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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Advanced Gas Separation Membrane Materials: Rigid Aromatic Polyimides

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To cite this Article Kim, Tae-Han , Koros, William J. and Husk, G. Ronald(1988) 'Advanced Gas Separation Membrane Materials: Rigid Aromatic Polyimides', Separation Science and Technology, 23: 12, 1611 — 1626
To link to this Article: DOI: 10.1080/01496398808075652
URL: http://dx.doi.org/10.1080/01496398808075652

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SEPARATION SCIENCE AND TECHNOLOGY, 23(12&13), pp. 1611-1626, 1988

ADVANCED GAS SEPARATION MEMBRANE MATERIALS: RIGID AROMATIC POLYIMIDES

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ABSTRACT

Permeabilities, solubilities, diffusivities, and selectivities for He/CH_4 and CO_2/CH_4 gas pairs are reported for four aromatic polyimides having systematic variations in intersegmental packing and intrasegmental mobility. As intersegmental packing is disrupted by bulky substituents, gas diffusivities are generally increased, but diffusivity selectivities of He/CH_4 and CO_2/CH_4 are correspondingly decreased. Simultaneous suppression of intrasegmental mobility and intersegmental packing, however, yields significant increases in both diffusivity and diffusivity selectivity, and consequently in permeability and permselectivity. For example, packing-disrupted and mobility-restricted 6FDA-DAF polyimide provides significantly higher permeabilities and permselectivities than commercially available polymers currently being used as membrane materials.

INTRODUCTION

It is very difficult to achieve the ideal material properties for gas separation membranes using commercially available polymers. Polymers with high permeability usually have low selectivity, while those

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with high selectivity have low permeability. A series of thermally stable polyimides has been prepared and studied in our laboratory. Preliminary results reported earlier[1], showed that some of these materials had both higher permeability and permselectivity than commercially available polymers currently being used as membrane materials.

New solubility and diffusivity data reported here will clarify the cause of these desirable properties. In addition, additional permeability, solubility, and diffusivity data for a new rigid polyimide, 6FDA-DAF, having even better separation properties are reported.

BACKGROUND AND THEORY

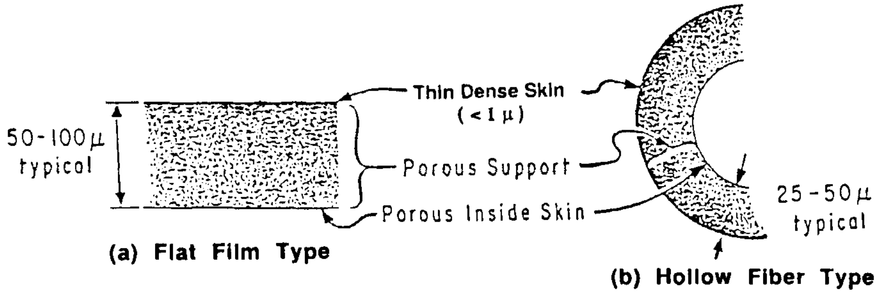
The permeation rate of a gas component, "i", can be expressed by Eq(1):

$$Q_i = \mathbf{P}_i \ A \ \left\{\frac{p_{i2} - p_{i1}}{l}\right\} \qquad (1)$$

where $\mathbf{P}_i$ is the gas permeability constant for a given membrane material, "A" is the membrane permeation area, "l" is the effective thickness of membrane, and p_{i2} and p_{i1} are the upstream and downstream partial pressures of component "i" respectively.

Economical gas permeation rates through permselective glassy polymer membrane were not achieved until two breakthroughs occurred: (i) asymmetric membrane structures and (ii) high permeation area packing approaches based on hollow fiber or spiral wound modules as shown in Figure 1 and Figure 2. The asymmetric membrane formation technology, discovered by Loeb and Sourirajan[2,3], enhanced permeation rates by reducing the effective thickness, l, in Eq(1). Hollow fibers used for membrane applications by Dow[4], Du Pont[5], and Monsanto[6] increase the permeation area, A, of membrane for a given volume of membrane module. Also asymmetric membranes in spiral wound form modules are sold by Separex/Air Products[7], Grace Membrane Products[8], and others.

