Gas Transport Properties of Asymmetric Polyimide Membrane with an Ultrathin Surface Skin Layer

H. Kawakami,* M. Mikawa, and S. Nagaoka

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

Received March 2, 1998; Revised Manuscript Received June 3, 1998

ABSTRACT: Here, a new possibility for gas separation is presented, using an asymmetric membrane, with an ultrathin and defect-free skin layer. The structure of the asymmetric membrane, prepared by a dry-/wet-phase inversion process, showed an ultrathin skin layer and spongelike structure characterized by the presence of macrovoids. The gas selectivity of the membrane increases with a decrease in the thickness of the surface skin layer, perhaps because the membrane with a thinner surface skin layer forms a more packed structure. The effect of the membrane's surface skin layer on gas permeability and selectivity is discussed.

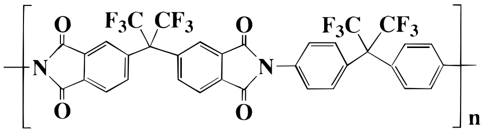
Introduction

The control of gas transport though polymer membranes is a primary concern in the development of new gas-separation membranes.[1] In this paper, we present a new possibility for gas separation, using an asymmetric membrane with an ultrathin, defect-free skin layer.

The structure and properties of polymer surfaces have received much attention because of their importance in practical applications. A recent study has revealed that surface effects lead to physical properties that differ substantially from those in the bulk material.[2] We have prepared a thin membrane of polyimide, a so-called asymmetric membrane, which consists of a thin, defect-free surface skin layer supported by a porous substructure. Recently, we reported that an asymmetric polyimide membrane with a surface skin layer 1 μm thick exhibits a greater gas selectivity than a dense membrane 50 μm thick and that the surface skin layer may provide a greater size and shape discrimination between the gas molecules.[3] Our goal has been to synthesize a new polymer membrane combining not only high gas permeability but also broad gas selectivity.

Here, we present the gas transport properties of an asymmetric polyimide membrane with an ultrathin skin layer. To focus on the effect of the membrane's surface skin layer on gas permeability and selectivity, we have prepared a series of asymmetric membranes with different skin layer thicknesses, varying from 10 to 200 nm.

6FDA-6FAP polyimide, which has a relatively high gas permeability coefficient and is highly soluble in organic solvents, was synthesized by using a chemical imidization reported in the literature.[4] The asymmetric 6FDA-6FAP membranes were prepared by a dry-/wet-phase inversion process.[5,6] During the initial stage of evaporation, a dry-phase separation occurs and an ultrathin skin layer is formed; during the next stage, which utilizes a coagulation medium, a wet-phase separation occurs and a porous substructure supporting the skin layer is formed. The membrane structure produced shows an ultrathin skin layer and a spongelike structure characterized by the presence of macrovoids.



6FDA-6FAP

The permeance and selectivity for CO_2, O_2, N_2, and CH_4 of the asymmetric membranes at 35 °C and at 76 cmHg have been measured without requiring an additional coating process.[7] The relationship between the CO_2/CH_4 selectivity and the apparent skin layer thickness is shown in Figure 1. The average CO_2/CH_4 selectivity of the membranes was 39; hence, the selectivity of most samples was greater than that determined for a solution-cast dense membrane. We found that the gas transport of the asymmetric membranes was predominantly carried out by a solution/diffusion mechanism and that the surface skin layer was essentially defect-free. The selectivities for O_2/N_2 and CO_2/CH_4 in the asymmetric membrane having an apparent skin layer thickness of 23 nm were 5.2 at an O_2 permeance of 3.5×10^{-4} [cm^3(STP)/(cm^2 s cmHg)] and 43 at a CO_2 permeance of 1.5×10^{-3} [cm^3(STP)/(cm^2 s cmHg)], respectively, where STP refers to standard temperature and pressure.[8]

