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Preparation of fluorinated polyimides with bulky structure and their gas separation performance correlated with microstructure



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ABSTRACT

The fluorinated polyimides with high fractional free volume were prepared from 6FDA and aromatic diamines with bulky triptycene and pendent phenyl moieties. These polymers showed excellent solubility, high thermal stabilities and outstanding mechanical properties. The correlation of gas separation performance with the microstructure of these polyimide membranes was investigated. The results indicated that the GSPI-P membranes based on the diamines with pendent phenyl moieties exhibited higher fractional free volumes than GSPI-T membranes derived from diamines with triptycene moieties; as a result, the former gave the much higher permeability coefficients. The gas permeability of these membranes is strongly depended on their free volume and also affected by fluorine content. The GSPI-P membranes also provided good selectivity for CO_2/CH_4 and CO_2/N_2 gas pairs because their appropriate cavity size is favorable to separate the CO_2 from the other gases.

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1. Introduction

Polymeric membranes have been received more and more attention because they play an important role in gas separation applications, such as hydrogen recovery [1,2], nitrogen generation [3] and carbon dioxide removal [4–9]. Gas separation by polymeric membranes has potential advantages of cost-effective, energyefficient and environmentally benign processes in many industries [10]. In the past decades, many different polymers have been investigated as gas separation materials, including rubbery polymers, such as poly(dimethylsiloxane) [11,12], and glassy polymers, such as polysulfone [13–16], poly(phenyl oxide) [17,18], cellulose acetate [19,20] and polyimides [21-23]. Glassy Aromatic polyimides are among the most attractive and promising gas separation materials owing to their admirable gas selectivity, excellent thermal stability, good mechanical properties and superior chemical resistance [24–26]. Moreover, their gas separation properties are easily tuned by numerous combinations between dianhydrides and diamines. However, most of aromatic polyimide membranes have low to moderate permeability because their high packing and low

* Corresponding authors. E-mail addresses: hxguo@iccas.ac.cn (H. Guo), fanlin@iccas.ac.cn (L. Fan). mobility of molecular chains restrain the diffusion of small molecules [27].

An ideal gas separation membrane should have both high permeability and high selectivity. Many efforts have been devoted to develop polyimide membranes with increasing permeability to specific gases without greatly impairing their inherent good selectivity. The introduction of packing-disrupting units into the polyimide backbone is the most effective way to reduce the chain packing, which can result in a high fractional free volume (FFV) in membrane to enhance the gas permeation properties [28]. Okamoto and his coworkers reported the permeability and selectivity of gases in fluorinated and non-fluorinated polyimides [29]. They found that polyimides with $-C(CF_3)_2$ linkages had lower chain packing density and revealed higher permeability with relatively higher selectivity. The polyimides based on 4,4'-(hexafluoroisopropylidene)diphthalic (6FDA) have been extensively investigated to fabricate high performance membranes [30,31]. The $-C(CF_3)_2$ linkages in 6FDA is believed to serve as a molecular spacer and a chain stiffener, which reduces the intra-segmental mobility and limits the chain packing thereby increasing the FFV [32]. Many other researches on development of high performance polyimide membranes are mainly focused on designing the aromatic diamines with bulky structure. The polyimides derived from methyl-substituted phenylenediamines and different dianhydrides have been developed by Tanaka et al. [33]. They claimed that the



methyl substituents in diamines restricted the internal rotation around the bonds between the phenyl rings and the imide rings; therefore, the rigidity and nonplanar polymer chain together with the bulky methyl groups made chain packing insufficient, resulting in high fraction of free space and high permeability. However, they also found that these polyimide membranes displayed very low selectivity. The bulky triptycene-based polyimides have been investigated by many researchers [34]. Triptycene is a symmetric three-dimensional, bulky and rigid structure composed of three phenyl rings bound together by a single hinge, which can disrupt chain packing and create void spaces. It is confirmed that the triptycene-based polyimides possessed high internal free volume, allowing fast molecular diffusion in membrane and resulting in high gas permeability. Calle et al. developed polyimide membranes from aromatic diamine containing bulky di-tert-butyl side groups, *i.e.*, 1,4-bis(4-aminophenoxy)2,5-di-tert-butylbenzene (TBAPB) and commercial dianhydrides [35]. They proved that the bulky di-tertbutyl side groups combined with rigid main chain could yield polyimides with fractional free volume as high as 0.199. The results indicated that the polyimide membranes derived from TBAPB displayed good permeability. However, like other high free volume glassy polymers, the significant improvement in gas permeability of polyimide membranes is not always accompanied by the similar improvement in selectivity [36]. The performance of polyimide membranes is still limited by the trade-off relationship between permeability and selectivity. Therefore, recent studies on polyimide membranes for gas separation have been done to develop new macromolecular structures with high fractional free volume but narrow cavity size distribution, which is favorable to gain the membranes with high permeability and maintained high selectivity [37]. However, to our knowledge, very few attempts have been carried out on the correlation between the microstructure and gas separation performance of polyimide membranes.

