

Gas Transport Property of Homo- and Copolyimides from Isomeric Thiaphthalic Dianhydride and Oxydianiline

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ABSTRACT: Gas transport properties of homo- and copolyimides prepared from 3,3',4,4'- and 2,2',3,3'-thiaphthalic dianhydride (*p*-TDPA and *m*-TDPA, respectively) with 4,4-oxydianiline (ODA) were investigated. The fractional free volume of *m*-TDPA-ODA is larger than that of *p*-TDPA-ODA, and the chain segmental mobility of the former is lower than that of the latter. The permeability coefficients of *m*-TDPA-ODA to H₂, CO₂, and O₂ are more increased by 48, 69 and 75%, at 30°C and 10 atm, respectively, than those of *p*-TDPA-ODA; but the permselectivities of *m*-TDPA-ODA for H₂, CO₂, and O₂ toward N₂ are more decreased by 33, 77, and 26%, respectively, than those of *p*-TDPA-ODA. The permeability coefficients and the diffusion coefficients of the copolyimides can be described by the following equations: $\log P = \Phi_p \log P_p + \Phi_m \log P_m$ and $\log D_a = \Phi_p \log(D_a)_p + \Phi_m \log(D_a)_m$, respectively. The variation of the permselectivity is controlled predominantly by diffusivity selectivity. These observations are interpreted in terms of variations in the fractional free volume of polyimides.
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INTRODUCTION

Aromatic polyimides have attracted much attention as membrane materials for gas separation because of their excellent performances.¹ In order to optimize polyimide membrane materials for gas separation, one needs to fully understand the relationship between the gas transport properties and the structure of polyimides. Therefore, it is necessary to investigate systematically the effect of the chemical structure on the gas transport properties of polyimides. A substantial amount of work has gone into investigating the relationship between the molecular structure of polyimides and the gas transport properties,¹⁻⁴ indicating that the molecular structures of polyimides have

a large effect upon gas permeability and permselectivity. Sykes and coworkers found that the polyimides from *meta*-diamines, such as *m*-methane dianiline and *m*-diamino-benzophenone, with pyromellitic dianhydride (PMDA) or benzophenone tetracarboxylic dianhydride (BTDA) have lower permeability and higher permselectivity compared with the corresponding polyimides from *para*-diamine.⁵ Stern and colleagues found that the polyimides from *m*-oxydianiline and PMDA or dicarboxyphenyl hexafluoropropane dianhydride (6FDA) have lower permeability and higher permselectivity compared with the corresponding polyimides from *para*-diamine.^{6,7} The similar effect has also been observed from other polyimides prepared from isomeric diamine.⁶⁻¹⁰ These results show that *meta*-diamine can improve the permselectivity at the cost of the permeability of the polyimides. Unfortunately, little knowledge about the polyimides from isomeric dianhydrides is known.

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It is desirable to know whether isomeric dianhydrides also play an important role on the permeability and permselectivity of polyimides. Therefore, in this article, we investigated the effect of the isomer of thiaphthalic dianhydride on the gas transport properties of the polyimides from 4,4'-oxydianiline (ODA).

BACKGROUND

The gas permeability coefficient (P) of a homogeneous polymer membrane can be written to be the product of a diffusion coefficient (D) and a solubility coefficient (S), as follows:

$$P = D \cdot S \quad (1)$$

where S , a thermodynamic factor, is controlled by the inherent condensability of the penetrant, by inherent interactions between the penetrant and the polymer, and by the amount of excess volume, i.e., free volume, existing in the glassy polymers; and D , a kinetic factor, is controlled by the free volume, by the chain segmental motion of the polymer, and by the size of the penetrant molecule.

The apparent diffusion coefficient D_a of rubber polymers can be measured by the method of time lag, as shown in the following equation:

$$D_a = l^2/(6\theta) \quad (2)$$

where l is the thickness of the membrane, and θ is the time lag. The apparent solubility coefficient S_a can be determined by dividing the permeability coefficient by the apparent diffusivity coefficient. Although eq. (2) does not exactly hold for glassy polymers, the apparent diffusion coefficient D_a and apparent solubility coefficient S_a of polyimides can be estimated by this method.

