Gas Permeability of Polyimides and Polypyrrolone Derived from 2,2'-*Bis*(p-trimellitoxyphenyl)hexafluoropropane Dianhydride

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SYNOPSIS

The permeability coefficients for H_2, O_2, and N_2 in four polyimides and one polypyrrolone based on 2,2'-*bis*(p-trimellitoxyphenyl)hexafluoropropane dianhydride were determined at 30°C and 1 atm. Systematic variations in chemical structure were found to lead to significant changes in permeabilities and selectivities. The relationship between the chemical structure of the polymers, some of their physical properties (d-spacing, fractional free volume), and their gas permeability behavior are discussed. Introduction of 2 flexible segments tends to increase permeability but decrease selectivity. Structural moieties, which simultaneously inhibit chain packing and intrasegmental mobility, may increase permeability while maintaining selectivity. Temperature dependency of gas permeabilities was also reported for polypyrrolone. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The transport properties of gases through polymers are of interest from both theoretical and technological points of view. Control of the gas permeability and selectivity of polymer membrane demand a good understanding of the relationships between the chemical structure of polymers and their gas permeability.

Polyimides and polypyrrolones, particularly with fluorine-containing functional groups, are considered very promising membrane materials because of their high gas selectivity, excellent physical properties, and versatile chemistry. Extensive studies have been done in recent years on the structure/permeability relationships of polyimides[1-14] and polypyrrolones.[15-18] The present work investigates the gas permeation properties of polyimides and polypyrrolone derived from 2,2'-*bis*(p-trimellitoxyphenyl)hexafluoropropane dianhydride. The effect of temperature on gas permeability of the polypyrrolone is also reported.

EXPERIMENTAL

Materials

The procedure to synthesize the dianhydride monomer, 2,2'-*bis*(p-trimellitoxyphenyl)hexafluoropropane dianhydride (BTFDA), by using trimellitic anhydride monoacid chloride and bisphenol AF was similar to that of Loncrini,[19] except acetone was used as solvent instead of benzene. The para-phenylene-diamine (p-PDA), 4,4'-diaminodiphenyl methylene (MDA), benzidine (BDA), 3,3',4,4'-tetramethyl-benzidine (TBDA), and 3,3'-diaminobenzidine (DAB) were purchased and purified prior to use.

The first two polymers in Figure 1 have been studied earlier and will be considered here for comparison with polymers based on BTFDA. The other polymers were synthesized by reacting stoichiometric amounts of amine and dianhydride in a solution of N,N'-dimethylacetamide (DMAc). The solid content of solutions totaled 10% by weight of the mixture.

The films were prepared by casting the precursor solutions on clean, dry glass plates and drying them for 1 h at 60°C. Thermal conversion of the films was then performed by heating in an oven for 1 h each at 100°C, 200°C, and 300°C under argon. Upon

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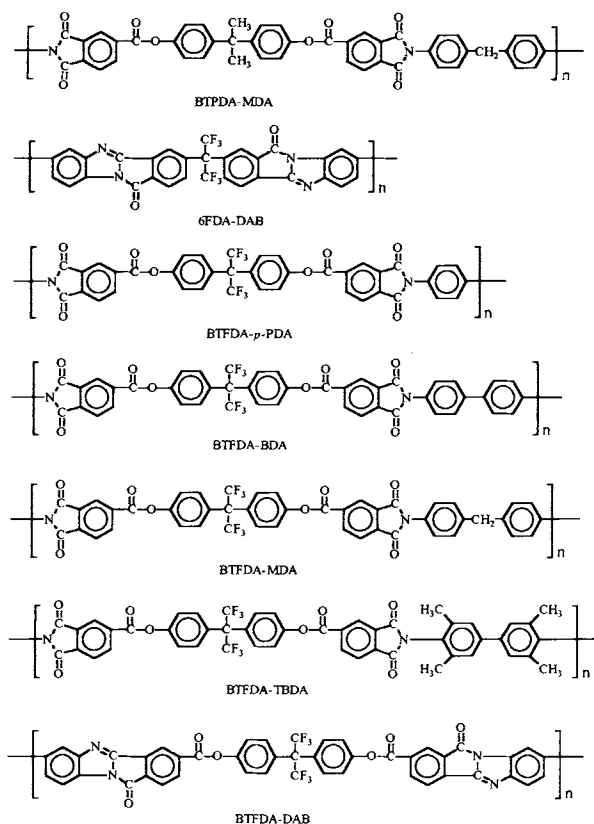
Figure 1 Polymers used in this study.

