Graphic Abstract

Analysis of Governing Factors Controlling Gas Transport Through Fresh and Aged Triptycene-based Polyimide Films

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Abstract

The fundamental gas transport properties and physical aging behavior of a series of triptycene-based polyimides with various substitution groups were investigated. Wide-angle x-ray diffraction revealed that the 6FDA-1,4-triptycene polyimides exhibit two chain packing domains with *d*-spacing values of ~ 6.7 Å and ~ 5.3 Å, corresponding to triptycene-induced chain packing disruption and chain segments lacking the triptycene moiety, respectively. Positron annihilation lifetime spectroscopy (PALS) showed a bimodal distribution of microcavity size made up of triptycene cleft cavities that are ~ 3 Å diameter and larger interchain cavities with an average diameter of ~ 7 Å. Additionally, PALS confirmed 6FDA-1,4-trip-CH₃ has the lowest fractional free volume, primarily due to smaller contributions from the interchain cavities, and 6FDA-1,4-trip-CF₃ has the largest fractional free volume. It was also found that the addition of substituent groups had a unique and positive effect on the aging properties over nine months, in which the addition of CH₃ and CF₃ groups led to permeability increases of $\sim 20\%$ and $\sim 40\%$, respectively. This is caused by the combination of the lowered driving force for physical aging, the substituent groups sterically hindering tighter packing with time, and the interconnectivity and/or unblocking of free volume over time through small-scale, local chain motion.

Keywords: Triptycene; gas separation membrane; physical aging; fractional free volume; polyimide

1. Introduction

Development of gas separation membranes have shown promise in the past couple of decades as a green and cost-effective alternative to current energy-intensive industrial standards of gas separations, such as cryogenic distillation and amine scrubbing.[1] However, designing suitable polymers with sufficient properties to truly compete with existing technologies has proven to be challenging. The most fundamental issue is the tradeoff between gas permeability and selectivity of most polymers, as was characterized by Robeson.[2,3] This leads to a primary design criteria – superior polymer membranes should have bulky groups and/or contorted, rigid backbones to create high fractional free volume (FFV) to provide pathways for fast diffusion, and the free volume elements should also have a narrow size distribution and/or the polymer backbone should be highly rigid to maintain the sieving capabilities. There have been several noteworthy polymers conforming to these design conditions, including polymers of intrinsic microporosity (PIMs), which are ladder polymers containing sites of contortion within a rigid backbone,[4–6] the highly substituted poly(1-trimethylsilyl-1-propyne) (PTMSP), known for its high oxygen permeability, [1,7,8] polyimides containing the rigid bridged bicyclic group, Tröger's base,[9] as well as several triptycene-based polymers, such as the polyimide 6FDA-DATRI, [10] the KAUST-PI series of ultramicroporous polyimides, [11,12] the Tröger's base- and triptycene-containing polymer PIM-Trip-TB,[13] and triptycene-based PIMs.[14]

We recently reported on a series of triptycene-based polyimides.[15] In designing the polymers, we were particularly interested in including the unique triptycene molecule due to its rigid, symmetric, three-dimensional structure made up of three benzene “blades” connected by a central hinge. The benzene blades are efficient in disrupting chain packing, which increases free volume; additionally, there are internal free volume elements in the clefts of triptycene blades, which can further add to the regular free volume.[16–20] These polymers exhibited a promising ability to be tuned via the addition of substituent groups (i.e. CH_3 and CF_3) neighboring the triptycene unit, which effectively altered the FFV and gas transport properties. The effect of the substituent group proved to be size-dependent; the methyl group was found to be relatively small enough compared to the clefts between triptycene blades to fill in some of the microcavities, following the proposed “partial filling” mechanism. Conversely, the introduction of the larger CF_3 groups led to increased fractional free volume.[15] This interesting trend prompted additional research into the governing mechanisms at molecular level behind gas transport

through the 6FDA-1,4-triptycene series, which is reported in this study. This investigation includes a thorough examination of chain packing and free volume through molecular simulation, wide angle x-ray diffraction (WAXD), positron annihilation lifetime spectroscopy (PALS), and determination of detailed fundamental gas transport properties, including diffusivity coefficients and solubility coefficients.

Besides the ability to perform well against the permeability/selectivity tradeoff, there are still several critical material attributes that must be met before the membranes can be considered for practical use. These include processability, thermal and mechanical stability, maintained sieving capability in the presence of the plasticizing gases, and stable performance over time.[1,21] One of the most detrimental issues to the recently-developed high fractional free volume polymers mentioned previously (e.g. PIMs) is the loss of performance over time, known as physical aging.[22–24] This phenomenon is the long-term densification of the polymer chains through short-range, local motion that results in an equilibrium chain packing conformation that is typically much denser. The driving force for physical aging can be expressed as the difference between the film's present specific volume (V) and the equilibrium specific volume (V_{∞}), i.e., $V - V_{\infty}$. [25] Written in this form, it can be seen clearly that the driving force for physical aging in high fractional free volume polymers is enhanced, as the V value is large. On the contrary, the 6FDA-1,4-triptycene series from our previous study[15] contain relatively flexible ether bonds, which should allow for more efficient packing during film formation, lowering V and consequently the driving force for physical aging, while the bulky triptycene moieties simultaneously create ample free volume for high permeabilities. Moreover, the free volume created by the triptycene molecule is expected to be resistant to age due to triptycene's rigid, shape-persistent structure and its possession of intrinsic (not conformation-based) internal free volume elements. These hypotheses are explored in this report through a physical aging study tracked by physical and gas transport properties (i.e. permeability, selectivity, diffusivity, solubility). Additionally, the effects of thermal annealing and non-solvent treatment on these triptycene-polyimides were investigated to provide feasible post-treatment approaches that might enhance membrane properties.

