondary ordinate,
8 further assist these comparisons. Additionally, dashed lines are drawn on these plots to
9 indicate the theoretical mass loss expected for complete, stoichiometric thermal
10 rearrangement.
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15 For TR polymers containing the same backbone structure, the ortho-functional
16 leaving group strongly affects the thermal reactivity of these polymers. The first row in
17 Figure 1 highlights these effects by comparing thermograms for three samples of HAB-
18 6FDA: HAB-6FDA-C (Figure 1A), which contains an acetyl leaving group, and HAB-
19 6FDA (Figure 1B) and HAB-6FDA-SS (Figure 1C), which contain hydroxyl leaving
20 groups. The poly(hydroxyimide)s have similar thermograms, but the onset temperature
21 and intensity of thermal rearrangement are much lower for HAB-6FDA-C. For HAB-
22 6FDA-C, thermal rearrangement can be detected below 300°C, but the hydroxyl-
23 functional samples do not lose mass until approximately 350°C. Moreover, the
24 derivative mass loss in the thermal rearrangement regime suggests faster reaction kinetics
25 for the poly(hydroxyimide)s than the acetate-functional polyimide. The maximum in the
26 derivative weight loss curve for the thermal rearrangement region is approximately 2.5 to
27 3 times stronger for the poly(hydroxyimide)s than for HAB-6FDA-C. Additionally, the
28 temperature range for thermal rearrangement of the poly(hydroxyimide)s is narrower than
29 that of HAB-6FDA-C, which indicates a more efficient reaction for the
30 poly(hydroxyimide)s.
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49 For the acetate-functional sample, the earlier onset and decreased intensity of
50 thermal rearrangement relates to the TR reaction mechanism. Partially converted
51 samples of HAB-6FDA-C contain some hydroxyl functionality, as determined from FTIR
52 and NMR experiments.^{8,16} The acetate functionality first degrades to acetic acid, leaving
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7 a phenolic structure, which then undergoes thermal rearrangement. This two-step
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9 mechanism likely decreases the efficiency of the overall reaction; however, the stability
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11 of the acetyl group and lower T_g of the polymer sample promotes an earlier onset
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13 temperature for thermal rearrangement.⁶
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15 Modifying the polyimide diamine can also influence thermal rearrangement
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17 reactivity. The center column of Figure 1 (i.e., Figure 1B and Figure 1E) compares the
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19 thermograms between 6FDA-containing polyimides. The polymers differ in their
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21 diamine structures: Figure 1B is the thermogram for HAB-6FDA, and Figure 1E is the
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23 thermogram for APAF-6FDA. The maximum derivative mass loss for HAB-6FDA is
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25 nearly three times that of APAF-6FDA, which indicates that HAB is more reactive than
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27 APAF. The hexafluoroisopropylidene groups that bridge the APAF diamine are strongly
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29 electron withdrawing, which is known to reduce the reactivity needed for forming high
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31 molecular weight polyimides.⁶² Our results suggest that similar principles apply for
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33 thermal rearrangement, whereby thermal rearrangement reactivity is lower for the APAF
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35 sample because of its hexafluoroisopropylidene functional group.
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38 Steric effects may also influence thermal rearrangement reactivity. For APAF-
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40 containing polyimides, changing the 6FDA dianhydride to a more flexible ODPA
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42 dianhydride increases the reactivity of the thermal rearrangement reaction, which has
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44 been attributed to the higher segmental mobility of ODPA-containing polyimides
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46 compared to more rigid, higher- T_g polyimides.^{5,56} Figure 1D presents the thermogram for
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48 APAF-ODPA. For the thermal rearrangement region of this plot, the peak height for the
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50 derivative mass loss is almost twice that of the APAF-6FDA polyimide in Figure 1E. In
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52 addition to these steric effects, carbonyl electrophilicity may also influence thermal
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54 rearrangement. One would expect that ODPA, which has weaker electron-withdrawing
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characteristics than 6FDA, may decrease the electrophilicity of the imide carbonyl,⁶³ thus decreasing the reactivity for thermal rearrangement. However, our ¹³C NMR results show similar chemical shifts between both imide carbonyls of approximately 166 ppm (cf., Supporting Information). Therefore, steric effects play a more significant role in increasing the thermal rearrangement reactivity for ODP-PA-containing polyimides compared to 6FDA-containing polyimides.

