

GAS TRANSPORT PROPERTIES OF A POLYIMIDE BASED ON 2,2-BIS (3,4-DECARBOXYPHENYL) HEXAFLUOROPROPANE AND *meta*-PHENYLENEDIAMINE

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Abstract By means of a vacuum time-lag method, gas transport properties of a polyimide based on 2,2-bis(3,4-decarboxyphenyl) hexafluoropropane dianhydride (6FDA) and *meta*-phenylenediamine (mPDA) have been measured as a function of upstream pressure and temperature. The results show that no gas-induced plasticization occurs for this polyimide in the upstream pressure range from 1 atm to 20 atm. The temperature dependence of P and D can be described by the Arrhenius equations. The activation energies of permeation and diffusion were obtained for the gas/polymer pair studied and correlated with the size of penetrant gas.

Keywords Polyimide; Membrane; Gas permeation; Gas separation

INTRODUCTION

During the past 30 years there has been growing interest in polyimide, a class of specialty polymers which has a substantial impact on a number of advanced technologies. Due to their excellent thermal and mechanical properties, the polyimides have been employed in many applications such as semiconductor devices, high-temperature adhesive, and high-performance composite materials^[1]. In addition to the already rich field of polyimide investigations, the aromatic polyimides have been especially employed as gas separation materials because of their surprisingly high permselectivity to CO_2/CH_4 ^[2-15].

It is well known that the most desirable gas separation membrane materials should have high permeability and high permselectivity as well as high mechanical and thermal stability. However, structural modifications which lead to the increase in polymer permeability usually cause losses in permselectivity and vice versa. This so-called "trade-off" relationship is well described in the literature^[16].

Expanding the performance envelope generally defined by this "trade-off" relationship is one goal of current research efforts. Among various polyimides, it was

found that polymers with 2,2-bis (3,4-decarboxyphenyl) hexafluoropropane dianhydride (6FDA) show both a higher gas permeability and a higher gas selectivity than do the general polyimides and the conventional polymers^[6-15]. In the present communication, gas permeability coefficient and diffusion coefficient for a 6FDA-based polyimide were measured to investigate the effects of pressure and temperature on gas permeability and diffusivity.

EXPERIMENTAL

Materials

The polyimide studied in this work was synthesized from 2,2-bis (3,4-decarboxyphenyl) hexafluoropropane dianhydride (6FDA) and meta-phenylenediamine (mPDA). Its glass transition temperature, which was determined using Rheometrix Solid Analyzer RSA II at a heating rate of 10°C/min and an oscillation frequency of 1 Hz, is 301°C and its density is 1.4732 g/cm³.

Carbon dioxide, oxygen, nitrogen, and methane were obtained from Messer Griesheim GmbH. The purity of CH₄ was stated by the supplier to be 99.5% or better and the purities of other gases were greater than 99.99%. All gases were used without further purification.

Membrane preparation

The sample was used in the form of nonporous planar membrane which were prepared by casting DMF solutions containing 20 wt% polymer onto glass plates and dried for 24 h at 100°C under vacuum. The membranes thus obtained were peeled from the glass plates and dried for another 24 h at 100°C under vacuum. The thickness of the dry membranes used for the permeability and diffusivity measurements varied from 20 to 40 μm.

Apparatus and experimental procedure

Mean permeability coefficients, P , and effective diffusion coefficients, D , were measured between 1 and 20 atm at 35°C, and at 10 atm for different temperature between 25 and 45°C by the vacuum time-lag method. Detail experimental procedure was described in the previous papers^[14-15]. From a single transient gas transport experiment, both permeability coefficient (P) and diffusion coefficient (D) can be obtained. The permeability is given by equation (1):

$$P = J_s \cdot \frac{l}{p_2 - p_1} \quad (1)$$

where l is the thickness of the membrane, J_s is the steady-state rate of gas permeation through a unit area of the membrane, p_2 and p_1 are the upstream and downstream pressures of the gas component, respectively. Effective diffusion coefficients were

calculated from the time-lag θ using equation (2):