2. Experimental

2.1 Preparation of triptycene-based polyimide films

The series of triptycene-based polyimides with variation in the substituent groups (Fig. 1) were prepared using the established solution casting procedures reported in our previously published study.[15] Using N-methyl-2-pyrrolidone (NMP) as the solvent, dense films were prepared ranging from 30-55 μm in thickness. The films were dried at 180 $^{\circ}\text{C}$ under vacuum for 24 h, soaked in methanol for 24 h to remove residual solvent, and dried again at 180 $^{\circ}\text{C}$ under vacuum for 24 h. Films denoted as “fresh” were characterized and tested directly after this second drying. Films denoted as “aged” were stored at atmospheric conditions for either 2.5 months or 9 months and then characterized. The feasibility of reversing physical aging was also studied, for which aged films were soaked in methanol for 24 h and then dried at 180 $^{\circ}\text{C}$ for 24 h under vacuum. Lastly, the effect of thermal treatment was investigated; after casting, these fresh films were annealed at 300 $^{\circ}\text{C}$ overnight under nitrogen protection.

Fig. 1. (a) Repeat unit structures of the 6FDA-1,4-triptycene polyimide series (b) Energy-minimized conformations of polymer segments of six repeat units.

2.2 Molecular Modeling of Polymer Conformations

The chain conformations were based off of polyimide segments with six repeat units and were constructed using Accelrys Materials Studio. Energy minimizations of each polyimide segment were performed in the Discover module using the COMPASS force field and the Smart algorithm for iteration.

2.3 Wide Angle X-Ray Diffraction (WAXD)

A wide-angle X-ray diffraction (WAXD) analysis was carried out to characterize polymer chain packing efficiency via quantifying the interchain d -spacing. A D8 Advance Davinci diffractometer with Cu K α radiation was used. It was operated at 40 mA and 40 kV with a scan speed of 5 seconds/step and 0.02° per step, scanning from 2θ value of 5° to 45°. Peak position was directly read from each WAXD pattern and d -spacing was calculated using Bragg's law:[26]

$$d = \frac{n\lambda}{2 \sin \theta} \quad (1)$$

where λ is the wavelength of 1.5418 Å for CuK α radiation and θ is the scattering angle corresponding to the peak.

2.4 Positron Annihilation Lifetime Spectroscopy (PALS)

Positron annihilation lifetime spectroscopy (PALS) was used to analyze the size and size distribution of the free volume elements in the triptycene-based polyimides at the atomic level. In this technique, positrons enter the material, and then either annihilate with free electrons in the material or form the bound state, positronium (Ps), existing in either the *ortho* (*o*-Ps) or *para* (*p*-Ps) spin state. Ps can only form in areas of low electron density, such as the void space within amorphous polymers.[27–29] It is the investigation of this *o*-Ps lifetime that can be correlated to the size of the voids throughout a material and shed light on the fractional free volume and free volume size distribution.

To perform the experiment, 1 cm x 1 cm squares of the polymer film were stacked into two 2 mm thick bundles and placed on either side of the positron source, which was a sealed Mylar envelope containing 1.5 x 10⁶ Bq of ²²NaCl. Measurements were carried out at room temperature and in a vacuum of 1 x 10⁻⁶ Torr. An EG&G Ortec fast-fast coincidence timing system was used to collect five files of 4.5 x 10⁶ integrated counts. Analysis was carried out using LT v9 software with a source correct of 1.609 ns and 4.002%.[30] The radius of the free

volume elements was determined using the Tao-Eldrup equation, which models the pores as infinite spherical potential wells:[31,32]

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0} \right) \right] \quad (2)$$

where τ_3 is the *o*-Ps lifetime, R is the radius of the pores, R_0 is the radius of the potential well, and $R_0 = R + \Delta R$, where ΔR was determined to be 1.66 Å based on the thickness of the electron layer within the potential well. This radius can then be used to find the fractional free volume using the following equation:[27]

$$f_v = CVI \quad (3)$$

where f_v is the fractional free volume determined by PALS, C is a constant equal to 0.0018 empirically determined from specific volume data, V is the spherical volume (Å³) determined using the radius found in Equation 2, and I is the intensity (%). The free-volume size distributions were determined using PASCAL software.[33]

2.5 Pure Gas Permeation Tests

Pure gas permeabilities were determined using the constant-volume, variable-pressure method at 35 °C. It should be mentioned that pure gas permeabilities of the 6FDA-1,4-triptycene polyimides we reported previously [15] were done at a collaborating facility and the films were not exactly fresh at the time when they were tested. Therefore, in this study, gas permeabilities of all polymer samples were retested in their truly “fresh” state (1 day after casting) on our permeation system so that reliable comparisons between the fresh films and the aged or treated membranes can be made. For the aged samples, the polymer membranes were tested for their gas permeabilities approximately 2.5 months or 9 months after being cast. Treated samples (i.e. annealed or methanol-soaked) were tested directly after the treatment was completed. Prior to measurement, the permeation system was evacuated and held under vacuum for at least 12 h to thoroughly degas the membrane. For nitrogen, feed pressures of 30, 80, 130, 180, and 230 psig were used and for methane and carbon dioxide, feed pressures of 30 and 130 psig were used. The upstream pressure was monitored by a Honeywell STJE high-pressure transducer. As the gas diffused across the membrane and collected in the isolated downstream volume, the steady-state pressure increase downstream was monitored with an MKS Baratron low-pressure transducer. The permeability (P) was calculated as follows:[34]

$$P_A = \frac{V_d l}{p_2 A R T} \left[\left(\frac{dp_1}{dt} \right)_{ss} - \left(\frac{dp_1}{dt} \right)_{leak} \right] \quad (4)$$

where V_d is downstream volume, l is membrane thickness, p_2 is upstream absolute pressure, A is gas transport film area, R is the gas constant, T is temperature, and $(dp_1/dt)_{ss}$ and $(dp_1/dt)_{leak}$ are steady-state rates of pressure rise in the downstream volume at fixed upstream pressure and at vacuum, respectively.