In this study, the novel aromatic diamines with pendent phenyl structures, *i.e.*, α, α -bis(4-amino-3,5-dimethyphenyl)-1-phenylmeth ane (BAPM), α, α -Bis(4-amino-3,5- dimethyphenyl)-1-(4'-fluorophen yl)methane (BAFM), and α,α -Bis(4-amino-3,5- dimethyphenyl)-1-(3',4',5'-trifluorophenyl)methane (BATFM), were synthesized. These diamines and the diamines with triptycene moieties, i.e., 1,4-bis(4aminophenoxy)triptycene (BAT) and 1,4-bis(4-amino-2-trifluorome thylphenoxy)triptycene (6FBAT) were polymerized with commercial available dianhydride 6FDA, respectively. The incorporation of the bulky triptycene and pendent phenyl moieties is expected to endow the polyimides with high fractional free volume and result in high gas permeability. The trifluoromethyl and methyl groups were also incorporated to the polymer backbone, in order to produce more free spaces and provide rigid main chain, which will thereby improve the gas permeability on the premise of maintaining high selectivity. The solubility, thermal and mechanical properties as well as gas separation performance of these fluorinated polyimides were evaluated. In order to clarify the relationship between gas separation performance and microstructure of membranes, the microstructure parameters, such as average interspacing distance and fractional free volume were determined by X-ray diffraction measurements and molecular dynamics simulation, respectively. These results were compared with the fractional free volume and cavity size obtained from experimental approach of positron annihilation measurements and discussed in detail.

2. Experimental

2.1. Materials

2,6-Dimethylaniline (>99%, Alfa Aesar), benzaldehyde (98.5%, Sinopharm Chemical Reagent Co., China), 4-fluorobenzaldehyde

(99%, J&K Chemical), 3,4,5-trifluorobenzaldehyde, potassium carbonate (Beijing Chemical Works, China) and concentrated hydrochloric acid (37 wt.%) were used as received. 4,4'-(Hexafluoroiso propylidene)diphthalic anhydride (6FDA) was dried in a vacuum oven at 150 °C for 12 h prior to use. Triptycene-based diamines, 1,4bis(4-aminophenoxy)triptycene (BAT) and 1,4-bis(4-amino-2trifluoromethylphenoxy)triptycene (6FBAT), were synthesized in our laboratory according to the literature [38]. Commercially available *N*-methyl-2-pyrrolidinone (NMP) and *N*,*N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure and dehydrated with 4 Å molecular sieves prior to use. Other solvents and regents were used as received.

2.2. Monomer synthesis

In a typical synthesized procedure of α,α -bis(4-amino-3,5dimethyphenyl)-1-phenylmethane (BAPM), 2,6-dimethylaniline (48.47 g, 0.4 mol) and 100 mL distilled water was placed into a three-necked round-bottom flask equipped with a mechanical stirrer and nitrogen inlet and outlet. The mixture was stirring at room temperature for 1 h until a cream yellow emulsion was obtained. Concentrated hydrochloric acid (37 wt.%, 47 mL) was then added dropwise over an hour and the reaction solution was maintained at 30-40 °C. After that, benzaldehyde (22.28 g, 0.21 mol) was added in batches followed by heated to 100 °C and kept refluxing for 12 h. The resulting nattier blue mixture was cooled to room temperature, and then, potassium carbonate (60 g) was added to neutralization. The BAPM was obtained by water vapor distillation to remove the by-product, which was then purified by recrystallization from ethanol to yield white powder (59.2 g, 93%). mp: 183–185 °C. ¹H NMR (CDCl₃, δ , ppm): 7.17–7.19 (t, 3H), 7.10-7.12 (d, 2H), 6.69 (s, 4H), 5.27 (s, 1H), 3.71 (s, 4H), 2.08 (s, 12H). Elemental analysis: Calculated for C₂₃H₂₆N₂ (330.47): C, 83.59%; H, 7.93%; N, 8.48%. Found: C, 83.14%; H, 7.96%; N, 8.28%.

The other two aromatic diamines, *i.e.*, α,α -bis(4-amino-3,5-dimethyphenyl)-1-(4'- fluorophenyl)methane (BAFM) and α,α -bis(4-amino-3,5-dimethyphenyl)-1-(3',4',5'- trifluorophenyl) methane (BATFM), were synthesized by the similar procedure, except the benzaldehyde was replaced by 4-fluorobenzaldehyde and 3,4,5-trifluorobenzaldehyde, respectively.

For BAFM, yield: 64.5 g, 93%. mp: 170–172 °C. ¹H NMR (CDCl₃, δ , ppm): 7.04–7.07 (t, 2H), 6.91–6.95 (t, 2H), 6.66 (s, 4H), 5.24 (s, 1H), 3.73 (s, 4H), 2.12 (s, 12H). Calculated for C₂₃H₂₅FN₂ (348.46): C, 79.28%; H, 7.23%; N, 8.04%. Found: C, 79.28%; H, 7.42%; N, 7.92%.

For BATFM, yield: 70.2 g, 91%. mp: $151-152 \circ C$, ¹H NMR (CDCl₃, δ , ppm): 6.69–6.72 (t, 2H), 6.63 (s, 4H), 5.16 (s, 1H), 3.73 (s, 4H), 2.13 (s, 12H). Calculated for C₂₃H₂₃F₃N₂ (384.44): C, 71.86%; H, 6.03%; N, 7.29%. Found: C, 72.06%; H, 6.09%; N, 7.04%.

2.3. Polymer synthesis

A series of fluorinated polyimides were prepared from dianhydride 6FDA and aromatic diamines, *i.e.*, BAT, 6FBAT, BAPM, BAFM and BATFM, respectively. In a typical experiment, GSPI-P3, which derived from 6FDA and BATFM, was prepared according to the following procedure.