$$D = \frac{l^2}{6\theta} \quad (2)$$

RESULTS AND DISCUSSION

The effect of upstream pressure on the pure gas permeability coefficient at 35°C is shown in Figure 1 in the form of semilogarithmic plots of permeability versus pressure. The straight lines in the Fig. 1 were obtained from least-squares regressions of the experimental data. As for most polyimides reported in the literatures^[12-15], the permeability coefficients are essentially independent of upstream pressure or tend to decrease slightly with increasing pressure. These results illustrate that gas-induced plasticization, which would be signalled by an increase in permeability with increasing upstream pressure, does not occur for this polyimide over the pressure range covered here. Resistance to plasticization is an important property of membrane materials, particularly in the high-pressure applications such as CO₂ stripping from

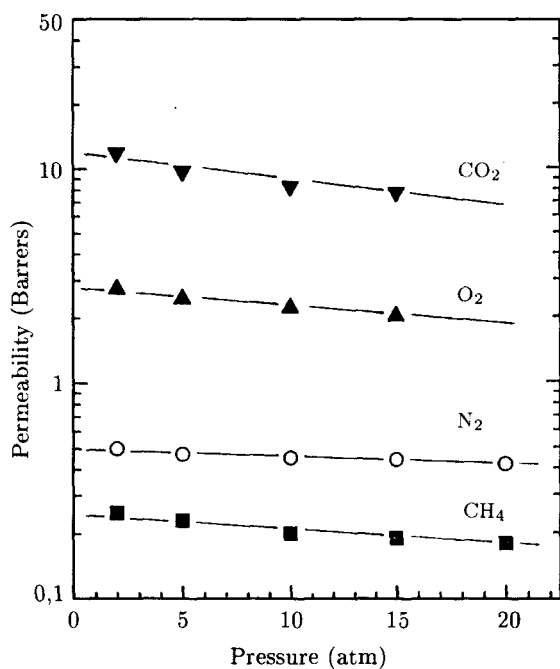


Fig. 1 Effect of pressure on the gas permeability coefficients of 6FDA/mPDA polyimide at 35°C

natural gas stream, since plasticized polymers usually exhibit markedly reduced selectivities to penetrant gas mixtures. The decrease in P with increasing gas pres-

sure observed in some cases for N_2 and CH_4 is probably due to a large experimental error at low pressures, because of the low permeation rates of these gases under these pressures.

The effect of temperature on permeabilities and diffusivities for CO_2 , O_2 , N_2 , and CH_4 at 10 atm upstream pressure were investigated. It was found that the temperature dependence of P and D for the polyimide can be described by the Arrhenius equation^[17]. As with all other polymers reported in the literature^[10], the general trend is that the gas permeabilities and diffusivities increase with temperature.

Table 1 Activation energies and pre-exponential factors for permeation and diffusion of four penetrants in the 6FDA/mPDA polyimide

Gas	CO_2	O_2	N_2	CH_4
E_p (kcal/mol)	2.36	2.35	3.99	4.81
E_d (kcal/mol)	7.00	5.71	6.62	9.19
$P_0 \times 10^{-2}$ (Barrers)	3.91	1.03	3.02	5.23
$D_0 \times 10^3$ (cm ² /s)	1.56	0.37	0.37	4.92

E_p and E_d as well as P_0 and D_0 obtained from the Arrhenius plots are given in Table 1. These parameters provide a convenient method for the calculation of permeabilities and diffusivities for each polymer-penetrant pair at a given temperature. However, these parameters are applicable only within the respective temperature range in which no significant thermal transition takes place for the polymer.

The permeation activation energies of the polyimide in Table 1 follow the same general trends as those reported by other investigators^[7,13,18], that is, E_p increases with penetrant size. Meares^[19] interpreted the diffusion of a penetrant as a process that occurs along a cylindrical volume defined by the penetrant diameter, σ , and the average length of its diffusion step, λ . According to this interpretation, the activation energy for diffusion and the penetrant diameter should be related by:

$$E_d = (\pi/4) \cdot \sigma^2 \cdot \lambda \cdot CED \quad (3)$$

where CED is the cohesive energy density of the polymer. Following equation (3), the E_d values should increase with the increase of the kinetic diameters of the gases. It is quite evident that the E_d values for CO_2 are higher than those expected, indicating that the relative magnitudes of E_d for CO_2 and O_2 are anomalous from their diameters.