A final comparison can be made between the thermal reactivity of the APAF-6FDA polyimide (cf., Figure 1E) and the APAF-6FCl polyamide (cf., Figure 1F). While the degradation regimes for both of these polymers occurs predominately above 450°C, the thermal rearrangement regime is quite different. The onset of thermal rearrangement for the polyimide begins at approximately 350°C. However, the polyamide begins to undergo thermal rearrangement around 250°C, indicating much higher thermal rearrangement reactivity for the 6FCl diacid chloride compared to the 6FDA dianhydride. This lower temperature window for thermal rearrangement further supports the work of Han *et al.* showing that TR polymers can be formed at much lower temperatures using polyamide-based precursors rather than polyimide-based precursors.²¹ In this study, near-quantitative thermal rearrangement can be achieved at temperatures 100°C lower for a polyamide-based sample than for a polyimide of similar backbone structure.

Figure 1. TGA thermograms of (A) HAB-6FDA-C, (B) HAB-6FDA, (C) HAB-6FDA-SS, (D) APAF-ODPA, (E) APAF-6FDA, and (F) APAF-6FCI. Figures (E) and (F) reproduced from Smith *et al.* with permission.³⁶ Theoretical mass loss was calculated as the mass loss expected for stoichiometric conversion of the polyimide or polyamide precursors to polybenzoxazoles (cf., Table 2).

Pure-gas permeabilities for the poly(hydroxyimide)s, poly(hydroxyamide), and corresponding TR polymers as a function of pressure

The pure-gas permeabilities of H₂, CH₄, N₂, O₂, and CO₂ and five selected permselectivities for the precursor poly(hydroxyimide)s, poly(hydroxyamide), and corresponding TR polymers are presented in Table 3. More complete data, including plots of permeability as a function of pressure for all gases and polymers, are recorded in the Supporting Information. H₂, CH₄, and CO₂ permeation properties for APAF-6FDA, APAF-6FCl and their corresponding TR polymers are taken from our previous work.³⁶

To more clearly show comparisons between transport properties for different gas pairs, upper bound plots for several gas pairs are shown in Figures 2 - 6. All TR polymer precursors are shown as open circles, and TR polymers are shown as open squares. Each precursor and analogous TR polymer are represented with the same colors, and discrete data points are shown for the permeability and selectivity of each pressure considered. The 2008 Robeson upper⁶⁴ bound is shown on each figure, and, where available, transport properties for common, commercially relevant polymers, such as tetrabromo polycarbonate (TBPC), cellulose acetate (CA), polysulfone (PSF), Matrimid[®], and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) are included.¹