BATFM (19.22 g, 0.05 mol) and anhydrous NMP (120 mL) were added to a completely dried 500 mL three-necked flask, which was equipped with a mechanical stirrer, a nitrogen inlet, a thermometer, and a Dean–Stark trap. The mixture was stirred at ambient temperature under nitrogen flow until BATFM was completely dissolved to give a homogeneous solution. Then, 6FDA (22.21 g, 0.05 mol), isoquinoline (0.25 g) and toluene (20 mL) were added and the solution was stirred in nitrogen at room temperature for 6 h. The reaction solution was gradually heated to 180 °C and

maintained at the temperature for 12 h, in which the water evolved in the procedure of imidization was removed simultaneously by azeotropic distillation. After the solution was cooled down to 80-100 °C, the viscous solution was poured slowly into excess ethanol to give pale-yellow, fiber-like precipitate, which was then collected by filtration, washed thoroughly with ethanol and dried in vacuum at 120 °C for 8 h.

The other fluorinated polyimides, *i.e.*, GSPI-T1 (6FDA/BAT), GSPI-T2 (6FDA/6FBAT), GSPI-P1 (6FDA/BAPM) and GSPI-P2 (6FDA/BAFM) were synthesized by the similar procedure, except BATFM was replaced by the other aromatic diamines.

2.4. Membrane preparation

The polyimide resin was dissolved in DMAc with stirring to give a homogeneous polyimide solution with a solid content of 20 wt.%. The polyimide solution was filtered by a 0.2-mm Teflon syringe filter and then spread onto a glass plate with a knife gap of 300 μ m on the Elcometer 4340 automatic film applicator. After that, the wet film was thermally baked in an oven at 80 °C for 2 h, 120 °C for 1 h, at 150 °C for 1 h and 180 °C for 1 h, successively. The free-standing polyimide membrane with the thickness of 40–50 μ m was obtained by immersion the glass plate in water followed by drying in an oven at 100 °C for 12 h.

2.5. Characterization

2.5.1. Measurements

¹H NMR spectra were performed on a Bruker Avance 400 Spectrometer operating at 400 MHz in CDCl₃. FTIR spectra were recorded on a Perkin-Elmer 782 Fourier transform spectrophotometer. The number average molecular weights (M_n) and polydispersities (M_w/M_n) were determined by gel permeation chromatography (GPC) on a Waters GPC system equipped with a Waters 1515 HPLC pump, a Waters 2414 differential refractometer, and three Styragel columns of HT-3, HT-4 and HT-5 using NMP containing 0.02 M LiBr as eluent at a flow rate of 1.0 mL/min at 40 °C. The system was calibrated using a series of monodisperse linear polystyrene standards. Solubility of polyimides was determined by dissolving polymer resins in different solvents with 15 wt.% of solid content at room temperature. The absolute viscosities of PI solutions in DMAc were measured on a Brookfield DV-II+ programmable viscometer at 25 °C. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were carried out using a TA Q100 and a TA Q50 instruments in nitrogen, respectively, at a heating rate of 10 °C/min. Mechanical properties were measured on an Instron-3365 tensile apparatus with $120 \times 10 \times 0.05$ mm specimens at 25 °C in accordance with Chinese national standard of GB/T 1040.3-2006 at a drawing rate of 5.0 mm/ min. Wide-angle X-ray diffraction (WAXRD) measurements were conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu/ Kα radiation, operated at 40 kV and 200 mA. The average interspacing distance (d-spacing) was determined based on the Bragg equation:

$$n\lambda = 2dsin\theta \tag{1}$$

where *d* is the d-spacing, θ is the scattering angle and n is an integer number (1, 2, 3 ...) related to the Bragg order.

2.5.2. Fractional free volume

The fractional free volume (FFV) of polyimide membranes was calculated by molecular dynamics (MD) simulation and measured by positron annihilation lifetime spectroscopy (PALS).

The molecular models for molecular dynamics simulation were built by Cerius² package from Accelrys. In model building, three molecular chains composed of dianhydride and diamine with 30 repeating units for each were set in a cubic simulation cell and optimize the trade-off between cell dimension and calculation time. All of the molecular models were treated with an energy minimization process over 1000 iterations to obtain a stable structure. Then, the MD calculations were performed under an NVT ensemble (fixed number of atoms, cell volume, and temperature) for duration of 1 ns at 308 K. The Newton second law of motion was employed to calculate the dynamic behaviors of molecules. The COMPASS force field was adopted for the theoretical calculations. The FFV of a membrane can be calculated by the following equation:

$$FFV = \frac{V - V_o}{V} = \frac{V - 1.3V_w}{V}$$
(2)

where V, V_o and V_w are the specific volume, occupied volume and the van der Waals volume of the polymer, respectively.

Positron annihilation measurements were performed with a fast-slow coincidence ORTEC system with a time resolution of 195 ps for the full width at half-maximum. The two identical pieces of samples were placed on either side of the ²²Na positron source, and then the sample-source-sample sandwich was placed between the two detectors to acquire the lifetime spectra. A total of 2×10^6 counts were accumulated for each spectrum to reduce the statistical error in the calculation of lifetimes. The positron annihilation spectra were de-convoluted using the LT-9 software. The raw data were resolved into three lifetime components, which assume a Gaussian distribution for the logarithm of the lifetime for each component. The third lifetime component of τ_3 (>0.5 ns) is assigned to the decay of orthopositronium (o-Ps) in the polymer free volume. The average cavity radius (*R*) in the polymer can be computed using the following semiempirical equation:

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1} \tag{3}$$

where τ_3 is the o-Ps lifetime, and ΔR is an empirical constant of 1.66 Å. Since the cavities are assumed to be spherical, the mean free volume of a cavity (*V*) and the relative fractional free volume (FFV) are given as the following equations (4) and (5), respectively.

$$V = \frac{4}{3}\pi R^3 \tag{4}$$

$$FFV = cVI_3 \tag{5}$$

where *c* is a material-dependent constant (defined as 10 in this paper), and I_3 is the corresponding intensity of τ_3 .