The ideal separation factors ($\alpha_{A/B}^*$, namely, overall selectivity) can be expressed according to following equation:

$$\alpha_{A/B}^* = P_A/P_B = [D_A/D_B] \cdot [S_A/S_B] \quad (3)$$

where P_A and P_B are the permeability coefficients for gases A and B , respectively; the ratio D_A/D_B , which is a kinetic in nature, is known as the diffusion selectivity; and the ratio S_A/S_B , which is a thermodynamic in nature, is known as the solubility selectivity. D_A/D_B and S_A/S_B represent the

contributions to the overall selectivity arising from differences in the diffusivity and solubility of the penetrant A and B , respectively.

Experimental

The isomeric dianhydrides that were used in this study were 3,3',4,4'- and 2,2',3,3'-thiaphthalic dianhydride (p -TDPA and m -TDPA, respectively), and diamine that was used in this study was 4,4'-oxydianiline (ODA). They were finally purified by vacuum sublimation before use in polymerization. The solvents N,N-dimethylacetamide (DMAc) was purified by drying with 4 Å molecular sieve for one week at 30°C, followed by distillation under nitrogen atmosphere. The purity of the permeation gases used was more than 99.9%.

The polyamic acid precursors were prepared by solution condensation of ODA with stoichiometric amount of p -TDPA or m -TDPA or mixtures of p -TDPA and m -TDPA (3/1, 1/1, or 1/3 in the p/m ratio) in dimethylacetamide. The polyamic acid precursors were cast membranes and then were thermal imidized. The procedure is the same as that described in a previous article.¹¹ Wide angle X-ray diffraction (WAXD) and the density were measured according to the methods described in the previous article.¹¹ The permeability coefficient P and diffusion time lag θ of the polyimides were measured using manometric apparatus at an upstream pressure of 10 atm and essentially zero pressure (not more than 10 mmHg) at the downstream. The apparent diffusion coefficient D_a was expediently evaluated from eq. (2). The apparent solubility coefficient S_a was evaluated from eq. (1). The procedure is the same as that described in a previous article.¹² The thicknesses of the polymer films, used for determining diffusion coefficients of CO₂, O₂, and N₂, were about 20–25 μm; that used for determining diffusion coefficients of H₂, is about 130–150 μm (six pieces of films).

RESULTS AND DISCUSSION

WAXD curves of all polyimides were broad and without obvious peak features, indicating that homo- and copolyimides from TDPA and ODA were all amorphous. Some physical properties of two homopolyimides were listed in Table I. From Table I, we can see that the thermooxidative stability of two homopolyimides is comparable. Intrinsic viscosity of m -TDPA–ODA is lower than that of

Table I Physics Properties of the Homopolyimides^a

Polyimide	η_{inh} (dL/g)	T_c (°C)	T_S (MPa)	E (%)	T'_S (MPa)	E' (%)
<i>p</i> -TDPA-ODA	1.05	535	121	15.0	129	64.7
<i>m</i> -TDPA-ODA	0.76	530	—	—	107	6.5

^a η_{inh} = intrinsic viscosity at *m*-cresol; T_c = beginning temperature of the weight loss at air; T_S and E = tensile strength and elongation at yield; and T'_S and E' = tensile strength and elongation at break.

