Gas Permeability of Asymmetric Polyimide Membranes with Partially Carbonized Skin Layer

Kenji FUKUI[†], Shoji NAGAOKA[†], Yoshiaki SUZUKI[‡], Masaya IWAKI[‡], and Hiroyoshi KAWAKAMI[†]

[†]Department of Applied Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

[‡]The Institute of Physical and Chemical Research, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Introduction

The gas separation process using polymer membranes has received much attention, because the membrane systems provide better energy efficiency than conventional separation methods. We reported the gas permeability through an asymmetric polyimide membrane with a thin and defect-free skin layer prepared by a dry-wet phase inversion process. In this paper, we describe an organic-inorganic hybrid membrane, which exhibits an asymmetric structure consisting of a carbonized skin layer and a polymeric porous substructure to synthesize a novel gas separation membrane combing high gas permeability and selectivity. In this preliminary study, the gas permeances of the asymmetric polyimide membranes irradiated with 50keV He^+ at fluences less than 3×10^{15} ions/cm^2 have been measured using a high vacuum apparatus with a Baratron absolute pressure gauge at 76 cmHg.[1)]

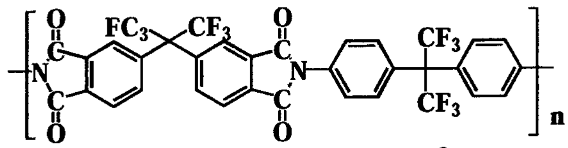
Experimental section

The polyimide, 6FDA-6FAP (scheme 1), was synthesized by chemical imidization of the poly (amic acid) precursors. Membranes with a different skin layer, approximately 80 nm and 4μm, were prepared by a dry-wet phase inversion process.[2)] Ion irradiation was performed on polyimide membranes and He^+ was used.

Gas permeances of carbon dioxide, oxygen, methane, and nitrogen were measured. The gas permeation measurements of the membranes were carried out at 35°C and 76 cmHg.

Results and Discussion

After ion-irradiating the asymmetric polyimide membranes, the absorbances of ATR-FTIR spectra and the Raman spectra changed dramatically between the virgin and irradiated membranes. Ion-beam irradiation induced changes in the chemical structure of the polyimide surface, and the changes strongly depended on the ion fluence.



Scheme 1 Chemical Structure of 6FDA-6FAP Polyimide.

The results of the gas permeance and selectivity of the asymmetric polyimide membranes for CO_2, O_2, N_2 and CH_4 at 35°C and 76 cmHg are shown in Table 1. The O_2 and CO_2 permeances of the asymmetric membranes irradiated at the fluence of less than 1×10^{13} (ions/cm^2) increased when compared with the asymmetric membrane before the ion irradiation. This suggests that the increase in the gas permeability indicates the formation of a more open space for the permeation of gas molecules in the asymmetric membrane irradiated at a low fluence. On the other hand, the (O_2/N_2) and (CO_2/CH_4) selectivities in the asymmetric membrane irradiated at the fluence of more than 1×10^{14} (ions/cm^2) increased with an increase in the He^+ influence.

Table 1 Effect of He^+ fluence on gas permeance and selectivity of He^+-irradiated asymmetric polyimide membranes at 35Å6 and 76cmHg[a].

He^+ fluence (ions/cm^2)	QO_2	QCO_2	QO_2/QN_2	QCO_2/QCH_4
Virgin	8.0	28	4.8	30
1Å˜10^{12}	10.0	35	4.8	32
1Å˜10^{13}	10.0	37	4.6	32
1Å˜10^{14}	7.4	27	4.6	30
1Å˜10^{15}	5.4	22	6.7	59
3Å˜10^{15}	3.3	15	7.8	79

[a]Apparent skin layer thickness is 80 Å] 3.7 nm.
$Q = 10^{-5}$cm^3(STP)/cm^2 sec cmHg.

References

(1) M. Iwase, A. Sannomiya, Y. Suzuki, M. Iwaki, H. Kawakami, *Macromolecules*, **37**, 6892-6897(2004).

(2) H. Kawakami, M. Mikawa, S. Nagaoka, *J. Appl. Polym. Sci.* **62**, 965-971(1996).

E-mail: kawakami-hiroyoshi@c.metro-u.ac.jp