In parallel with an effort to improve asymmetric and/or hollow fiber membrane formation, material structure-property studies related to the permeability, $\mathbf{P}_i$, in Eq(1) have occurred[9-20], but only a few of these studies reported desirable materials showing significantly higher permeabilities and permselectivities than commercial polymers[1,13-15,20].



ASYMMETRIC MEMBRANES

Figure 1: Schematic representation of asymmetric membranes.

Similarly as in Eq(1), the ratio of permeation rates, Q_i/Q_j, can be expressed by Eq(2):

$$\frac{Q_i}{Q_j} = \left\{\frac{\mathbf{P}_i}{\mathbf{P}_j}\right\} \left\{\frac{p_{i2} - p_{i1}}{p_{j2} - p_{j1}}\right\} \tag{2}$$

where $(\mathbf{P}_i/\mathbf{P}_j)$ is the intrinsic permselectivity of the membrane material.

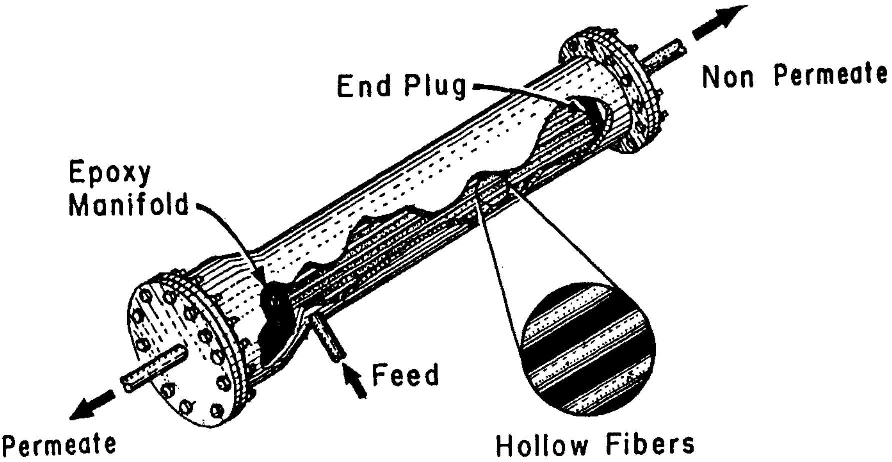
In this paper, we will consider improvements in permeability, P_i, and permselectivity, $(\mathbf{P}_i/\mathbf{P}_j)$, which are intrinsic properties of the thin dense skin layer shown in Figure 1.

To understand the $\mathbf{P}_i$ and $(\mathbf{P}_i/\mathbf{P}_j)$ behavior as related to the chemical structures of constituent polymers, the following discussion provides a useful framework.

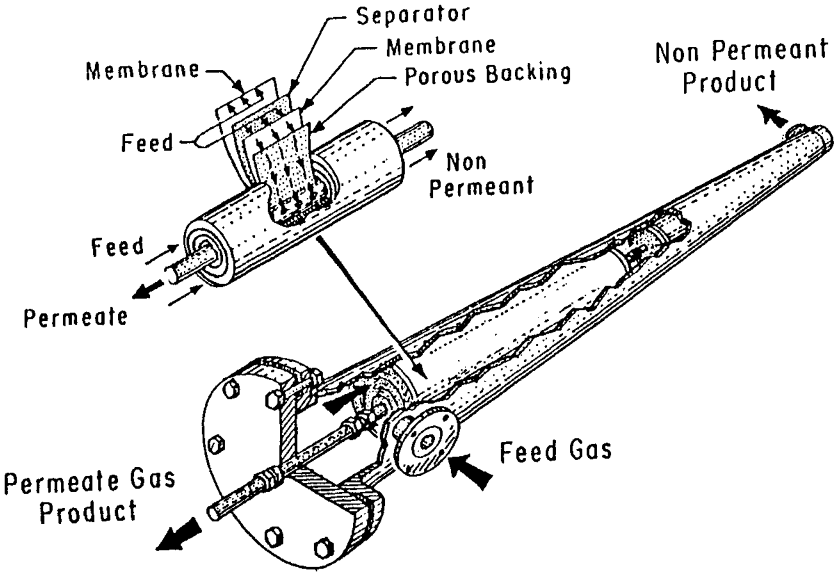
* The permeability of a membrane, $\mathbf{P}_i$, is defined by Eq(3):

$$\mathbf{P}_i \equiv \frac{N_i}{(p_{i2} - p_{i1})/l} \tag{3}$$

where N_i is the local flux of a given gas component penetrating across the membrane. The permeability is determined by the diffusivity and the solubility of the



