Gas permeation and mechanical properties of thermally rearranged (TR) copolyimides

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Abstract

Gas transport and mechanical properties are reported for a series of copolyimides and their corresponding thermally rearranged (TR) analogs. Random copolyimides of APAF/HAB-6FDA with various compositions were synthesized via chemical imidization from 2,2'-bis (3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF), 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), and 2,2'-bis-(3,4-dicarboxy-phenyl) hexafluoropropane dianhydride (6FDA). These copolyimides were thermally treated at temperatures between 350 °C and 450 °C to prepare TR polybenzoxazoles (PBOs). Pure gas permeabilities of H₂, CH₄, N₂, O₂, and CO₂ were measured at 35 °C with upstream pressures ranging from 3 to 17 atm. In general, gas permeability increased and selectivity decreased as TR conversion increased. Gas permeability also increased with increasing APAF content in the polyimides as a result of higher fractional free volume (FFV) imparted by the extra hexafluoroisopropylidene group in APAF. Stress-strain relationships were recorded for the polyimides and their TR analogs. As polyimides underwent thermal rearrangement, samples became more rigid, and tensile stress and elongation at break decreased. A similar trend in mechanical properties was also observed as APAF content increased, which was attributed to the lower molecular weight of APAF-containing polymers, resulting from the lower reactivity of APAF relative to that of HAB.

Keywords: Thermally rearranged; polybenzoxazole; HAB; 6FDA; APAF; mechanical property

1. Introduction

CO₂ removal from natural gas is a growing application for membrane technology [1]. Compared with traditional amine absorption technology, membranes are attractive due to lower capital cost and energy consumption, smaller footprint, ease of process integration, and lower maintenance costs [1-4]. Today, many commercial membrane systems in gas separation applications are based on hollow fibers prepared via phase inversion [2]. Hollow fibers have a high packing density, i.e., high membrane surface area per unit volume. During a typical spinning process, a viscous polymer solution or dope is pumped through an extrusion die to form hollow fibers with a cylindrical shape. Then, the fiber passes through a short air gap before entering a coagulation bath that solidifies the polymer into an asymmetric porous structure and removes the solvent [1, 5]. During this process, the fiber needs sufficient mechanical integrity to survive the tension applied to draw the fiber through the coagulation bath and along the spin line. Additionally, the manufacturing of membrane modules from hollow fibers can apply significant mechanical forces to the membranes. Furthermore, transportation, installation, and operation can subject membranes to a variety of continuous as well as periodic stresses and shocks. Therefore, new materials synthesized and characterized for gas separation applications should have favorable combinations of gas transport and separation properties and have sufficient mechanical properties to survive manufacturing, transport, installation, and operation.

In 2007, Park et al. reported gas transport properties of a family of polymers known as thermally rearranged (TR) polymers [6], which exhibited exceptional CO₂ permeability and CO₂/CH₄ selectivity, good resistance to plasticization, and excellent chemical resistance [6-8]. These TR polymers are often polybenzoxazoles (PBO) prepared by thermal treatment of polyimide precursors bearing *ortho*-position functional groups [8]. Because these PBOs are

typically insoluble in common organic solvents, the ability to prepare them from soluble polyimide precursors allows TR polymers to be fabricated into hollow fibers using conventional technology and then thermally treated to form the PBOs with desirable transport properties [5, 9].

Since the initial report by Park et al., many studies have explored structure-property relationships of various TR polymers. The effects of various *ortho*-position functional groups [10-13] and glass transition temperature (T_g) of polyimide precursors [14, 15] on free volume and gas transport properties have been investigated. Copolymers of PBO-polyimide [13, 16, 17], PBO-polypyrrolone [18], and PBO-polyamide [19] have been studied to combine the excellent gas separation properties of PBO with benefits from other families of materials. In addition to single-gas permeation and sorption studies [8, 20], mixed-gas permeation [6, 21], water vapor transport [22], and pervaporation of aromatic/aliphatic hydrocarbon mixtures [23] have also been reported for different TR polymers. Simulation studies using molecular dynamics and Monte Carlo methods have been performed to understand the influence of free volume and free volume distribution on gas transport properties of these materials [24, 25]. Until now, however, relatively few studies have documented the mechanical properties of TR polymers and copolymers [6, 17, 26].

Mechanical properties of polymers depend on many parameters, such as molecular weight, molecular weight distribution, temperature, sample preparation history, and experimental technique [27-29]. For this reason, comparison of mechanical properties among different studies is difficult. As a result, mechanical properties, such as tensile stress and elongation at break, are commonly reported in ranges. TR polymers, despite their good gas separation characteristics, tend to become more brittle as thermal rearrangement proceeds [30]. Recently, some studies focused on improving mechanical properties of TR polymers by either blending PBO with other

polyimides [17] or introducing spirobisindane moieties into the PBO structure [26]. These strategies have shown promising improvements in mechanical properties, but usually at the expense of gas transport properties.

This study aims to characterize gas transport and mechanical properties of a series of copolyimides and their corresponding TR analogs. Polyimide precursors based on 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB), 2,2'-bis (3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF), and 2,2'-bis-(3,4-dicarboxy-phenyl) hexafluoropropane dianhydride (6FDA) were prepared using a conventional two-step process including condensation polymerization of dianhydride and diamine followed by chemical imidization [8, 9]. Chemical structures of polyimides and corresponding PBOs considered in this study are presented in Fig. 1. Based on previous studies, PBOs prepared from APAF-6FDA typically have better gas transport properties than those prepared from HAB-6FDA, due in part to the higher free volume of APAF-6FDA [8, 31]. On the other hand, because the 6F unit in APAF is strongly electron withdrawing, APAF is a weaker nucleophile than HAB, which decreases the reactivity of APAF-based polyimides compared to analogous HAB-based polyimides, thus yielding polyimides with lower molecular weights, all other factors being equal [32, 33]. Higher molecular weight often leads to better mechanical properties [28]. By comparing gas transport and mechanical properties of copolyimides and their TR polymers, this study seeks to elucidate the apparent tradeoff between gas transport and mechanical properties.

Fig. 1. Chemical structures of monomers, polyimide precursor, and TR polymer considered in this study.

