

Gas Separation Properties of Aromatic Polyetherimides from 1,4-Bis(3,4-dicarboxyphenoxy)benzene Dianhydride and 3,5-Diaminobenzic Acid or Its Esters

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SYNOPSIS

The gas transport properties of a series polyetherimides, which were prepared from 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA) with 1,3-phenylenediamine or 3,5-diaminobenzic acid (DBA) or its esters are reported. The effects of carboxylic group ($-\text{COOH}$) and carboxylic ether groups ($-\text{COOR}$), at five positions of 1,3-phenylenediamine moiety, on H_2 , CO_2 , O_2 , and N_2 permeability, diffusivity, and solubility of the polyetherimides were investigated. The gas permeability, diffusion, and solubility coefficients of the polyetherimides containing COOR are bigger than those of HQDPA-PDA, but the ideal separation factors and ideal diffusivity selectivity factors are much smaller than that of HQDPA-PDA because COOR decreases chain segmental packing efficiency and increases chain segmental mobility. The permeability coefficients of HQDPA-DBA to H_2 , CO_2 , and O_2 are bigger than those of HQDPA-PDA; the ideal separation factors for gas pairs H_2/N_2 , CO_2/N_2 , and O_2/N_2 are also much bigger than those of HQDPA-PDA. Both the diffusion coefficients of CO_2 and O_2 and the ideal diffusivity selectivity factors for CO_2/N_2 and O_2/N_2 are bigger than those of HQDPA-PDA because COOH decreases both chain segmental packing efficiency and chain segmental mobility. The copolyimides, which were prepared from 3,5-diaminobenzic acid and 3,5-diaminobenzic esters, have both high permeability and high permselectivity. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Membrane technology such as hydrogen recovery from petrochemical recycle and purge gas streams, separating carbon dioxide from nature gas, and preparation of nitrogen- or oxygen-enriched air has been widely used for gas separation in industry.¹ The key to gas separation based on membrane method is high performance membrane materials as well as preparing technology of the applicable membrane, such as hollow fiber. To develop favorable membrane materials for gas separation, a substantial amount of work has gone into investigation of the relationship between the molecular structure of polymers and the permeability and permselectivity, indicating that the molecular structures of polymers affect

strongly on the permeability and permselectivity and that aromatic polyimide is a class of very promising membrane material for gas separation.²⁻⁸ The polyimides possess high performance, such as high gas permselectivity, excellent mechanical properties, outstanding thermal stability, and excellent chemical resistance. However, there is still a general trend within the family of polyimides that polyimides with high permeability have low permselectivity, and others with high permselectivity have low permeability. In last decade, remarkable success has been achieved that enhances both permeability and permselectivity of polyimides by controlling chemical structure.^{1,8} For example, the studies made by Koros and colleagues indicated that incorporating some bulky structure elements into the backbone of the polyimides based on dicarboxyphenyl hexafluoropropane dianhydride (6FDA) can increase gas permeability with only minimum permselectivity losses.⁹⁻¹² Recent work in our laboratory shows

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that the substitution of some groups onto the aromatic rings of diamines can simultaneously increase both permeability and permselectivity of the polyetherimides based on 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HQDPA).^{13,14} It promoted us to further investigate the effect of substituting diamine structure on the gas separation properties of the HQDPA-based polyetherimides.

In the present study, the gas transport properties of HQDPA-based polyetherimides prepared from 3,5-diaminobenzic acid (DBA) or its ester were investigated to further understand the relationship between the diamine structure and gas separation properties of HQDPA-based polyetherimides.