(a) Hollow Fiber Module



(b) Spiral Wound Module

Figure 2: Schematic representation of high permeation-area packing.

penetrant. The contributions of the two factors can be seen clearly when p_{i1} is negligibly small compared with p_{i2} as it will be in the data reported here with a vacuum downstream. In this case, the permeability can be expressed by Eq(4):

$$\mathbf{P}_i = D_i \quad S_i \tag{4}$$

where the solubility coefficient, S_i, is equivalent to the secant slope of the sorption isotherm evaluated at the upstream conditions. The average diffusivity, D_i, can be determined by dividing permeability by the solubility coefficient.

When the downstream pressure, p_1, is negligible, as in the present study, the gas separation factor, $\alpha_{i/j}$, defined by Eq (5), is rigorously equal to the ratio of permeabilities of components "i" and "j" under mixed gas feed conditions [21].

$$\alpha_{i/j} \equiv \frac{(y_i/y_j)}{(x_i/x_j)} \tag{5}$$

$$\alpha^*_{i/j} \equiv \frac{\mathbf{P}_i}{\mathbf{P}_j} \tag{6}$$

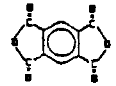
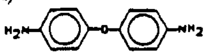
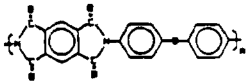
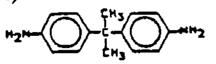
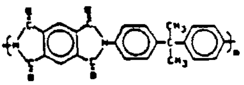
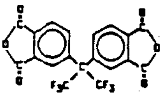
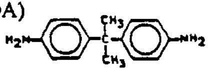
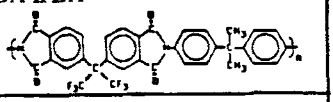
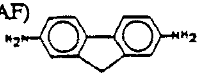
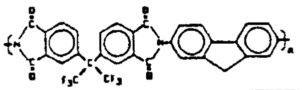
where x_i and y_i are the mole fractions of component "i" at the upstream and downstream sides of the membrane respectively. The ideal separation factor, $\alpha^*_{i/j}$, provides a valuable measure of the intrinsic permselectivity of a membrane material for mixtures of "i" and "j".

If Eq (4) is substituted into Eq (6), the ideal separation factor can be broken into two parts;

$$\alpha^*_{i/j} = \left\{\frac{D_i}{D_j}\right\} \left\{\frac{S_i}{S_j}\right\} \tag{7}$$

where (D_i/D_j) is called the diffusivity selectivity, and (S_i/S_j) is the solubility selectivity. The diffusivity selectivity arises from the inherent ability of polymer matrices to function as size and shape selective media. This ability is primarily determined by such factors as polymer segmental mobility and intersegmental packing. The solubility selectivity on the other hand, is determined by the difference in the condensibilities of the two penetrants as well as chemical interactions of the penetrants with the particular polymer that the membrane is composed of.

Table 1: Chemical structures of systematically varied polyimides and monomers.

Dianhydride	Diamine	Polymer
Pyromellitic Dianhydride (PMDA) 	Oxydianiline (ODA) 	PMDA-ODA 
	Isopropylidenedianiline (IPDA) 	PMDA-IPDA 
Hexafluoro-dianhydride (6FDA) 	Isopropylidenedianiline (IPDA) 	6FDA-IPDA 
	Diaminofluorene (DAF) 	6FDA-DAF 

In a previous study[1], some polyimide materials were shown to have both significantly higher permeability and permselectivity than commercially available polymers for various gas pairs , but detailed solubility and diffusivity data were not available at that time. In this paper, therefore, we report new solubility and diffusivity data that further clarify the basis for the desirable properties of rigid aromatic polyimides and extend the range of materials to include a new member in the family.