2. Experimental

2.1. Synthesis

HAB-6FDA, APAF-6FDA, and copolyimide precursors were prepared using a conventional two-step process including condensation polymerization of dianhydride and diamine followed by chemical imidization [9]. HAB and APAF were purchased from Chriskev (Overland Park, KS) and 6FDA was purchased from Alfa Aesar (Word Hill, MA). To prepare the monomers for synthesis, HAB and APAF were heated at 50 °C and 120 °C, respectively, under full vacuum for 12 h. To prevent degradation, the monomers were shielded from light by placing aluminum foil around the monomer container and over the window of the vacuum oven. 6FDA was heated to 200 °C under partial vacuum for 6 h and then cooled to 120 °C under full

vacuum to remove any water resulting from hydrolyzed dianhydride rings. *N*-methyl-2-pyrrolidinone (NMP, anhydrous), pyridine (99.9%), acetic anhydride (99.5%), and dimethylacetamide (DMAc, anhydrous) were purchased from Sigma Aldrich (St. Louis, MO).

A typical synthesis of polyimide was as follows: 20 mmol of diamine (i.e., APAF, HAB, or a mixture of APAF and HAB) was added to a three-neck flask and dissolved in 44 mL of NMP under a nitrogen purge. After at least 30 min of rigorous stirring, 20 mmol of 6FDA was added along with another 44 mL of NMP to make a 15% (grams of monomers / mL of NMP) solution. The three-neck flask was placed in an ice bath, and the solution was stirred for 12 h to form the poly(amic acid). Then, the poly(amic acid) was imidized using a standard chemical imidization method [8, 32]. For every mole of diamine, 8 moles of acetic anhydride and 8 moles of pyridine were added simultaneously to the reaction flask. Additional NMP was added to reduce the solution concentration to 8% (grams of monomers / mL of solvents (i.e., NMP, acetic anhydride, and pyridine)). The reaction flask was placed in an oil bath and held at 80 °C for 24 h. Afterwards, the solution was precipitated in a non-solvent. For HAB-6FDA, the non-solvent was methanol, and for APAF-6FDA and the copolyimides, the non-solvent was a 70:30 (v/v) mixture of methanol:deionized water. Following precipitation, the resulting polyimide was heated under vacuum at 100 °C for 24 h, 150 °C for 24 h, and 200 °C for 48 h to dry the polymer.

For APAF/HAB-6FDA copolyimides, the naming convention is AH followed by the mole fraction of APAF-6FDA used in the copolymers synthesis. For example, AH(0.75) refers to a copolyimide prepared with 75 mol% of APAF-6FDA and 25 mol% of HAB-6FDA. ¹H NMR spectra of copolymers (cf., Supplementary Information) verified that the mole ratio of monomers used in the synthesis corresponded to the expected composition of the final copolymer. The protocol to synthesize copolyimides was identical to that used for APAF-6FDA.

APAF and HAB were added simultaneously to the reaction flask during synthesis, and the amount added was based on the desired molar ratio of the copolymer. Chemical structures of the resulting homopolymers and copolymers are presented in Fig. 1.

2.2. Film casting

Dense films of 25-40 μm were prepared by controlled evaporation of polyimide solutions. A polymer solution containing 3 grams of polymer per 100 grams of solvent was prepared by dissolving the polyimide in DMAc. The well-mixed solution was filtered through a 5.0 μm Millex-LS PTFE filter (SLLS025NS, Millipore, Billerica, MA, USA) and cast onto a clean, flat, and level glass plate. The solution was initially heated to 80 $^{\circ}\text{C}$ under a partial vacuum of about -25 cmHg for 24 h and then at 100 $^{\circ}\text{C}$ for another 24 h. During this process, solvent from headspace of the vacuum oven was occasionally removed by partially opening both the vacuum valve and the vent valve to maintain a pressure of -25 cmHg. Next, the samples were held at 100 $^{\circ}\text{C}$ under full vacuum for 12 h. Afterwards, films were immersed in deionized water and detached from the glass plate. Finally, the films were sandwiched between two glass plates covered with aluminum foil and heated under full vacuum at 200 $^{\circ}\text{C}$ for 24 h. Solvent removal was confirmed using thermogravimetric analysis.

2.3. TR polymer conversion

Polyimide samples were converted to PBOs by thermal treatment in a Carbolite three-zone hinged tube furnace (Model HZS 12/-/600, Watertown, Wisconsin, USA) for a given amount of time ("Time at Rearrangement Temperature" in Table 1) at a given final temperature ("Rearrangement Temperature" in Table 1). The tube furnace was purged with nitrogen at 900 mL/min. Polymer samples were sandwiched between two ceramic plates inside a ceramic boat. Metal spacers were inserted between the ceramic plates to allow nitrogen to reach the

samples. Polyimide samples were initially heated to 300 °C at 5 °C/min and held at 300 °C for 1 h to ensure complete imidization [8, 20]. Afterwards, the films were heated at 5 °C/min to the final rearrangement temperature of either 350 °C for 1 h, 400 °C for 1 h, or 450 °C for 30 min. Finally, the samples were cooled to ambient temperature at 10 °C/min. These conditions were chosen to minimize polymer degradation and to be consistent with earlier reports [8, 11, 12]. By-products of thermal rearrangement have been characterized using TGA-mass spectroscopy by Smith et al. [20]. Chemical structures of PBOs derived from polyimides considered in this study are presented in Fig. 1. Although linear structures are drawn for PBOs, interchain thermal rearrangement may occur, resulting in a crosslinked PBO structure [6]. Percent TR conversion, as presented in Table 1, is defined as 100 times the ratio of the actual mass loss upon thermal rearrangement to the theoretical mass loss:

$$\% TR Conversion = \frac{Actual Mass Loss}{Theoretical Mass Loss} \times 100 \quad (1)$$

This calculation was based on the assumption that any polyimide segment that underwent thermal rearrangement was converted to its corresponding polybenzoxazole segment. The implications and limitations of this methodology have been discussed by Sanders et al. [11].

Table 1. Thermal rearrangement conditions and percent TR conversions for samples considered in this study.

Sample		Rearrangement Temperature (°C)	Time at Rearrangement Temperature (min)	TR Conversion (%)
HAB-6FDA	PI	-	-	-
	TR350	350	60	37
	TR400	400	60	59
	TR450	450	30	74
AH(0.25)*	PI	-	-	-
	TR350	350	60	43
	TR400	400	60	56
	TR450	450	30	78
AH(0.5)*	PI	-	-	-
	TR350	350	60	40
	TR400	400	60	58
	TR450	450	30	72
AH(0.75)*	PI	-	-	-
	TR350	350	60	47
	TR400	400	60	58
	TR450	450	30	83
APAF-6FDA	PI	-	-	-
	TR350	350	60	40
	TR400	400	60	62
	TR450	450	30	81

Note: *AH(x) indicates a copolyimide synthesized with x mole fraction of APAF-6FDA and (1-x) mole fraction of HAB-6FDA.