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	HAB-6FDA PI	HAB-6FDA-SS PI	APAF-ODPA PI	APAF-6FDA PI	APAF-6FCI PA	HAB-6FDA-C PI			
H ₂	41 ± 1	43 ± 1	15 ± 1	60 ± 4	36.6 ± 0.9	37.8 ± 0.9			
CO ₂	12.3 ± 0.4	11.0 ± 0.4	1.7 ± 0.1	13.3 ± 0.4	10.5 ± 0.3	12.0 ± 0.3			
O ₂	2.89 ± 0.08	2.73 ± 0.09	0.60 ± 0.03	4.2 ± 0.2	3.24 ± 0.09	3.18 ± 0.07			
N ₂	0.42 ± 0.01	0.42 ± 0.01	0.071 ± 0.003	0.70 ± 0.02	0.59 ± 0.02	0.56 ± 0.01			
CH ₄	0.136 ± 0.006	0.135 ± 0.004	0.020 ± 0.001	0.171 ± 0.005	0.23 ± 0.01	0.313 ± 0.007			
N ₂ /CH ₄	3.1 ± 0.2	3.2 ± 0.1	3.5 ± 0.2	4.1 ± 0.2	2.57 ± 0.09	1.80 ± 0.05			
CO ₂ /CH ₄	91 ± 5	82 ± 4	87 ± 6	78 ± 3	46 ± 2	38 ± 1			
CO ₂ /N ₂	28.9 ± 0.8	26.0 ± 0.9	25 ± 1	19.0 ± 0.6	17.8 ± 0.5	21.6 ± 0.7			
H ₂ /CH ₄	304 ± 8	318 ± 9	740 ± 50	350 ± 30	160 ± 4	121 ± 4			
O ₂ /N ₂	6.8 ± 0.3	6.4 ± 0.3	8.4 ± 0.6	5.9 ± 0.3	5.5 ± 0.2	5.7 ± 0.2			
	HAB-6FDA TR	HAB-6FDA-SS TR	APAF-ODPA TR	APAF-6FDA TR	APAF-6FCI TR	HAB-6FDA-C TR 350	HAB-6FDA-C TR 400	HAB-6FDA-C TR 450	
H ₂	111 ± 3	218 ± 6	56 ± 2	592 ± 28	238 ± 6	95 ± 2	290 ± 20	530 ± 10	
CO ₂	50 ± 1	108 ± 3	7.1 ± 0.6	446 ± 35	127 ± 3	35.3 ± 0.6	160 ± 10	410 ± 10	
O ₂	13.5 ± 0.4	28.9 ± 0.8	4.9 ± 0.2	121 ± 7	38.2 ± 0.9	8.9 ± 0.2	39 ± 3	100 ± 2	
N ₂	2.7 ± 0.1	6.4 ± 0.2	0.82 ± 0.03	32 ± 2	9.2 ± 0.2	1.62 ± 0.03	8.7 ± 0.6	25.3 ± 0.6	
CH ₄	1.67 ± 0.05	3.9 ± 0.1	0.42 ± 0.01	20 ± 1	5.5 ± 0.1	0.77 ± 0.01	5.6 ± 0.4	18.2 ± 0.4	
N ₂ /CH ₄	1.64 ± 0.06	1.64 ± 0.07	2.0 ± 0.1	1.6 ± 0.1	1.67 ± 0.06	2.10 ± 0.05	1.6 ± 0.2	1.39 ± 0.04	
CO ₂ /CH ₄	30 ± 1	28 ± 1	41 ± 2	22 ± 2	23.2 ± 0.8	46 ± 1	28 ± 3	22.4 ± 0.7	
CO ₂ /N ₂	18.3 ± 0.6	16.9 ± 0.6	20.7 ± 0.8	14 ± 2	13.8 ± 0.4	21.7 ± 0.5	18.2 ± 0.2	16.1 ± 0.5	
H ₂ /CH ₄	66 ± 2	56 ± 2	135 ± 5	29 ± 2	43 ± 1	123 ± 3	52 ± 5	29.1 ± 0.8	
O ₂ /N ₂	4.9 ± 0.2	4.5 ± 0.2	5.9 ± 0.3	3.8 ± 0.3	4.2 ± 0.1	5.5 ± 0.2	4.5 ± 0.5	3.9 ± 0.1	

Table 3. Pure-gas permeabilities (in Barrer) of H₂, CO₂, O₂, N₂, and CH₄ for polyimides (PI), the poly(hydroxyamide) (PA), and their analogous TR polymers. Pure-gas selectivities for N₂/CH₄, CO₂/CH₄, CO₂/N₂, H₂/CH₄, and O₂/N₂ are also shown. Data are reported for 35°C and an upstream pressure of 10 atm. Data for HAB-6FDA-C samples taken from ref ¹⁵.

Figure 2. Upper bound comparison for the CO₂/CH₄ gas pair. Polyimide and polyamide precursors are shown as open circles, and TR polymers are shown as open squares. Literature data are shown as gray circles from Robeson's database,⁶⁴ and additional industrially relevant polymers (tetrabromo polycarbonate (TBPC), cellulose acetate (CA), polysulfone (PSF), Matrimid[®], and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)) are highlighted from the review by Sanders *et al.*¹ Data points are plotted for pure-gas permeability determined between approximately 1 and 50 bar with the exception of the HAB-6FDA and HAB-6FDA-SS polyimides, which are only plotted for pressures below their CO₂ plasticization pressure point. Data for HAB-6FDA and HAB-6FDA-SS partially overlap data for APAF-6FDA. The change of permeability and selectivity with increasing pressure is indicated for the APAF-6FDA TR polymer. APAF-6FCI TR polymer shows increasing selectivity with increasing CO₂ pressure, which likely indicates some CO₂ plasticization.³⁶ This figure was modified and reproduced from Smith *et al.* with permission.³⁶

Figure 3. Upper bound comparison for the CO₂/N₂ gas pair. Polyimide and polyamide precursors are shown as open circles, and TR polymers are shown as open squares. Literature data are shown as gray circles from Robeson's database,⁶⁴ and additional industrially relevant polymers (tetrabromo polycarbonate (TBPC), cellulose acetate (CA), polysulfone (PSF), Matrimid[®], and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)) are highlighted from the review by Sanders *et al.*¹ Data points are plotted for pure-gas permeability determined between approximately 1 and 50 bar with the exception of the HAB-6FDA and HAB-6FDA-SS polyimides, which are only plotted for pressures below their CO₂ plasticization pressure point. The change of permeability and selectivity with increasing pressure is indicated for the APAF-6FDA TR polymer.

