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Gas transport properties of polyimides and polypyrrolone containing ester linkage

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Four polyimides and one polypyrrolone derived from 2,2'-bis(*p*-trimellitoxyphenyl) propane dianhydride were synthesized and the transport properties of H_2, O_2 and N_2 in these polymers were measured at 30°C and 1 atm (1.01×10^5 Pa). Values of permeability and permselectivity were significantly affected by diffusivity and diffusivity selectivity, respectively. The polypyrrolone shows simultaneously increased permeability and permselectivity over the analogous polyimides. The introduction of a methyl group into the backbone of polyimide results in an increase in permeability and permselectivity. Replacement of the rigid moiety in polyimide with a more flexible segment leads to increased permeability but decreased permselectivity.

(Keywords: polyimide; polypyrrolone; gas separation)

INTRODUCTION

In the past decade, gas membrane technology has been found useful for a variety of separations[1-5]. New membrane materials with higher permeability and permselectivity are required to continue to advance this new technology and to allow expansion to additional applications.

Aromatic polyimide and polypyrrolone, which have a high degree of thermal and chemical resistance, are prospective materials for polymer membranes[6-12]. The diffusion and solution properties of gases in polymeric membranes are both closely related to the chemical and physical structures of the polymer. Extensive investigations have been done to correlate the structure of polymers with their permeation properties[13-15]. Eastmond *et al.*[16] have studied the permeabilities of isomeric poly(ether imide)s.

In this study, four polyimides and one polypyrrolone containing an ester group in the backbone were synthesized and the effects of the chemical structure of these polymers on permeability are discussed.

BACKGROUND AND THEORY

The transport of a gas through a polymeric membrane is described by a permeability (P), which can be expressed as the product of the diffusivity (D), and the solubility (S), of the gas in the membrane[17] as shown in equation (1):

$$P = DS \tag{1}$$

The diffusivity of the gas in the membrane was computed from the time-lag method[18]:

$$D = l^2/6\theta \tag{2}$$

where θ is the time lag (s), and l is the thickness of membrane. The solubility can then be calculated from P and D.

When the pressure of the gases downstream from the membrane is much lower than their upstream pressure[17], an assessment of the permselectivity $\alpha_{A/B}$ of a membrane may be obtained from the ratio of the respective permeabilities (P_A/P_B). Then the permselectivity can be thought of in terms of a diffusivity selectivity (D_A/D_B) and a solubility selectivity (S_A/S_B) as represented in the following equation[19]:

$$\alpha_{A/B} = P_A/P_B = (D_A/D_B)(S_A/S_B) \tag{3}$$

The fractional free volume, which is the ratio of specific free volume to polymer specific volume, gives a better representation of the degree of openness of a polymer matrix[20,21]. An estimate of the occupied volume of the polymer is made by using a group contribution method such as that of Bondi[22] or Van Krevelen and Hoftyzer[23].

EXPERIMENTAL

Materials

The polymers used in this study, which are shown in *Figure 1*, were synthesized in this laboratory. The monomers used are shown in *Figure 2*. The 4,4'-diaminodiphenyl ether (ODA), benzidine (BDA), 3,3'-dimethyl-benzidine (DBDA) and 4,4'-diaminodiphenyl methylene (MDA) were purchased. A four-step synthesis was used to obtain the 3,3', 4,4'-tetraaminodiphenyl ether (TADPE) from 4,4'-diaminodiphenyl ether[24]. The procedure to synthesize the 2,2'-bis(*p*-trimellitoxyphenyl) propane dianhydride (BTPDA) by using trimellitic anhydride monoacid chloride and bisphenol A is similar to that of Loncrini[25].

The polymers were synthesized by reacting stoichiometric amounts of amines and dianhydrides in a solution

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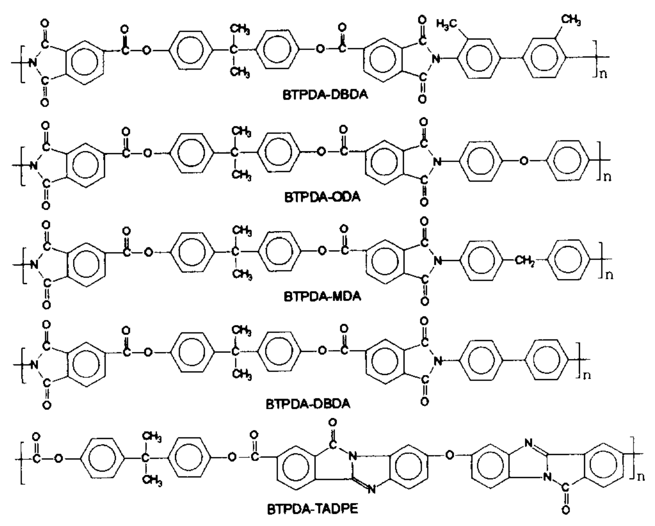