2.5.3. Permeability measurements

A barometric permeation method was employed to determine steady state pure gas permeability at 23 °C according to international standard of ISO 15105-1. The membranes were degassed in the permeation apparatus on both sides under high vacuum before testing. The downstream pressure was kept below 10^{-2} mbar, while the upstream pressure was maintained at 1 bar. For the permeation experiments, the gases of CO₂, O₂, N₂ and CH₄ with purity higher than 99.99% were used. Under conditions of steady state of permeation, the permeability coefficient (*P*) is determined from the slope of the downstream pressure versus the time plot (dp(t)/dt) according to the following equation:

$$P = \frac{273}{76} \frac{Vl}{ATp_0} \frac{dp(t)}{dt}$$
(6)

where *V* is the calibrated permeate volume, *l* and *A* are the effective thickness and area of the tested membrane, respectively, *T* is the measurement temperature in K and p_0 is the pressure of the feed gas in the upstream chamber. The permeation measurement results were determined by the average value of three specimens for each test condition.

The ideal selectivity for a pair of gases A and B is calculated from the following equation:

$$\alpha_{A/B} = P_A/P_B \tag{7}$$

where P_A and P_B are the permeability coefficients of A and B, respectively.

3. Results and discussion

3.1. Monomer synthesis

The aromatic diamines with pendent phenyl group, *i.e.*, BAPM, BAFM and BATFM, were synthesized by a typical electrophilic substitution reaction as shown in Scheme 1. The 2,6-dimethylaniline was reacted with benzaldehyde or fluorobenzaldehyde under the catalysis of concentrated hydrochloric acid, followed by neutralization with potassium carbonate. In this procedure, the excess benzaldehyde and fluorobenzaldehyde, which performed not only as reactants but also as good solvents, were used to ensure a sufficient reaction and to afford the resultants in high yield (91–93%).

The chemical structures of the synthesized diamines were confirmed by ¹H NMR, FTIR and elemental analysis. Fig. 1 shows the ¹H NMR spectra of the compounds BAPM, BAFM and BATFM, in which all the protons in the structures could be assigned clearly according to the integral values of the intensity. The signals assigned to the protons in the methyl groups, H₁, were detected at 2.08–2.13 ppm. The protons in amino groups resonated in the range of 3.71–3.73 ppm. The signals assigned to proton in the methylidyne group, H₂, shifted to downfield region of



Scheme 1. Synthesis of diamines with pendent phenyl structure.



Fig. 1. ¹H NMR spectra of BAPM (a), BAFM (b) and BATFM (c) in CDCl₃.

5.16–5.27 ppm on account of the conjugative effect from the phenyl group. The aromatic protons, H_3 – H_6 , resonated in the region of 6.63–7.19 ppm. The aromatic protons adjacent to methyl group (H_3) were observed at 6.63–6.69 ppm with the relatively lower chemical shift due to the electron-donating effect of adjacent methyl groups. It is noticed that the fluorine atom affects the chemical shift of protons in the pendent phenyl group significantly. The signal assigned to H_4 in BAPM appeared at 7.10–7.12 ppm, which shifted to 6.91–6.95 ppm for BAFM and 6.69–6.72 ppm for BATFM because of the strong electron-withdrawing effect of the fluorine atoms.

The structures of these aromatic diamines were further confirmed by means of FTIR spectra. As shown in Fig. 2, the



Fig. 2. FTIR spectra of BAPM, BAFM and BATFM.

characteristic absorptions due to the N–H stretching vibration of amino groups and the C–H stretching vibration of methyl groups in the region of $3300-3500 \text{ cm}^{-1}$ and $2800-3000 \text{ cm}^{-1}$, respectively, were detected for all of diamines. Whereas, the characteristic absorptions around 1620 cm⁻¹ were assigned to the C=C vibration of phenyl groups. Meanwhile, the absorptions assigned to C–F stretching vibration at 1228 and 1151 cm⁻¹ were detected for fluorinated diamines BAFM and BATFM. The latter gave the relatively stronger signal due to the higher fluorine content. In addition, the elementary analysis values of these monomers were in good agreement with the calculated ones. The characterization results demonstrated that the aromatic diamines BAPM, BAFM and BATFM were successfully synthesized and the obtained monomers were pure enough to be employed for preparation of polyimides.

3.2. Polymer synthesis and characterization

A series of fluorinated polyimides were synthesized *via* one-pot solution polycondensation from dianhydride 6FDA and aromatic diamines with bulky triptycene and pendent phenyl moieties in NMP as shown in Scheme 2. It is considered that the one-pot method is suitable for low reactive monomers to synthesize soluble PIs, however, the polycondensation should be implemented at elevated temperature in order to get the polymer with high molecular weight. Initially, 6FDA and aromatic diamine were reacted at the ambient temperature in the presence of isoquinoline, which acted as a catalyst, to give poly(amic acid). After that, the intermediate without isolation was thermally cyclodehydrated at elevated temperature to give the corresponding polymer. The water by-product was removed by azeotropic distillation with toluene to ensure the thermal cyclization being processed completely. The fiber-like precipitates in pale-yellow were obtained by pouring the viscous polymer solution slowly into excess of ethanol, indicating that the polymers have relatively high molecular weight.