cooling, the films were removed from the glass plates by submersion in water and then dried.

Apparatus and Gases

The measurements of gas permeability were performed at 30°C and 1 atm on a K-315N-01 GTR Measurement Apparatus (RSK Rikaseiki Kogyo Co., Ltd., Japan). The purity of the gases used in this work was 99.5% or higher.

X-ray Diffraction

The WAXD measurements were performed on a Rigaku Dmax-3B X-ray diffractometer. The mean intersegmental distance was taken to be represented by the d-spacing obtained from maxima in WAXD spectra as suggested by O'Brien et al.[20] The d-spacings of the polymers are shown in Table I.

Density and Fractional Free Volume

The densities of the polymers used in this study, shown in Table I, were measured at 25°C using aqueous calcium nitrate. A Paar DMA45 Density Meter was used to determine the density of the solution.

Once the density of the polymer is known, the fractional free volume (FFV) can be estimated by Lee's method,[21] which uses the group contribution correlation of Van Krevelen[22] for calculation of Van der Waals volumes. The specific occupied volume of the double bonded nitrogen was taken from Bondi.[23]

RESULTS AND DISCUSSION

The permeability and selectivity data measured at 30°C and 1 atm for H_2, O_2, and N_2 for the polymers are summarized in Table II. A general trend of permeability increases, correlated with selectivity decreases, is observed for the polymers. In each polymer, the permeability of H_2 (having the smallest kinetic diameter) is the highest, and is followed by those of the progressively larger penetrants.

The diffusivity (D) listed in Table III was determined by the time-lag method,[25,26] and the solubility (S) shown in Table IV was calculated by dividing the permeability by the diffusivity. Referring to Tables II, III, and IV, it can be seen that differences

Table I Physical Properties of the Polymers

Polymer	Density (g/cm³)	d-Spacing (Å)	Fractional Free Volume (FFV)
BTPDA[a]-MDA[24]	1.324	5.0	0.1108
6FDA[b]-DAB[17]	1.391	6.3	0.1933
BTFDA-p-PDA	1.501	4.9	0.1142
BTFDA-BDA	1.464	5.1	0.1161
BTFDA-MDA	1.406	5.4	0.1431
BTFDA-TBDA	1.316	6.0	0.1697
BTFDA-DAB	1.399	5.8	0.1668

[a] 2.2'-bis(p-trimellitoxyphenyl)propane dianhydride (BTPDA).
[b] 2.2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA).

Table II   Permeabilities of the Polymers at 30°C and 1 atm

Polymer	Permeability (Barrers[a])			Ideal Selectivity	
	H_2	O_2	N_2	H_2/N_2	O_2/N_2
BTPDA–MDA[24]	4.65	0.293	0.0457	101	6.4
6FDA–DAB[17]	74.4	7.75	1.44	52	5.3
BTFDA-p-PDA	4.36	0.251	0.0355	123	7.0
BTFDA–BDA	5.01	0.348	0.0517	97	6.7
BTFDA–MDA	11.8	0.917	0.164	72	5.6
BTFDA–TBDA	38.0	3.02	0.549	69	5.5
BTFDA–DAB	13.3	0.977	0.155	86	6.3

[a] Barrer = 10^{-10} (cm^3 [STP] cm)/(cm^2 sec cmHg).

in both diffusivity and solubility affect the permeability of the polymers. However, larger differences are apparent in diffusivity than in solubility. That is, the diffusivity is the principal factor that alters the permeability even though the solubility makes a measurable contribution. The selectivity is also controlled by the diffusivity selectivity, not the solubility selectivity. The diffusivity is mainly determined by the packing density and the segmental mobility.