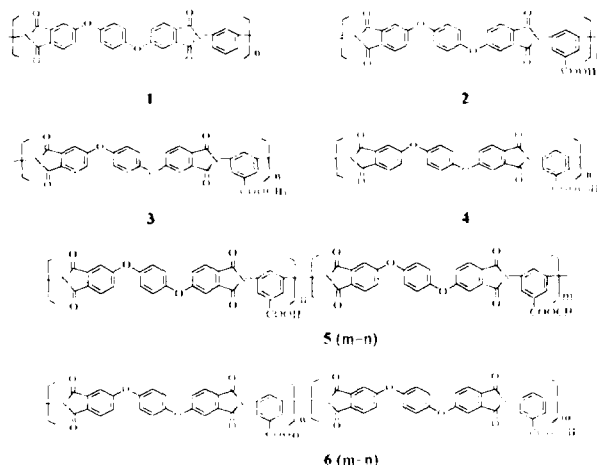
EXPERIMENTAL

Materials

The diamines used for this study were 1,3-phenylenediamine (PDA), 3,5-diaminobenzic acid (DBA), methyl 3,5-diaminobenzoate (MDBA), and ethyl 3,5-diaminobenzoate (EDBA). HQDPA, MDBA, and EDBA were prepared in our laboratory. PDA and DBA were purchased from Shanghai Chemical Agent Factory (P. R. China) and from Aldrich Chemical Co., respectively. All the monomers were finally purified by vacuum sublimation or recrystallization before use in polymerization. The solvent dimethylacetamide (DMAc) was dried at 30°C with 4Å molecular sieve for one week, followed by distillation under nitrogen atmosphere. The purity of the permeation gases used was more than 99.95%.

Apparatus and Procedure

The polyetheramic acid precursors were prepared by solution condensation of HQDPA with stoichiometric amount of diamine in DMAc. The polyetheramic acid precursors were cast membranes and were then thermal imidized. The procedure is the same as that described in previous paper.¹³ The polyimide membranes obtained were about 30 μm in thickness. The molecular structure of the polyetherimides is shown in Scheme 1. The membranes were characterized according to the procedure described in a previous paper.¹³ The permeability coefficients (P) of the polyimides to H₂, CO₂, O₂, and N₂ were measured using manometric apparatus in the temperature range from 30 to 150°C. The downstream pressure was kept essentially zero (not more than 10 mmHg), and the upstream pressure was maintained at 7 atm. The apparent diffusion coefficients



Scheme 1 Chemical structure of the polyetherimides studied.

(D) were estimated from time-lag data at 30°C, according to eq. (1):

$$D = l^2/6\theta \quad (1)$$

where l is membrane thickness and θ is the time lag.¹⁵ The apparent solubility coefficients (S) were estimated from eq. (2).

$$S = P/D \quad (2)$$

The thicknesses of the polymer films, used for determining diffusion coefficients of CO₂, O₂, and N₂, were about 30 μm; that used for determining diffusion coefficients of H₂ is about 150 μm (five pieces of films).

RESULTS AND DISCUSSION

Characterization of Polyetherimides

Some physical properties of the HQDPA-based polyetherimides studied are listed in Table I. Wide angle X-ray diffraction (WAXD) curves of all polyetherimides were broad and structureless, indicating that the polyetherimides were amorphous. The special free volume (SFV), and the fractional free volume (FFV) of the polyetherimides were calculated by eqs. (3)–(5):

$$V_f = M/\rho - 1.3V_w \quad (3)$$

$$\text{SFV} = V_f/M \quad (4)$$

$$\text{FFV} = \text{SFV} \cdot \rho \quad (5)$$

where, V_f is the free volume of smallest repeat unit, M is the weight of smallest repeat unit, ρ is the density of polyetherimide at 25°C, and V_w is van der Waals volume calculated by the group contribution method, reported by Lee¹⁶ and Bondi.¹⁷

Gas Transport Properties

The permeability coefficients of the representative polyetherimide, 2, to H₂, CO₂, O₂, and N₂ are illustrated in the form of Arrhenius plots in Figure 1. It is obvious that a linear relationship exists between $\log P$ and $1/T$ in each polyetherimide. In other words, the Arrhenius equation holds

$$\log P = \log P_0 - E_p/(2.303RT) \quad (6)$$

where R is the universal gas constant, T is the absolute temperature (K), and E_p is the apparent activation energy of gas permeation. Because all the HQDPA-based polyetherimides studied here were in the glassy state in the experimental temperature range, the apparent activation energy of gas permeation does not change with temperature.

