

## 기체분리용 신규 고투과선택성 유기고분자막

최정익, 정철호, 박호범, 이영무\*  
한양대학교 화학공학과

### Novel High Permeable and Selective Polymer Membrane for Gas Separation

Jung Ik Choi, Chul Ho Jung, Ho Bum Park, Young Moo Lee\*  
School of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

#### 1. Introduction

Nanoporous solids are extensively regarded as promising materials for a wide range of technological applications [1-3]. in adsorption, catalysis and separation. Up to now, modern highly nanoporous materials have consisted primarily of inorganic components [4-5] such as activated carbons, zeolites, silica gel, carbon-silica and alumina. Here we report highly nanoporous organic polymers containing large and accessible surface areas above 500 m<sup>2</sup>g<sup>-1</sup> and micropores with dimensions in the range < 2nm. Compared to conventional microporous polymers having high free volume [9] or organic network polymers [6], the present nanoporous polymers show an excellent molecular sieving effect even for gas pairs with small molecules, as well as ultrapermeable characteristics in gas separation. This is successfully achieved by inducing regioisomerism for non-linear and rigid main-chain conformation obtained during thermal molecular rearrangement in functionalized glassy polymers, which are soluble and can be processed readily in versatile forms such as film, fibre and powder. The present method and its related analogous approach should provide a new blueprint for high-performance nanoporous organic polymer materials, available for adsorbents, electrode material, membranes, and so on.

#### 2. Experimental

To obtain high free volume polymers, we designed three kinds of functionalized polyimides as illustrated in Fig. 1. Bulky groups such Hexafluoroisopropylidene linkage  $-(CF_3)_2C-$  has been considered in the design of the

polymers in order to compensate for probable reduction of gas permeability due to the formation of the more rigid structure after heat treatment. Usually, the introduction of bulky groups into a rigid polymer matrix can disrupt the degree of chain packing, thereby increasing free volume and lead to high permeability without a significant loss of selectivity. In addition, to control the region of the rigid chain, monomers having different swivel groups (6FDA, OPDA, and BPDA) were introduced in the design. The change of such a flat package region was expected to result in the difference of the sieving effect, as often found in rigid polymers.

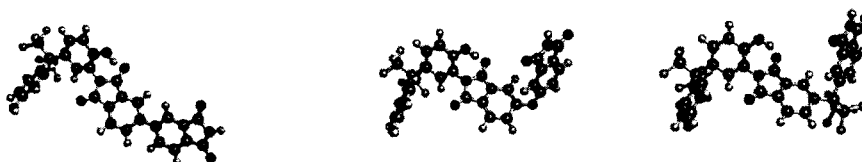


Fig. 1. Chemical structure of the 6FDA-APAF, OPDA-APAF, and BPDA-APAF

Polyimides were synthesized by a conventional two-step process in which the poly(amic acids) were firstly formed and then the polyimides were completed by thermal imidization. For instance, to a 100 mL flask purged with nitrogen was added APAF (3.663g, 10 mmol) and NMP (24.42 mL). The mixture was stirred to form a clear, brown solution at ambient temperature. 6FDA (4.443g, 10mmol) and NMP (29.62 mL) was added to this APAF solution in order to achieve the 15 %(w/v) solid contents. The reaction was mechanically stirred for 5 h at ambient temperature to give a viscous yellow solution. These solutions were dried under a vacuum for 2 h at 40 °C and for 2 h at 80 °C. Then, poly(amic acid) films were transformed to hydroxyl-containing polyimides (HPI) by heating for 1 h at 100 °C, 1h at 200 °C, and 1 h at 300 °C under a vacuum. The HPIs (6FDA-APAF, BPDA-APAF, OPDA-APAF) were thermally converted to polybenzoxazoles by heating the films under an Ar flow [ $<150 \text{ cm}^3 \text{ (STP)/min}$ ] in a quartz tube furnace supported on an alumina holder plate. The Ar flow was precisely controlled by a mass flow controller (MKS instruments, MASS-FLO, Andover, MA, USA). A 4.5-cm-i.d., 70-cm-long quartz tube with a glass end cap was used for heating in a muffle furnace equipped with four heating elements to minimize the axial and radial temperature gradients. The length of the effective heating zone was 30 cm. The final heating temperature and duration time were predetermined from thermal gravimetric

analysis(TGA) coupled with mass spectroscopy (MS). Each HPI films was heated up to 350 °C, 400 °C, 450 °C, and 500 °C under a Ar purge flow for 1 h, respectively. Eventually, heat-treated films were slowly cooled to room temperature.

### 3. Results and Discussion

For the TGA thermogram of HPI, a well-defined weight loss comprising 11.13% of the sample weight was observed between 400 oC and 500 oC. Calculations revealed that expulsion of 2 mol of carbon dioxide per repeat unit would exactly account for this weight loss.