p-TDPA-ODA. However, the intrinsic viscosities of the copolyimides from *m*-TDPA and *p*-TDPA are comparable to *p*-TDPA-ODA (higher than 1.0 dL/g). Comparison with *p*-TDPA-ODA, *m*-TDPA-ODA is brittle, but it is strong and tough enough to be used for making membrane. Previous investigation found that *m*-TDPA-ODA has a higher glass transition temperature ($T_g = 288^\circ\text{C}$) than *p*-TDPA-ODA ($T_g = 267^\circ\text{C}$). *p*-TDPA-ODA has strong sub- T_g transition at 138°C , but *m*-TDPA-ODA does not possess sub- T_g transition.¹³ This indicated that the chain segmental mobility of *m*-TDPA-ODA is much lower than that of *p*-TDPA-ODA. It can be expected from molecular structure (see Fig. 1) that the chain segmental packing density of *m*-TDPA-ODA is lower than that of *p*-TDPA-ODA due to changes in molecular structure and conformation and in chain segmental mobility. In fact, the density of *m*-TDPA-ODA is lower than that of *p*-TDPA-ODA, and the fractional free volume of the former is higher than that of the latter. Figure 2 is the plots of the density (ρ) and the fractional free volume (FFV) versus the ratio of (*m*-TDPA/*p*-TDPA) in the copolyimides. The fractional free volume was the ratio of the specific free volume over specific volume measured at 25°C . The specific free volume was estimated by the method of Lee¹⁴ that used the group contribution correlation of Bondi¹⁵ for calculation of van der Waals volume. As shown in Figure 2, the density of copolyimides is linearly

decreased, and the fractional free volume of copolyimides is linearly increased.

In general, the polyimides from *meta*-diamines have lower permeability but higher permselectivity than those from *para*-diamines.^{6–10} The main reason is that the polyimides from *meta*-diamines have lower fractional free volume and lower chain segment mobility (related to higher T_g and higher sub- T_g transition) than those from *para*-diamine (related to lower T_g and lower sub- T_g transition). However, the effect of dianhydride isomers on the permeability and permselectivity is opposite to that of diamine isomers. *m*-TDPA-ODA, with higher fractional free volume and lower chain segment mobility ($T_g = 288^\circ\text{C}$ and no sub- T_g transition), possesses permeability coefficients of to H_2 , CO_2 , O_2 , and N_2 higher than *p*-TDPA-ODA, with lower fractional free volume and higher chain segment mobility ($T_g = 267^\circ\text{C}$ and sub- T_g transition = 138°C). Furthermore, the relative increase of the permeability coefficients due to the dianhydride variation is larger for a bigger molecular gas than a smaller one. In the other words, replacing *p*-TDPA with *m*-TDPA is more effective in causing an increase in the permeability coefficients of the bigger molecular gas than those of the smaller one. Consequently, the ideal separation factors of *p*-TDPA-ODA for gas pairs H_2/N_2 , CO_2/N_2 , and O_2/N_2 are larger than those of *m*-TDPA-ODA. These facts indicate that the mainly reason of the *meta*-polyimide having higher permeability and lower permselectivity than the *para*-polyimide is that the former possesses higher fractional free volume than the latter.

Figures 3 and 4 are plots of the permeability coefficients and the ideal separation factors versus *m*-TDPA content in the copolyimides. As shown in Figure 3, the permeability coefficient of each gas increases linearly with the increase of *m*-TDPA content in the copolyimides. In other words, the relationship between the permeability coefficients and the composition of the copolyimides, from TDPA isomers, are in accord with the

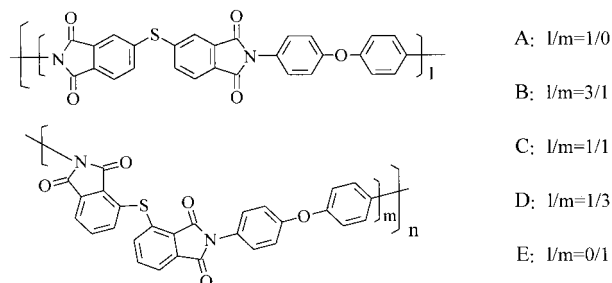


Figure 1 Chemical structure of the polyimides from thianththalic dianhydride isomers.