Comparison of BTFDA–MDA and BTPDA–MDA

As can be seen from a comparison of BTPDA–MDA and BTFDA–MDA, the permeability of BTFDA–MDA for H_2, O_2, and N_2 increases by 1.5, 2.1, and 2.6 times, respectively. Meanwhile, the selectivity of BTFDA–MDA for H_2/N_2 and O_2/N_2 decreases by 29 and 13%, respectively. The only difference in chemical structure of the two polymers is that BTFDA–MDA contains —C(CF$_3$)$_2$—

moiety instead of the —C(CH$_3$)$_2$— moiety in BTPDA–MDA.

Earlier work by Coleman and Koros[11] showed that substitution of the bulkier —C(CF$_3$)$_2$— central moiety for —C(CH$_3$)$_2$— moiety in the diamine segment of polyimide leads to simultaneous disruption in intermolecular packing and suppression of intrarotational flexibility, and resulted in a significant increase in permeability of all gases and negligible decrease in selectivity. It is certain that substitution of the bulkier —C(CF$_3$)$_2$— moiety for the —C(CH$_3$)$_2$— moiety in the dianhydride segment also leads to simultaneous packing disruption and inhibition of rotational motions of the polyimide. The disruption of chain packing is reflected by the data in Table I, indicating an increased d-spacing of BTFDA–MDA (d = 5.4 Å) over that of BTPDA–MDA (d = 5.0 Å). The increased inhibition of chain packing is also indicated by the increased FFV (0.1431 versus 0.1108). Thus, inhibition of chain packing and restriction of rotational

Table III   Diffusivities of the Polymers at 30°C and 1 atm

Polymer	Diffusivity[a]			Ideal Diffusivity Selectivity	
	H_2	O_2	N_2	H_2/N_2	O_2/N_2
BTPDA–MDA[24]	289	7.36	1.87	154	3.9
6FDA–DAB[17]	2680	69.2	14.6	182	4.7
BTFDA-p-PDA	156	3.36	0.768	203	4.4
BTFDA–BDA	210	5.55	1.34	157	4.1
BTFDA–MDA	443	14.5	3.81	116	3.8
BTFDA–TBDA	1380	39.9	11.9	116	3.6
BTFDA–DAB	658	11.8	2.70	243	4.4

[a] Unit: 10^{-9} cm^2/s.

Table IV   Solubilities of the Polymers at 30°C and 1 atm

Polymer	Solubility[a]			Ideal Solubility Selectivity	
	H_2	O_2	N_2	H_2/N_2	O_2/N_2
BTPDA–MDA[24]	1.61	3.98	2.44	0.660	1.6
6FDA–DAB[17]	2.78	11.2	9.81	0.283	1.1
BTFDA-p-PDA	2.79	7.43	4.62	0.604	1.6
BTFDA–BDA	2.39	6.27	3.86	0.619	1.6
BTFDA–MDA	2.67	6.31	4.30	0.621	1.5
BTFDA–TBDA	2.76	7.56	4.61	0.599	1.6
BTFDA–DAB	2.02	8.29	5.38	0.375	1.5

[a] Unit: 10^{-3} (cm^3 [STP] cm)/(cm^3 cmHg).

motion tend to increase permeability while maintaining selectivity.

Comparison of Polyimides Based on BTFDA

Because the central moiety of the diamine in the polyimides is varied, both intersegmental packing and intrasegmental mobility are affected. The permeability coefficients for a given gas in the four polyimides increase in the polyimide order

$$P(BTFDA\text{-}p\text{-PDA}) < P(BTFDA\text{–BDA})$$
$$< P(BTFDA\text{–MDA}) < P(BTFDA\text{–TBDA})$$

The d-spacing and FFV increase in the same polyimide order (cf. Table I), indicating increased disruption of chain packing.