The diffusion coefficients (D) were determined using the time lag method at 30 psig and 35 °C:[34,35]

$$D = \frac{l^2}{6\theta} \quad (5)$$

where l is the membrane thickness and θ is the time lag. The solubility coefficients (S) are then determined based on solution-diffusion model of gas transport in dense polymer membranes:

$$P = D \times S \quad \text{or} \quad S = P/D \quad (6)$$

Additionally, the selectivity can be divided into its solubility and diffusivity components, as is shown below:

$$\alpha_{A/B} = \alpha_{D,A/B} \times \alpha_{S,A/B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B} \quad (7)$$

3. Results and Discussion

3.1 Chain Packing and Fractional Free Volume (FFV)

In the macromolecular design of new polymers for gas separation membrane applications, polymer structures leading to films with high fractional free volume (FFV) are typically desired to provide pathways for efficient gas transport. One method of generating free volume is through the disruption of polymer chain packing, which can be achieved typically through the inclusion of bulky groups, such as the triptycene molecule in this study.

Furthermore, size sieving properties can be regulated through the size distribution of the free volume elements. The symmetric, shape-persistent triptycene molecule with regularly occurring intrinsic microvoids is expected to facilitate in a narrow free volume size distribution. Also, the addition of substituent groups (i.e. CH_3 and CF_3) can act as a method to finely tune the free volume of the polymers, as will be discussed further in this section.

Molecular modeling was first conducted to visualize and compare the chain conformations as a function of substituent group. Fig. 1b shows the energy-minimized conformations of the three triptycene polyimide chain segments containing six repeat units. It can be seen that compared to the CH₃-substituted and the *para* polymers, the CF₃-substituted polymer assumes a much more tortuous backbone structure due to the steric hindrance introduced by the bulky trifluoromethyl groups. This stiffer, kinked structure prevents tight chain packing and contributes to the highest fractional free volume of 6FDA-1,4-trip_CF₃ among the three polyimides. Conversely, the more flexible nature of the CH₃ and *para* polymers allow for more efficient chain packing and therefore, a lower FFV as discussed later.

The interchain distance was investigated with wide angle x-ray diffraction (WAXD), which provides quantitative insights into chain packing efficiency and is closely related to fractional free volume and consequent transport properties. As indicated by the broad peaks in Fig. 2, all three 6FDA-1,4-triptycene polyimides were found to be completely amorphous. Typically, one broad peak correlating to the average intersegmental distance (*d*-spacing) dominates the amorphous glassy polymer spectrum (e.g. Matrimid[®][36,37] and 6FDA-DATRI[10] in Table 1); however, for the triptycene-based polymers, multiple peaks can be observed signifying the rich structural hierarchy associated with triptycene units. Similar multi-peak patterns have been seen in the literature for microporous polymers, such as polymers of intrinsic microporosity, PIM-1.[38] Although these polymers still form amorphous films, the peaks are generally assigned to domains of different chain packing efficiency. For example, in PIM-1, the largest *d*-spacing of 11.9 Å can be ascribed to the adjacent spiro-carbons, the peak at 6.6 Å represents the loose packing resulting from the kinked ladder-type backbone, the 4.9 Å position can be assigned to the more efficiently packed chains, and lastly the peak at 3.8 Å is typical of π - π stacking.[38–40]

Looking at the triptycene-based polyimide series, the unsubstituted 6FDA-1,4-trip_*para* polymer and the 6FDA-1,4-trip_CH₃ polymer display two diffraction peaks (A and B on Fig. 2), while three peaks can be detected in the 6FDA-1,4-trip_CF₃ polymer (A, B, and C on Fig. 2). The *d*-spacing data is tabulated in Table 1. The first set of peaks in the A position, corresponding to *d*-spacing from 6.5 – 6.8 Å, can be assigned to the general amorphous packing of the polymer chains. It is thought that this spacing can be attributed to bulky triptycene units disrupting chain packing. Looking at peak B, tighter chain packing with *d*-spacing from 5.2 – 5.4 Å can be

ascribed to the domain possibly made up of the chain segments lacking the bulky triptycene unit. Lastly, a peak around 4.0 Å, which is typical of π - π stacking,[41] appears in the spectrum of the CF₃ substituted polymer. The spectra of the two relatively flexible polymers, 6FDA-1,4-trip_ para and 6FDA-1,4-trip_CH₃, are very similar with peak A having the highest intensity and peak B appearing as a shoulder. However, 6FDA-1,4-trip_CF₃ shows a significantly different pattern in that peak A is present as more of a shoulder and peak B appears as the strongest peak. This difference could be due to the more tortuous packing conformation of the CF₃ polymer, as discussed previously. It's possible that the stiffer, distorted polymer backbone, brought about by the CF₃ groups, causes the effect of the bulky triptycene units to be less distinct, somewhat merging the two domains discussed above into a broader peak centered at the “B” location.

Fig. 2. WAXD patterns of the 6FDA-1,4-triptycene polyimide series. The vertical lines labeled A, B, and C represent amorphous polymer chain packing, a more-ordered chain-packing domain, and π - π stacking, respectively.

Table 1

Diffraction peak position (2θ) and d -spacing values in WAXD patterns

Sample	2 θ (°)			d -spacing (Å)		
	A	B	C	A	B	C
6FDA-1,4-trip_CH ₃	13.0	17.1	-	6.8	5.2	-
6FDA-1,4-trip_ para	13.7	16.5	-	6.5	5.4	-
6FDA-1,4-trip_CF ₃	13.2	17.1	22.2	6.7	5.2	4.0

6FDA-DATRI[10]	16.4	-	-	5.5	-	-
Matrimid®[36,37]	5.5	-	-	5.7	-	-

As reported in our previous publication,[15] the 6FDA-1,4-triptycene polyimides were found to be high fractional free volume materials whose gas transport properties proved to be tunable based on the structure of triptycene monomers (i.e. the variation of side groups neighboring the triptycene moiety). Using the group contribution method,[42–44] it was found that 6FDA-1,4-trip_CH₃ had the lowest fractional free volume (FFV) of 15.1%, followed by 6FDA-1,4-trip_ para at 15.6%, with the highest being 6FDA-1,4-trip_CF₃ at 18.3%.[15] This trend was primarily attributed to the differences in substituent size relative to the internal free volume space defined by the shape of bulky triptycene units, in which the methyl groups were small enough to partially reside in this space while the trifluoromethyl groups were large enough to add to the chain disruption and increase the overall free volume.