Table 1 summarized the physical properties and GPC data of the fluorinated polyimides. It can be seen that all the polyimides were produced in high yields of 96–98%. The fluorine contents of GSPI-T1~GSPI-P3 ranged from 13.0 to 22.5%. These polymers showed reasonable high molecular weight and narrow molecular weight distribution with M_n and M_w in the range of $3.64-5.60 \times 10^4$ g/mol and $8.27-11.12 \times 10^4$ g/mol, as well as M_w/M_n of 1.93-2.27, respectively.

Fig. 3 shows the FTIR spectra of the fluorinated polyimides, in which the characteristic absorptions of imide groups were observed at about 1780 cm⁻¹ (C=O, asymmetric), 1720 cm⁻¹ (C=O, symmetric) and 1370 cm⁻¹ (C–N, asymmetric), respectively. Meanwhile, the characteristic N–H stretching vibration of animo group in poly(amic acid) at around 3300–3500 cm⁻¹ were not detected, indicating that the polymers were imidized completely. Moreover, the absorptions assigned to stretching vibration of C–F at 1250 and 1140 cm⁻¹ were also observed in the spectra of these polymers. The results demonstrated that the fluorinated polyimides had the expected chemical structures.

The solubility of the fluorinated polyimides was measured by dissolving the polyimide resins in different organic solvents with 15 wt.% of solid content at room temperature. It is known that aromatic polyimides generally have poor solubility in common organic solvents because of their strong chain interaction of imide rings. However, the fluorinated polyimides synthesized in this study could be easily dissolved in many organic solvents except in ethanol as shown in Table 2. The good solubility of these polyimides is due to the synergetic effects of the bulky triptycene and pendent phenyl moieties as well as the fluorine groups in the polymer structure, which disrupt the regularity of the molecular chains and hinder the dense chain stacking, consequently, permitting solvent to dissolve the polymers more easily [39].

The solubility of these polyimides was also quantitatively evaluated. Fig. 4 depicts the dependence of the absolute viscosities of polyimide solutions in DMAc on the solid contents. The absolute viscosities of these polyimides in DMAc with 20 wt.% of solid content were no more than 1250 mPa·s at 25 °C, which exhibited a gradually increasing for GSPI-T polyimides and an abruptly enhancing for GSPI-P polyimides as the solid content in excess of 25 wt.%. Moreover, the absolute viscosity of these polyimide solutions with same concentration increased in the order of GSPI-



Scheme 2. Synthesis of fluorinated polyimides.

Table 1Physical properties and GPC data of fluorinated polyimides.

PI	Yield (%)	F ^a (%)	GPC data			
			$M_n imes 10^{-4}$	$M_w imes 10^{-4}$	M_w/M_n	
GSPI-T1	98	13.0	5.60	11.12	1.98	
GSPI-T2	97	22.5	5.20	10.28	1.98	
GSPI-P1	97	15.4	4.46	9.01	2.02	
GSPI-P2	97	17.6	5.04	9.75	1.93	
GSPI-P3	96	21.6	3.64	8.27	2.27	

^a F: fluorine content.



Fig. 3. FTIR spectra of fluorinated polyimides.

T2<GSPI-T1<GSPI-P3<GSPI-P2<GSPI-P1. It is noted that the solubility depended on their backbone structure. The GSPI-T polyimides showed better solubility than GSPI-P polyimides due to the presence of bulky triptycene structure and flexible polymer backbone. It is also found that the polyimides with relative higher fluorine content gave the lower absolute viscosity although they have the similar backbone. For instance, the absolute viscosity of GSPI-P3 (21.6% of fluorine content) at the solid content of 30 wt.% was 3.42×10^4 mPa s, which was only half of that for GSPI-P1 (15.4% of fluorine content). The bulky fluorinated substituents both in the polymer main chain and side chain could inhibit the close chain packing, which leading to the improvement of polymer solubility. The polymer solutions were very stable and no phase separation or precipitation was observed after storage for several weeks.

The thermal and mechanical properties of these polyimides were evaluated and the results are summarized in Table 3. These polyimides exhibited excellent thermal stability with glass transition temperatures (T_g) for GSPI-T and GSPI-P polyimides around 300 °C and 330 °C, respectively. The relatively higher T_g values of GSPI-P polyimides are attributed to their more rigid polymer main chains. It has been reported that the methyl substituents in the

Solubility	of f	luorinated	polvimic	les.

Table 2



Fig. 4. Dependence of the absolute viscosity of polyimide solution in DMAc on solid content.

ortho position to the imide ring in polyimide structure restricted the rotation of nitrogen atom along the phenyl ring, which in turn increase the T_g of polyimides [40]. Moreover, TGA results revealed that these polymers were thermally stable up to 496 °C without obvious weight loss in nitrogen. In comparing these polyimides, it can be seen that the GSPI-P polyimides gave the decomposition temperatures at 5% and 10% weight loss (T_5 and T_{10}) 15–22 °C lower than GSPI-T polyimides. This may correspond to the loss of methyl substituents in GSPI-P polyimides [41], although they have more rigid backbone than GSPI-T polyimides.