Among the four polyimides, BTFDA-p-PDA shows the lowest permeability and the highest selectivity. This corresponds to the flat, rigid, and easily packed p-PDA segment in the polyimide, as stiffer polymers are better able to discriminate between penetrant molecules of different sizes and shapes. The introduction of BDA moiety may cause a disruption of chain packing and some increase in the intrasegmental motion, which increases the permeabilities of all gases (benefits the larger penetrants) and decreases the selectivities. Since the disruption of chain packing is more severe in BTFDA–MDA, BTFDA–MDA has higher permeabilities and lower selectivities than BTFDA–BDA does. The hindrance of chain packing of BTFDA–MDA would appear from the increased d-spacing. The d-spacing of BTFDA–MDA is 5.4 Å, whereas it is 5.1 Å for BTFDA–BDA. The restriction of chain packing in BTFDA–MDA is also evidenced by its larger FFV.

Compared with BTFDA–BDA, the permeability of BTFDA–TBDA for H_2, O_2, and N_2 increases by 6.6, 7.7, and 9.6 times, respectively, while the selectivity of H_2/N_2 and O_2/N_2 decreases by only 29% and 18%, respectively. Undoubtedly, the four methyl groups in the backbone can inhibit not only intersegmental packing but also intrasegmental rotation of the connected benzene rings and imide rings. As a result, the introduction of four methyl group to the backbone leads to a significant permeability increase in all gases and negligible selectivity decrease.

Comparison of BTFDA–BDA and BTFDA–DAB

As shown in Table II, the polypyrrolone BTFDA–DAB is more permeable than the analogous polyimide BTFDA–BDA by 1.7, 1.8, and 2.0 times for H_2, O_2, and N_2, respectively. The selectivity of H_2/N_2 and O_2/N_2 decreases by 11% and 6%, respectively.

The increased permeabilities of BTFDA–DAB may be primarily due to the disruption of chain packing. The four-condensed-ring structure in the polypyrrolone makes the backbone much more rigid compared with the analogous polyimide containing two-condensed-ring structure. Thus, the chain packing is disrupted in the polypyrrolone. The packing disruption of the polypyrrolone is supported by its larger d-spacing (5.8 Å versus 5.1 Å) and higher FFV (0.1668 versus 0.1161). This results in increased permeabilities for all gases (especially for the larger penetrants) and in definitely decreased selectivities. In fact, not only the intersegmental chain packing but also the intrasegmental mobility of the polypyrrolone were inhibited because of its extremely rigid backbone. The disruption of chain packing leads to increased permeability, and the suppression of intrasegmental motion tends to raise

the selectivity. Both of the above effects result in an apparent increase in permeability without a large corresponding decrease in selectivity. We hypothesize that structural moieties which inhibit chain packing while simultaneously inhibiting torsional motion about flexible linkages on the polymer backbone tend to increase permeability while maintaining selectivity.

Comparison of 6FDA–DAB and BTFDA–DAB

Referring to Table II, it can be seen that 6FDA–DAB is more permeable than BTFDA–DAB. The increased permeability of 6FDA–DAB for each gas results in decrease in selectivity.