2.4. Characterization

The chemical structures of the polyimides were confirmed using a Varian NOVA 500MHz nuclear magnetic resonance spectrometer (NMR). ¹H NMR spectra were recorded using solutions of about 10% (w/v) polymer in deuterated dimethyl sulfoxide (d-DMSO).

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 Thermogravimetric Analyzer (Newcastle, DE). TGA scans were conducted in N₂ (UHP grade,

Airgas) at 5 °C/min ramp rate. Nitrogen flow rate was maintained at 40 mL/min in the TGA balance and 60 mL/min in the sample chamber.

The glass transition temperatures (T_g) of polyimides were measured using a TA Instruments Q100 differential scanning calorimeter (DSC). Samples were heated at 10 °C/min from 25 °C to 300 °C under a N₂ flow rate of 50 mL/min. The transition of the midpoint of the heat capacity step change in the first scan was taken as the T_g .

Density was determined based on Archimedes' principle using a Mettler-Toledo balance (Mettler-Toledo GmbH, P706039) equipped with a density kit [34]. The liquid used for the density kit was *n*-heptane because it did not sorb into polyimides and TR polymers to a measurable extent over the time scale of the measurement.

Inherent viscosity of the polyimides was determined at 25 °C using a Cannon-Fenske viscometer (PN: 7988-37, Ace Glass, Vineland, NJ, USA) using a procedure described elsewhere [35]. A solution of 0.5 g polymer/dL solution was prepared by dissolving samples in NMP. The viscometer was rinsed with the solution three times before viscosity measurements were undertaken.

Mechanical properties were measured using a Universal Testing Machine (Model AGS-X, Shimadzu, Kyoto, Japan). Pneumatic grips were used to make sure equal force was applied to each sample upon mounting. In addition, the grips were rubber-coated to prevent polymer samples from slipping during testing. Films used for tensile testing in this study ranged in thicknesses between 80 and 100 µm. Samples were cut into a dog-bone shape, in accordance with ASTM D-1708-13 standard [36]. This standard was used to accommodate the small dimensions and thicknesses of the typical polymer films used in this study. After a sample was

mounted in the grips, it was pulled at 1 mm/min until it broke. A stress-strain plot was prepared for each sample tested, and tensile stress and elongation at break were recorded. At least five samples were tested for each material. The Young's modulus was estimated by taking the ratio of stress to strain in the initial linear region of each stress/strain plot.

2.5. Gas permeation

Pure-gas permeability coefficients were measured using a constant volume-variable pressure method [37]. A gas at a feed pressure of P_o was applied to the upstream side of the film, and gas permeated through the film into a calibrated downstream chamber of volume, V . Permeabilities of H_2 , CH_4 , N_2 , O_2 , and CO_2 were measured in that order at 35 °C and feed pressures ranging from 3 to 17 atm for the polyimides and their TR analogs. The permeability of gas A, P_A , was calculated as follows [37]:

$$P_A = \frac{Vl}{P_oRTA} \left[\left(\frac{dp}{dt} \right)_{ss} - \left(\frac{dp}{dt} \right)_{leak} \right] \quad (2)$$

where l is film thickness, R is the gas constant, T is absolute temperature, A is film area, and $\left(\frac{dp}{dt} \right)_{leak}$ and $\left(\frac{dp}{dt} \right)_{ss}$ are the rates of pressure rise in the downstream volume during the leak test and when the gas permeation through the film is at pseudo-steady state, respectively. The leak test was conducted by isolating the downstream and upstream sections of the permeation system and monitoring changes in the downstream pressure for about 1 h. Permeabilities are reported in units of Barrer, where 1 Barrer is $10^{-10} \frac{cm^3 (STP) cm}{cm^2 s cmHg}$. Pure-gas selectivity, $\alpha_{A/B}$, is defined as the ratio of pure-gas permeabilities [37]:

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

where P_A is the permeability coefficient of the more permeable gas, and P_B is the permeability of the less permeable gas.

3. Results and Discussion

3.1. Synthesis and ^1H NMR characterization

Polyimide precursors were prepared by an initial condensation reaction of diamine (HAB and/or APAF) and dianhydride (6FDA) followed by chemical imidization [9]. First, a poly(amic acid) intermediate was obtained from the step-growth polymerization of the diamine and dianhydride monomers. In the case of copolymerization, typically only random copolymers result from such one-step condensation reaction [38]. Formation of random copolymers occurs because polycondensation usually allows extensive interchange among monomers and leads to equilibrium-controlled products, in which monomers are randomly distributed in the copolymer chains [38]. The resulting poly(amic acid) was subsequently imidized using a standard chemical imidization method [9].

^1H NMR was used to confirm the chemical structures of polyimides. Representative examples of the ^1H NMR spectra for HAB-6FDA and APAF-6FDA are presented in Fig. 2. A peak associated with the NMR solvent, d-DMSO, appears at 2.5 ppm, and the proton from the acetate functionality appears at 2.2 ppm [39]. The aromatic proton resonances are between 7.4 and 8.2 ppm, and the peak assignments are shown accordingly. No peak corresponding to carboxylic acids was observed above 10 ppm [39], so that the poly(amic acid) was fully imidized. The composition of the copolymers was also confirmed. ^1H NMR spectra of the copolyimides are included in Supplementary Information.

Fig. 2. ^1H NMR spectra and peak assignments for HAB-6FDA and APAF-6FDA.

3.2. TGA characterization

Fig. 3 presents TGA scans for the homopolymers and copolymers. The labels “HAB” and “APAF” indicate HAB-6FDA and APAF-6FDA, respectively, and the copolymer naming convention was defined earlier. Consistent with previous studies, TGA scans of TR polymers typically display a two-stage mass loss [6, 8, 20]. The first stage, in this case between 300 °C and 450 °C, is associated primarily with thermal rearrangement. The second stage, in this case starting at around 500 °C, is attributed mainly to thermal degradation. As shown in Fig. 3A, TGA scans show similar thermal stability for all polymers up to 500 °C. The slight difference between the thermal behavior of HAB-6FDA and APAF-6FDA, as shown in Fig. 3B, which focuses on TGA regions between 200 °C and 450 °C, may be attributed to the slightly higher theoretical mass loss for TR conversion of HAB-6FDA (24.3% mass loss) relative to that of APAF-6FDA (20.0% mass loss). As polymers begin to degrade at higher temperatures (e.g.,

500 °C), there is a greater mass loss in samples with higher APAF content, which may be attributed to the degradation of hexafluoroisopropylidene units in APAF [7, 40].

Fig. 3. Thermogravimetric analysis of polymers considered in this study. These experiments were performed as described in the Experimental section. (A) Complete scan up to 800 °C. (B) Scan focusing on the region between 200 °C and 450 °C.