The unoriented fluorinated polyimide membranes could be prepared by solution casting and solvent evaporation. All the membranes presented excellent mechanical property with the tensile strength of 90–115 MPa, the Young's modulus of 2.1–2.9 GPa, and the elongation at break of 4.3–7.4%, respectively. The strong and tough property of these polyimide membranes are owing to their strong chemical bond in the main chains [25].

3.3. Gas transport properties and their correlation with microstructure

The gas transport properties of these fluorinated polyimide membranes were investigated using a constant-volume, pressurevariable gas permeation method. The gas permeability coefficients of CO₂, O₂, N₂ and CH₄ as well as the ideal selectivity for gas pairs are listed in Table 4. It can be observed that, in all cases, the order of permeability was $P(CO_2) > P(O_2) > P(N_2) > P(CH_4)$. This order coincides with the kinetic diameter of gas molecules (CO₂, 3.30 Å; O₂, 3.46 Å; N₂, 3.64 Å; CH₄, 3.80 Å), indicating that the size-sieving is a dominant factor for gas separation in these membranes. As comparing the permeability of these polyimide membranes, it is noted that the GSPI-P membranes revealed much higher permeability coefficients than the GSPI-T membranes combined with an

PI	NMP	<i>m</i> -Cresol	DMAc	THF	Dioxane	Chloroform	Acetone	Ethanol
GSPI-T1	++	++	++	++	++	++	+	_
GSPI-T2	++	++	++	++	++	++	++	-
GSPI-P1	++	++	++	++	++	++	++	-
GSPI-P2	++	++	++	++	++	++	++	-
GSPI-P3	++	++	++	++	++	++	++	-

 a ++: soluble at room temperature; +: partially soluble; -: insoluble even on heating.

Iddle 5		
Thermal and mechanical	properties of fluorinated	polvimides. ^a

PI	$T_g (^{\circ}C)$	T_d (°C)	T ₅ (°C)	T ₁₀ (°C)	T _S (MPa)	T _M (GPa)	E _b (%)
GSPI-T1	300	507	523	540	100	2.8	4.6
GSPI-T2	295	504	523	540	115	2.9	4.3
GSPI-P1	332	496	503	520	100	2.6	5.5
GSPI-P2	331	501	508	524	90	2.5	5.0
GSPI-P3	336	496	501	520	96	2.1	7.4

^a T_g: determined by DSC; T_d: onset decomposition temperature; T₅, T₁₀: the decomposition temperature at 5% and 10% weight loss, respectively; T_S: tensile strength; T_M: Young's modulus; E_b : elongation at break.

improvement in selectivity. For example, $P(CO_2)$ and $P(CH_4)$ for the GSPI-P1 membrane are 10.3 and 5.9 times for the GSPI-T1 membrane, respectively, meanwhile, the $\alpha(CO_2/CH_4)$ for the former is 1.8 times of the latter. It is worth to mention that the CO₂ and CH₄ permeability of GSPI-P membranes is superior to the commercially available Matrimid membrane, which has $P(CO_2)$ of 10 barrer and $P(CH_4)$ of 0.28 barrer [42,43], without significant loss of selectivity.

It is well known that the permeability and selectivity of dense polymer membranes are strongly depended on their microstructure. The average interspacing distance (d-spacing) is considered to represent the distance between segments of different chains and correlate with the permeability coefficient of membranes [44]. The X-ray diffraction patterns of fluorinated polyimides were investigated and the d-spacing values of these polymers were determined from the angle of maximal peaks by Bragg's equation. A broad amorphous halo is observed for all the polyimides as shown in Fig. 5. The amorphous nature of these polyimides is attributed to the presence of bulky $-C(CF_3)_2$ - group in the dianhydride combined with bulky triptycene moiety or pendent phenyl group in the diamine, resulting in loose chain packing and aggregation. It can be seen that GSPI-T polyimides revealed the relatively broader diffraction peaks than GSPI-P ones, which suggested the bulky triptycene moiety is more efficient to separate molecular chains from dense arrangement. The GSPI-T and GSPI-P polyimides gave the maximal peaks at 13.3°-13.5° and 15.0-15.2° that correspond to the d-spacing of 6.57–6.64 Å and 5.83–5.97 Å, respectively. From the XRD pattern of GSPI-T2, a shoulder diffraction peak on the high angle side ($2\theta = 16.7^{\circ}$) with d-spacing of 5.31 Å is also observed. This peak could be assigned to interlocking of phenyl rings of triptycene perpendicular to polymer chain, and then $\pi - \pi$ interactions between phenyl rings [34].

Generally, the permeability of penetrant gases in a polymer membrane enhances with the d-spacing increasing. The permeability for both GSPI-T and GSPI-P membranes showed an increasing trend accompanied with the d-spacing increasing due to incorporation of bulky trifluoromethyl or fluorine substituents. However, as comparing the GSPI-P and GSPI-T membranes, it is unexpected that the former exhibited significantly higher permeability coefficients, although they gave the smaller d-spacing than the latter. We suspect that the gas permeation in membrane may

Table 4

Permeability coefficient and selectivity of fluorinated polyimide membranes at 1 bar and 23 $^\circ\text{C}.$

PI	P (barrer) ^a			$\alpha (P_A/P_B)$				
	CO ₂	02	N_2	CH ₄	CO ₂ /CH ₄	CO_2/N_2	O_2/N_2	N ₂ /CH ₄
GSPI-T1	11.65	4.10	1.57	0.78	14.9	7.4	2.6	2.0
GSPI-T2	28.26	7.22	2.07	1.06	26.7	13.6	3.5	2.0
GSPI-P1	120.20	21.20	4.99	4.57	26.3	24.1	4.2	1.1
GSPI-P2	119.10	21.59	5.03	4.41	27.0	23.7	4.3	1.1
GSPI-P3	142.61	27.07	7.11	6.62	21.5	20.1	3.8	1.1

^a Permeability in barrers, where 1 barrer = 10^{-10} cm³(STP)cm/cm² s cmHg.