Figure 4. Upper bound comparison for the N_2/CH_4 gas pair. Polyimide and polyamide precursors are shown as open circles, and TR polymers are shown as open squares. Literature data are shown as gray circles from Robeson's database,⁶⁴ and additional industrially relevant polymers (tetrabromo polycarbonate (TBPC), cellulose acetate (CA), polysulfone (PSF), Matrimid[®], and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)) are highlighted from the review by Sanders *et al.*¹ Data points are plotted for pure-gas permeability determined between approximately 1 and 50 bar. The change of permeability and selectivity with increasing pressure is indicated for the APAF-6FDA TR polymer.

Figure 5. Upper bound comparison for the H₂/CH₄ gas pair. Polyimide and polyamide precursors are shown as open circles, and TR polymers are shown as open squares. Literature data are shown as gray circles from Robeson's database,⁶⁴ and additional industrially relevant polymers (cellulose acetate (CA), polysulfone (PSF), Matrimid[®], and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)) are highlighted from the review by Sanders *et al.*¹ Data points are plotted for pure-gas permeability determined between approximately 1 and 50 bar. The change of permeability and selectivity with increasing pressure is indicated for the APAF-6FDA TR polymer. This figure is modified and reproduced from Smith *et al.* with permission.³⁶

Figure 6. Upper bound comparison for the O₂/N₂ gas pair. Polyimide and polyamide precursors are shown as open circles, and TR polymers are shown as open squares. Literature data are shown as gray circles from Robeson's database,⁶⁴ and additional industrially relevant polymers (tetrabromo polycarbonate (TBPC), cellulose acetate (CA), polysulfone (PSF), Matrimid[®], and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)) are highlighted from the review by Sanders *et al.*¹ Data points are plotted for pure-gas permeability determined between approximately 1 and 50 bar. The change of permeability and selectivity with increasing pressure is indicated for the APAF-6FDA TR polymer.

Effect of thermal rearrangement on transport properties

Conversion of all poly(hydroxyimide) and poly(hydroxyamide) precursors to TR polymers resulted in increased gas permeability and a concomitant decreases in selectivity, which resulted in transport properties that roughly paralleled the upper bound. A vast body of work in the literature reports improvements in permeability-selectivity property sets for TR polymers compared to their precursors,^{2-4,7,8,15,57-59,65-67} and these improvements have been attributed to increases in free volume and a narrowing in free