3.3. DSC characterization

The glass transition temperatures of the polyimides considered in this study are presented in Table 2. A single T_g was observed for each polyimide, consistent with that observed for typical random copolymers [41]. The T_g decreases as APAF content increases. For example, the T_g of HAB-6FDA (279 °C) is 21 °C and 33 °C higher than that of AH(0.5) and APAF-6FDA, respectively. Adding hexafluoroisopropylidene (i.e., 6F) units to other polymer backbones also decreases T_g [42]. Table 3 presents data comparing physical, thermal, and gas transport properties of several linear aromatic polymers with and without 6F groups in the repeat unit. For example, the T_g of 6FDA-6FpDA (320 °C) is 41 °C lower than that of BPDA-6FpDA (361 °C) [43], and the T_g of HFPSF (192 °C) is 39 °C lower than that of BIPSF (231 °C) [44, 45].

Table 2. Glass transition temperatures of polyimides considered in this study.

Sample	T _g (°C)
HAB-6FDA	279
AH(0.25)	265
AH(0.5)	258
AH(0.75)	250
APAF-6FDA	246

Table 3. Comparison of thermal and gas transport properties of selected polyimides from this study with those of some relevant polymers. Unless otherwise noted, all gas transport data are reported at 35 °C and an upstream pressure of 10 atm.

Polymer	T _g	FFV	Permeability (Barrer)			Selectivity			Ref.
			CO ₂	CH ₄	O ₂	CO ₂ /CH ₄	O ₂ /N ₂	N ₂ /CH ₄	
HAB-6FDA	279	0.157	9.8	0.255	2.76	38	5.7	1.89	This Study
APAF-6FDA	246	0.172	15.4	0.363	4.8	42	5.5	2.40	This Study
BPDA-6FpDA	361	0.161	27.4	0.76	6.65 ^a	36.0	5.5 ^a	1.60	[43]
6FDA-6FpDA	320	0.190	63.9	1.60	16.3 ^a	39.9	4.7 ^a	2.17	[43]
BIPSF	231	0.154	5.6	0.25	1.3 ^a	22	5.5 ^a	0.96	[45]
HFPSF	192	0.168	12	0.55	3.4 ^b	22	5.1 ^b	1.22	[44]

^a Data at 2 atm^b Data at 5 atm

Fig. 4 presents experimental and estimated values of T_g as a function of APAF content (wt. fraction). The T_g 's were estimated using the Fox equation [46]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (4)$$

where w_1 and w_2 are weight fractions of homopolymer 1 and 2, respectively, and T_{g1} and T_{g2} are the glass transition temperatures of homopolymer 1 and 2, respectively. As shown in Fig. 4, the experimental and estimated T_g values are in reasonable agreement.

Fig. 4. Experimental and predicted values of T_g as a function of APAF content in the copolyimide. Predicted T_g was estimated using the Fox equation [Equation (4)] [46].

3.4. Gas permeation properties

Fig. 5 (A-D) presents gas permeability as a function of upstream pressure for AH(0.5) polyimide and its partially rearranged TR analogs. Permeability coefficients of the more condensable gases, such as CO_2 and CH_4 [20], generally decrease with upstream pressure. On

the other hand, permeability coefficients of the less condensable gases, in this case H₂, N₂, and O₂ [20], are essentially independent of feed pressure. These trends are typical of glassy polymers and are consistent with the dual-mode model [47, 48]. Similar results were also observed for other materials, and figures recording their gas permeability coefficients versus feed pressure are included in Supplementary Information.

Fig. 5. Permeability as a function of upstream pressure at 35 °C for: (A) AH(0.5) polyimide, (B) AH(0.5) TR350 60min (40% TR conversion), (C) AH(0.5) TR400 60min (58% TR conversion), and (D) AH(0.5) TR450 30min (72% TR conversion).

Table 4 presents permeability coefficients of the polymers considered in this study at 35 °C and an upstream pressure of 10 atm. Uncertainties in permeabilities, estimated via propagation of errors [49], are included in Supplementary Information. As presented in Fig. 5 and Table 4, as TR conversion increases, gas permeability increases. For example, CH₄ permeability increases by a factor of more than 100, from 0.34 Barrer for AH(0.5) polyimide to 37 Barrer for AH(0.5) TR450. Earlier studies reported increases in permeability upon thermal rearrangement and attributed those increases to increases in diffusion coefficients [8], due to increased fractional free volume (FFV) of the polymer [50]. FFV of these materials will be discussed in Section 3.5.

Table 4. Pure-gas permeability for polyimides and their TR polymers at 35 °C and an upstream pressure of 10 atm.

Sample		Permeability (Barrer)				
		CH ₄	N ₂	O ₂	CO ₂	H ₂
HAB-6FDA	PI	0.255	0.482	2.76	9.8	33.2
	TR350	0.72	1.53	8.2	29.9	90
	TR400	5.9	9.7	42	164	284
	TR450	20.6	27.0	104	410	510
AH(0.25)	PI	0.31	0.62	3.5	12.4	41
	TR350	0.83	1.92	10.3	36.9	109
	TR400	5.0	8.5	37	143	278
	TR450	41	55	195	730	850
AH(0.5)	PI	0.34	0.69	3.8	13	41
	TR350	0.71	1.82	10.4	35	108
	TR400	4.6	8.9	40	150	288
	TR450	37	52	175	660	880
AH(0.75)	PI	0.35	0.77	4.3	14.5	44
	TR350	1.58	3.8	18.8	66	162
	TR400	7.5	14.1	59	220	400
	TR450	91	121	380	1430	1400
APAF-6FDA	PI	0.363	0.87	4.8	15.4	50
	TR350	0.98	2.68	14.0	48	134
	TR400	13.3	22.7	87	325	510
	TR450	96	128	390	1410	1340

Fig. 6 presents the experimental and estimated gas permeability coefficients in the copolyimides as a function of APAF-6FDA content (in volume percent). The volume fraction of APAF-6FDA, φ_{APAF} , was estimated as follows [51, 52]:

$$\varphi_{APAF} = w_{APAF} \frac{\rho}{\rho_{APAF}} \quad (5)$$

where w_{APAF} is the mass fraction of APAF-6FDA in the copolymer, and ρ and ρ_{APAF} are the measured densities of the copolymer and APAF-6FDA homopolymer, respectively. As shown in Fig. 6, there is a good correlation of gas permeability with APAF-6FDA content. Permeability coefficients of all gases generally increase with APAF content, probably due to disruption of polymer chain packing imparted by the bulky 6F units in APAF, leading to an increase of fractional free volume [44, 53]. The lines in Fig. 6 represent estimated permeability of the copolymers, P_A , based on the following model [54]:

$$\ln P_A = \varphi_{APAF} \ln P_{APAF} + (1 - \varphi_{APAF}) \ln P_{HAB} \quad (6)$$

where P_{APAF} and P_{HAB} are the permeability coefficients of HAB-6FDA and APAF-6FDA, respectively. As shown in Fig. 6, the permeability coefficients of the copolymers are in good agreement with the model.