To provide more quantitative insight into the free volume size and size distribution of the triptycene-based polyimides at the atomic level, a positron annihilation lifetime spectroscopy (PALS) study was carried out. As previously discussed, the lifetime of the *o*-Ps (τ_3) can be correlated to the average void size throughout the material. Most conventional amorphous glassy polymers, such as polycarbonate [27] (See Table 2), are monomodal and show only one average free volume size;[45] however, polymers with relatively high fractional free volume, such as Matrimid® polyimide [46] and PIM-1,[47] may result in *o*-Ps lifetime data that best conform to a bimodal distribution of free volume size,[30] indicating two types of microcavities present in these materials. The 6FDA-1,4-triptycene series falls into this latter category showing a bimodal size distribution of microcavities centered around 2.9 Å and 6.9 Å (Fig. 3). Tsui et. al. estimated the internal free volume in the cleft between two arene blades of triptycene molecule to be ~31 Å³ by considering the void space as a triangular prism made up of an approximate triangle of the van der Waals surfaces of the phenyls with a width defined by the *para* hydrogens of the phenyls.[20] Although the internal free volume is estimated as a triangular prism, if the volume of 31 Å³ is taken to be a sphere, the diameter would be around 3.9 Å. It can be seen from Fig. 3 and Table 2, the smaller microcavities in the triptycene polyimides have a diameter around 2.9 Å. Taking into consideration the approximations made and the possibility of partial filling of this internal free volume by segments of the polymer chains, it is assumed that these smaller

microcavities can be attributed to the internal free volume between the arene blades. The second average pore size, around 6.9 Å in diameter, can be attributed to the interchain free spaces brought about by inefficient chain packing.

The nature of the microcavities depend on the substituent groups neighboring the triptycene unit in the polymer backbone. As can be seen from Figure 3, the microcavities of both categories vary in diameter across the polymer series, as indicated by peak position; in concentration, as indicated by peak intensity; and in size distribution, as indicated by the broadness of the peak. Beginning with the small microcavities attributed to the clefts between the arene blades, it is hypothesized that the size, size distribution, and intensity are tailored by the degree of filling of the clefts with portions of the polymer chain. The size distribution for the smaller cavity of the non-substituted *para* polymer is wider (FWHM = 1.0) compared to the CH₃-substituted polymer (FWHM = 0.7). As shown in Fig. 1b, 6FDA-1,4-trip_ *para* has the most flexible backbone in the series; it is possible that the flexible nature allows for tighter packing conformations and faster local motion with various parts of the polymer chains partially residing in the clefts of the triptycene moiety, causing a range in the degree of filling of the cleft and, therefore, a broader distribution of sizes for these small microcavities. Conversely, the CH₃-substituted polymer has the narrowest size distribution, suggesting that methyl groups might act as a facilitator in restricting other parts of the polymer chain from residing in the clefts so there is more of a tendency for the clefts to be either entirely unoccupied or entirely filled. The lower intensity of this peak for the CH₃-substituted polymer compared to the *para* polymer supports the hypothesis that some of these cleft voids are completely filled and inaccessible. The triptycene cleft pores of the CF₃-substituted polymer have the largest diameter of the series, although its size distribution (FWHM = 1.0) is comparable to the *para* polymer. This supports the hypothesis that the CF₃ groups are too large to partially fill the triptycene clefts like the methyl groups of the CH₃-substituted polymer. On the other hand, the CF₃-substituted polymer had the lowest peak intensity of the small microcavities. As is shown in Fig. 1(b), this polymer is the most tortuous of the series, allowing for disrupted packing. The loose packing conformation could allow for a portion of the cleft voids to connect with the larger interchain voids. This is supported by analyzing and comparing the size, size distribution, and peak intensity of the large microvoids across the series, which is discussed further in the next paragraph.

Similarly, it is apparent that the size, size distribution, and intensity of the larger microcavities are also affected by the substituent group. The *para* polymer shows the smallest pore size (6.76 Å) with a relatively broad size distribution (FWHM = 0.7) and the highest intensity. As discussed before, the flexible nature of the polymer chain allows for more compact packing configurations, leading to the smaller cavity size; however, the inclusion of the triptycene still causes significant packing interruption, causing a higher number of these voids to form. The CH₃-substituted polymer has the next largest pore size with a diameter of 6.82 Å, coupled with the lowest intensity and narrowest size distribution (FWHM = 0.5). The proposed mechanism that the methyl groups are residing in and partially filling some of the free volume voids generated by the triptycene units is in agreement with these findings, particularly the low intensity and narrow size distribution. Lastly, the CF₃-substituted polymer shows the largest pore size with a similar intensity and size distribution (FWHM = 0.7) as the *para* polymer. The combination of this polymer's stiffer backbone and possession of bulky substituent groups prohibits efficient chain packing, which generates larger pore sizes and higher intensity in 6FDA-1,4-trip_CF₃.

Fig. 3: Microcavity diameter and size distribution determined by PALS measurements for the triptycene-1,4-polyimides. The inset table displays the full-width at half-maximum (FWHM) values for each peak.

It is a combination of size and intensity of the free volume elements that determine the overall fractional free volume (FFV) of the material. Using Equation 3, the fractional free volume was determined for each average lifetime (τ_3 and τ_4) and then combined to obtain the overall fractional free volume. These values (f_{v3} , f_{v4} , f_v) are listed in Table 2. It was found that the overall FFV trend determined by PALS mirrors what was found in our previous study using group contribution method,[15] where FFV increases from 6FDA-1,4-trip_CH₃ to 6FDA-1,4-trip_ *para* to 6FDA-1,4-trip_CF₃. Looking at the breakdown of the contributions to f_v , it can be seen that the contribution from the small cavities attributed to the clefts of the triptycene molecules (f_{v3}) is the minor component of the overall FFV. Also, this element is relatively constant across the series. Although the cleft cavity diameter of the *para* polymer was smaller than those of the substituted polymers, its higher intensity brings the fractional free volume up to a comparable value to those of the substituted polymers. The major contributing factor to the overall FFV is the free volume based on the interchain microcavity (f_{v4}). Although the CH₃-substituted polymer has the mid-sized diameter for the interchain pores, when combined with its low intensity, it presents the lowest overall FFV. Similarly, although the *para*-substituted polymer shows the highest intensity for the interchain cavities, its small cavity diameter brings the overall FFV below the CF₃-substituted polymer, whose combination of large interchain diameter and high intensity produces the highest overall FFV.