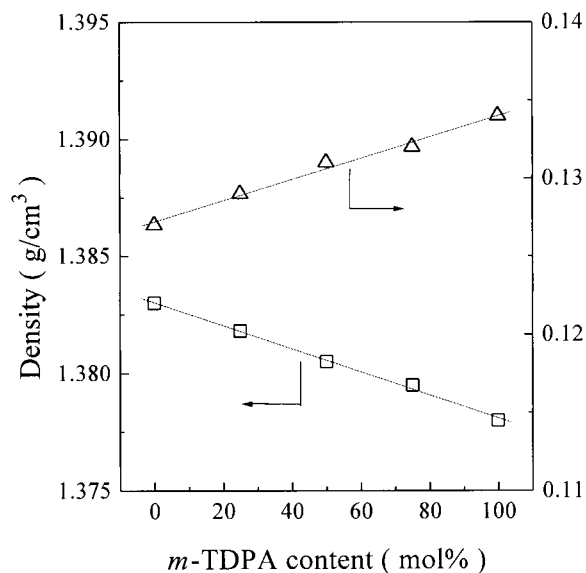


Figure 2 Plots of the density and the fractional free volume versus the *m*-TDPA content in copolyimides.

simple additivity rule suggested by Paul,¹⁶ which, i.e., can be given by eq. (4), as follows:

$$\log P = \Phi_p \log P_p + \Phi_m \log P_m \quad (4)$$

where P is the permeability coefficient of the copolyimide; P_p and P_m are the permeability coefficients of *p*-TDPA-ODA and *m*-TDPA-ODA, respectively; and Φ_p and Φ_m are *p*-TDPA and *m*-TDPA content in the copolyimide, respectively.

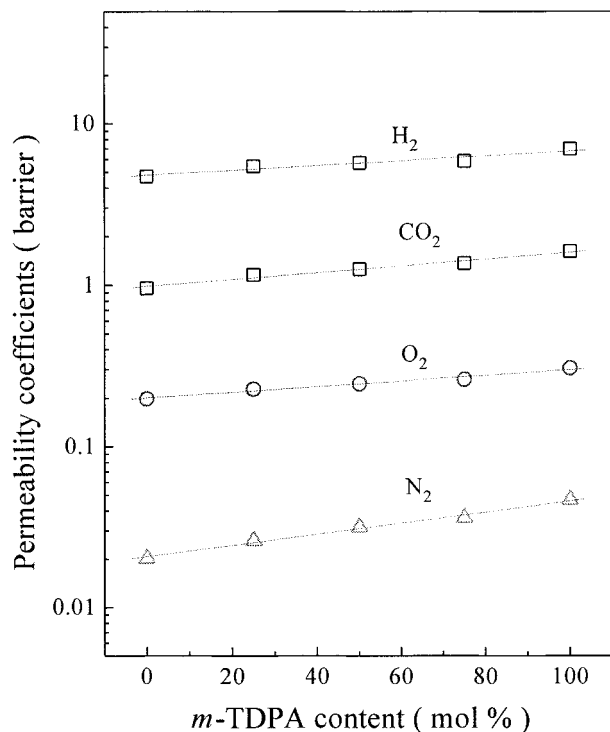


Figure 3 Plots of the permeability coefficients versus the *m*-TDPA content in copolyimides. 1 Barrer = 10^{-10} cm³ (STP) · cm/cm² · s · cmHg.