The permeability coefficients of the polyetherimides to H₂, CO₂, O₂, and N₂ at 30 and 100°C are listed in Table II. The apparent activation energies (E_p) for the permeation of H₂, CO₂, O₂, and N₂ calculated from the slopes are summarized in Table III. The ideal separation factors of the polyetherimides for H₂/N₂, CO₂/N₂, and O₂/N₂ at 30 and 100°C are summarized in Table IV. The apparent diffusion coefficients and the ideal diffusivity selectivity factors of four homopolyetherimides at 30°C are listed in Table V. The solubility coefficients and ideal solubility selectivity factors of four homopolyetherimides for H₂/N₂, CO₂/N₂, and O₂/N₂ at 30°C are listed in Table VI. The permeability coefficient (P) can be shown to be a product of a diffusion coefficient (D), and a solubility coefficient (S):

$$P = D \cdot S \quad (7)$$

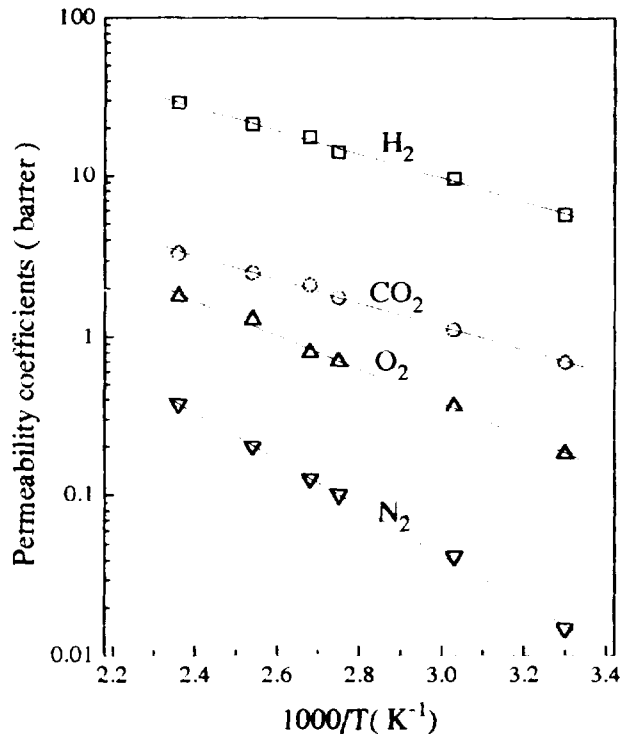


Figure 1 Temperature dependence of the permeability coefficients of HQDPA-DBA 1 barrer = 10^{-10} cm³ (STP) · cm/cm² · s · cm Hg.

where S , a thermodynamic factor, can be determined by the inherent condensability of the penetrant gas, by polymer-penetrant gas molecule interactions, and by the amount of excess volume; namely, free volume, existing in the glassy polymers, and D , a kinetic factor, can be determined by dividing the permeability coefficient by the solubility coefficient. The ideal separation factor ($\alpha_{A/B}^*$), namely, overall selectivity, can be expressed according to eq. (8):

Table I Physical Properties of the Polyetherimides

Polyetherimide	Glass Transition	Density	Specific Free Volume	Fractional Free Volume
	Temperature			
	(°C)	ρ (g/cm ³)	(SFV) (cm ³ /g)	(FFV)
	(T_g)			
1	262	1.380	0.086	0.119
2	286	1.384	0.096	0.133
3	248	1.371	0.094	0.129
4	241	1.353	0.096	0.130
5	269	1.379	0.095	0.131
6	265	1.371	0.096	0.131