The triptycene-based polyimide series shows similar PALS data to the commercial Matrimid[®] polyimide with a bimodal distribution in which the major contributing factor to the overall fractional free volume is the larger cavity. Comparing the two cavities, Matrimid[®]'s small cavity, 1.98 Å in diameter, is significantly smaller than that of the 6FDA-1,4-triptycene series with an average diameter of 2.93 Å; however, the larger cavity is approximately the same size as the interchain cavities of the 6FDA-1,4-triptycene series with diameters around 7 Å. Despite the similar cavity sizes, it can be seen that the f_v value of Matrimid[®] is significantly lower than the triptycene-based polyimides, which can be attributed to the low Matrimid[®] intensities. Comparing the 6FDA-1,4-triptycene series to PIM-1, the triptycene-based polyimides have significantly smaller cavity sizes and fractional free volumes, caused by their relatively flexible and less tortuous backbones compared to the highly rigid, kinked backbone of PIM-1. However, this high fractional free volume of PIM-1 can act as a driving force for physical aging,

causing deterioration of gas transport properties over time.[22] This will be discussed further in a later section.

Table 2

Microcavity size and size distribution characterizations by PALS

Sample Name	Lifetimes (ns)		Intensities (%)		
	τ_3	τ_4	I_3	I_4	
6FDA-1,4-trip_CH ₃	0.895 ± 0.082	2.682 ± 0.044	9.06 ± 1.37	9.53 ± 0.58	
6FDA-1,4-trip_ <i>para</i>	0.867 ± 0.029	2.642 ± 0.033	10.87 ± 0.57	10.68 ± 0.55	
6FDA-1,4-trip_CF ₃	0.903 ± 0.009	2.853 ± 0.037	8.27 ± 0.36	10.30 ± 0.20	
Polycarbonate[27]	2.06 – 2.25	-	40.4 – 45.6	-	
Matrimid®[46]	0.678	2.852	8.3	3.78	
PIM-1[47]	1.67 ± 0.05	4.13 ± 0.05	10.47 ± 0.21	11.20 ± 0.32	
Sample Name	Pore Sizes (Å)		Fractional Free Volume (%)		
	Diameter 3 (d_3)	Diameter 4 (d_4)	f_{v3}	f_{v4}	f_v
6FDA-1,4-trip_CH ₃	2.95 ± 0.30	6.82 ± 0.06	0.22	2.85	3.07
6FDA-1,4-trip_ <i>para</i>	2.85 ± 0.11	6.76 ± 0.05	0.24	3.11	3.35
6FDA-1,4-trip_CF ₃	2.98 ± 0.03	7.07 ± 0.05	0.21	3.42	3.63
Polycarbonate[27]	5.80 – 6.14	-	-	-	-
Matrimid®[46]	1.98	7.06	0.61 ^a	1.25 ^a	1.31 ^a
PIM-1[47]	5.06	8.64	1.27	6.80	8.07

^aCalculated with Equation 3 for consistency

3.2 Analysis of Fundamental Gas Permeation Properties

Our previous study examined the gas transport properties of the 6FDA-1,4-triptycene series.[15] It was found that pure gas permeability (P) is sensitive to the substituent groups neighboring the triptycene units. Based on our proposed “partial filling” mechanism, the relatively small CH₃ group filled some of the microcavities generated by the triptycene unit, leading to a decrease in FFV in comparison to the unsubstituted *para* polymer. Conversely, the relatively large CF₃ side groups were bulky enough to further disrupt chain packing and led to the largest FFV of the series. The combined effects of CH₃ groups filling microcavities and CF₃ groups disrupting chain packing carried through to the gas permeabilities, which showed an increasing trend in the order of 6FDA-1,4-trip_CH₃ < 6FDA-1,4-trip_ *para* < 6FDA-1,4-trip_CF₃ for all testing gases, as shown in Table 3. It can also be seen from Table 3 that, despite the increase in permeability across the polymer series, the selectivity was well-maintained; it is

believed that the small cleft microcavities associated with the triptycene unit facilitate in maintaining the sieving capability of the polymers as they are comparable in size to the gas molecules ($\sim 3\text{-}4\text{ \AA}$). This study takes a more detailed look at the gas transport properties of these triptycene-based polyimides by breaking the permeability (P) down into its two fundamental contributing factors, the diffusivity (D) and the solubility (S). Most glassy polymers' gas transport properties are controlled by a size-sieving mechanism, in which diffusion through free volume spaces dominates. This is the case for the 6FDA-1,4-trip series in this study. As shown in Table 3, the diffusivity coefficients (D) increased in accordance with the FFV trend, moving from 6FDA-1,4-trip-CH₃ to 6FDA-1,4-trip-*para* and lastly to 6FDA-1,4-trip-CF₃. The diffusivities are enhanced more significantly for those gases with a larger kinetic diameter. For example, D_{CH_4} increases 138% from $1.0 \times 10^{-9}\text{ cm}^2/\text{s}$ for 6FDA-1,4-trip-CH₃ to $2.4 \times 10^{-9}\text{ cm}^2/\text{s}$ for 6FDA-1,4-trip-CF₃, while D_{CO_2} only increases 116% from $9.8 \times 10^{-9}\text{ cm}^2/\text{s}$ for 6FDA-1,4-trip-CH₃ to $21 \times 10^{-9}\text{ cm}^2/\text{s}$ for 6FDA-1,4-trip-CF₃. The solubility coefficients (S) are also affected by the structural changes in the triptycene-polyimide series although at a much less profound level. Glassy polymers are typically governed by dual-mode sorption, in which there are two contributing components, Henry's law sorption and Langmuir sorption. The Henry's law component corresponds to the gas sorption into the densified polymer matrix and the Langmuir portion relates to the sorption in the non-equilibrium excess free volume.[35] Generally, there is an increase in solubility for the *para* polymer compared to the CH₃-substituted polymer; this can mostly likely be attributed to an increase in the Langmuir sorption due to an increase in FFV. Conversely, the CF₃-substituted polymer shows lower solubilities than 6FDA-1,4-trip-*para* and similar solubilities to 6FDA-1,4-trip-CH₃, despite having higher FFV than both polymers. This is probably due to a reduction in the Langmuir affinity parameter describing the interactions between the gas molecules and the polymer matrix, as has been seen in other studies investigating the effect of fluorinated polymer backbones.[48]