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7 volume distribution or, in certain cases, the formation of a bimodal free volume
8 distribution that occurs during the TR process.^{2,4,21,65,67-69}
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11 To investigate the role of thermal rearrangement on transport properties for our
12 samples, we first discuss our results in comparison with other studies in the literature and
13 then compare permeability and selectivity of our precursor and TR polymer samples
14 using free volume theory.
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19 Guo *et al.* and Sanders *et al.* investigated pure-gas permeabilities and selectivities
20 for HAB-6FDA polyimides, including a solution-imidized polyimide, similar to the one
21 investigated in this study, but prepared via an ester acid synthesis route and cast under
22 slightly different conditions.^{8,10} Upon partial conversion of this sample at 350°C, CO₂
23 permeability increased by over a factor of 5, and CO₂/CH₄ selectivity increased by 40%,
24 leading to an improvement in transport properties relative to the upper bound. Treatment
25 temperatures of 400 and 450°C further increased permeability, but resulted in decreases
26 in selectivity that moved these samples further from the upper bound. In fact, these
27 authors reported very little improvement relative to the upper bound for their HAB-6FDA
28 polyimide and most highly converted TR polymer, similar to the results we have
29 determined in this study.^{8,10}
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42 The synthesis route used to prepare polyimide precursors can strongly affect TR
43 polymer transport properties. Early studies on TR polymers focused exclusively on
44 preparing samples from polyimides that were thermally imidized in the solid state,^{2,3,57,59}
45 but it soon became apparent that TR polymer transport properties were affected by
46 precursor synthesis route. The first paper describing these effects, by Han and
47 colleagues,⁴ investigated the effect of polyimide synthesis route on transport properties
48 for APAF-6FDA TR polymers, which were thermally rearranged at 450°C for 60 min.
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7 Interestingly, in an upper bound comparison, they observed that TR polymers formed
8 from solid-state imidized polyimides had property sets well beyond those formed from
9 solution-imidized analogs; in fact, CO₂ permeabilities were over an order of magnitude
10 higher.⁴ Han *et al.* showed that these results were predominately related to the physical,
11 not chemical structure of TR polymers: permeabilities correlated with differences in
12 fractional free volume as determined by positron annihilation lifetime spectroscopy,
13 among other characterization tests.⁴ For our study on HAB-6FDA, we also observed
14 higher permeabilities for the TR polymer prepared from solid-state imidized polyimides.
15 For CO₂, permeabilities were approximately twice as high. These results suggest a
16 similar mechanism of transport for our samples and the APAF-6FDA samples reported
17 by Han *et al.*⁴ However, unlike the APAF-6FDA samples, our TR polymers exhibited
18 only minor shifts in their relation to the upper bound front: the solid-state imidized TR
19 polymers (i.e., -SS) had higher permeabilities but similar or reduced selectivities relative
20 to their solution imidized analogs. The molecular origins of these differences may relate
21 to sample preparation (e.g., conversion times of either 30 or 60 min) or to the difference
22 in polymer backbone chemistry (e.g., HAB-6FDA versus APAF-6FDA).
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41 Transport properties for the samples considered in this study tracked with free
42 volume. In general, permeability increases and selectivity decreases with increasing free
43 volume. Figures 7A and 7B present the relationship between free volume on
44 permeability and selectivity for each sample. For the regions of these plots with
45 overlapping data between precursors and TR polymers (i.e., the region between $V_f^{-1} \approx 5$
46 and 6 nm^{-3}), TR polymer have higher permeabilities but lower selectivities than
47 polyamides and polyimides with similar free volume. Such behavior suggests either
48 broader free volume distributions for the TR polymers or some more complicated
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scenario, such as the formation of bimodal distributions. However, within our limited set of data, it is difficult, and perhaps overly speculative, to determine which of these interpretations, or combinations of these interpretations, are most suitable. Interestingly, the largest disparities in Figure 7 occur for the H_2/CH_4 , CO_2/CH_4 , and N_2/CH_4 gas pairs. For these gas pairs, the TR polymers consistently have permeabilities and selectivities that are further from the upper bound than polyimides with similar free volume.

Figure 7. Comparison of (A) permeability and (B) selectivity as a function of average free volume element size determined by PALS. Precursors are shown as circles and TR polymers are shown as squares. Exponential fits to all data are shown to guide the eye.

Effect of chemical structure on transport properties

Figure 2 - 6 elucidate several structure-property relationships for polyimides and TR polymers. First, replacement of the hexafluoroisopropylidene-containing dianhydride with an ether-containing dianhydride has the strongest effect on gas permeability. Among the polyimide precursors, APAF-ODPA had permeabilities that were consistently

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7 lower than those of APAF-6FDA. For N₂ and CH₄, these permeabilities were nearly an
8 order of magnitude lower. Similar trends in permeability have been reported for other
9 ether versus hexafluoroisopropylidene-functional polyimides for propylene/propane
10 separation. In a study by Shimazu *et al.*, replacing a hexafluoroisopropylidene-functional
11 group with an ether-functional group reduced propylene permeability by nearly an order
12 of magnitude, and this decrease in permeability was almost exclusively associated with a
13 decrease in gas diffusivity.⁷⁰ The effect of ether versus hexafluoroisopropylidene
14 structure is even more pronounced for the TR polymers. In the polyimides, for example,
15 structural modification of ether to hexafluoroisopropylidene functionality increases CO₂
16 permeability by a factor of 8, but, for their corresponding TR polymers, this structural
17 modification increases CO₂ permeability by a factor of 62. In terms of the solution-
18 diffusion model, increases in permeability between polyimides and TR polymers is most
19 strongly correlated with increases in diffusivity.^{14,16} Therefore, replacing the rigid
20 hexafluoroisopropylidene-functional 6FDA with a more flexible ether-functional ODPA
21 results in more significant differences in permeability for TR polymers than their
22 corresponding polyimide precursors.

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24 Replacing the aromatic biphenyl diamine, HAB, with an aromatic
25 hexafluoroisopropylidene-functional diamine, APAF, resulted in slight increases in
26 permeability for the polyimides, but very large differences in permeabilities for the TR
27 polymers. At 10 atm, the APAF-6FDA polyimide had CO₂ and N₂ permeabilities that
28 were nearly 10% and 70% higher, respectively, than those of the HAB-6FDA polyimide.
29 However, after conversion, CO₂ and N₂ permeabilities were nearly 900% and 1200%
30 higher for the APAF-6FDA TR polymer compared to the HAB-6FDA TR polymer.
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These results, along with those for APAF-ODPA, highlight the importance in selecting highly permeable precursors when designing TR polymers with high permeability.

