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

Hui TONG (佟辉)[a,c], Chenchen HU (胡晨晨) [b,c], Hongxia GUO (郭洪霞) [b,c], Lin FAN (范琳) [a,c] *

[a] Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Haidian District, Beijing 100190, China;

[b] Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Haidian District Beijing 100190, China;

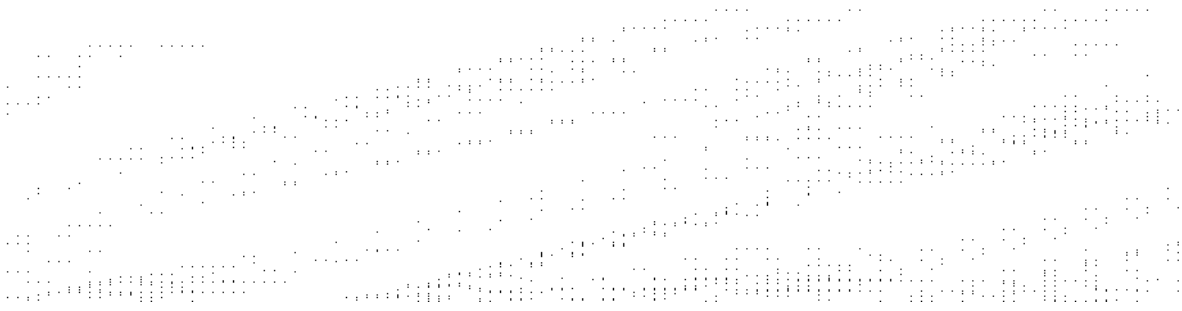
[c] School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Yuquan Rd, Shijingshan District, Beijing 100049, China;

Tel: +86-10-62564819; Fax: +86-10-62569562; E-mail: fanlin@iccas.ac.cn

Aromatic polyimides are one of the most attractive materials for gas separation due to their combination properties, *e.g.*, excellent thermal stability, good mechanical properties, outstanding chemical resistance, and high gas selectivity. They are especially suitable for using in some extreme situations, such as, high temperature, high pressure, or existence of harsh substances [1-2]. However, conventional polyimide membranes possess low gas permeability on account of the strong attractive force between intra/inter-molecules, which also lead to poor processability. In the past decades, many attempts have been made to enhance the gas permeability of polyimide membranes under the premise of maintaining their inherent good gas selectivity [3]. Fluorinated polyimides containing 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) have been identified as materials exhibiting both high gas permeability and selectivity [4]. In addition, introduction of bulky moiety into the polymer backbone, to disturb the chain packaging and consequently increase the free volume, is also an efficient way to improve the permeability of polyimide membranes [5].

In this research, aiming at development the polyimide membranes with enhanced gas permeability, a serial of novel fluorinated aromatic polyimides derived from 6FDA and aromatic diamines with bulky triptycene or pendent phenyl structures were synthesized. The effect of the structure on the thermal and mechanical properties of these polyimides was evaluated. The correlation of gas separation performance with the microstructure of these polyimide membranes was investigated.

The fluorinated aromatic polyimides were prepared *via* one-pot solution polycondensation at high temperature as shown in Scheme 1. These polyimides exhibited good thermal stability and mechanical properties, which gave the T_g of 295-336^{o}C and tensile strength of 90-115 MPa.



Scheme 1. Synthesis of fluorinated aromatic polyimides.

The gas separation properties of these membranes were measured under 1 atm at 23°C and summarized in Table 1. The fluorinated polyimide membranes exhibited permeability in the order of $P(CO_2)>P(O_2)>P(N_2)>P(CH_4)$, which enhanced with the decreasing of kinetic diameter of gases. 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 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.