GSPI-T1, d=6.57Å GSPI-T2, d=6.64Å/5.31Å GSPI-P1, d=5.83Å GSPI-P2, d=5.88Å GSPI-P3, d=5.97Å 0 10 20 30 40 50 60 20 (°)

Fig. 5. XRD patterns of fluorinated polyimides.

not only correlate with the average distance of chain segments but also rely on the free spaces in microstructure. In addition, GSPI-P polyimides displayed relatively sharper XRD curves, suggesting a certain degree of regularity in the interchain distance. This result is probably related to their better gas selectivity especially for gas pair of CO_2/CH_4 and CO_2/N_2 .

The free volume is the sum of the static voids which are created by chain packing or transient gaps generated by thermally induced chain rearrangement and provides the diffusing molecules a lowresistance path for their transport. The fractional free volumes of these polymers were investigated by both molecular dynamics simulation and experimental approach in order to clarify the relationship between gas permeability and microstructure of membrane. Fig. 6 is a schematic representation of a simulated molecular cell of GSPI-P3, in which three molecular chains composed of 6FDA and BATFM with 30 repeating units for each were set in the cubic cell. The blue and the gray areas in the simulation cell are related to the free volume and the occupied volume of GSPI-P3, respectively. The fractional free volume of fluorinated polyimides were calculated from the specific volume and the occupied volume of the polymer based on their optimized model structure.

Table 5 presents the density, cell length, specific volume and occupied volume obtained by molecular dynamics simulation as well as the fractional free volume (FFV_{sim}) for fluorinated polyimide membranes. The density of these polymers in stable state in the simulation cell varied from 1.180 to 1.346 g/cm³, which is relatively low compared to other 6FDA based polyimides [45]. The cell lengths for GSPI-P membranes were around 45 Å, whereas that for GSPI-T membranes increased to 46.96-48.52 Å, as a result, the latter gave the higher specific volume than the former. However, the GSPI-P membranes exhibited the lower occupied volume than GSPI-T ones, which finally lead to the larger FFV_{sim} values. It is noted that the FFV_{sim} results for these polyimide membranes are inconsistent with the finding from the corresponding d-spacing. We consider that the bulky triptycene groups in GSPI-T polyimides may separate molecular chains more effectively than pendent phenyl groups in GSPI-P polyimides and result in larger d-spacing and specific volume. However, the triptycene groups in the polymer chains also occupy more volume, as a consequence, providing less free volume. It is worth to mention that GSPI-P membranes exhibited the FFVsim of 0.2274-0.2517, which is higher than most of 6FDA based polyimide [46]. The larger FFV of GSPI-P membranes is



Fig. 6. Schematic representation of a simulated molecular cell of GSPI-P3.

directly associated with their higher gas permeability as illustrated in Table 4, even though they gave narrower d-spacing than GSPI-T membranes.

The relationships between CO₂ permeability and their simulated fractional free volume for these polyimide membranes are depicted in Fig. 7. For GSPI-T membranes, FFV_{sim} values enhanced with the incorporation of large trifluoromethyl substituents in the backbone due to their steric hinder effect, which coincides with their changing trend of d-spacing. Therefore, the GSPI-T2 revealed improved CO₂ permeability than GSPI-T1. On the other hand, for GSPI-P membranes, an unanticipated decreasing in FFV_{sim} values accompanied with the introducing of fluorine substituents in the pendent phenyl group was observed. According to the simulation results listed in Table 5, it is found that the cell length and specific volume for GSPI-P membranes showed a slight decreasing combined with an increasing in occupied volume with the enhancing of fluorine content. The decreasing in FFV_{sim} of GSPI-P membranes can be explained by the filling effect of fluorine atoms. As shown schematically in Fig. 8, the specific volume for all the GSPI-P membranes is dominated by the bulky pendent phenyl moieties. As the fluorine substituents are incorporated to the pendent phenyl rings, the fluorine atoms will fill in the internal space and result in less free volume. A similar filling effect of trifluoromethyl and methyl groups for pentiptycene-based polyimides has been reported by Luo et al. [47]. However, it is difficult to understand that the permeability coefficients for GSPI-P membranes are in the order of GSPI-P1 \approx GSPI-P2<GSPI-P3, which is in conflict with the order of FFVsim. Stern et al. pointed that the polar fluorine-containing groups could induce specific interactions with the penetrant molecules, and such interactions can significantly enhance the solubility process, which was favorable to gas permeation [48]. We speculate that the permeability increasing related with the specific



Fig. 7. Relationship between CO₂ permeability and simulated fractional free volume of fluorinated polyimide membranes.

interaction effect of fluorine substituents for GSPI-P3 is superior to the permeability decreasing caused by the reduction of FFV, as a result, it revealed the relatively higher permeability. From this point of view, we can say that the opposite effects on the permeability achieved a good balance for GSPI-P2 because of the less fluorine atoms in the side chain, which gave the permeability coefficient similar to GSPI-P1.

