

Sorption and transport properties of gases in aromatic polyimide membranes

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Abstract

A series of aromatic polyimide membranes were synthesized using direct polycondensation of various diamines containing flexible ether groups and bulky substituents with various aromatic dianhydrides. It is expected to promote the gas permeability of the polyimide membrane and maintain similarly gas selectivity by introduction of bulky groups. It was found that the gas permeability of aromatic polyimide membranes increased and the gas selectivity decreased with increasing fractional free volume and *d*-spacing. In addition, the gas permeability had good correlation with the γ -transition temperature and the thermal expansion coefficient. The bulky hexafluoroisopropylidene group introduced into the polyimide backbone could efficiently promote the gas permeability while the gas selectivity decreased slightly. Because the gas diffusivity coefficient and diffusivity selectivity controlled gas permeability and selectivity, respectively, the diffusivity effect dominated the gas separation behavior. The sorption behavior of aromatic polyimide membrane can be well explained using the dual-sorption model. The experimental data indicated that the aromatic polyimide membrane had excellent oxygen/nitrogen separation performance.

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1. Introduction

Membrane-based gas separation has emerged as a commercially important technology for replacement, or use in combination with, traditional gas separation methods such as pressure swing adsorption, cryogenic distillation and amine absorption. Therefore, gas separation membrane systems have received much attention. Various membrane materials have been synthesized for gas separation applications in the last two decades. An important element contributing to gas separation technology success is the development of new membrane materials with high permeability and selectivity. The gas permeability and selectivity control using polymer

membranes has become a subject of intense research in both the industrial and academic fields because of the importance of developing new membrane separation processes [1–8]. In recent years, special attention has been concentrated on the relationship between the membrane polymer structure and gas separation properties.

It has been reported that the major physicochemical factors influencing polymer gas permeability and permselectivity control are (1) the mobility of the polymer chains, as reflected in many cases by the glass or sub-glass transition temperature of the polymer, (2) the intersegmental spacing, used to measure the mean free polymer volume, and (3) the penetrant–polymer interactions, as reflected by the solubility of the penetrant gases in polymers. It is well known that there are few specific polymer interactions with permanent gases such as oxygen and nitrogen at relatively low gas pressures

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(below 10 atm). The exception is carrier-mediated transport. Thus, for a given permanent gas, the permeation properties depend primarily on the packing density and the polymeric chain mobility. The former has been frequently interpreted in terms of the free volume, specific volume and *d*-spacing. The *d*-spacing can be examined through dynamic mechanical analysis (DMA) [9–12].

Polyimide gas separation properties exhibit low permeability coefficients, high selectivity, good thermal stability and thin film formability, making them attractive for this application. Numerous works were performed to modify the physical and chemical properties of polyimides, aiming at acquiring good gas separation performance [13–18]. Recent studies demonstrated that both permeability and selectivity might be enhanced by the incorporation of bulky pendent groups in glassy polymeric membranes to simultaneously decrease the chain packing efficiency and hinder torsional mobility [19–21]. There have been many active studies on novel polyimides that are structure modified in order to enhance gas permeability and selectivity. Hirayama et al. studied 32 kinds of polyimide films synthesized from diamines and BPDA, 6FDA, or PMDA [22]. The authors concluded that the diffusivities of amorphous polyimides were not clearly correlated with the *d*-spacing or fractional free polyimide film volume. This fact indicates that the total free space or mean segment distance may not be proper for explaining gas diffusion. A similar investigation performed by Yang et al. [30] examined polyimides with great chain stiffness that displayed much higher CO₂ permeability coefficients. However, the ideal selectivity was similar. A representative example is the 6FDA series polyimide. Fluorinated polyimides containing 6FDA have been identified as materials exhibiting both high permeability and selectivity [23–26]. Tanaka et al. [27] has studied the gas solubility and permeability coefficients of a series of fluorinated and non-fluorinated polyimides. They found that 6FDA-based polyimide has better gas separation properties than other polyimides. Shimazu et al. [24] investigated the relationship between the chemical structure and permeation properties of 1,3-butadiene and *n*-butane in various 6FDA-based polyimides. They indicated that 6FDA-based polyimides exhibited high separation performance compared with some conventional glassy polymers. However, even in the 6FDA series polyimide, which exhibits both high gas permeability and high selectivity, it has been difficult to over-

come the trade-off relationship between the gas permeability and selectivity.

In this study, the polyimide membranes were synthesized from the diamines containing flexible ether groups and bulky substituents, 1,4-bis(4-aminophenoxy) 2-*tert*-butylbenzene (BATB) and 3,3',5,5'-tetramethyl-bis[4-(4-aminophenoxy)phenyl]sulfone (TMBPS), with the dianhydrides having various linkages in the backbones, we hope to improve gas permeability of the polyimide membranes and maintain gas selectivity by introducing bulky groups. Meanwhile, the variation in polymer-structure influences the gas transport properties was investigated in detail.

2. Experimental

2.1. Materials

BATB-based polyimide membranes were prepared by the conventional two-step polymerization of BATB with various dianhydrides. To a stirred solution of 2.5 mmol of BATB in 13.5 ml DMAc, was added gradually 2.5 mmol of dianhydride. The mixture was stirred at room temperature for 2 h under argon atmosphere. The inherent viscosities of the poly(amic acid) were in the range of 1.2–1.8 dl/g. The poly(amic acid) solution thus obtained was spread on a glass plate and the solvent was removed at 80 °C. Imidization was carried out through thermal cyclodehydration of the poly(amic acid) membrane by heating at 110, 150, 180, 210, 250, and 300 °C for 20 min, respectively. TMBPS-based polyimide membranes were also prepared by the same method. Scheme of the polyimides synthetic route and the reaction pairs of polyimides were shown in Fig. 1 and Table 1, respectively.

2.2. Characterization

A Perkin-Elmer differential scanning calorimeter (Perkin-Elmer DSC7) was used to measure the glassy transition temperature, T_g , of the membranes at a heating rate of 10 °C/min. The dynamic mechanical property ($\tan \delta$) of the polyimide membranes was measured with a Perkin-Elmer dynamic mechanical analyzer (Perkin-Elmer DMA7e) at a heating rate of 5 °C/min from –150 to 350 °C using a stainless steel extension probe. The film extension mode was used at a fre-

Table 1
The reaction pairs of polyimides

Polyimides	Diamine	Dianhydride
BATB–6FDA		4,4'-Hexafluoroisopropylidenebisphthalic anhydride
BATB–BPDA	1,4-Bis(4-aminophenoxy)2- <i>tert</i> -butylbenzene	3,3',4,4'-Biphenyltetracarboxylic dianhydride
BATB–BTDA		3,3',4,4'-Benzophenonetetracarboxylic dianhydride
BATB–DSDA		4,4'-Sulfonyldiphthalic anhydride
TMBPS–6FDA	3,3',5,5'-Tetramethyl-bis[4-(4-aminophenoxy)phenyl]sulfone	4,4'-Hexafluoroisopropylidenebisphthalic anhydride
TMBPS–ODPA		4,4'-Oxydiphthalic anhydride
TMBPS–BTDA		3,3',4,4'-Biphenyltetracarboxylic dianhydride

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