Fig. 6. Experimental and predicted pure-gas permeability coefficients as a function of APAF content in polyimides. Permeability coefficients were measured at 35 °C and an upstream pressure of 10 atm. Lines represent permeability values calculated from Equation (6).

Pure-gas selectivities of several gas pairs for polymers considered in this study are presented in Table 5, and selectivities as a function of APAF content are presented in Fig. 7(A-E). The lines in Fig. 7 represent selectivity values based on permeability coefficients calculated using Equation (6). Uncertainties in pure-gas selectivities were determined based on uncertainties in permeability coefficients using the propagation of errors method [49]. Selectivities of AH(0.5) polyimide are not presented in Fig. 7 because the uncertainties in its permeability coefficients were large due to thickness variations in the particular sample used for the permeation measurements. As shown in Fig. 7, the estimated selectivity values are in reasonable agreement with the experimental values.

Pure-gas selectivities of H₂/N₂ (Fig. 7A) and CO₂/N₂ (Fig. 7B) generally decrease as APAF content increases, a trend that is consistent with typical tradeoffs between permeability

and selectivity in glassy polymers and often reflects decreases in diffusion selectivity as free volume increases [55, 56]. This trend is less obvious for O₂/N₂ (Fig. 7C), where the differences among selectivity values are typically within experimental uncertainties, which may be due to the very similar kinetic diameters of O₂ (3.46 Å) and N₂ (3.64 Å) [2]. Interestingly, for CO₂/CH₄ (Fig. 7D), and to a more significant extent in N₂/CH₄ (Fig. 7E), selectivity increases somewhat with APAF content. For example, selectivities of CO₂/CH₄ and N₂/CH₄ in APAF-6FDA are 11% and 27% higher, respectively, than those in HAB-6FDA. Similar behavior was also observed for partially rearranged TR polymers, and plots of their pure-gas selectivities as a function of APAF content are included in Supplementary Information.

Robeson speculated that fluorinated polymers may suppress hydrocarbon solubility, thereby increasing N₂/CH₄ solubility selectivity [56]. This effect was confirmed by Merkel et al. [57] and Prabhakar et al. [58], and it is consistent with hydrocarbon solubility depression in fluorinated liquids [59]. Earlier studies by Pasternak et al. reported relatively high light-gas (e.g., N₂) solubility and low hydrocarbon (e.g., CH₄) solubility in fluorine-containing tetrafluoroethylene-hexafluoropropylene copolymer (FEP) [60]. As presented in Table 3, N₂/CH₄ selectivity of 6FDA-6FpDA is 38% higher than that of BPDA-6FpDA [43], and 6FDA-6FpDA has more 6F linkages in its repeat unit than BPDA-6FpDA. Similarly, N₂/CH₄ selectivity of 6F-containing HFPSF is 27% higher than that of BIPSF (cf., Table 3), which does not contain 6F groups [44, 45]. In this study, as APAF content in the copolyimide increases, the relative amount of 6F groups increases. Therefore, the observed increase in N₂/CH₄ selectivity, and possibly CO₂/CH₄ selectivity, is likely related to the aforementioned sorption effects, since diffusion selectivity is likely decreasing as APAF content increases (cf., Fig. 7A-7B).

Table 5. Pure-gas selectivity of common gas pairs for polyimides and their TR polymers at 35 °C and an upstream pressure of 10 atm.

Sample		Selectivity				
		CO ₂ /CH ₄	O ₂ /N ₂	H ₂ /N ₂	N ₂ /CH ₄	CO ₂ /N ₂
HAB-6FDA	PI	38	5.7	69	1.89	20.3
	TR350	42	5.4	59	2.13	19.5
	TR400	28	4.3	29	1.64	16.9
	TR450	19.9	3.9	18.9	1.31	15.2
AH(0.25)	PI	40	5.7	66	2.00	20
	TR350	44	5.4	57	2.31	19.2
	TR400	29	4.4	33	1.70	16.8
	TR450	18	3.5	15	1.3	13.3
AH(0.5)	PI	38	5.5	60	2.0	19
	TR350	49	5.5	59	2.6	19.2
	TR400	33	4.5	32	1.93	16.9
	TR450	18	3.4	17	1.41	12.7
AH(0.75)	PI	41	5.6	57	2.2	18.8
	TR350	42	5.0	43	2.4	17
	TR400	29	4.2	28	1.9	16
	TR450	16	3.1	11.6	1.3	11.8
APAF-6FDA	PI	42	5.5	57	2.40	17.7
	TR350	48	5.2	50	2.7	17.7
	TR400	24.4	3.8	22.5	1.71	14.3
	TR450	14.7	3.0	10.5	1.33	11.0

Fig. 7. Experimental and predicted pure-gas selectivity of (A) H_2/N_2 , (B) CO_2/N_2 , (C) O_2/N_2 , (D) CO_2/CH_4 , and (E) N_2/CH_4 as a function of APAF content in polyimides. Gas transport properties were measured at 35 °C and an upstream pressure of 10 atm. Lines represent selectivity values calculated from Equation (6).

Fig. 8A and 8B present pure CO₂ permeability and CO₂/CH₄ selectivity as a function of TR conversion. CO₂ permeability becomes increasingly sensitive to TR conversion as conversion increases, which is consistent with earlier reports on TR polymers [8, 12]. For example, for AH(0.75), CO₂ permeability increases from 66 Barrer at 47% TR conversion to 220 Barrer at 58% TR conversion, and finally to 1430 Barrer at 83% TR conversion. As APAF content in partially converted TR polymers increases, CO₂ permeability generally increases as well. For example, CO₂ permeability of APAF-6FDA TR450 is 240% and 110% higher than that of HAB-6FDA TR450 and AH(0.5) TR450, respectively. Similar trends were also observed for other gases. One exception to this trend is that AH(0.5) TR450 has lower CO₂ permeability than AH(0.25) TR450. Apparently, at the same treatment conditions, AH(0.5) TR450 has undergone less thermal rearrangement (72% TR conversion) than AH(0.25) TR450 (78% TR conversion). Since gas permeability is sensitive to conversion, especially at higher TR conversions, small differences in TR conversion can result in large changes in gas permeability [11]. Interestingly, AH(0.75) TR450 and APAF-6FDA TR450 have similar CO₂ permeability values. This similarity in permeability may be due to a slightly higher TR conversion in AH(0.75) TR450 (83% TR conversion) than in APAF-6FDA TR450 (81% TR conversion). As will be discussed below, these two samples also have similar fractional free volume values, which is consistent with their similar permeabilities.