Table 1. Permeability coefficient and selectivity of fluorinated polyimide membranes

PI	P (barrer) [a]				α (P_A/P_B) [b]			
	CO_2	O_2	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} $cm^3(STP)cm/cm^2 \cdot s \cdot cmHg$.
[b] The ideal selectivity, $\alpha=P_A/P_B$;

The fractional free volumes (FFV) of these polymers were calculated by molecular dynamics (MD) simulation and measured by positron annihilation lifetime spectroscopy (PALS) in order to clarify the relationship between gas permeability and microstructure of membrane. Figure 1 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 FFV_{sim} of fluorinated polyimides were calculated from the specific volume and the occupied volume of the polymer based on their optimized model structure.

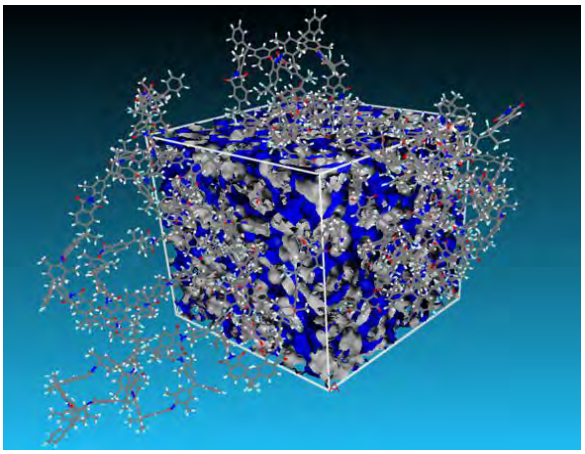


Figure 1. Schematic representation of a simulated molecular cell of GSPI-P3

Table 2 presents the cell length, specific volume and occupied volume obtained by molecular dynamics simulation as well as the fraction free volume (FFV_{sim}) for these membranes. 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. 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 specific volume. However, the triptycene groups in the polymer chains also occupy more

volume, as a consequence, providing less free volume. The larger FFV of GSPI-P membranes is directly associated with their higher gas permeability as illustrated in Table 1.

Table 2 . The cell length, specific volume, occupied volume and the calculated FFV_{sim} by simulation cells as well as the free volume radius (R) and the FFV_{PALS} determined by PALS for fluorinated polyimide membranes

PI	Cell length (Å)	Specific volume ($Å^3$)	Occupied volume ($Å^3$)	FFV_{sim}	R (Å)	FFV_{PALS}
GSPI-T1	46.96	103558	81376	0.2142	3.33	0.1069
GSPI-T2	48.52	114211	88574	0.2245	3.40	0.1590
GSPI-P1	45.44	93805	70196	0.2517	3.45	0.2224
GSPI-P2	45.25	92584	70260	0.2411	3.44	0.2197
GSPI-P3	45.27	92781	71683	0.2274	3.42	0.2082

The positron annihilation lifetime spectroscopy (PALS), 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 membranes. The average cavity radii (R) and the corresponding fractional free volumes (FFV_{PALS}) are also listed in Table 2. 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 FFV_{sim} results, demonstrating the reliable FFV results were obtained from molecular simulation method. Meanwhile, the average cavity radii for GSPI-P were in the range of 3.42-3.45 Å, while that for GSPI-T slightly decreased to 3.33-3.40 Å. 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. 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 CO_2 (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 CO_2 and prevent the other larger gaseous molecules, which providing them improved CO_2/CH_4 and CO_2/N_2 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.

References

[1] L.M. Tao, H.X. Yang, J.G. Liu, L. Fan, S.Y. Yang. *Polym*er, **2009**, 50, 6009-6018.
[2] Y. Xiao, B. T. Low, S.S. Hosseini, T.S. Chung, D.R. Paul. *Prog. Polym. Sci.* **2009**, 34, 561-580
[3] W. -H. Lin, T.S. Chung. *J. Memb. Sci*. **2001**, 186, 183-193.
[4] W. Qiu, C. -C. Chen, M.R. Kincer, W.J. Koros. *Polymer*, **2011**, 52, 4073-4082.
[5] T. Nakagawa, S. Tomoi, K. Goto. *J. Photopolym. Sci. Technol.* **2003**, 16, 277-278.