EXPERIMENTAL

Materials

The chemical structures of four polyimides and constituent monomers are shown in Table 1. Poly (pyromellitimides) of oxydianiline (ODA), and isopropylidenedianiline (IPDA) were prepared by the reaction of these diamines with pyromellitic dianhydride (PMDA). The precursor polyamic acids were solvent cast from dimethylacetamide (DMAC) and thermally imidized at over 285 °C to form tough films[22]. Detailed procedures and influences of the casting process on gas transport properties of films have been reported [23]. Based on this earlier study, care was exercised to effectively prevent second-order effects due to variation in film preparation protocols from obscuring the primary effects due to chemical structure variations in the present study.

The fluorinated dianhydride, 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis-1,3-isobenzofurandione (6FDA) was also reacted with each of the diamines, IPDA and 2,7-fluorenediamine (DAF) [22]. Because these polyimides are soluble, it was possible to effect chemical imidization with acetic anhydride, and to solution cast films. Specifically, in the case of 6FDA-IPDA, solutions of 4 % of polymer by weight in methylene chloride were cast on clean glass plates, and dried at room temperature for 30 minutes to remove most of the solvent, and then lifted carefully from the plates. The film was finally dried in a vacuum oven at 80 °C for 12 hours and at 250 °C for 24 hours. In the case of 6FDA-DAF, which is not soluble in methylene chloride, 4 % of polymer by weight in DMAC was cast on a clean glass plate, and dried at 100 °C for 2 hours to remove most of the solvent, and then lifted from the plate. The film was finally dried in a vacuum oven at 250 °C for 24 hours.

Equipment and Procedures

Gas permeabilities were determined at 35 °C over a pressure range of 1-20 atm for He, CO_2, and CH_4 using an apparatus described in a previous report[1]. The equipment allows measurement of gas permeation rates by detection of the rate of accumulation of penetrants in the evacuated downstream receiver using an accurate pressure transducer with a full scale range of 10 mmHg.

Gas solubilities were determined using sorption apparatus and an experimental procedure described previously[24,25]. Sorption data for each gas were collected over the same pressure range as for the permeation experiments.

Wide angle x-ray diffraction (WAXD) measurements for the films were performed on a Philips x-ray diffractometer with Cu Kα radiation, $\lambda = 1.54$ Å. The d-spacing value was calculated for each polymer using Bragg's law[26], $n\lambda = 2d \sin\Theta$. In this case, d-spacing provides a measure of intersegmental distance between polymer backbones[27].

RESULTS AND DISCUSSION

Permeability and Permselectivity

Permeabilities versus selectivities of He/CH_4 and CO_2/CH_4 gas pairs are plotted in Figure 3 for a representative group of commercial polymers often considered for this application as well as for the polyimides in the current study. Among the commercial polymers, one can see a general trend; polymers with higher selectivities usually have lower permeabilities , and the others with higher permeabilities have lower selectivities[28]. For example, Poly(vinyl fluoride) has a high selectivity of He/CH_4, but a relatively low permeability of helium, while silicone rubber with a high permeability has a low selectivity. PMDA-ODA and PMDA-IPDA deviate favorably from the general plot of the permeabilities and selectivities of the conventional polymers. Specifically, these materials have higher selectivity than the standard material correlation line at an equivalent value of permeability. If the two polyimides are compared, however, one finds that they still follow the conventional rule of high selectivity and low permeability correlation.

Comparison of the other two pairs: (PMDA-IPDA and 6FDA-IPDA), (6FDA-IPDA and 6FDA-DAF) shows a fundamental deviation from the conventional relationship between permeability and selectivity. In both cases, the permeabilities and selectivities are increased simultaneously for He/CH_4 and CO_2/CH_4 gas pairs. This desirable improvement can be clarified in the following section which provides a discussion of diffusivity and solubility factors as related to the changes in intersegmental packing and intrasegmental mobility of the constituent polymers.