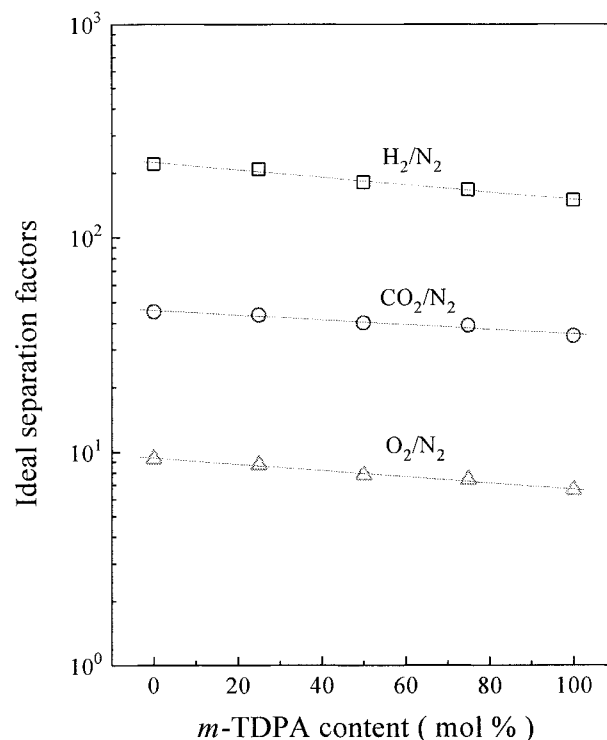


Figure 4 Plots of the ideal separation factors versus the *m*-TDPA content in copolyimides.

Table II Apparent Diffusion Coefficients and Apparent Solubility Coefficients of the Polyimides^a

Polyimide	D_{H_2}	D_{CO_2}	D_{O_2}	D_{N_2}	S_{H_2}	S_{CO_2}	S_{O_2}	S_{N_2}
<i>p</i> -TDPA-ODA	1440	1.01	5.17	0.743	0.324	94.6	3.83	2.72
Copolyimide (B)	1650	1.21	5.89	0.942	0.328	96.5	3.85	2.77
Copolyimide (C)	1710	1.28	6.31	1.12	0.332	97.7	3.88	2.82
Copolyimide (D)	1760	1.39	6.65	1.25	0.334	98.1	3.91	2.88
<i>m</i> -TDPA-ODA	2040	1.64	7.70	1.59	0.338	98.6	3.95	2.91

^a Unit $D = 10^{-9} \text{ cm}^2/\text{s}$; $S = 10^{-2} \text{ cm}^3 (\text{STP})/\text{cm}^3 \cdot \text{cmHg}$.

This indicates that the fractional free volume is a main factor to control the permeability of the copolyimides from TDPA isomers. When *m*-catenation increased, the N_2 permeability coefficients increase more significantly than the others. As a result, the permselectivity coefficients of gas pairs H_2/N_2 , CO_2/N_2 , and O_2/N_2 decreased with the increase of content of *m*-catenation in the copolyimides.

The time lag method was used to obtain apparent diffusion coefficients of the various polyimides to H_2 , CO_2 , O_2 , and N_2 . Table II listed the apparent diffusion coefficients and the apparent solubility coefficients calculated by eq. (1). Note first that the apparent diffusion coefficients for each gas are increased linearly with the increase of the *m*-TDPA content in the polyimides, which agrees with the relationship between the permeability coefficients and the *m*-TDPA content in the polyimides. In other words, the relationship between the apparent diffusion coefficients and the composition of the copolyimides, from TDPA isomers, are also in accord with the simple additivity rule, which, i.e., can be given by eq. (5):

$$\log D_a = \Phi_p \log(D_a)_p + \Phi_m \log(D_a)_m \quad (5)$$

where D_a is the apparent diffusion coefficient of the copolyimide; $(D_a)_p$ and $(D_a)_m$ are the apparent diffusion coefficients of *p*-TDPA-ODA and *m*-TDPA-ODA, respectively; and Φ_p and Φ_m are *p*-TDPA and *m*-TDPA content in the copolyimide, respectively. This is because that the apparent diffusion coefficient for given gas is determined mainly by the free volume of polymers, and the fractional free volume increases linearly with the increase of *m*-TDPA content in the copolyimides. One can see that the apparent solubility coefficients for CO_2 , O_2 , and N_2 also increase with the increase of *m*-TDPA content in these polyimides, but the magnitude of the increase in apparent

solubility coefficient for each gas is much smaller than that in apparent diffusion coefficient.