From the permeability results in Figure 5, all of the poly(hydroxyimide)s except APAF-ODPA reached or surpassed Robeson's 2008 H₂/CH₄ upper bound. To investigate the morphology of these materials, Figure 8 presents H₂ permeability and H₂/CH₄ selectivity as a function of free volume for all samples considered in this study. From these results, the tradeoff between free volume and permeability/selectivity is clear. However, compared to the other precursors and TR polymers, HAB-6FDA, HAB-6FDA-SS, and APAF-6FDA have unusually high selectivities relative to their given free volume, indicating that the hydroxyl group in these polyimides along with their rigid backbone structure, may provide a benefit to selectivity for the polyimides. On the other hand, APAF-ODPA, which also contains hydroxyl groups, may not have transport properties above the upper bound due to its flexible ether linkage.

Figure 8. Comparison of (A) H₂ permeability and (B) H₂/CH₄ selectivity as a function of average free volume element size determined by PALS. Precursors are shown as open circles, and TR polymers are shown as open squares. Error bars represent one standard deviation in uncertainty. Exponential fits to all data are provided to guide the eye.

Effect of polyamide versus polyimide precursor on transport properties

The APAF-6FDA polyimide had transport properties that were closer to the upper bound than those of the APAF-6FCl polyamide. Similar results were reported by Park *et al.*² and Han *et al.*²¹ for APAF-6FDA-SS and APAF-6FCl, respectively. Despite APAF-6FDA and APAF-6FCl TR polymers having nearly identical structures, these polymers showed differences in transport properties for all gases considered. These differences are presumably related to the non-equilibrium nature of these materials, meta/para versus strictly para configuration for the two samples, and differences in crosslinking.³⁶

Study of conditioning and plasticization effects with hysteresis loops

In the presence of high concentrations of condensable gases such as CO₂, polymer membranes can undergo plasticization and conditioning.^{25,71-73} Plasticization is often observed when polymers undergo penetrant-induced swelling, which often increases gas diffusion. Conditioning of a polymer upon exposure to condensable gases also influences polymer swelling. However, this term is used to describe relatively long-lived changes in transport properties that result after removing a condensable penetrant. To separate the effects of plasticization and conditioning, permeability hysteresis curves were recorded to document the effect of CO₂ exposure on transport properties.

The first set of samples considered are poly(hydroxyimide)s formed from thermal imidization in solution and their corresponding TR polymers. The hysteresis loops for HAB-6FDA and APAF-6FDA are shown in Figures 9 and 10, respectively. Similar to APAF-6FDA, APAF-ODPA showed no plasticization pressure point and little hysteresis (cf., Supporting Information). For the HAB-6FDA polyimide, a plasticization pressure is

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7 observed for the first pressurization step between approximately 10 and 15 atm, which is
8 a similar location for the plasticization pressure of HAB-6FDA-C.³² Such plasticization
9 pressures are also common for other polyimides, such as untreated Matrimid[®] (DAPI-
10 BTDA),⁷⁴ MDA-6FDA polyimide,⁷⁵ 6FpDA-6FDA,²⁸ and uncrosslinked DAM:DABA-
11 6FDA.⁷⁶ However, after thermal rearrangement, Figure 9B indicates no plasticization
12 pressure for the HAB-6FDA TR polymer. Similar suppression of plasticization due to
13 thermal rearrangement has been documented by Gleason *et al.*³² In addition to
14 plasticization, hysteresis results show a strong conditioning effect for the polyimide, but
15 more limited conditioning in the TR polymer. At 10 atm, CO₂ permeability is over 200%
16 higher for HAB-6FDA polyimide upon depressurization. However, CO₂ permeability is
17 only 20% higher for the HAB-6FDA TR polymer. Upon re-pressurization, the polyimide
18 has higher permeability, but the TR polymer has almost completely recovered. Within
19 the uncertainty of the measurements, the first and second pressurization steps overlap for
20 the TR polymer for almost every pressurization point. In contrast, permeability is
21 consistently higher for the second pressurization step compared to the first for the
22 precursor polyimide.
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Figure 9. CO₂ hysteresis loops for HAB-6FDA (A) polyimide and (B) TR polymer.