Comparison of PMDA-ODA and PMDA-IPDA

Permeabilities of helium and CO_2 are increased as the ODA part is replaced by IPDA as shown in Figure 3, but selectivities are decreased correspondingly. To clarify the changes in permeabilities and permselectivities, solubility and diffusivity factors are compared in Table 2 for the two polymers as well as the other two polyimides, 6FDA-IPDA and 6FDA-DAF, and typical commercial glassy polymers. As the ODA part is replaced by IPDA, S_{He} and SCO_2 are increased slightly, probably due to the increased free space in IPDA material as reflected by the d-spacing data. Even though the solubility increase makes a measurable contribution, the diffusivity is the principle factor that alters the permeability and permselectivity so significantly for both the He/CH_4 and CO_2/CH_4 gas pairs.

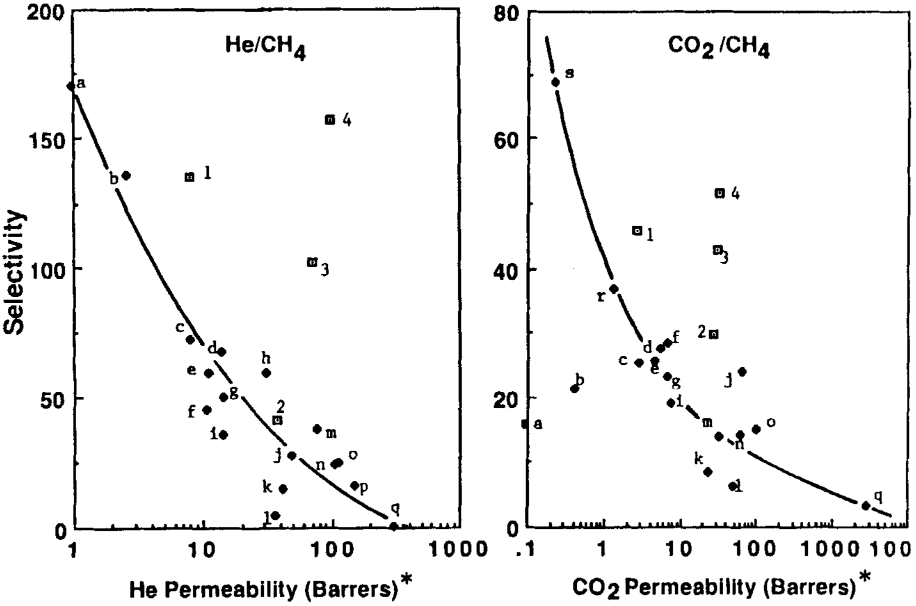


Figure 3:

Comparison of polyimides to typical permeability vs selectivity tradeoffs for most polymers. { 1 = PMDA-ODA, 2 = PMDA-IPDA, 3 = 6FDA-IPDA, 4 = 6FDA-DAF } { a = Poly(vinyl fluoride), b = Poly(hydroxy ether), c = Poly(ether sulfone), d = Cellulose Acetate, e = Polysulfone, f = Poly(methyl acrylate), g = Polycarbonate, h = Poly(tetramethyl bis A isophthalate), i = Polyarylate, j = Poly(tetramethyl bis L sulfone), k = Polystyrene, l = Ethyl Cellulose, m = Poly(tetramethyl cyclobutane diol carbonate), n = Poly(phenylene oxide), o = Poly(tetraisopropyl bis A sulfone), p = Poly(tetramethyl bis L terephthalate), q = Silicone Rubber, r = ULTEM®, s = KAPTON®} [28]

* 1 Barrer = 10^{-10} cm^3 (STP) cm / (cm^2 sec cm Hg)

The PMDA part in the two polyimides is believed to be flat and rigid, while ODA and IPDA have tetrahedral swivel points at the center of each diamine. Therefore it will be primarily the ODA or the IPDA part that provides intrasegmental mobility and intersegmental packing disruption in the two polymers. As the central moiety of the diamine is varied from -O- to the bulkier $-C(CH_3)_2-$, intersegmental packing becomes more restricted, but the intrasegmental mobility change is relatively small as discussed previously[1]. The significant packing disruption effect is reflected by the change in the d-spacing data determined by the wide angle x-ray diffraction. The d-spacing determined in this manner is a convenient measure of intersegmental distance between the polymeric molecules[27], even though it does not reflect the detailed complex effects of space filling by side groups such as $-CH_3$ or $-CF_3$. Specifically, PMDA-IPDA having bulky $-CH_3$ groups in the diamine provides larger d-spacing than PMDA-ODA, and consequently higher permeability, solubility, and diffusivity, but lower permselectivity and diffusivity selectivity.