The ideal selectivities of the 6FDA-1,4-triptycene polyimides were also broken down into their contributing factors of diffusivity selectivity (α_D) and solubility selectivity (α_S) shown in Table 3. For the CO₂/CH₄ gas pair, the diffusivity selectivity factor is the overruling component of the overall selectivity due to the large difference in kinetic diameter of the gas molecules. This difference in size is particularly important for diffusion in the small triptycene cleft cavities with a diameter around $3\text{ \AA}$ (see Table 2). Moving across the series, the solubility selectivities for

CO₂/CH₄ stayed relatively constant for all the polymers; however the diffusivity selectivity showed a clear decrease with the addition of the CF₃ groups, corresponding to the increase in FFV. For the CO₂/N₂ gas pair, different trends in diffusivity selectivity and solubility selectivity were observed due to different transport governing factors for this gas pair: permeation of CO₂ has a significant solubility contribution whereas N₂ transport is completely diffusivity-dominated; additionally, the two gases are closer in size compared to the CO₂/CH₄ gas pair. The combination of these effects caused the solubility selectivity to be the primary factor in the overall selectivity. As shown, the CO₂/N₂ diffusivity selectivities were fairly stable for the series; however, the solubility selectivities clearly showed dependency on substitution, with 6FDA-1,4-trip_ para being the highest due to the highest CO₂ solubility because of increased FFV over the CH₃-substituted polymer and improved polymer/gas interactions compared to the CF₃-substituted polymer, as previously discussed.

Table 3

Gas transport properties of the fresh 6FDA-1,4-tripycene polyimides. Permeability (P), selectivity (α), diffusivity (D), and solubility (S) were determined at 2 atm and 35 °C.

	Permeability, P (barrer)			Selectivity, α		
	CH ₄	N ₂	CO ₂	CO ₂ /CH ₄	CO ₂ /N ₂	
6FDA-1,4-trip_CH ₃	0.21 ± 0.005	0.36 ± 0.007	9.3 ± 0.2	45	26	
6FDA-1,4-trip_ <i>para</i>	0.31 ± 0.007	0.52 ± 0.01	14 ± 0.3	46	27	
6FDA-1,4-trip_CF ₃	0.49 ± 0.02	0.87± 0.03	21 ± 0.6	42	24	
	Diffusivity, D (10 ⁻⁹ cm ² /s)			Solubility, S (10 ⁻² cm ³ (STP)/(cm ³ cmHg))		
	CH ₄	N ₂	CO ₂	CH ₄	N ₂	CO ₂
6FDA-1,4-trip_CH ₃	1.0 ± 0.01	6.3 ± 0.1	9.8 ± 0.08	2.0 ± 0.07	0.6 ± 0.02	9.5 ± 0.2
6FDA-1,4-trip_ <i>para</i>	1.3 ± 0.03	8.4 ± 0.3	13 ± 0.2	2.3 ± 0.1	0.6 ± 0.04	11 ± 0.4
6FDA-1,4-trip_CF ₃	2.4 ± 0.1	15 ± 0.8	21 ± 0.8	2.0 ± 0.1	0.6 ± 0.05	9.7 ± 0.6
	Diffusivity Selectivity, α_D			Solubility Selectivity, α_S		
	CO ₂ /CH ₄		CO ₂ /N ₂	CO ₂ /CH ₄		CO ₂ /N ₂
6FDA-1,4-trip_CH ₃	9.6		1.6	4.7		17
6FDA-1,4-trip_ <i>para</i>	9.7		1.5	4.8		18
6FDA-1,4-trip_CF ₃	8.7		1.4	4.8		16

3.3 Physical Aging Behavior

Many highly permeable glassy polymers suffer from physical aging, or the collapse of free volume as the polymer chains shift towards their equilibrium packing over time, causing deterioration of the gas permeabilities. This is especially an issue for very high free volume polymers, such as PIMs, TPIMs, and PIM-TBs. The rigid, highly contorted structures of PIMs induces large amounts of non-equilibrium free volume, greatly increasing the driving force for physical aging.[22] In contrast to PIMs, it was expected that given the relatively flexible nature of the 6FDA-1,4-triptycene series (Fig. 1b), the polymer chains would be able to assume a packing conformation fairly close to the equilibrium packing, minimizing $(V-V_\infty)$ and consequently lowering the driving force for physical aging. Additionally, the fraction of the internal free volume delineated by the shape of triptycene unit is considered to be truly intrinsic to the polymer structure, which is most likely not subjected to conventional physical aging. For all polymers of the series, it was found that the aging effect was strongly dependent on the presence and the nature of substituent groups neighboring the triptycene unit, as shown in Fig. 4. As a general observation, the substituted polyimides showed excellent resistance to physical aging while the unsubstituted *para* polymer exhibited typical loss of gas permeabilities upon physical aging, which seemed to suggest the critical role of substituent group in providing resistance to physical aging for microporous polymers.

Fig. 4. The dependence of (a) N₂ (b) CO₂ and (c) CH₄ permeability on feed pressure for fresh and aged 6FDA-1,4-tripycene polyimides. (▲ represents 6FDA-1,4-trip_CF₃, ● represents 6FDA-1,4-trip_ para, and ■ represents 6FDA-1,4-trip_CH₃. Tested at 35 °C.)