Table III summarizes the diffusivity selectivity coefficients and solubility selectivity coefficients of the polyimides for H_2 , CO_2 , and O_2 over N_2 . The apparent diffusion coefficients decrease in the order of $H_2 > O_2 > CO_2 > N_2$. The apparent solubility coefficients for H_2 , CO_2 , O_2 , and N_2 in these polyimides decrease in the order $CO_2 > O_2 > N_2 > H_2$, which is the decreasing order of inherent condensability of these gases.¹⁷ CO_2 possesses high inherent condensability results that its solubility coefficient is much larger than that of the others. The solubility selectivity for gas pair CO_2/N_2 in all the polyimides studied is much higher than the diffusivity selectivity. Consequently, the overall selectivity for gas pair CO_2/N_2 is quite high, although the diffusivity selectivity very low (about 1.0). In other words, high overall selectivity of the polyimides for gas pair CO_2/N_2 is resulted mainly from high solubility selectivity. In contrast to the gas pair CO_2/N_2 , the diffusivity selectivity of the polyimides for gas pair O_2/N_2 is higher than solubility selectivity of that. Therefore, high overall selectivity of these polyimides for the gas pair O_2/N_2 resulted mainly from diffusivity selectivity. The solubility selectivity and diffusivity selectivity for the gas pair H_2/N_2 are opposite. Although the solubility selectivity for the gas pair H_2/N_2 is less than 1 (about 0.12), the ideal separation is still quite high (more than 100) due to high diffusivity selectivity (more than 1000).

With the increase of *m*-TDPA content in the polyimides, the various selectivity for gas pairs H_2/N_2 , CO_2/N_2 , and O_2/N_2 are linearly decreased. The overall selectivity, diffusivity selectivity, and solubility selectivity for the gas pair H_2/N_2 are decreased by 48, 51, and -3%, respectively, with an increase of *m*-TDPA content in the polyimides; those for the gas pair CO_2/N_2 are decreased by 26, 24, and 3%, respectively, and those for gas

Table III Diffusivity Selectivity and Solubility Selectivity of the Polyimides

Polyimide	Diffusivity Selectivity			Solubility Selectivity		
	H ₂ /N ₂	CO ₂ /N ₂	O ₂ /N ₂	H ₂ /N ₂	CO ₂ /N ₂	O ₂ /N ₂
<i>p</i> -TDPA-ODA	1940	1.36	6.96	0.119	34.9	1.41
Copolyimide (B)	1750	1.28	6.25	0.118	34.8	1.39
Copolyimide (C)	1530	1.14	5.63	0.118	34.6	1.38
Copolyimide (D)	1410	1.11	5.33	0.117	34.1	1.36
<i>m</i> -TDPA-ODA	1280	1.03	4.84	0.116	33.9	1.36

pair O₂/N₂ are decreased by 33, 30, and 4%, respectively. These facts show that the decreases of the overall selectivity for gas pairs H₂/N₂, CO₂/N₂, and O₂/N₂ result mainly from the decrease of the diffusivity selectivity.

CONCLUSIONS

In contrast to the polyimides from isomeric diamines, the polyimide, from *m*-TDPA with ODA, possesses a larger fractional free volume than that from *p*-TDPA with ODA; and the former has a lower chain segmental mobility than the latter. The permeability of *m*-TDPA-ODA is higher than that of *p*-TDPA-ODA, but the permselectivity of *m*-TDPA-ODA is lower than that of *p*-TDPA-ODA. The permeability coefficients and the diffusion coefficients decrease linearly with the increase of *m*-TDPA content in the copolyimides and can be described by the following equations: $\log P = \Phi_p \log P_p + \Phi_m \log P_m$ and $\log D_a = \Phi_p \log (D_a)_p + \Phi_m \log (D_a)_m$, respectively. The increase of the permeability resulted predominantly from the increase of diffusivity, and the decrease of the permselectivity resulted mainly from the decrease of diffusivity selectivity.

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