The chain packing of 6FDA–DAB is disrupted compared with BTFDA–DAB, which tends to open the matrix. The packing disruption effect of 6FDA–DAB is again supported by the increased d-spacing and FFV of the polymer, as shown in Table I. The opening of the matrix leads to increased permeabilities for all gases, especially for the larger penetrants. In fact, the permeabilities of H_2, O_2, and N_2 in 6FDA–DAB are 4.6, 6.9, and 8.3 times greater than that in BTFDA–DAB, respectively; whereas the selectivity of H_2/N_2 and O_2/N_2 decreases by 65% and 19%, respectively. Generally, a tradeoff exists between the permeability and selectivity of polymer membranes. However, the permeability of 6FDA–DAB increases significantly without causing precipitous drops in selectivity. This may be attributed to restriction of both intersegmental packing and intrasegmental mobility. Unlike BTFDA–DAB, 6FDA–DAB does not contain a flexible ester group; thus the rotational resistance of the 6FDA segment is much greater than for the BTFDA segment. That is, replacement of BTFDA with 6FDA introduces very significant increases in the resistance to motion around flexible "joints" in the polymer backbone,
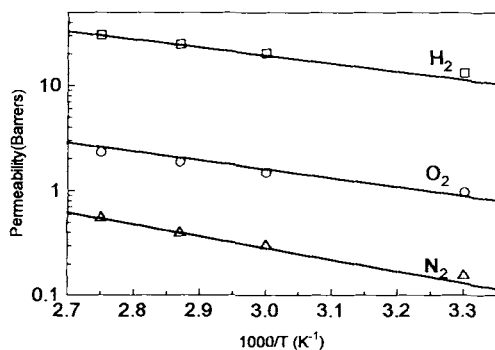
Figure 2 Arrhenius correlations of permeability of various gases in BTFDA–DAB at 30–90°C and 1 atm.

Table V Temperature Dependence of Permeabilities[a] and Selectivities of BTFDA–DAB at 1 atm

Temperature (°C)	30	60	75	90
P_{H_2}	13.3	20.3	24.8	30.3
P_{O_2}	0.977	1.49	1.88	2.33
P_{N_2}	0.155	0.302	0.398	0.548
α_{H_2/N_2}	86	67	62	55
α_{O_2/N_2}	6.3	4.9	4.7	4.3

[a] Unit: Barrers.

which causes a tendency to give increased precision in size and shape selectivity. As a result, simultaneous inhibition of both inherent intrasegmental mobility and intersegmental packing for 6FDA–DAB increases the permeabilities of all gases significantly without correspondingly large decreases in selectivity.

Temperature Dependence of Gas Permeation of BTFDA–DAB

As shown in Table V, the permeabilities of BTFDA–DAB for all gases increase with increased temperature, whereas the selectivities decrease correspondingly. For example, at 90°C the permeability of H_2 increases by 1.3 times and the selectivity of H_2/N_2 decreases by 36%.

The effects of temperature on permeability can be described by an Arrhenius-type expression[27,28]:

$$P = P_0 \exp(-E_p/RT) \tag{1}$$

where P_0 is the preexponential factor and E_p is the apparent activation energy for permeation. The equation is valid only within temperature ranges that do not span significant thermal transitions of the polymers.

Figure 2 shows gas permeabilities of the three penetrants (H_2, O_2, and N_2) plotted as functions of temperature in the Arrhenius form of BTFDA–

Table VI Permeation Activation Energies for Various Gases in BTFDA–DAB

Gas	H_2	O_2	N_2
E_p (kcal/mol)	2.98	3.15	4.20

DAB. These permeabilities appear to follow Arrhenius behavior over the temperature range studied, and the dependence of permeabilities on temperature is the same as in other glassy polymers.

The activation energies of permeation, computed from the data in Figure 2 using eq (1), are listed in Table VI. As expected, H_2 has the smallest E_p, and is followed by the general trend, which is also the order of increasing kinetic molecular diameter of the penetrants.

CONCLUSION

Systematic variations in chemical structure were found to lead to significant changes in permeabilities and selectivities, providing a wide range of gas separation properties. Since replacement of the flat, rigid, and easily packed moiety in polyimide with a more flexible segment may cause a disruption of chain packing and some increase in intrasegmental motion, the permeability increases but the selectivity decreases. Structural alterations (i.e., introduction of a bulkier group, polypyrrolone structure moiety, and reduction of motion around mobile "joints" in the backbone) which inhibit chain packing while simultaneously inhibiting rotational motion on the polymer backbone tend to increase permeability while maintaining selectivity. The temperature dependency of gas permeation in the BTFDA–DAB can be well described by the Arrhenius form within a temperature range of 30–90°C.

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