Figure 1 Polymers used in this study

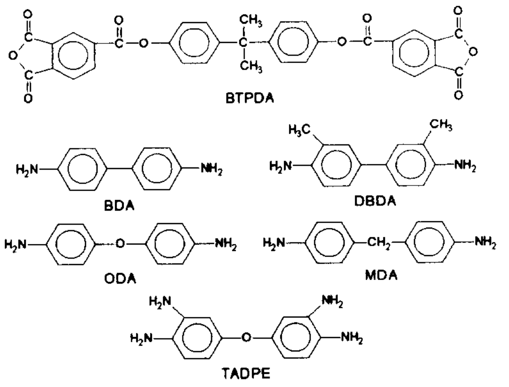

Figure 2 Monomers used in this study

of *N,N*-dimethylacetamide (DMAc), of which the solid contents totalled 10% by weight. After stirring for 4 h at room temperature, the solution of precursor was filtered and stored in a refrigerator until needed for film casting.

Film preparation

The films were prepared by casting the solutions of polyamic acid precursors on clean and dried glass plates and heating at 60°C for 1 h to evaporate most of the solvent. Then the plates were placed in an oven and kept at 100, 200 and 290°C each for 1 h with a slow flow of argon through the oven. After cooling, the films were removed from the glass plates by soaking in water and dried.

Permeability measurements

The measurement of gas permeability was performed on a K-315N-01 GTR measurement apparatus (RSK Rikaseiki Kogyo Co., Ltd). The purity of the gases used in the study was at least 99.5%. The pure gas permeability was measured at 30°C and 1 atm (1.01×10^5 Pa).

Density and fractional free volume

The densities of the polyimides and polypyrrolone are shown in *Table 1*. Since these polymers are insoluble in methylene chloride and chloroform, macroscopic densities were measured at 25°C using methylene chloride and chloroform mixtures of various compositions. The densities of the mixtures were measured with a PAAR DMA45 Density Meter (Austria).

Once the densities of the polymers are known, the fractional free volumes can be estimated by the method of Lee[26]. The volume occupied by the atoms is estimated by summing over the various atoms present for each type of bonding and configuration. The specific occupied volume of the double-bonded nitrogen was taken from Bondi[22].

RESULTS AND DISCUSSION

The permeability, diffusivity and solubility data for H_2, O_2 and N_2 in these polymers at 30°C and 1 atm are listed in *Tables 2, 3* and *4*, respectively.

Table 1 Physical properties of polymers

Polymer	Density ($g\,cm^{-3}$)	Fractional free volume
BTPDA-DBDA	1.281	0.1290
BTPDA-ODA	1.341	0.1171
BTPDA-MDA	1.324	0.1108
BTPDA-BDA	1.355	0.09726
BTPDA-TADPE	1.315	0.1470

Table 2 Permeability and permselectivity of polymers

	Permeability (barrer[a])			Ideal permselectivity	
Polymer	H_2	O_2	N_2	H_2/N_2	O_2/N_2
BTPDA-DBDA	6.46	0.405	0.0512	126	7.9
BTPDA-ODA	4.83	0.310	0.0484	100	6.4
BTPDA-MDA	4.65	0.293	0.0457	101	6.4
BTPDA-BDA	0.723	0.0459	0.00647	112	6.9
BTPDA-TADPE	7.36	0.434	0.0585	126	7.4

[a] 1 barrer = $10^{-10}\,cm^3[STP]\,cm\,cm^{-2}\,s^{-1}\,cmHg^{-1}$

Table 3 Diffusivity and diffusivity selectivity of polymers

	Diffusivity ($cm^2\,s^{-1} \times 10^{-9}$)			Ideal diffusivity selectivity	
Polymer	H_2	O_2	N_2	H_2/N_2	O_2/N_2
BTPDA-DBDA	396	10.57	2.22	178	4.76
BTPDA-ODA	329	8.78	2.06	152	3.79
BTPDA-MDA	289	7.36	1.87	154	3.94
BTPDA-BDA	53.6	1.67	0.327	164	5.1
BTPDA-TADPE	402	10.21	2.23	180	4.46

Table 4 Solubility and solubility selectivity of polymers

	Solubility[a]			Ideal solubility selectivity	
Polymer	H_2	O_2	N_2	H_2/N_2	O_2/N_2
BTPDA-DBDA	1.63	3.83	2.31	0.706	1.66
BTPDA-ODA	1.47	3.53	2.35	0.656	1.69
BTPDA-MDA	1.61	3.98	2.44	0.660	1.63
BTPDA-BDA	1.35	2.75	1.98	0.682	1.45
BTPDA-TADPE	1.83	4.25	3.09	0.608	1.51

[a] $10^{-3}\,cm^3[STP]\,cm^{-3}\,cmHg^{-1}$

It is generally accepted that transport of gases in non-porous glassy polymers obeys the solution-diffusion mechanism. Diffusivity values of different gases in a given polymer depend predominantly on size and shape while solubility values depend on attraction between the gases and the polymer. Since there is no extreme attraction between the three gases of H_2, O_2, N_2 and the six polymers, the values of solubility are similar while those of diffusivity are obviously different, so the permselectivity is determined by the diffusivity selectivity.

