# "Reverse Permselectivity" of $N_2$ over $CH_4$ in Aromatic Polyimides

## INTRODUCTION

The presence of significant supplies of natural gas containing nitrogen contamination in the range of 5–15% makes it desirable to have membranes which preferentially pass $N_2$ while rejecting $CH_4$ as a high pressure nonpermeate product. Upgrading of the heating value of such gas supplies without the need to recompress the resultant product stream would be a significant advantage. Unfortunately, the permeability of $N_2$ is lower than that of $CH_4$ for most polymer materials as indicated by the representative list given in Table I.[1] A series of polymers have, however, been synthesized in our laboratory which show so-called "reverse permselectivity" of $N_2$ over $CH_4$. The detailed synthesis of such materials, all of which are aromatic polyimides, has been described in detail earlier.[2] The purpose of the present note is to clarify the apparent cause of such an unusual phenomenon. The $N_2$ permeabilities and the permselectivities of $N_2$ over $CH_4$ for the polyimides are reproduced in Table II. The equipment and procedures for the gas permeation and sorption experiments are the same as described earlier.[2-4]

## DISCUSSION

Permeabilities and sorption isotherms of $N_2$ and $CH_4$ for one of the polyimides shown in Table II are plotted against upstream pressure in Figures 1 and 2. This member of the family was selected for more detailed study, since it displayed the highest $N_2$ permeability in the group. As is the case for most other polymers, the solubility coefficient of $N_2$ in this polyimide, which is equivalent to the secant slope of the sorption isotherm ($C_{N_2}/p_{N_2}$) evaluated at a given pressure, is lower than that of $CH_4$. Methane has a higher solubility coefficient than nitrogen in most media since the higher critical temperature of $CH_4$ (191 K vs. 126 K for $N_2$) makes it more condensible than $N_2$.[5] Since neither component is expected to display significant specific interactions with most polymers, the solubility coefficients are largely governed by their respective tendencies to exist in a condensed state corresponding to sorption in a polymer.[6-8]

The permeability coefficient of a penetrant $i$, $P_i$, is equal to a product of diffusivity and solubility coefficients as shown in eq. (1). For conditions such as considered here, where the downstream pressure is negligible, the average diffusivity, $\bar{D}_i$, can be determined by dividing the permeability of Figure 1 by the solubility, $\bar{S}_i$, determined from Figure 2 at a given upstream pressure[9]:

$$P_i = \bar{D}_i \bar{S}_i \tag{1}$$

Again when the downstream pressure of the permeation system is negligibly small, the ideal gas separation factor, $\alpha^*_{N_2/CH_4}$, which is a measure of the intrinsic permselectivity of a membrane for mixture of $N_2$ and $CH_4$, becomes equal to the true separation factor. The ideal separation factor can be broken into two parts as in eq. (2):

$$\alpha^*_{N_2/CH_4} = \frac{P_{N_2}}{P_{CH_4}} = \left(\frac{\bar{D}_{N_2}}{\bar{D}_{CH_4}}\right)\left(\frac{\bar{S}_{N_2}}{\bar{S}_{CH_4}}\right) \tag{2}$$

where $(\bar{D}_{N_2}/\bar{D}_{CH_4})$ and $(\bar{S}_{N_2}/\bar{S}_{CH_4})$ are referred to as diffusivity selectivity and solubility selectivity of $N_2$ over $CH_4$.

Table III provides a comparison of permeabilities, solubilities, diffusivities, and their selectivities of $N_2$ over $CH_4$ for various polymers including the polyimide (PMDA–IPDA). The solubility selectivity of $N_2$ over $CH_4$ is within the range of 0.2–0.4 for all polymers considered in the table. The diffusivity of $N_2$ is higher than that of $CH_4$ in all the polymers for both the rubbery and

TABLE I

Permeabilities of $N_2$ and $CH_4$ for Various Polymers near Room Temperature

| Polymer | $P_{N_2}$ (Barrers)[a] | $P_{N_2}/P_{CH_4}$ | Reference |
|---|---|---|---|
| Silicone rubber | 280 | 0.30 | 5 |
| Natural rubber | 8.1 | 0.27 | 5 |
| FEP (Teflon) | 2.2 | 0.37 | 5 |
| Neoprene | 1.1 | 0.42 | 5 |
| Methyl rubber | 0.36 | 0.60 | 5 |
| Poly(phenylene oxide) | 4.1 | 0.95 | 6 |
| Polymethylacrylate | 0.19 | 0.80 | 7 |
| Polycarbonate | 0.27 | 0.93 | 8 |
| Cellulose acetate | 0.22 | 0.73 | 9 |
| Polysulfone | 0.18 | 1.0 | 10 |