Fig. 8. Pure CO₂ permeability (A) and pure gas CO₂/CH₄ selectivity (B) as a function of percent TR conversion for HAB-6FDA (●), AH(0.25) (◆), AH(0.5) (▲), AH(0.75) (▼), and APAF-6FDA (■) at 10 atm and 35 °C.

As presented in Table 5, for certain gas pairs, such as O₂/N₂, CO₂/N₂, and H₂/N₂, selectivities generally decrease monotonically with TR conversion. For example, pure CO₂/N₂ selectivity of HAB-6FDA decreases monotonically from 20.3 for the polyimide to 15.2 for the TR450 sample. This observation is qualitatively consistent with the gas permeability/selectivity tradeoff found in other TR polymers [55, 56]. On the other hand, for gas pairs that involve methane, such as CO₂/CH₄ and N₂/CH₄, selectivities initially increase at low TR conversions (30-40%) before decreasing at higher TR conversions. This trend is clearly demonstrated in Fig. 8B. For example, CO₂/CH₄ selectivity of APAF-6FDA initially increases from 42 for the polyimide to 48 for the TR350 sample (40% TR conversion), and then decreases monotonically to 24.4 and 14.7 for TR400 (62% TR conversion) and TR450 samples (81% TR conversion), respectively. Sanders et al. reported a similar observation and attributed the initial increase in

selectivity to changes in free volume distribution at the onset of thermal rearrangement that inhibits CH₄ diffusion and, therefore, favors selectivities of gas pairs involving CH₄ [8, 11]. Interestingly, as shown in Fig. 8B, at TR conversions higher than about 50%, CO₂/CH₄ selectivity values of all materials are similar. Even though CO₂/CH₄ selectivity for APAF-6FDA TR450 ($\alpha_{\text{CO}_2/\text{CH}_4} = 14.7$) is 26% lower than that of HAB-6FDA TR450 ($\alpha_{\text{CO}_2/\text{CH}_4} = 19.9$), that difference may be attributed to differences in percent TR conversions (81% for APAF-6FDA TR450 vs. 74% for HAB-6FDA TR450). Apparently, the choice of diamine (HAB or APAF) and the polyimide precursor composition do not strongly influence the size-sieving ability of these polymers for CO₂/CH₄ separation at high TR conversions. Similar trends were also observed for other gas pairs presented in Table 5.

The CO₂/CH₄ separation performance of materials considered in this study is compared with that of several relevant polymers on an upper bound plot, as shown in Fig. 9. For all samples, TR conversion increases from left to right. As thermal rearrangement proceeds, CO₂/CH₄ separation performance shifts to the right and eventually traverses the 1991 upper bound. Some samples, such as AH(0.75) TR450 and APAF-6FDA TR450, approach the 2008 upper bound. In addition, the partially converted TR polymers cover a wide range of gas separation characteristics, so desired gas permeability and selectivity can be tuned with APAF content and thermal rearrangement conditions.

Fig. 9. Permeability/selectivity tradeoff plot for HAB-6FDA (●), AH(0.25) (◆), AH(0.5) (▲), AH(0.75) (▼), and APAF-6FDA (■). Gas transport results were measured at 35 °C and an upstream pressure of 10 atm. TR conversion increases from left to right. Transport data of polysulfone (PSF) [61], Matrimid [62], and cellulose acetate (CA) [63] are also included for reference. The lines are the 1991 and 2008 upper bound limits [55, 56].

3.5. Fractional free volume

Fractional free volume was estimated as follows [8]:

$$FFV = \frac{V - V_0}{V} \quad (7)$$

where V is the measured specific volume of the polymer sample, which is the inverse of polymer density. V_0 is the occupied volume of the polymer and was estimated using the group contribution method as follows [64, 65]:

$$V_0 = 1.3 \sum V_w \quad (8)$$

where V_w is the van der Waals volumes of the various groups comprising the polymer backbone [64, 65]. For partially rearranged TR copolymers, V_0 was calculated as follows [11]:

$$V_0 = w_{APAF} [c_{APAF} V_{0,APAF-PBO} + (1 - c_{APAF}) V_{0,APAF-PI}] + (1 - w_{APAF}) [c_{HAB} V_{0,HAB-PBO} + (1 - c_{HAB}) V_{0,HAB-PI}] \quad (9)$$

where w_{APAF} is the mass fraction of APAF-6FDA in the copolymer, and c_{APAF} and c_{HAB} are the fractional TR conversions of APAF-6FDA and HAB-6FDA, respectively, on a mass basis (see Equation (1)). $V_{0,APAF-PI}$ and $V_{0,APAF-PBO}$ are the occupied volumes of APAF-6FDA polyimide and its corresponding PBO (cm^3/g), respectively. Likewise, $V_{0,HAB-PI}$ and $V_{0,HAB-PBO}$ are the occupied volumes of HAB-6FDA polyimide and its corresponding PBO (cm^3/g), respectively.

Calculation of occupied volume using Equation (9) was made within the bounds of two limiting assumptions. The first is that any polyimide segments remaining in the polymer following partial rearrangement would retain its initial acetate functionality [8, 11]. During thermal rearrangement, the acetate groups in polyimides are generally believed to convert to hydroxyl groups before rearranging to a final benzoxazole structure [8, 20]. However, since partially converted PBOs are typically insoluble in common organic solvents, precise composition of partially rearranged structures is difficult to determine. Serendipitously for HAB-6FDA and APAF-6FDA, the occupied volumes of acetate-containing and hydroxyl-containing polyimides differ by less than 2% [8]. Therefore, the aforementioned assumption regarding polymer structure has a small effect on overall fractional free volume. A more detailed discussion of the implications of this assumption for polyacetylimides and PBOs was reported earlier by Sanders et al. [12].