Interestingly, the gas selectivity of the asymmetric membrane increased with decreasing thickness of the surface skin layer (Figure 1). To elucidate the thickness-dependence of the gas selectivity, we measured the permeability of the membrane for the four gases over the temperature range of 15−45 °C. Activation energies for the permeance (ΔEp) of the asymmetric polyimide membranes with apparent skin layer thicknesses of 47, 95, and 150 nm are shown in Figure 2. The ΔEp value of the four gases decreased in the order $CH_4 > N_2 > O_2 > CO_2$, the trend being in accord with that measured for other polyimides.[9] Also, the ΔEp clearly was enhanced with decreasing skin layer thickness. These results suggest that some contributions affect the growth of potential barriers for gas permeability, as reflected in the increase in ΔEp on the surface of the

---

* To whom correspondence should be addressed. Tel: +81-426-77-1111 (ext.) 4975. Fax: +81−426−77−2821. E-mail: kawakami-hiroyoshi@c.metro-u.ac.jp.

S0024-9297(98)00317-9 CCC: $15.00

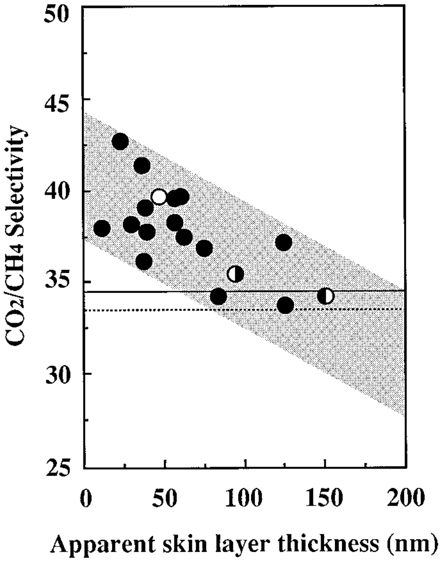


Figure 1. Effect of apparent thickness of the skin layer on CO_2/CH_4 selectivity for the asymmetric 6FDA-6FAP membranes at 35 °C and at 76 cmHg. Apparent skin layer thickness = 47 (open circle), 95 (right-half-darkened circle), 150 (left-half-darkened circle) nm. The (CO_2/CH_4) selectivity of dense 6FDA-6FAP membranes with a thickness of 50 μm annealed at 150 °C for 80 and 15 h is shown by the solid and dotted lines, respectively.

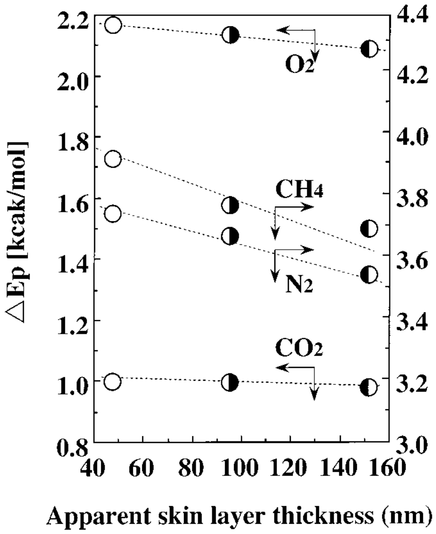


Figure 2. Effect of apparent of the thickness skin layer on the ΔEp for the asymmetric 6FDA-6FAP membranes at 35 °C and at 76 cmHg. Symbols for apparent skin layer thickness as shown in Figure 1.

polyimide having a thinner surface layer, so that the gas selectivity increases for the asymmetric membranes with an ultrathin surface skin layer.

The glassy polymers such as polyimides possess "excess" free volume and enthalpy relative to the extrapolated equilibrium liquid state. The thermal annealing below sub-T_g influences the packing density of the membrane in a time- or temperature-dependent manner, since the annealing reduces both volume and enthalpy.[10] The asymmetric and dense membranes used in this study were annealed at 150 °C for 15 h and at 150 °C for 15 or 80 h, respectively. ΔH values for the asymmetric membranes with skin layer thicknesses of 47, 95, and 150 nm were 7.8, 5.7, and 4.7 mJ/mg, respectively, and those for the dense membranes annealed for 15 and 80 h were 1.9 and 7.9 mJ/mg, respectively. The ΔH value of the asymmetric membrane is enhanced with decreasing thickness of the surface skin layer, which may result because the asymmetric membrane with a thinner surface skin layer forms a more packed structure.