[a] 1 Barrer $= 10^{-10}$ (cm$^3$ (STP) cm/cm$^2$ s cm Hg).

glassy materials; however, a significant difference is seen between the diffusivity selectivity of the polyimide and all of the other polymers in Table II. The diffusivity selectivity measures the inherent ability of polymer matrices to function as size and shape selective media for the two penetrants. This ability is primarily determined by such factors as polymer segmental mobility, intersegmental packing, and the size and shape difference between the two penetrants. The size difference between $N_2$ and $CH_4$ is very small; however, the 3.64 Å kinetic diameter of $N_2$ compared to the 3.8 Å value for $CH_4$ favors $N_2$ slightly.[10] Unfortunately, for rubbery materials such as natural rubber and silicone rubber, a broad distribution of segmental motions produces a correspondingly broad distribution of intersegmental gap sizes responsible for gas diffusion. This situation causes all rubbery media to have very poor ability to distinguish subtly different sizes and shapes and, hence, low values of diffusivity selectivity. Therefore, the solubility selectivity dominates in the permselectivity determinations for the rubbery materials to provide lower permeability of $N_2$ relative to that of $CH_4$.

Glassy materials such as polycarbonate and polysulfone show relatively high diffusivity selectivity, but it is not sufficiently high to offset the undesirable solubility factor. Therefore, the permselectivity is close to 1.0, so that the permeabilities of $N_2$ and $CH_4$ are close to each other in both polycarbonate and polysulfone. For the aromatic polyimide, PMDA–IPDA, the diffusivity selectivity dominates and yields a higher permeability for $N_2$ than for $CH_4$. The strong size and shape selective function of the polyimide family is believed to be due to the limited mobility of the polymer backbone segments which presumably leads to a relatively narrow distribution of effective intersegmental gap sizes responsible for diffusion.[2,11]
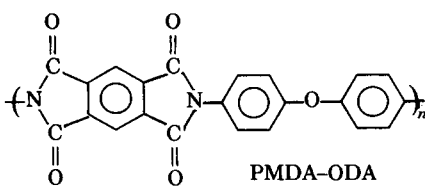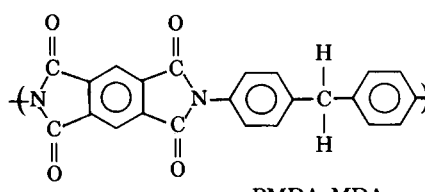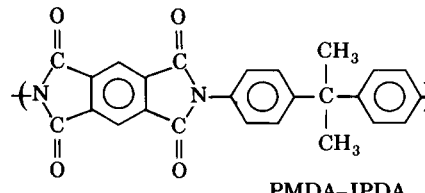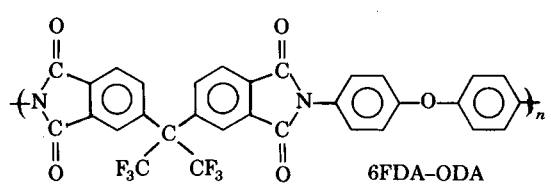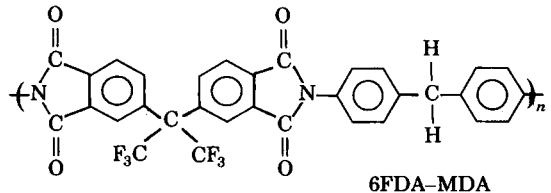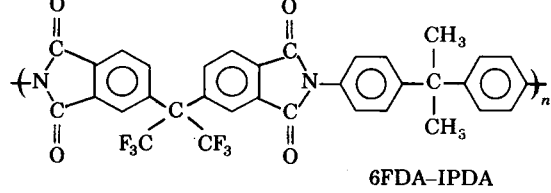
Solubility data for the other five polyimides in Table II are still being collected. When the data collection is completed, the interesting reverse permselectivity in the polyimide family can be further clarified by consideration of the detailed relationship between polymer structure and diffusivity selectivity for the complete family of materials shown in Table II. The magnification of the desired effect may then be pursued through tailoring the chemical structure of polymers so that the new polymers having higher $N_2$ permeability with still acceptable permselectivities can be developed.

## CONCLUSIONS

In most polymers, the solubility of $N_2$ is lower than that of $CH_4$ due to the lower critical temperature of $N_2$. On the other hand the diffusivity of $N_2$ is higher than that of $CH_4$ due to the smaller kinetic size of $N_2$. Among conventional rubbery and glassy polymers, the diffusivity selectivity of $N_2$ over $CH_4$ is small and tends to be overcome by the solubility selectivity. Consequently, the permeability of $N_2$ is smaller than that of $CH_4$ for almost all polymers that have been reported to date.