In particular, the unsubstituted *para* polymer with 9-month age showed a decrease (~39-45%) in permeabilities. This follows typical aging behavior seen for glassy polymers, and is considered relatively minor compared to many high fractional free volume polymers. An example is the triptycene-based polymer, TPIM-1. While TPIM-1 maintains permeabilities of an order of magnitude higher even after aging ($P_{N_2, \text{aged}} = 7.1$ barrer), in just 15 days TPIM-1 has a 70% decrease in nitrogen permeability, and decreases even further to 98% loss in P_{N_2} by 26 months of age.[22] Although 6FDA-1,4-trip_ para showed decreased gas permeabilities with age, the introduction of substituent groups, i.e. CH₃ and CF₃, causes the polymer films to display an unusual increase in gas permeabilities over time. For instance, the CH₃-substituted polymer showed a 24% increase in N₂ permeability from 0.35 to 0.43 barrer with 9 months of aging and the CF₃-substituted polymer showed a 39% increase from 0.87 to 1.21 barrer in 9 months, as shown in Fig. 4. It seems that introducing substituent groups next to the triptycene unit is instrumental in improving the polymer's resistance to physical aging, which might be due to two

synergistic effects: 1) the local motion of substituent groups over time may cause interconnecting or unblocking of microcavities (e.g. chain movement causing a CH₃ group to free a triptycene cleft) leading to increased overall free volume and thus permeability, and 2) the substituent groups sterically hinder the polymer chains from tighter packing, especially in the case of the bulky CF₃-substituent groups which effectively stiffen the polymer backbone, and lower charge transfer complex (CTC) interactions.[49] This also explains the more pronounced aging-induced permeability increase on 6FDA-1,4-trip_CF₃ compared to 6FDA-1,4-trip_CH₃. To further investigate this aging phenomenon, another 6FDA-1,4-trip_CF₃ film was prepared and allowed to age only 2.5 months. As shown in Fig. 4, it was found that the permeabilities of this film lied in between the fresh film permeabilities and the permeabilities of the films aged for 9 months, as was expected.

In addition to standard aging experiments, a couple of film treatments including thermal annealing and non-solvent treatment and their effects were explored. For the 6FDA-1,4-trip_CF₃ polymer, a fresh film was prepared and subjected to high-temperature treatment at 300 °C overnight under nitrogen protection. When tested for pure gas permeabilities (see Table S1), it was found that the thermally treated film displayed the highest permeabilities, which is in agreement with the idea that annealing treatment above the T_g of the polymer can expedite the polymer chains in achieving the fully aged, equilibrium conformation. In looking at nitrogen, the thermal treatment caused an increase of 93% from the fresh film permeability. For the aged 6FDA-1,4-trip_*para* polymer, the restoration of original gas transport properties was explored by using non-solvent treatment. It has been shown that permeabilities can be enhanced by soaking the aged polymer film in a non-solvent such as methanol, which swells the polymer chains restoring non-equilibrium free volume present before the long-term chain relaxation.[50] Following a similar approach, the aged 6FDA-1,4-trip_*para* film was subjected to this treatment by soaking the film in methanol for 24 h and drying at 180 °C under vacuum for 24 h before it was retested for its pure gas permeabilities. While the methanol treatment was successful in reversing the physical aging, the permeabilities were only recovered to ~78% of the original values (e.g. P_{N2,Recovered} = 0.40 barrer while P_{N2,Fresh} = 0.52 barrer).

As captured in the Robeson's upper bound plots, generally an increase in permeability is accompanied by a decrease in selectivity. However, as shown in Fig. 5, even though the substituted triptycene-based polyimides show an increase in permeability with age, their

selectivities do not decline. The aged 6FDA-14-trip_CH₃ films actually showed a slight increase in selectivity with age, with fresh CO₂/CH₄ and CO₂/N₂ selectivities of 45 and 26 respectively, and aged CO₂/CH₄ and CO₂/N₂ selectivities of 47 and 27 respectively. Additionally, while 6FDA-1,4-trip_CF₃ shows a significantly larger permeability increase with age than the CH₃ counterpart, it still maintains selectivities with no significant change over time. In addition to aging effects, the effect of film conditioning on selectivity can also be explored. While the 6FDA-1,4-trip_CF₃ maintained selectivity with age, the annealing treatment caused a decrease in selectivity. For example, the CO₂/CH₄ selectivity decreased from 42 for the fresh film to 37 for the 300 °C-annealed film. This is unsurprising in light of the large increase in permeability, indicating increased FFV, brought about by the thermal treatment. Conversely, the methanol treatment carried out on the aged 6FDA-1,4-trip_ *para* film resulted in similar selectivities as the fresh films (e.g. $\alpha_{\text{CO}_2/\text{CH}_4, \text{Fresh}} = 46$ and $\alpha_{\text{CO}_2/\text{CH}_4, \text{Recovered}} = 46$), supporting the hypothesis that the non-solvent exchange can facilitate in restoring chain packing in the aged film similar to the originally fresh film. The conservation of selectivities in this series of polymers can be attributed to the rigid, shape-persistent nature of the triptycene structure unit with its ability to impart uniform molecular voids via the clefts between the benzene blades. The combination of increased permeability and maintained selectivities allow the substituted triptycene-based polyimides to move along a rather lateral trend towards the upper bound with age and annealing, as shown in Fig. 5. These properties would be desirable to implement in industry where membrane operations often suffer from deterioration of gas permeabilities with time; therefore, it is important to note that these aging properties are dependent on film thickness and the aging rate exponentially decreases with film thickness. In this study, film thicknesses ranged from 30-55 μm , whereas in industry film thickness are often as small as 100 nm, which may result in different rates of aging.[51] It would be an interesting extension of this work to study how the polymers behaved with age on a thin film scale.

Fig. 5. Permeability/selectivity tradeoff for 6FDA-1,4-trip films with varying treatments (i.e. aged, methanol-soaked, annealed), tested at 35 °C and 10 atm. Solid symbols represent fresh film. Open symbols represent treated films. $\blacktriangle$ ($\triangle$) represents 6FDA-1,4-trip_ CF_3 , $\bullet$ ($\circ$) represents 6FDA-1,4-trip_ para , and $\blacksquare$ ($\square$) represents 6FDA-1,4-trip_ CH_3 .