The second assumption employed in estimating FFV is that both APAF-6FDA and HAB-6FDA segments in a copolyimide would undergo the same extent of TR conversion at a given thermal treatment. In other words, c_{APAF} equals c_{HAB} in Equation (9). For example, the measured percent TR conversion for AH(0.5) TR400, based on mass loss, is 58% (cf., Table 1). Because APAF-6FDA has a lower T_g than HAB-6FDA, APAF segments in AH(0.5) can potentially begin the rearrangement process at a lower temperature and reach a higher TR conversion than HAB segments [15]. However, because the precise composition of APAF and HAB segments in a partially rearranged copolyimide is not known, for the V_0 calculation, both APAF and HAB segments in AH(0.5) TR400 were simply assumed to achieve 58% conversion to PBOs. Table 6 presents the occupied volumes of polyimides and selected PBOs considered in this study. Fortuitously, the occupied volumes of HAB-6FDA PI and APAF-6FDA PI differ from their respective PBOs by less than two percent. For example, the occupied volume of APAF-6FDA PI ($0.5632 \text{ cm}^3/\text{g}$) is 1.3% higher than that of APAF-6FDA PBO ($0.5557 \text{ cm}^3/\text{g}$), and the occupied volume of HAB-6FDA PI ($0.5898 \text{ cm}^3/\text{g}$) is 0.3% lower than that of HAB-6FDA PBO ($0.5996 \text{ cm}^3/\text{g}$). Because of this similarity in occupied volumes between polyimides and their corresponding PBOs, for a particular copolymer at a specific rearrangement condition, assuming that both HAB and APAF segments achieve the same TR conversion has a small effect on estimated FFV values.

Table 6. Occupied volumes of polyimides and selected PBOs considered in this study.

Sample	V ₀ (cm ³ /g)
HAB-6FDA PI	0.5980
AH(0.25) PI	0.5880
AH(0.5) PI	0.5789
AH(0.75) PI	0.5707
APAF-6FDA PI	0.5632
HAB-6FDA PBO	0.5996
APAF-6FDA PBO	0.5557

Estimated FFV values of polymers considered in this study as a function of TR conversion are shown in Fig. 10. Uncertainties in FFV values were calculated according to the propagation of errors method based on uncertainties in the density measurements of at least three samples [49]. FFV generally increases as APAF content increases. For example, FFV of APAF-6FDA is 9.6% and 3.6% higher than that of HAB-6FDA and AH(0.5), respectively. This trend is attributed to a disruption in polymer chain packing imparted by the extra 6F groups in APAF. For all polymers, FFV increases as TR conversion increases, which is similar to previous reports in other TR polymers [7, 8, 10-12]. For example, FFV of AH(0.5) increases from 0.166 for the polyimide to 0.206 for the TR450 sample. Depending on the polyimide precursor, the total increase in FFV upon thermal rearrangement is in the range of 0.04 to 0.07. The density and FFV values are tabulated in Supplementary Information.

Fig. 10. Fractional free volume as a function of percent TR conversion for HAB-6FDA (●), AH(0.25) (◆), AH(0.5) (▲), AH(0.75) (▼), and APAF-6FDA (■). Uncertainties were estimated based on uncertainties in density measurements using the propagation of errors method [49].

Fig. 11 presents CO₂ permeability of the copolymers as a function of reciprocal FFV. Both TR conversion and FFV of a given copolyimide increase from right to left. There is a good correlation between FFV and CO₂ permeability, suggesting that permeability depends strongly on gas diffusivity [8]. Similar behavior was also observed for other gases, and plots of their permeabilities as a function of reciprocal FFV are included in Supplementary Information. Because the precise structure of partially converted samples at a given conversion is not known, the calculated FFV values should be viewed as approximations, which may contribute to some of the scatter in Fig. 11. A similar observation has been reported in other TR polymers [8, 12]. In addition, as reported by Sanders et al. [8], other factors, such as changes in free volume

distribution upon TR conversion, can also influence gas transport properties in ways that are not captured by average FFV values alone [6, 8, 12].

Fig. 11. CO₂ permeability as a function of 1/FFV for HAB-6FDA (●), AH(0.25) (◆), AH(0.5) (▲), AH(0.75) (▼), and APAF-6FDA (■). The permeability data were measured at 35 °C and an upstream pressure of 10 atm.

3.6. Mechanical properties

Mechanical properties of polymer films depend on many factors, such as casting procedure, temperature, molecular weight, molecular weight distribution, rate of tensile deformation, and extent of any crosslinking or branching [27]. Therefore, for any comparison, it is important to adhere to a strict sample preparation method and testing protocol. All of the films prepared for tensile testing were cut into a dog-bone shape and ranged in thicknesses between 80 and 100 μm . Inherent viscosity was measured to provide a qualitative comparison of the

samples' molecular weights. Mechanical properties, along with inherent viscosity, for all polyimides and their TR polymers are presented in Table 7.

Table 7. Inherent viscosity and mechanical properties of polyimides and TR polymers considered in this study.

Sample		Inherent Viscosity	Tensile Stress (MPa)	Elongation at break (%)	Young's modulus (GPa)
HAB-6FDA	PI	0.54	153 ± 3	7.1 ± 0.2	3.54
	TR350		107 ± 1	4.9 ± 0.2	2.68
	TR400		85 ± 2	4.0 ± 0.2	2.51
	TR450		62 ± 3	2.9 ± 0.1	2.52
AH(0.25)	PI	0.40	140 ± 1	5.5 ± 0.1	3.44
	TR350		108 ± 2	5.2 ± 0.1	2.71
	TR400		77 ± 1	3.7 ± 0.1	2.45
	TR450		*	*	*
AH(0.5)	PI	0.29	119 ± 3	5.2 ± 0.1	3.07
	TR350		101 ± 6	4.6 ± 0.4	2.54
	TR400		71 ± 3	3.3 ± 0.2	2.41
	TR450		*	*	*
AH(0.75)	PI	0.19	76 ± 3	2.9 ± 0.2	2.93
	TR350		67 ± 4	2.5 ± 0.2	2.88
	TR400		*	*	*
	TR450		*	*	*
APAF-6FDA	PI	0.18	65 ± 5	2.5 ± 0.2	2.90
	TR350		*	*	*
	TR400		*	*	*
	TR450		*	*	*

*Samples were too brittle for tensile testing

Fig. 12 presents stress (in MPa) as a function of strain (percent of original sample length) for HAB-6FDA polyimide and its TR analogs. Stress-strain plots for other materials in this study are reported in Supplementary Information. Among these samples, HAB-6FDA polyimide has the highest tensile stress (153 MPa), elongation at break (7.1%), and the Young's modulus (3.54 GPa). As TR conversion increases, both tensile stress and elongation at break decrease.