Comparisons of polyimides

The permeability of BTPDA-BDA is lower than that of BTPDA-ODA and BTPDA-MDA because of the rigid BDA linkages in the former polymer. For the same reason, the permselectivity of BTPDA-BDA is larger.

The increased permeability for H_2, O_2 and N_2 is primarily due to increase in diffusivity of these gases. Replacement of the flat, rigid and easily packed BDA moiety by ODA or MDA, while holding the BTPDA segment constant, may restrict chain packing and cause some increase in intrasegmental motion in the polyimide. The hindrance of packing is shown by the fractional free volume changes given in *Table 1*. Both effects, packing hindrance and increase in intrasegmental mobility, cause an increase in permeability and a decrease in permselectivity of the polymers.

Compared with BTPDA-BDA, the permeability of BTPDA-DBDA for H_2, O_2 and N_2 increases by 7.9, 7.8 and 6.9 times, respectively, and the permselectivity of H_2/N_2 and O_2/N_2 also increases by 12% and 14%.

The introduction of a large side group, such as methyl, in the backbone can inhibit intersegmental chain packing, which appears to increase the permeability of penetrants. This is reflected in values of the fractional free volume (FFV) of the two polymers. The FFV of BTPDA-DBDA is 0.1290 whereas it is 0.09726 for BTPDA-BDA. On the other hand, the methyl group in the biphenylene ring can also inhibit intrasegmental rotation, which would probably increase the permselectivity. The two factors result in an apparent increase in permeability of gases and a slight increase, instead of a decrease, in permselectivity. Thus the methyl group in the backbone increases the permeability of penetrant gases with a simultaneous increase in permselectivity.

Comparisons of polyimide and polypyrrolone

The BTPDA-TADPE polypyrrolone is more permeable than the BTPDA-ODA polyimide by 20% or more for all the gases studied in the present work. The permselectivity of H_2/N_2 and O_2/N_2 of the polypyrrolone is 26% and 16% higher than that of the polyimide, respectively. Referring to *Tables 3* and *4*, it can be seen that the diffusivity is the principal factor that alters permeability and permselectivity. For H_2, O_2 and N_2, the diffusivity is increased by 22, 16 and 8%, respectively.

Since the backbone of the polypyrrolone contains a four-condensed-ring structure, which shows extremely high rigidity compared with that of the polyimide with two-condensed-ring structure, the greater diffusivity of BTPDA-TADPE relative to BTPDA-ODA may be due to the hindrance of chain packing in the polypyrrolone. This effect is reflected in the values of fractional free volume, which are 0.1470 and 0.1171 respectively for the polypyrrolone and the polyimide. It has been demonstrated that a significant increase in diffusivity and diffusivity selectivity can be obtained by simultaneously inhibiting intrasegmental motion and intersegmental chain packing[27,28]. For polypyrrolone, the four-condensed-ring moiety it contains can inhibit not only chain packing, but also internal rotation about flexible linkages on the polypyrrolone backbone. The inhibition of chain packing tends to increase the diffusivity and the suppression of chain segmental motion in the polypyrrolone leads to a greater diffusivity selectivity.

Generally, the great hindrance of chain packing may allow for high permeability and relatively low permselectivity, but the inhibition of internal rotation about flexible linkages and the decrease of concentration of mobile linkage in the polymer repeat unit can greatly increase permselectivity. As a result, the permeability and permselectivity of polypyrrolone are higher than those of the analogous polyimide.

CONCLUSIONS

The introduction of a methyl group into the backbone of BTPDA-BDA leads to a significant increase in permeability of H_2, O_2 and N_2, while the permselectivity is also increased.

The relatively soft polyimides BTPDA-ODA and BTPDA-MDA show higher permeability for all gases than the rigid BTPDA-BDA, whereas the permselectivity decreased. The reason is that the soft segments of the two polyimides may inhibit chain packing and promote intrasegmental rotation.

The permeability and permselectivity of polypyrrolone are larger than those of the analogous polyimide. The much higher rigidity of the backbone of polypyrrolone may inhibit chain packing, therefore leading to increased permeability, while the suppression of chain segmental motions in the polypyrrolone leads to a greater permselectivity. The increase in permeability and permselectivity may be primarily due to an increase in the diffusivity and diffusivity selectivity, respectively.

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