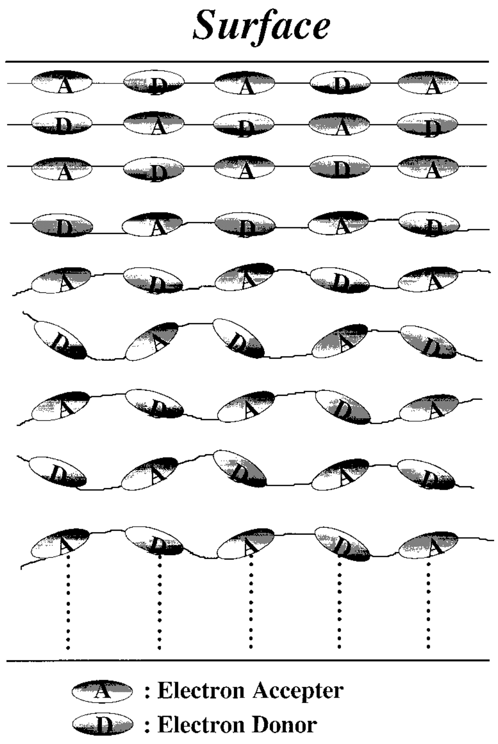


Figure 3. Schematic model describing the polyimide formation in the membrane.

Subjecting a glassy polymer membrane to sub-T_g annealing acts to increase the density because of the decreasing mobility of the chain segments; as a result, the gas selectivity of the annealed membrane is greater than that of the original membrane.[11] The selectivity of the dense membranes also increases with annealing time, as shown in Figure 1, and the trend in results for the membrane agrees that observed for other glassy polymers. According to this argument, the dense membrane annealed for 80 h with a ΔH of 7.9 mJ/mg should exhibit a large gas selectivity, equal to or even greater than that determined for the asymmetric membrane. We suggest the following aspects of the high gas selectivity in the asymmetric membrane: As is well-known, both the structure and dynamics of aromatic polyimides are largely determined by the intermolecular and intramolecular charge-transfer interactions between the polymer chains, since the aromatic polyimides contain an alternating sequence of electron-rich donor and electron-deficient acceptor molecules.[12] Recently, we reported that the asymmetric polyimide membrane made by dry-/wet-phase inversion exhibited a stronger formation of the charge-transfer complex than did the dense membrane. This means that donor and acceptor molecules in the surface skin layer are able to approach each other more closely and better allow a π-electron density, in comparison with those in the dense membrane Figure 3. Additionally, the parallel ring−ring contacts such as $\pi-\pi$ stacking may take place strongly between aromatic systems in the surface skin layer. Koros reports that the gas selectivities of the asymmetric membranes prepared from polysulfone, polycarbonate, and polyestercarbonate are greater than those of the dense membranes and suggests that these higher selectivities could result from the high polymer packing density in the skin layer.[2a,b] We also propose that the packed structure in the surface skin layer formed by the intermolecular interactions provides a high degree of size and shape discrimination between the gas molecules.

We have shown that an asymmetric membrane with an ultrathin, defect-free skin layer is a promising gas-separation material that enhances not only the gas permeability but also the gas selectivity. Control of the intermolecular interactions in the surface skin layer appears to account for the success of the membrane. In future research we will try to discover how to control the above interactions.

Acknowledgment. This work was partially supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

References and Notes

(1) (a) Spillman, R. W. *Chem. Eng. Prog.* **1989**, *85*, 41. (b) Koros, W. J.; Fleming, G. K. *J. Membrane Sci.* **1993**, *83*, 1. (c) Bhide, B. D.; Stern, S. A. *J. Membrane Sci.* **1993**, *81*, 209.