Table II Permeability Coefficients of the Polyetherimides*

Polyetherimide	30°C				100°C			
	H ₂	CO ₂	O ₂	N ₂	H ₂	CO ₂	O ₂	N ₂
1	3.75	0.598	0.149	0.016	11.3	1.70	0.586	0.111
2	5.67	0.683	0.179	0.015	17.1	2.10	0.793	0.125
3	5.33	1.18	0.234	0.034	15.3	2.37	0.787	0.160
4	7.79	2.26	0.529	0.077	19.2	4.18	1.33	0.292
5	5.70	0.957	0.207	0.023	16.2	2.34	0.802	0.147
6	7.03	1.34	0.321	0.036	19.2	3.25	1.12	0.207

* Unit: Barrer [10^{-10} cm³(STP) · cm/cm² · s · cm Hg].

$$\alpha_{A/B}^* = P_A/P_B = [D_A/D_B] \cdot [S_A/S_B] \quad (8)$$

where P_A and P_B are the permeability coefficients for gases A and B , respectively; the ratio D_A/D_B , which is kinetic in nature, is known as the “diffusivity selectivity” or ideal diffusivity selectivity factor, and the ratio S_A/S_B , which is thermodynamic in nature, is known as the “solubility selectivity” or ideal solubility selectivity factor. 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. As shown in Figure 1, the permeability coefficients of the polyetherimides for four gases decrease, at each temperature, in the following order: $P_{H_2} > P_{CO_2} > P_{O_2} > P_{N_2}$. This is also the order of increasing kinetic molecular diameters of the penetrant gases ($H_2 < CO_2 < O_2 < N_2$).¹⁸ The ideal separation factors decreases in the following order: $H_2/N_2 > CO_2/N_2 > O_2/N_2$. The diffusion coefficients decrease in the following order: $H_2 > O_2 > CO_2 > N_2$. The apparent solubility coefficients for 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 increased order of inherent condensability of these gases. CO_2 possesses high inherent condensability results that its solubility coef-

ficient is much larger than others. Although the solubility selectivity for gas pair H_2/N_2 in all the polyimides studied is not more than one, the overall selectivity for gas pair H_2/N_2 is also quite high due to very high diffusivity selectivity. The solubility selectivity for the gas pair CO_2/N_2 in the polyimides studied is much higher than the diffusivity selectivity. Consequently, the overall selectivity for the gas pair CO_2/N_2 is quite high. In other words, high overall selectivity of the polyimides for the gas pair CO_2/N_2 is mainly because of high solubility selectivity. In contrast to the gas pair CO_2/N_2 , the diffusivity selectivity of the polyimides for the gas pair O_2/N_2 is higher than the solubility selectivity. Therefore, high overall selectivity of these polyimides for the gas pair O_2/N_2 results from diffusivity selectivity.

Comparison of HQDPA-DBA and HQDPA-PDA

Carboxylic group ($-COOH$) is a strong polar substituent. Polyetherimide with carboxylic group HQDPA-DBA (2), has high H-bond energy and high orientation energy. The result is that 2 has much higher cohesive energy than HQDPA-PDA (1). Furthermore, there can be intermolecular cross-link structure in 2. Consequently, the glass transition temperature of 2 is much higher than 1, and the chain segmental mobility is much lower than 1. Carboxylic group is also a bulky substituent that restricts the chain segmental package. Hence, the special free volume and the fractional free volume of 2 is higher than 1. The polymers with high fractional free volume and low chain segmental mobility, especially cross-link structure, possess high permeability and high permselectivity. Therefore, the permeability coefficients of 2 to H_2 , CO_2 , and O_2 are larger than those of 1, and the ideal separation factors of 2 for H_2/N_2 , CO_2/N_2 , and O_2/N_2 are much larger than those of 1. The permeability coefficients

Table III Apparent Activation Energy of Gas Permeation Through the Polyetherimides*

Polyetherimide	H ₂	CO ₂	O ₂	N ₂
1	14.6	13.9	18.4	26.1
2	14.8	15.3	20.3	28.7
3	13.3	9.37	15.3	20.6
4	12.1	8.26	12.4	18.1
5	14.0	12.1	18.2	24.9
6	13.5	11.9	16.8	23.5

* Unit: kJ/mol.