No plasticization pressure and little conditioning at feed pressures up to 50 bar are observed for TR polymers prepared from poly(hydroxyimide)s. Interestingly, the APAF-6FDA and APAF-ODPA polyimides (cf., Figure 10 and the Supporting Information, respectively) showed no plasticization pressure point and little hysteresis. For the APAF-ODPA polyimide, the difference in plasticization pressure response may relate to crosslinking occurring during solvent removal. The HAB-6FDA polymer had a 0% gel fraction after a three day exposure test in DMAc with a Soxhlet extractor, but the APAF-ODPA sample had a gel fraction of 49.8%. Solvent was removed from all of the poly(hydroxyimide)s at 270°C, which is slightly above the T_g of APAF-ODPA (266°C) but below the T_g of the other poly(hydroxyimide)s. The solvent removal temperature being above the T_g may allow sufficient chain flexibility in APAF-ODPA to induce crosslinking. Interestingly, the APAF-6FDA polyimide, which did not show a

plasticization pressure, also had a 0% gel fraction like HAB-6FDA. A macromolecular explanation for the relative stability of APAF-6FDA is currently unknown.

Nearly identical hysteresis curves were observed for the solution and solid-state thermally imidized HAB-6FDA samples. The HAB-6FDA-SS polyimide also had a 0% gel fraction, dissolving after a three day exposure test to DMAc, so it is presumably not crosslinked. The hysteresis curve for HAB-6FDA-SS is included in the Supporting Information.

Figure 10. CO₂ hysteresis loops for APAF-6FDA (A) polyimide and (B) TR polymer.

Similar to the APAF-6FDA polyimide, the APAF-6FCl polyamide hysteresis loop in Figure 11A shows no indication of plasticization pressure. The APAF-6FCl TR hysteresis loop in Figure 11B did not show a plasticization pressure either, but there was a stronger hysteresis effect for this sample compared to that of its polyamide precursor. Moreover, at lower pressures, differences in permeabilities are observed between the first

and second pressurization steps suggesting some plasticization. The APAF-6FCI TR polymer appears to show slight increases in CO₂/CH₄ selectivity with increasing pressure (cf., Figure 2), so although no plasticization pressure is observed, this sample may be undergoing slow structural relaxation during these experiments.

Figure 11. CO₂ hysteresis loops for APAF-6FCI (A) polyamide and (B) TR polymer.

Olefin-paraffin permeation properties of APAF-6FDA TR polymer

Ethylene and ethane permeation results are presented in Figure 12A the propylene and propane results are presented in Figure 12B for the APAF-6FDA TR polymer. Dual-mode behavior is observed at low activities, which is indicated by decreasing permeability with increasing pressure.⁷⁷ Furthermore, paraffin permeability is lower than olefin permeability, and olefin/paraffin permeabilities increase in the following order: C₃H₈ < C₂H₆ < CH₄ ≈ C₃H₆ < C₂H₄. At the experimental temperature considered (i.e.,

35°C), ethylene and ethane are both supercritical gases, which necessitated an extrapolation of their saturation fugacities to the temperature of interest to determine their gas phase activities.⁷⁸ Propylene and propane, however, are below their critical temperature, so their saturation fugacities were determined from the Wagner equation.⁷⁸

For our olefin and paraffin experiments, non-idealities in pressure-based permeabilities need to be corrected. Otherwise, misleading conclusions regarding plasticization could be gleaned from these results. From Equation 1 in the experimental section, permeability is calculated from a pressure- and thickness-normalized flux across a film. For gases that exhibit strong non-idealities, such as olefins and paraffins, the pressure-normalized flux needs to be replaced with a fugacity-normalized flux. Figure 13 presents normalized permeabilities for C₂H₄, C₂H₆, C₃H₆, C₃H₈, and CO₂ as a function of activity. Figure 13A presents permeabilities calculated based on pressure, and Figure 13B presents permeabilities calculated based on fugacity. Clearly, the most disparate interpretation between these plots occurs for C₂H₄ and C₂H₆. When considering pressure-based permeabilities (cf., Figure 13A), these results indicate that no plasticization pressure point is reached for either gas. However, when considering fugacity-based permeabilities, a clear plasticization pressure point is observed at activities near 0.30. While the trend for changes in permeability for C₃H₆ and C₃H₈ is similar between pressure and fugacity-based permeability, we present these data (cf., Figure 12B) on a fugacity basis for consistency with our olefin/paraffin study. At the activities considered for CO₂, there are differences in CO₂ permeability when calculated with pressure or fugacity. However, the trends in CO₂ permeation remain the same regardless of the calculation method used. Therefore, we have reported CO₂

permeabilities based on pressure, but we have calculated C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 permeabilities based on fugacity.