Comparison of PMDA-IPDA and 6FDA-IPDA

The replacement of PMDA with 6FDA provides very desirable improvements in both permeabilities and permselectivities as shown in Figure 3. Specifically, permselectivities are improved by 2.5 times (He/CH_4) to 1.44 times (CO_2/CH_4), in addition to the improvement in permeabilities of helium and CO_2.

In a previous paper[1], we hypothesized that the changes in permeability and permselectivity might be primarily due to the changes in diffusivity factors. Table 2 supports the previous hypothesis and shows that solubility factors change little when compared with diffusivity factors. High diffusivity selectivities for the He/CH_4 and CO_2/CH_4 gas pairs are also consistent with the high diffusivity selectivity for the N_2/CH_4 gas pair in these rigid backbone polymers as reported earlier[29].

We have also proposed the following hypothetical explanation for the effects caused by replacement of PMDA with 6FDA, while holding the IPDA segment constant. In the PMDA-IPDA polymer, the PMDA section is flat ("packable") and rigid. A PMDA chain segment that directly neighbors another PMDA segment should be much less able to permit gas molecule diffusion than when such a PMDA segment neighbors an ODA or IPDA segment in the random glassy matrix. The presence of the ODA or IPDA part of the repeat unit is, therefore, believed to be principally responsible for the intersegmental spacing and intrasegmental motions useful for gas diffusion in the PMDA-IPDA material.

Replacement of PMDA with 6FDA, while holding the IPDA segment constant, causes both a packing disruption and an increase in the number of internal swivel points per repeat unit of polymer. The packing disruption effect is again supported by the d-spacing change as shown in Table 2. One might expect both effects of packing disruption and an increase in the number of internal swivel points to raise the permeability, and to reduce the selectivity of the resultant polymer. This view, however, is oversimplified, because an additional effect also results from the 6FDA substitution in the IPDA polymer. As noted earlier[1], the average number of mobile -C(CH3)2- linkages is decreased by 32 % per unit volume in the 6FDA-IPDA compared to the PMDA-IPDA material. Along with this reduction in the concentration of $-C(CH_3)_2-$ linkages comes a simultaneous introduction of mobility-restricted $-C(CF_3)_2-$ linkages. Both these factors actually reduce the total intrasegmental mobility and make the matrix more selective. This hypothesis is consistent with the observed behavior for these two polymers.

Comparison of 6FDA-IPDA and 6FDA-DAF

The difference between 6FDA-IPDA and 6FDA-DAF typifies the most ideal case for improving the gas separation properties of polymer membranes. As shown in Figure 3, permselectivities of He and CO_2 over CH_4 are further improved due to the substitution of the IPDA with mobility-restricted DAF. As a result, in this 6FDA-DAF material, the permeability of helium is 12 times higher than in PMDA-ODA, and is 9 times higher than in typical glassy polysulfone. The permselectivity of He/CH_4 in 6FDA-DAF is 16 % higher than in PMDA-ODA, and 2.6 times higher than in polysulfone.

Recall that for the PMDA-IPDA and 6FDA-IPDA, replacement of PMDA with 6FDA caused a reduction in rotational mobility and an increase in intersegmental spacing. Additional replacement of IPDA with DAF further restricts intrasegmental mobility, because the diamine part is no longer flexible in this 6FDA-DAF. The increase in permeability due to the substitution of DAF for IPDA was surprising. Before performing the permeability and solubility measurements, we had anticipated that the permselectivity in 6FDA-DAF material would be higher than in 6FDA-IPDA and permeabilities would be somewhat lower. To clarify the unexpected higher permeability results, we measured the x-ray diffraction for these two materials, and observed that 6FDA-DAF has slightly larger d-spacing than 6FDA-IPDA, as shown in Table 2.