Table IV Ideal Separation Factors of the Polyetherimides

Polyetherimide	30°C			100°C		
	H ₂ /N ₂	CO ₂ /N ₂	O ₂ /N ₂	H ₂ /N ₂	CO ₂ /N ₂	O ₂ /N ₂
1	237	37.4	9.4	102	15.3	5.3
2	386	45.5	12	137	16.8	6.3
3	155	34.7	6.9	89.4	14.8	4.9
4	103	29.4	6.9	65.8	14.3	4.6
5	247	41.2	9.0	111	15.9	5.5
6	203	37.6	9.0	92.7	15.7	5.4

of 2 to H₂, CO₂, and O₂ increase by 51, 14, and 17%, respectively, at 30°C and at 7 atm, compared with 1; while the ideal separation factors for H₂/N₂, CO₂/N₂, and O₂/N₂ increase 41, 22, and 27%, respectively, compared with 1. There is not any special interaction between the gases used in this study and the carboxylic group in the polyetherimide. Therefore, the difference of the solubility and solubility selectivity between 1 and 2 to each gas is rather small. However, the fractional free volume of 2 increases by about 12% than that of 1. The diffusivity is controlled mainly by the free volume, by the chain segmental motion of polymer, and by the size of the penetrant molecule. Hence, the diffusion coefficients of 2 to H₂, CO₂, O₂, and N₂ are much larger than those of 1, and the ideal diffusivity selectivity factors of 2 for H₂/N₂, CO₂/N₂, and O₂/N₂ are much larger than those of 1; although the chain segmental mobility of the former is lower than the later. These facts show that the high permselectivity of 2 is results primarily from the high diffusivity selectivity.

Comparison of HQDPA-3,5-diaminobenzoate and the Others

Carboxylic ether groups (—COOR) differ from carboxylic group in many respects. First, the volumes of carboxylic ether groups are much larger than that of carboxylic group. Second, carboxylic ether groups are flexible substituents and have a strong plasticization,

but the carboxylic group does not. Third, carboxylic ether groups are inert substituents and do not react with amine in the process of imidization of polyamide acid precursor. Therefore, the polyetherimides that were prepared from 3,5-diaminobenzoate possess lower glass transition temperature, namely, higher chain segmental mobility than 1 and 2 and lower chain segmental package density, e.g., higher fractional free volume or high special free volume than 1 but slightly lower higher fractional free volume or high special free volume than 2.

Diffusivity is determined by the free volume, by the chain segmental motion of polymers, and the size of the penetrant molecule. The result is that the 3,5-diaminobenzoate-based polyetherimides, with higher fractional free volume and lower glass transition temperature, possess higher diffusivity to each gas than the others. The strong plasticization of —COOR causes a large increase of N₂ (with big molecular kinetic diameter) diffusion coefficients than that of H₂, CO₂, and O₂ (with small molecular kinetic diameter). Consequently, the diffusivity selectivity of the HQDPA-3,5-diaminobenzoate for H₂/N₂, CO₂/N₂, and O₂/N₂ are much lower than those of the other polyetherimides. Although solubility of polymer is determined by free volume, the increase of the fractional free volume of the polyetherimide causes only a small increase of the solubility coefficients and results in only a minute decrease of the solubility selectivity in this case. One

Table V Diffusion Coefficients and Ideal Diffusivity Selectivity Factors of the Polyetherimides at 30°C*

Polyetherimide	H ₂	CO ₂	O ₂	N ₂	H ₂ /N ₂	CO ₂ /N ₂	O ₂ /N ₂
1	837	0.974	3.44	0.671	1247	1.45	5.1
2	1233	1.08	4.05	0.607	2032	1.78	6.7
3	1085	1.63	4.81	1.19	912	1.37	4.0
4	1500	2.80	9.40	2.33	644	1.20	4.0

* Unit: 10⁻⁹ cm²/s.