To obtain fundamental insights into the aging phenomenon, the diffusivity coefficients and solubility coefficients of the aged and treated (i.e. methanol-soaked and 300 °C-annealed) films were determined using the time-lag method. These results are tabulated in Table S1 and CO_2 results are represented in Fig. 6 as an example. Plots for N_2 and CH_4 are included in Supporting Information as Fig. S1-S4. It's apparent that the main contributing factor to the changes in permeability upon aging or thermal treatment is the change in the diffusivity coefficient. For example, when breaking down the ~29% permeability increase for CO_2 from 8.0 barrer for the fresh CH_3 film to 10 barrer for the aged one, the diffusivity coefficient exhibited a 21% increase while the solubility coefficient only showed less than 3% increase. This diffusion-dominated effect suggests that over time the polymer chains are rearranging to increase and/or redistribute the free volume throughout the material, possibly through interconnecting or unblocking microcavities, as previously proposed. Generally, selectivities showed no significant change with aging; however, the thermal treatment of 6FDA-1,4-trip_ CF_3 led to a slight decrease in selectivity, which was analyzed for its diffusivity selectivity and solubility selectivity components shown in Table S1 in supporting information. For the CO_2/CH_4 gas pair, the

solubility selectivity remains relatively stable but the diffusivity selectivity suffers a decrease, which is indicative of increasing FFV or interconnectivity of existing microcavities. As previously discussed for the CO₂/N₂ gas pair, solubility selectivity is a major contributing factor and for the annealed film the solubility selectivity decreases compared with the fresh film, since the treatment more greatly enhanced the N₂ solubility than the CO₂ solubility, most likely through the increase of free volume elements that are of sufficient size for N₂ sorption.

Fig. 6. (a) CO₂ diffusivity coefficient for 6FDA-1,4-triptycene series films determined by time-lag method; (b) CO₂ solubility coefficients. Tested at 35 °C and 2 atm.

Because the gas transport data suggest an increase in or redistribution of the fractional free volume in the substituted polymers with age, a WAXD analysis was done on the 6FDA-1,4-trip_CF₃ samples aged for 9 months and treated at 300 °C and the 6FDA-1,4-trip_ para sample aged for 9 months. These treated-film spectra were compared to their respective fresh film spectra as displayed in Fig. 7. It is apparent from Fig. 7 (a) that there was little change in the chain packing of 6FDA-1,4-trip_ para over time, as the “fresh” and “aged” spectra are nearly identical, suggesting that only local segmental motions occur in the aged sample. However, as shown in Fig. 7 (b), the CF₃-substituted polymer shows a marked change in the WAXD pattern of aged and treated samples. Most noticeably, there is a shift in relative peak intensities. As previously discussed, the three peaks presented in the 6FDA-1,4-trip_CF₃ spectrum are thought to be attributed to a less-ordered domain with chain-disrupting triptycene units (peak A, $d = 6.70$ Å), a more-ordered domain lacking triptycene moieties (peak B, $d = 5.18$ Å), and π - π stacking of triptycene unit (peak C, $d = 4.00$ Å), moving from low to high 2θ values. In the spectrum of fresh

film, the peak for the more-ordered domain (B) has the highest intensity; however, for both aged and thermally-treated films, the diffraction profile changes so that peak A, attributed to the less-ordered domain, has the highest intensity. This suggests that the fractional free volume is redistributing over time to increase the amount of microvoids with the larger d -spacing around 6.7 Å compared to the amount of voids with smaller d -spacing of 5.3 Å. [49,52] This change supports the idea of possible free volume interconnectivity and is in alliance with the increase of permeability for both the aging treatment and the thermal treatment. The similar “aged” and “300 °C” spectra also supports that thermal treatment above the T_g can facilitate chain movement in reaching the packing conformation that is likely eventually achieved through the aging process. In addition to the shift in peak intensity, there is also a slight shift in the positions of peaks A and B. Peak A moves from a 2θ value of $\sim 13.2^\circ$ and d -spacing of 6.70 Å for the fresh film to $\sim 13.0^\circ$ and 6.80 Å for the aged and annealed films. Peak B moves from a 2θ value of $\sim 17.1^\circ$ and d -spacing of 5.18 Å for the fresh film to $\sim 16.8^\circ$ and 5.27 Å for the aged film and finally to $\sim 16.6^\circ$ and 5.34 Å for the 300 °C-treated film. These increases in interchain spacing further corroborates the increase in permeability with age.

Fig. 7. (a) WAXD patterns of fresh and aged 6FDA-1,4-trip_{para} films (b) WAXD patterns of fresh, aged, and thermally-treated 6FDA-1,4-trip_{CF₃} films (Vertical dashed lines indicate the approximate peak positions)

4. Conclusions

The governing factors controlling chain packing, fractional free volume, and gas transport properties were thoroughly investigated for a series of triptycene-based polyimides.

WAXD analysis showed that the triptycene-based polyimides have two packing domains – one containing the triptycene moieties with a larger d -spacing and one lacking triptycene units with a slightly reduced d -spacing. Additionally, the triptycene units impart two different types of free volume within the polymer films, as was revealed by PALS. The internal free volume of the triptycene clefts presents itself in small cavities with a diameter of ~ 3 Å, which helps in maintaining the sieving capabilities of the membranes, despite increased permeabilities. Secondly, the triptycene units help disrupt chain packing, creating interchain cavities with a diameter of ~ 7 Å that facilitate in increased permeability. The PALS data confirms the FFV trend increasing from 6FDA-1,4-trip_CH₃ < 6FDA-1,4-trip_ para < 6FDA-1,4-trip_CF₃, which supports the “partial filling” mechanism of the methyl groups in 6FDA-1,4-trip_CH₃. It was determined that the substituted triptycene polyimides possess unique aging properties, presenting with increased permeabilities and maintained selectivities. This is probably due to the relatively flexible nature of the polyimide backbones allowing for initial packing close to the equilibrium conformation and small scale, local motions over time causing interconnectivity and/or unblocking of cavities. This hypothesis is supported by increased diffusivity coefficients for the CH₃- and CF₃-substituted polymers with time and a change in the 6FDA-1,4-trip_CF₃ WAXD pattern, in which the intensity shifted towards the peak corresponding to the larger d -spacing around 6.7Å, coupled with a slight increase in d -spacing for the more-ordered domain around 5.3Å. These insights on the packing behavior and physical aging in the triptycene-based polyimides can be applied toward future polymer design for gas separation membranes.

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