Fortunately, for aromatic polyimides in the present study, the diffusivity selectivity is significantly higher than in other polymers, while the solubility selectivity is similar to those in other

TABLE II

Permeabilities of $N_2$ and $CH_4$ at 35°C and 10 atm for a Series of Aromatic Polyimides Synthesized in Our Laboratory

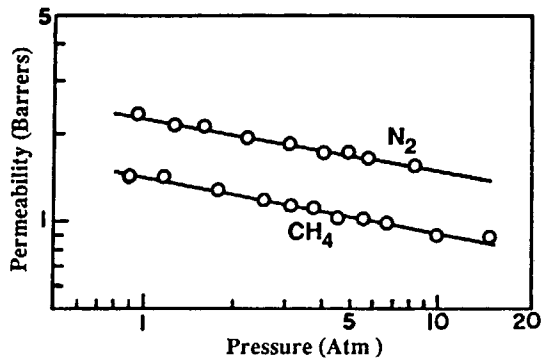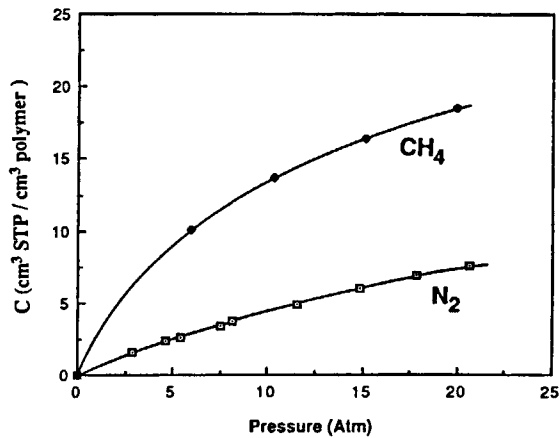| Polymer | $P_{N_2}$ (Barrers)[a] | $P_{N_2}/P_{CH_4}$ | Density (g/cm$^3$) |
|---|---|---|---|
| PMDA–ODA | 0.10 | 1.75 | 1.41 |
| PMDA–MDA | 0.20 | 1.84 | 1.35 |
| PMDA–IPDA | 1.50 | 1.67 | 1.28 |
| 6FDA–ODA | 0.83 | 2.18 | 1.43 |
| 6FDA–MDA | 0.81 | 1.88 | 1.40 |
| 6FDA–IPDA | 1.33 | 1.90 | 1.35 |

[a] 1 Barrer = $10^{-10}$ (cm$^3$ (STP) cm/cm$^2$ s cm Hg).

Fig. 1.  Permeabilities of $N_2$ and $CH_4$ in PMDA–IPDA at 35°C.



Fig. 2.  Sorption isotherms of $N_2$ and $CH_4$ in PMDA–IPDA at 35°C.

TABLE III

Comparison of Permeabilities, Solubilities, Diffusivities, and Their Selectivities for Various Polymers near Room Temperature at 10 atm

| Polymer | $P_{N_2}$[a] | $P_{N_2}/P_{CH_4}$ | $\bar{S}_{N_2}$[b] | $\bar{S}_{N_2}/\bar{S}_{CH_4}$ | $\bar{D}_{N_2}$[c] | $\bar{D}_{N_2}/\bar{D}_{CH_4}$ | Reference |
|---|---|---|---|---|---|---|---|
| PMDA–IPDA | 1.50 | 1.67 | 0.44 | 0.33 | 259 | 5.00 | This study |
| Polycarbonate | 0.27 | 0.93 | 0.14 | 0.28 | 141 | 3.31 | 8 |
| Polysulfone | 0.18 | 1.00 | 0.21 | 0.40 | 65 | 2.51 | 10 |
| Natural rubber[d] | 8.10 | 0.27 | 0.056 | 0.22 | 11,000 | 1.22 | 5 |
| Silicone rubber[d] | 280 | 0.30 | 0.15 | 0.27 | 144,000 | 1.23 | 5 |

[a] Barrers = $10^{-10}$ (cm$^3$ (STP) cm/cm$^2$ s cm Hg).
[b] (cm$^3$ (STP)/cm$^3$ (polymer) atm).
[c] $\times 10^{10}$ (cm$^2$/s).
[d] At unknown pressure.

materials. The large diffusivity selectivity factor dominates in determination of permselectivity of $N_2$ over $CH_4$, so that the permeability of $N_2$ is higher than that of $CH_4$ in the case of the aromatic polyimide family. At the same time, due to the somewhat inhibited packing of chain segments in some of the members in this family of polyimides, rather high $N_2$ permeabilities can be achieved. The combination of these two factors indicates the possibility of application of some of these materials as commercial membrane materials.

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