Table VI Solubility Coefficients and Ideal Solubility Selectivity Factors of the Polyetherimides at 30°C*

Polyetherimide	H ₂	CO ₂	O ₂	N ₂	H ₂ /N ₂	CO ₂ /N ₂	O ₂ /N ₂
1	0.45	61.4	4.33	2.38	0.19	25.8	1.8
2	0.48	63.5	4.42	2.47	0.19	25.7	1.8
3	0.50	72.4	4.86	2.86	0.17	25.3	1.7
4	0.53	80.8	5.63	3.31	0.16	24.4	1.7

* Unit: 10⁻² cm³(STP)/cm³ · cm Hg.

can also see this fact from the data listed in Table VI. This indicates that the increase in the permeability and the decrease in the permselectivity of the polyetherimides, from 1 to HQDPA-3,5-diaminobenzoate (3 and 4) mainly is caused by increase diffusivity and by decrease in diffusivity selectivity. For example, CO₂ permeability coefficient, diffusion coefficient, and solubility coefficient 3 increase by 97, 67, and 18% more, respectively, than 1; while the CO₂/N₂ deal separation, ideal diffusivity selectivity, and ideal solubility selectivity factors of 3 decrease by 21, 17, and 2% more, respectively, than those 1.

Copolyetherimides offer the possibility of preparing membrane materials with favorable gas separation property, i.e., both high permeability and high permselectivity, which is not obtained with the homopolyetherimides. The chain segmental package and chain segmental mobility of the copolyetherimides (5 and 6), which were prepared from 3,5-diaminobenzoic acid and 3,5-diaminobenzoic esters, are between those of 2 and those of 3 or 4. This causes the permeability and permselectivity of 5 to be between that of 2 and 3, and the permeability and permselectivity of 6 to be between that of 2 and 4. Paul¹⁹ has suggested that the mean permeability coefficient P of a copolymer can be estimated from the values of P_i of its i constituent homopolymers by means of the following relation:

$$\ln P = \sum_i q_i \ln P_i \quad (9)$$

where q_i is the volume-fraction of the i constituent homopolymer. The agreement between the experimental and calculated permeability coefficients, by means of eq. (9), for copolymers 5 and 6 is satisfactory. For example, the permeability coefficients of H₂, CO₂, O₂, and N₂ through 6 at 30°C is 6.69, 1.27, 0.314, and 0.035 barrer, respectively. The differences between the experimental values and calculated values are not more than 10%.

CONCLUSION

The structure of the diamines affects strongly on the gas transport properties of HQDPA-based polyetherimides from 1,3-phenylenediamine or 3,5-diaminobenzoic acid or its ester. The general trends of the increase of permeability, correlated with the decrease of permselectivity, is not observed for HQDPA-based polyetherimides herein. The polyetherimides, that prepared from 3,5-diaminobenzoic esters, with low chain segmental package and high chain segmental mobility due to carboxylic ether group strong plasticization, possess high permeability and low permselectivity. HQDPA-DBA, with both low chain segmental package and low chain segmental mobility, holds much high permselectivity. The variation of the permeability and permselectivity of the polyetherimides studied here is caused predominantly by the change of diffusivity and diffusivity selectivity. HQDPA-DBA/MDBA(1/1) and HQDPA-DBA/EDBA(1/1) have both high permeability and high permselectivity. These copolymers exhibit a balance of excellent thermal and chemical stability, high mechanical strength, favorable processability, and good H₂/N₂ separation properties, so they are favorable gas separation membrane materials for hydrogen recovery from various industrial purge gases.

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