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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_CH_3 has the lowest fractional free volume, primarily due to smaller contributions from the interchain cavities, and 6FDA-1,4-trip_CF_3 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 CH_3 and CF_3 groups led to permeability increases of ~20% and ~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.

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

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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 to 55 μm in thickness. The films were dried at 180 °C under vacuum for 24 h, soaked in methanol for 24 h to remove residual solvent, and dried again at 180 °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 °C for 24 h under vacuum. Lastly, the effect of thermal treatment was investigated; after casting, these fresh films were annealed at 300 °C overnight under nitrogen protection.

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

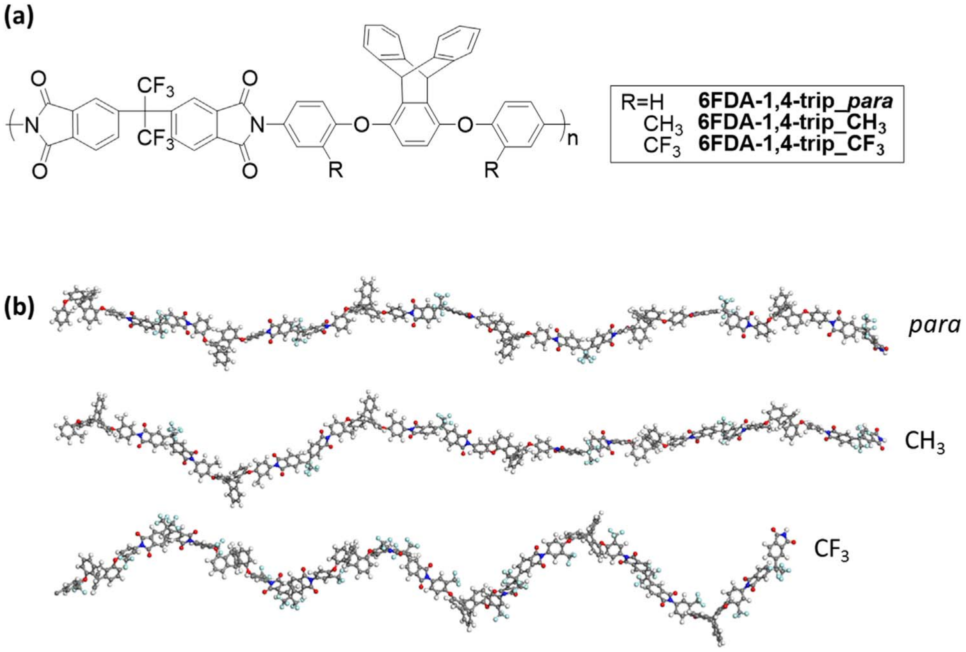

Fig. 1. (a) Repeat unit structures of the 6FDA-1,4-triptycene polyimide series. (b) Energy-minimized conformations of polymer segments of six repeat units.