Figure 12. Permeability of ethylene, ethane, propylene, and propane as a function of feed fugacity in APAF-6FDA TR at 35°C. Olefins are shown as open circles, and paraffins are shown as filled circles. Uncertainties were estimated as one standard deviation based on the propagation of error technique described by Bevington and Robinson.⁷⁹

Figure 13. Comparison of normalized permeabilities as a function of activity when permeability is calculated based on (A) upstream pressure or (B) upstream fugacity for APAF-6FDA TR.

Upper bound data is presented for ethylene/ethane in Figure 14 and for propylene/propane in Figure 15. Pure-gas selectivities were calculated by fitting a smooth fit to the data in Figure 12 and determining the ratio of permeabilities over the range of pressure considered. Therefore, the ethylene/ethane data points represent permeabilities and selectivities up to approximately 46 atm, and the propylene/propane data points represent permeabilities and selectivities up to approximately 8.5 atm. For ethylene/ethane separation, the selectivity of the APAF-6FDA TR polymer is < 3 , and this data lies below the upper bound. However, for propylene/propane, the APAF-6FDA TR polymer falls above the current upper bound.

The polymer upper bound for ethylene/ethane and propylene/propane are defined by a limited number of polymers, and the polymers closest to the upper bound are 6FDA-containing polyimides.^{33,80} For the ethylene/ethane gas pair, 6FDA-NDA polyimide defines the upper bound,⁸⁰ and for the propylene/propane gas pair, 6FDA-DDBT and 6FDA-TrMPD polymers define the upper bound.³³ Therefore, certain chemical structures that have upper bound separation performance for the ethylene/ethane gas pair may not have upper bound separation performance for the propylene/propane gas pair, and *vice versa*, which appears to be the case here for APAF-6FDA TR polymer. Nevertheless, these results indicate that TR polymers formed from near-upper bound precursor polyimides may be of interest for olefin/paraffin separation.

Figure 14. Upper bound comparison for C_2H_4/C_2H_6 .⁸⁰ The APAF-6FDA TR polymer data is presented up to pressures of approximately 46 atm.

Figure 15. Upper bound comparison for C_3H_6/C_3H_8 .³³ The APAF-6FDA TR polymer data is presented up to pressures of approximately 8.5 atm.

CONCLUSIONS

Several polyimides and a polyamide containing reactive functional groups suitable for forming thermally rearranged polymers were synthesized. These polymers include three polyimides (i.e., HAB-6FDA, APAF-6FDA, APAF-ODPA) and a polyamide (i.e., APAF-6FCl). Thermogravimetric analysis shows that the HAB-containing polymers are more reactive than those containing APAF moieties. Furthermore, the flexible ether linkage in ODPA increases the reactivity of the thermal rearrangement reaction relative to 6FDA-containing polyimides. Higher combinations of gas permeability and selectivity are observed for polyimides compared to polyamides and for polyimides containing hexafluoroisopropylidene linkages. Additionally, TR polymers

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7 formed from better performing precursors are typically closer to the upper bound,
8 indicating that transport properties for TR polymer precursors can be used to gauge the
9 relative performance of TR polymers. One exception to this correlation is for TR
10 polymer precursors formed from different synthesis routes. For HAB-6FDA, TR
11 polymers synthesized from a solid-state imidized polyimide were slightly closer to the
12 upper bound than the sample synthesized via thermal imidization in solution. Differences
13 in transport properties between these samples likely relates to differences in their casting
14 and imidization procedure (i.e., thermal processing history). Plasticization and
15 conditioning of all samples were analyzed by CO₂ permeability hysteresis curves. HAB-
16 6FDA samples (thermally imidized in solution and in the solid-state) were the only
17 samples to show evidence of plasticization in permeability pressures curves. Conversion
18 of HAB-6FDA to its corresponding TR polymer resulted in increased permeability and
19 no plasticization pressure. None of the other samples showed CO₂ plasticization
20 pressures up to 50 bar, which may indicate plasticization resistance for several TR
21 polymer precursors. The TR polymer formed from APAF-6FDA was tested for C₂H₄,
22 C₂H₆, C₃H₆, and C₃H₈ permeability, and this sample showed separation performance
23 beyond the polymer upper bound for propylene/propane separation. These transport
24 results may indicate that the APAF-6FDA TR polymer may have a favorable diffusion
25 selectivity for C₃H₆/C₃H₈, similar to other highly selective glassy polymers for this
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