Fluorinated Polyimide Membranes and Their Gas Separation Properties

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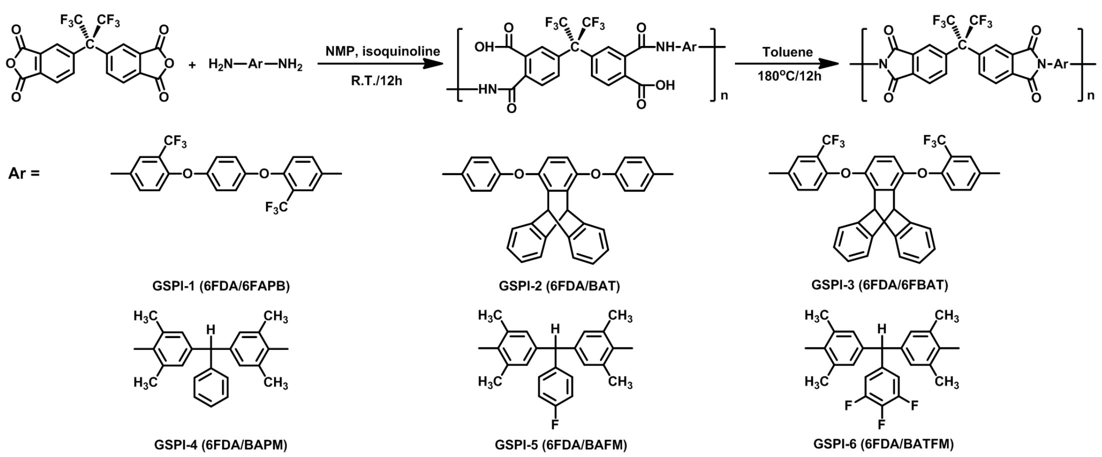
Aromatic polyimides are one of the most attractive materials for gas separation due to their combination properties, *e.g.*, excellent thermal stability, good mechanical properties, outstanding chemical resistance, and high gas selectivity. They are especially suitable for using in some extreme situations, 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, a serial of novel fluorinated aromatic polyimides were synthesized based on 6FDA and aromatic diamines, aiming at development the polyimide membranes with enhanced gas separation properties. The effect of the structure on the thermal and mechanical properties, as well as gas separation properties of these polyimide membranes was investigated.

The fluorinated aromatic polyimides were prepared *via* one-pot solution polycondensation at high temperature (Scheme 1). These polyimide membranes exhibited good thermal stability and mechanical properties, which gave the T_g of 260-336^oC 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^oC

and summarized in Table 1. The fluorinated polyimide membranes exhibited permeability in the order of CO_2>O_2>N_2>CH_4, which enhanced with the decreasing of kinetic diameter of gases. The GSPI-1 membrane gave the lowest permeability coefficient than the other membranes. This is related to its flexible and linear polymer structure, which allows the chain rotation and packing. The GSPI-4~GSPI-6 membranes exhibited relatively higher permeability coefficients, which is due to their large free volume caused by the large pendent phenyl groups in the structure. However, the GSPI-2 and GSPI-3 membranes revealed the permeability coefficients not much higher than the GSPI-1 membranes, although they have bulky triptycene structure in the polymer chain. This may be caused by the chain stacking in some extent due to their flexible polymer backbone. It is also found that GSPI-4~GSPI-6 membranes displayed enhanced selectivity for CO_2/CH_4 and CO_2/N_2 as comparing with the other membranes. It is considered that the large pendent phenyl groups in the diamine moiety combined with the rigid polymer backbone could prevent the chain packaging and hinder the chain rotation; as a result, the permeability and selectivity of membrane could be improved simultaneously.

Table 1. The gas separation properties of fluorinated polyimide membranes

	Permeability [a] (Barrer)				Selectivity [b] (α)			
	O_2	N_2	CH_4	CO_2	O_2/N_2	CO_2/CH_4	CO_2/N_2	N_2/CH_4
GSPI-1	4.95	0.62	0.31	4.90	8.0	15.8	7.9	2.0
GSPI-2	4.29	1.14	0.80	14.26	3.8	17.9	12.5	1.4
GSPI-3	7.71	1.71	0.99	24.56	4.5	24.8	14.4	1.7
GSPI-4	21.20	4.99	4.57	120.20	4.2	26.3	24.1	1.1
GSPI-5	21.59	5.03	4.41	119.10	4.3	27.0	23.7	1.1
GSPI-6	27.07	7.11	6.62	142.61	3.8	21.5	20.0	1.1

[a] Permeability in barrers, where 1 barrer =10^{-10} cm^3 (STP) cm/cm^2 s cm Hg;
[b] The ideal selectivity, $\alpha = P_A/P_B$;

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