The free volume in a polymeric membrane generally consists of many isolated spaces with variable volume and size, which provides variation in the membrane permeability and selectivity [49]. The positron annihilation lifetime spectroscopy, an experimental approach to determine the size and concentration of free volume cavities in a polymeric membrane, was adapted to verify the FFV results derived from theoretical simulating and furthermore understand the gas separation performance of these fluorinated polyimide membranes. The positronium lifetimes, intensities, average cavity radii and the corresponding fractional free volumes (FFV_{PALS}) are summarized in Table 6. The FFV_{PALS} values for GSPI-T and GSPI-P polyimides were in the range of 0.1069-0.1590 and 0.2082-0.2224, respectively. It can be seen that the changing trend of FFV_{PALS} values was completely consistent with that of FFVsim results, demonstrating the reliable FFV results were obtained from molecular simulation method. It is also found that GSPI-P membranes gave the longer τ_3 combined with higher I_3 values as comparing to GSPI-Tones. Meanwhile, the average cavity radii for the former were in the range of 3.42–3.45 Å, while that for the latter slightly decreased to 3.33–3.40 Å. The lifetime (τ_3) and intensity (I_3) of orthopositronium have been found to be correlated well with the local free volume in polymers in which τ_3 is proportional to the size of the free volume cavity and the I_3 is proportional to their number concentration [50]. Therefore, it can be deduced that the superior gas permeability of GSPI-P membranes is attributed to their larger mean cavity size and the higher free volume. The intensity and the average cavity radius for GSPI-T membranes showed an increasing

Table 5

The density, cell length, specific volume and occupied volume of simulation cells as well as calculated fraction free volume for fluorinated polyimide membranes.

PI	Density (g/cm ³)	Cell length(Å)	Specific volume (Å ³)	Occupied volume (Å ³)	FFV _{sim}
GSPI-T1	1.286	46.96	103558	81376	0.2142
GSPI-T2	1.346	48.52	114211	88574	0.2245
GSPI-P1	1.180	45.44	93805	70196	0.2517
GSPI-P2	1.226	45.25	92584	70260	0.2411
GSPI-P3	1.280	45.27	92781	71683	0.2274



Fig. 8. Schematic of filling effect of fluorine substituent for GSPI-P membranes.

Table 6

The positronium lifetime, intensity, free volume radius and fractional free volume for fluorinated polyimide membranes.

PI	τ_3 (ns)	I ₃ (%)	R (Å)	FFV _{PALS}
GSPI-T1	2.56 ± 0.03	6.93 ± 0.15	3.33	0.1069
GSPI-T2	2.66 ± 0.02	9.66 ± 0.19	3.40	0.1590
GSPI-P1	2.73 ± 0.02	12.91 ± 0.19	3.45	0.2224
GSPI-P2	2.72 ± 0.02	12.90 ± 0.20	3.44	0.2197
GSPI-P3	2.68 ± 0.02	12.46 ± 0.19	3.42	0.2082

trend along with the incorporation of fluorinated groups, in contrast, those for GSPI-P membranes exhibited a decreasing trend due to the filling effect of fluorine atoms. The corresponding FFV_{PALS} values of these polyimides revealed the similar changing. It is also noted that the GSPI-P membranes have the appropriate cavity size (R = 3.42 - 3.45 Å), which is larger than the dynamic radius of CO₂ (3.30 Å) and smaller than that of the other gaseous molecules (3.46–3.80 Å). The specific cavity size of GSPI-P membranes made them favorable to transport the CO₂ and prevent the other larger gaseous molecules, which providing them improved CO₂/CH₄ and CO₂/N₂ selectivity. The GSPI-T2 membrane displayed selectivity comparable to GSPI-P ones because of the similar cavity size, whereas, gave much lower permeability coefficients due to the lower FFV_{PALS}. These results suggested that the gas transport properties of fluorinated polyimide membranes were strongly dependent on their microstructure. The large quantity of free volume combined with appropriate cavity size in polymeric membranes is beneficial to improve their permeability and selectivity simultaneously.

4. Conclusions

The novel aromatic diamines with pendent phenyl structure, *i.e.*, BAPM, BAFM and BATFM, were synthesized and characterized. These diamines and the diamines with triptycene moieties were successfully polymerized with commercial available dianhydride 6FDA via one-pot solution polycondensation at high temperature to gain the GSPI-P and GSPI-T polyimides, respectively. These polyimides exhibited excellent solubility in various organic solvents due to the presence of bulky triptycene and pendent phenyl moieties. They also revealed high thermal stabilities and outstanding mechanical properties, which made them suitable for further investigation of gas transport properties. The GSPI-P membranes revealed much higher permeability coefficients than the GSPI-T membranes combined with good selectivity. The larger fractional free volume of GSPI-P membranes is directly associated with their higher gas permeability, even though they gave narrower d-spacing than GSPI-T membranes. The GSPI-P membranes also provided good selectivity for CO_2/CH_4 and CO_2/N_2 gas pairs. According to the positron annihilation measurements, it is found that the cavity size of GSPI-P membranes is larger than the dynamic radius of CO₂ and smaller than that of the other gaseous molecules, which made them favorable to separate the CO_2 from the other gases. These results suggested that the large quantity of free volume combined with appropriate cavity size in polymeric membranes is beneficial to improve their permeability and selectivity simultaneously.

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