A possible cause for the lower diffusion activation energy of O_2 compared to those of CO_2 is the strongy quadrupole moment of the CO_2 molecule^[13], which may induce specific interactions between CO_2 and the polar groups in the polyimides, such as CF_3 and $C=O$ groups in the polymer chain. On the other hand, the O_2 molecule is nonpolar. Stern et al.^[13] suggested that the specific CO_2 /polymer interactions may

hinder the mobility of the CO₂ molecules in the polymer matrix. To activate this hindered mobility, more energy should be needed, thus, $E_d(\text{CO}_2) > E_d(\text{O}_2)$. Another possible reason for the anomalies mentioned above is the difficulty in estimating the accurate diameter of CO₂ molecule because of its nonspherical nature. Stern et al.^[13] suggested that the CO₂ molecule may have a larger effective size, possible between its kinetic diameter of 0.33 nm and its collision diameter of 0.394 nm.

Acknowledgement One of the authors, Dr. Xu Zhikang, is thankful to Zentrum für Technologische Zusammenarbeit of TU Berlin for a fellowship.

REFERENCES

- [1] Mittal, K.L., "Polyimides", Plenum Press, New York, N.Y., 1984
- [2] Mi, Y., Stern, S.A., Trohalaki, S., *J. Membr. Sci.*, **1993**, 77, 41
- [3] Tanaka, K., Okano, M., Toshino, H., Kita, H., Okamoto, K., *J. Polym. Sci., Polym. Phys. Edn.*, **1992**, 30, 907
- [4] Matsumoto, K., Xu, P., Nishikimi, T., *J. Membr. Sci.*, **1993**, 81, 15
- [5] Langsam, M., Burgoyne, W.F., *J. Polym. Sci., Polym. Chem. Ed.*, **1993**, 31, 909
- [6] Tanaka, K., Kita, H., Okano, M., Okamoto, K., *Polymer*, **1992**, 33, 585
- [7] Costello, L.M., Koros, W.J., *J. Polym. Sci., Polym. Phys. Ed.*, **1995**, 33, 135
- [8] Coleman, M.R., Koros, W.J., *J. Polym. Sci., Polym. Phys. Ed.*, **1994**, 32, 1915
- [9] Coleman, M.R., Koros, W.J., *J. Membr. Sci.*, **1990**, 50, 285
- [10] Matsumoto, K., Xu, P., *J. Appl. Polym. Sci.*, **1993**, 47, 1961
- [11] Coleman, M.R., Kohn, R., Koros, W.J., *J. Appl. Polym. Sci.*, **1993**, 50, 1059
- [12] Zoia, G., Stern, S.A., St. Clair, A.K., Pratt, J.R., *J. Polym. Sci., Polym. Phys. Ed.*, **1994**, 32, 53
- [13] Stern, S.A., Liu, Y., Feld, W.A., *J. Polym. Sci., Polym. Phys. Ed.*, **1993**, 31, 939
- [14] Xu, Z.K., Boning, M., Schultze, J.D., Li, G.T., Springer, J., Glatz F.P., Mulhaupt, R., *Polymer*, **1997**, 38, 1573
- [15] Xu, Z.K., Boning, M., Springer, J., Steinhauser, N., Mulhaupt, R., *Polymer*, **1997**, 38, 581
- [16] Robeson, L.M., *J. Membr. Sci.*, **1991**, 62, 165
- [17] Stannett, V.T., "Diffusion in Polymers", John Wiley & Sons, New York, 1971
- [18] Costello, L.M., Koros, W.J., *J. Polym. Sci., Polym. Phys. Ed.*, **1994**, 32, 701
- [19] Meares, P., *J. Am. Chem. Soc.*, **1954**, 76, 3415