For example, tensile stress and elongation at break of HAB-6FDA TR450 are both 59% lower than those of the polyimide precursor. Additionally, the Young's modulus, which characterizes sample stiffness [66], also decreases with increasing TR conversion. For example, the Young's modulus of HAB-6FDA TR450 is about 30% lower than that of HAB-6FDA polyimide precursor. Such decreases in mechanical properties is likely due to the increased rigidity of TR polymers relative to the polyimide precursor, resulting in more brittleness and less stiffness of the sample [17, 67]. Similar behavior was also observed for other polyimides and TR polymers in this study. For copolymers at higher TR conversions, some samples were too brittle for tensile testing, as they typically cracked upon mounting into the pneumatic grips of the testing machine. In the case of APAF-6FDA, none of the thermally rearranged samples had enough mechanical integrity for tensile testing.

Fig. 12. Stress-strain relationship of HAB-6FDA polyimide and its corresponding TR analogs.

Fig. 13 presents the stress-strain relationship for all the polyimides in this study. As APAF content increases in the polyimide, both tensile stress and elongation at break decrease. For example, relative to those of HAB-6FDA, tensile stress and elongation at break of APAF-6FDA are 58% and 65% lower, respectively. Similar trends are also observed for the Young's modulus, as presented in Table 7. For example, the Young's modulus of APAF-6FDA is 17% lower than that of HAB-6FDA. Because HAB is a more reactive monomer than APAF, as previously discussed, HAB is likely to yield polyimides with higher average molecular weight. As presented in Table 7, inherent viscosity, which qualitatively describes the molecular weight of a sample, decreases as APAF content increases. Many studies have shown that for low molecular weight polymers, mechanical properties generally improve as molecular weight increases [27, 68, 69]. Because the TR polymers considered in this study are relatively brittle, a detailed investigation of the influence of molecular weight on mechanical properties is beyond the scope of this study.

Fig. 13. Stress-strain relationship of polyimides considered in this study.

Table 8 compares mechanical properties of selected polymers from this study with those of several relevant commercial polymers of interest and other TR polymers. The tensile stress of polyimides in this study is either similar to or higher than that of the selected commercial polymers. On the other hand, polyimides from this study are more brittle than commercial materials. For example, the elongation at break of HAB-6FDA is 85% and 58% lower than that of polysulfone and cellulose acetate, respectively [63, 70].

Table 8. Comparison of mechanical properties of selected polyimides and TR polymers from this study with those of selected commercial polymers and other TR polymers.

Sample	Tensile Stress (MPa)	Elongation at break (%)	References
Polysulfone (Udel P-1700)	54.2	48	[70]
Matrimid [®] 5218	87.1	21.1	[71]
Cellulose acetate ¹	14.0	17.0	[63]
spiroTR-PBO-6F	82.3	20.0	[26]
spiroTR-PBO-PM	79.2	17.3	[26]
spiroTR-PBO-BP	94.4	14.9	[26]
spiroTR-PBO-BPA	69.9	19.7	[26]
HAB-6FDA TR	137	4.5	[17]
HAB-6FDA TR (75%) / 4MPD-6FDA	193	13	[17]
HAB-6FDA TR (50%) / 4MPD-6FDA	238	21	[17]
HAB-6FDA TR (25%) / 4MPD-6FDA	280	25	[17]
4MPD-6FDA	390	29	[17]
HAB-6FDA PI	153	7.1	This study
HAB-6FDA TR350	107	4.9	This study
HAB-6FDA TR400	85	4.0	This study
HAB-6FDA TR450	62	2.9	This study
AH(0.25) PI	140	5.5	This study
AH(0.5) PI	119	5.2	This study
AH(0.75) PI	76	2.9	This study
APAF-6FDA PI	65	2.5	This study

¹degree of substitution = 2.84

Some recent studies combined thermally rearrangeable polyimides with other materials in an attempt to improve mechanical properties. Li et al. prepared TR polymers derived from spirobisindane-containing polyhydroxyimides and hypothesized that the unique structure with a spiro-center induced entanglement of polymer chains and reduced elongational stress [26]. As presented in Table 8, these spiro-PBOs demonstrated not only high tensile stress (69.9 – 94.4 MPa), but also elongation at break values ranging from 15% to 20%, which is about four times higher than the TR polymers from this study. However, because molecular weights ranging from

59,100 to 104,000 were reported for the spiro-containing polyimide precursors, it is not possible to separate the respective contributions of chemical structure and molecular weight to mechanical properties [26]. In a separate study, Scholes et al. blended a thermally rearrangeable polyimide (HAB-6FDA) with a non-TRable polyimide (4MPD-6FDA) that provided additional flexibility [17]. Mechanical properties of HAB-6FDA TR reported by Scholes et al. were different from those reported in this study, probably because different polyimide precursors and thermal treatment conditions were used. For example, the TR polymers reported by Scholes et al. were derived from polyhydroxyimides and thermally treated at 450 °C for 1 h [17], whereas the HAB-6FDA TR polymers from this study were derived from polyacetylimides and thermally treated at different conditions. Nevertheless, Scholes et al. demonstrated that mechanical properties could be improved significantly by incorporating 4MPD-6FDA in the polymer blend. For example, with 25 wt.% of 4MPD-6FDA in the blend, tensile stress and elongation at break increased by 40% and 190%, respectively, relative to those of HAB-6FDA TR. However, similar to the study by Li et al., Scholes et al. did not quantify the impact of molecular weight on mechanical properties.

4. Conclusions

Thermally rearranged (TR) copolymers were prepared from a series of random copolyacetylimide precursors based on HAB-6FDA and APAF-6FDA. Structures of the homopolyimides and copolyimides were confirmed by ¹H NMR, and thermogravimetric analysis (TGA) showed similar thermal stability for all samples. A single glass transition temperature (T_g) was observed for the copolyimides, which is consistent with that observed for typical random copolymers. Pure-gas permeabilities of CH₄, H₂, N₂, O₂, and CO₂ were measured in that

order at 35 °C and at upstream pressures ranging from 3 atm to 17 atm. As polyimides undergo thermal rearrangement, gas permeability increases and becomes increasingly sensitive to conversion at higher TR conversions. In addition, as APAF content increases, gas permeability coefficients increase. The bulky hexafluoroisopropylidene units in APAF help disrupt polymer chain packing, resulting in higher fractional free volume (FFV) and gas permeability. As percent TR conversion increases, samples traverse the 1991 CO₂/CH₄ upper bound and approach the 2008 upper bound. For all samples, tensile stress, elongation at break, and Young's modulus decreased as percent TR conversion increased, as a result of the increased rigidity of PBOs. This decrease in mechanical properties was also observed with increasing APAF content, which is attributed to the lower molecular weight of the samples as a result of the lower reactivity of APAF relative to HAB. At higher TR conversions, some samples were too brittle to undergo tensile testing.

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