(2) (a) Pinnau, I.; Hellums, M. W.; Koros, W. J. *Polymer* **1991**, *32*, 2612. (b) Pfromm, P. H.; Pinnau, I.; Koros, W. J. *J. Appl. Polym. Sci.* **1993**, *48*, 2161. (c) Calvert, P. *Nature* **1996**, *384*, 311. (d) Frank, B.; Gast, A. P.; Russell, T. P.; Brown, H. R.; Hawker, C. *Macromolecules* **1996**, *29*, 6531. (e) Henn, G.; Bucknall, D. G.; Stamm, M.; Vanhoorne, P.; Jerome, R. *Macromolecules* **1996**, *29*, 4305.

(3) (a) Kawakami, H.; Mikawa, M.; Nagaoka, S. *J. Appl. Polym. Sci.* **1996**, *62*, 965. (b) Kawakami, H.; Mikawa, M.; Nagaoka, S. *J. Membrane Sci.* **1997**, *137*, 241.

(4) (a) Mohammed, H. K.; Sung, C. S. P.; Huang, S. J. *Macromolecules* **1992**, *25*, 3751. (b) Kawakami, H.; Anzai, J.; Nagaoka, S. *J. Appl. Polym. Sci.* **1995**, *57*, 789. (c) Kawakami, H.; Nagaoka, S. *ASIO J.* **1995**, *41*, M379.

(5) (a) Pinnau, I.; Koros, W. J. *J. Appl. Polym. Sci.* **1991**, *43*, 1491. (b) Pinnau, I.; Koros, W. J. *J. Membrane Sci.* **1992**, *7*, 81.

(6) Compositions of casting solution used for the preparation of asymmetric membranes were 11 wt % polyimide, 59 wt % methylene chloride, 20.5−23 wt % 1,1,2-trichloroethane, and 7−9.5 wt % 1-butanol. The apparent skin layer thickness of the membrane was controlled by the compositions of 1,1,2-trichloroethane and 1-butanol. The polymer solutions were filtered and subsequently degassed. The solutions were cast on glass plates with a knife gap of 250 μm and air-dried there for 15 s. After the evaporation, the membranes were coagulated in methanol, washed for 12 h, air-dried for 24 h, and finally dried in a vacuum oven at 150 °C for 15 h to remove all solvents.

(7) CO_2, O_2, N_2, and CH_4 used in this study were represented to be at least 99.9 mol % and were used without further purification. Asymmetric 6FDA-6FAP membranes were mounted on a permeation cell of 1.0 cm^2 surface area. Gas permeances at pressure up to 760 cmHg were determined with a high vacuum apparatus (Rika Seiki Inc. K-315-H). The pressures on the upstream and downstream sides were detected with a Baratron absolute pressure gauge. The error in permeance was estimated as $\pm 0.1-0.5\%$.

(8) The apparent thickness of the skin layer of the defect-free asymmetric membrane was calculated from the permeability coefficient by the equation $L = P/Q$, where L is the apparent skin layer thickness, P is the gas permeability coefficient measured from the dense membrane, and Q is the gas permeance of asymmetric membrane. The O_2/N_2 selectivity of a 6FDA-6FAP dense membrane was 4.7.

(9) Costello, L. M.; Koros, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1995**, *33*, 135.

(10) (a) Chan, A. H.; Paul, D. R. *J. Appl. Polym. Sci.* **1979**, *24*, 1539. (b) Jain, S. C.; Simha, R. *Macromolecules* **1982**, *15*, 1522.

(11) (a) Chan, A. H.; Paul, D. R. *J. Appl. Polym. Sci.* **1980**, *25*, 971. (b) Kawakami, H.; Mikawa, M.; Nagaoka, S. *J. Membrane Sci.* **1996**, *118*, 223.

(12) (a) Ishida, H.; Wellinghoff, S. T.; Baer, E.; Koening, J. L. *Macromolecules* **1980**, *13*, 826. (b) Hasegawa, M.; Mita, I.; Kochi, M.; Yokota, R. *Polymer* **1991**, *32*, 3225. (c) Hasegawa, M.; Okuda, K.; Morimoto, M.; Shindo, Y.; Yokota, R.; Kochi, M. *Macromolecules* **1997**, *30*, 5745.

MA9803178