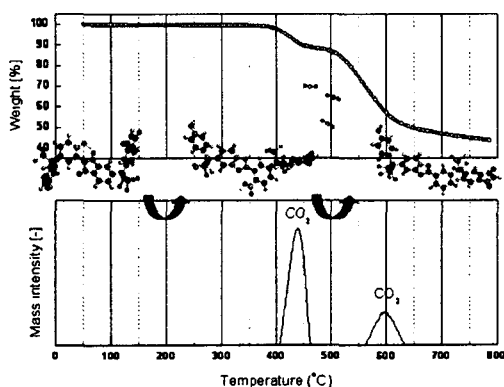


Fig. 2. TGA-MS curves of polyimide made from 6FDA-APAF monomers

The *d*-spacing value of HPI and PBO is 5.48 and 6.00. The change in the *d*-spacing from PI to PBO can serve as an indicator of the amount of room available for penetrating small molecules. The decrease of average *d*-spacing from HPI (300°C) to PBO (450°C) is a somewhat unexpected result. Originally, oxazole ring is more rigid and flat than imide ring so that the transformation of an imide ring into an oxazole ring will give denser chain packing to final PBO membranes. but the experimental result shows the inverse data. Surprisingly, it was found that PBO membranes derived from HPIs showed superior O<sub>2</sub> permeability and desirable O<sub>2</sub>/N<sub>2</sub> selectivity (Fig. 3), jumping by far the upper bound line of conventional polymer membranes<sup>3</sup>. A PBO-450 membrane based on BHPI have a maximum gas separation performance as O<sub>2</sub> permeability is 1360 Barrer (1 Barrer = 1 · 10<sup>-10</sup> cm<sup>3</sup>(STP)·cm/cm<sup>2</sup>·sec·cmHg) and O<sub>2</sub>/N<sub>2</sub> ideal separation factor is 7.6. This was a wholly unexpected result. The O<sub>2</sub>/N<sub>2</sub> separation performance of pure HPI membranes is still placed below the upper bound. However, the O<sub>2</sub> permeabilities of HPI

membranes treated at higher temperatures ( $> 300\text{ }^{\circ}\text{C}$ ) systematically increases with increasing final heating temperature. The difference in early chemical structure of HPI membranes affected final gas permeability and selectivity as well, but with the same tendency to the heat treatment. However, noticeably, the separation performances of all HPI membranes treated at  $500\text{ }^{\circ}\text{C}$  (seemingly partial carbonized membranes) is converged on the similar area, as compared to samples treated below  $450\text{ }^{\circ}\text{C}$ , less depending upon initial chemical structure owing to accompanying the decomposition of main chains at this temperature. That is, they are not polymers any longer.

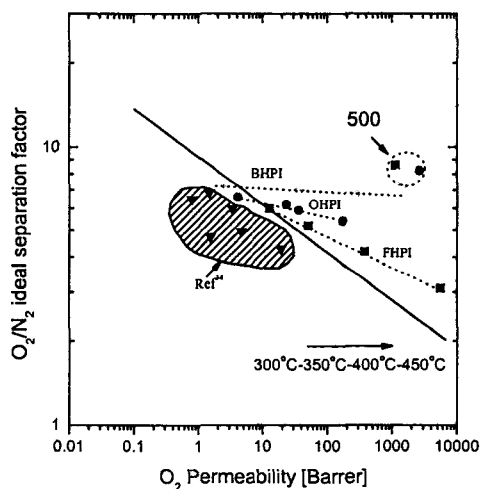


Fig. 3.  $\text{O}_2$  permeability vs.  $\text{O}_2/\text{N}_2$  ideal separation factor of HPIs and their derivative PBOs prepared in this study

#### 4. Conclusions

In this work, a new class of polymer membrane has been developed for improved gas separation. Usually PBO membranes have been regarded as an organic molecular sieving material, expecting high selectivity but low gas permeability because the PBO has very stiff chain packing, analogous to the semi-rigid polyimides. However, The remarkable gas permeation properties and separation performance in the PBO membranes derived from HPIs were found. The gas separation performance of PBOs heat-treated at above  $350\text{ }^{\circ}\text{C}$  exceeds the upper bound limit of conventional polymer membranes, particularly, for air separation. To reveal unusual gas permeation and

separation behavior of the PBOs derived from HPIs, the physical properties of PBOs obtained from experimental values were compared with those from molecular simulation method using molecular modeling programs (Hyperchem 7.0 and Cerius 2 (version 4.2)). However, two results were not coincided with each other. This might be caused by the difference that a PBO polymer chain generated in amolecular simulation method is not the same as the present PBO derived from HPI. Eventually, from the nitrogen sorption isotherm in PBO at -196 °C, the main contribution to high gas permeability and desirable separating-ability in PBO membranes is the formation of connected free volume (microvoid, or cavity) caused by the evolution of CO<sub>2</sub> gas molecules in the rigid glassy matrix, altogether with the increase of the fractional free volume due to bulky linkages and the deformation of original polyimide segments.

### **Acknowledgement**

This work was supported by Carbon Dioxide Reduction & Sequestration Center, one of 21st Century Frontier R&D Programs funded by the Ministry of Science and Technology.

### **Reference**

1. M. E. Davis, Ordered porous materials for emerging applications. *Nature* 417, 813-821 (2002)
2. A. Corma, From microporous to mesoporous molecular sieve materials and their use in catalysis, *Chem. Rev.* 97, 2372-1419 (1997)
3. S. M. Kuznicki. et al, A titanosilicate molecular sieve with tunable pores and its use in gas separation, *Nature* 412, 720-724 (2001)
4. M. E. Davis, R. F. Lobo, Zeolite and molecular sieve synthesis, *Chem. Mater.* 4, 756-768 (1992)
5. T. Masuda, E. Isobe, T. Higashimura, K. Takada, poly[1-(trimethylsilyl)-1-propyne]: a new high polymer synthesized with transition-metal catalysts and characterized by extremely high gas permeability, *J. Am. Chem. Soc.* 105, 7473-7474 (1983)
6. N. B. McKeown, S. Makhseed, P. M. Budd, Phthalocyanine-based nanoporous network polymers, *Chem. Commun.* 2780-2781 (2002)