The following hypothesis might help understand the surprising permeability and d-spacing result. Although

Table 2: Comparison of permeabilities, solubilities, diffusivities, and their selectivities for He/CH_4 and CO_2/CH_4 gas pairs in various polymers at 35 °C and 10 atm.

(a) He/CH_4 gas pair

Polymer	P_{He} (Barrers)	$\frac{P_{He}}{P_{CH_4}}$	S_{He} (cc/cc atm)	$\frac{S_{He}}{S_{CH_4}}$	D_{He} ($\times10^8$ cm^2/sec)	$\frac{D_{He}}{D_{CH_4}}$	d-spacing (Å)
PMDA-ODA	8.0	134.9	0.053	0.056	115	2,441	4.6
PMDA-IPDA	37.1	41.1	0.062	0.047	455	876	5.5
6FDA-IPDA	71.2	102.1	0.079	0.066	685	1,546	5.7
6FDA-DAF	98.5	156.3	0.096	0.060	780	2,608	5.9
Polysulfone*	10.8	60.0	-	-	-	-	-
Polycarbonate**	14.0	50.0	0.03	0.057	355	876	5.1

(b) CO_2/CH_4 gas pair

Polymer	P_{CO_2} (Barrers)	$\frac{P_{CO_2}}{P_{CH_4}}$	S_{CO_2} (cc/cc atm)	$\frac{S_{CO_2}}{S_{CH_4}}$	D_{CO_2} ($\times10^8$ cm^2/sec)	$\frac{D_{CO_2}}{D_{CH_4}}$	d-spacing (Å)
PMDA-ODA	2.71	45.9	3.65	3.84	0.56	11.9	4.6
PMDA-IPDA	26.8	29.7	5.00	3.77	4.10	7.9	5.5
6FDA-IPDA	30.0	42.9	4.24	3.53	5.38	12.1	5.7
6FDA-DAF	32.2	51.1	5.02	3.14	4.88	16.3	5.9
Polysulfone*	4.6	25.6	2.05	3.87	1.71	6.37	-
Polycarbonate**	6.5	23.2	2.05	3.90	2.50	6.17	5.1

* A.J. Erb and D.R. Paul, *J. Membr. Sci.*, *8*, 11-22, (1981).

** W.J. Koros, A.H. Chan, and D.R. Paul, *J. Membr. Sci*, *2*, 165-190, (1977).

the DAF part of the imide repeat unit is planar and tends to pack well, the 6FDA part is non-planar and restricts efficient packing of the polymer molecules. In typical non-crystalline polymers such as 6FDA-DAF and 6FDA-IPDA, one can not expect a high order of segmental arrangement. Therefore a dianhydride may neighbor either another dianhydride or a diamine. In the case of dianhydride-dianhydride neighboring, 6FDA-DAF and 6FDA-IPDA may have similar packing tendency, because the ease of packing will be governed by the bulky 6FDA part in both polymers. In the case of dianhydride-diamine neighboring, 6FDA-DAF may have even looser packing tendency than 6FDA-IPDA, because the geometrical shape of 6FDA would be closer to that of IPDA than that of DAF. This hypothesis is consistent with higher permeabilities, higher solubilities, and larger d-spacing in 6FDA-DAF than in 6FDA-IPDA; however additional work is required to demonstrate its validity. The smaller CO_2 diffusivity for 6FDA-DAF than for 6FDA-IPDA might be due to extremely low intrasegmental mobility in DAF material.

CONCLUSIONS

For a given family of polymers such as polyimides, systematically "opening up" the polymer matrix by suppressing intersegmental packing tends to increase the permeability and to decrease the selectivity. Systematically inhibiting intrasegmental mobility around backbone swivel points tends to increase the diffusivity selectivity and permselctivity. Simultaneous suppression of intersegmental packing while inhibiting intrasegmental motion can yield significant increases in both diffusivity and diffusivity selectivity, and consequently permeability and permselectivity. The relative packing disruptive effects caused by systematic structure variations seem to be well characterized by WAXD d-spacings for a series of closely related materials.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of Department of Energy, Basic Energy Sciences Program, under grant No. DF-FG05-86ER13507. Also donation of 6FDA monomer by American Hoechst /Celanese Corporation is gratefully acknowledged.

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