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### Structure/Permeability and Permselectivity Relationship of Polyetherimides from 1,4-Bis(3,4-Dicarboxyphenoxy) Benzene Dianhydride. III

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## **STRUCTURE/PERMEABILITY AND PERMSELECTIVITY RELATIONSHIP OF POLYETHERIMIDES FROM 1,4-BIS(3,4-DICARBOXYPHENOXY) BENZENE DIANHYDRIDE. III**

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### **ABSTRACT**

Gas permeability coefficients of a series of aromatic polyetherimides prepared from 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA) and four (methylene dianiline)s with a methyl side group to H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> were measured under 7 atm and within a temperature range from 30 to 150°C. The gas permeabilities and permselectivities of these polymers were compared with those of the HQDPA-based polyetherimides from methylene dianiline (MDA) and isopropylidene dianiline (IPDA). The number and position of the methyl side groups on the benzene rings of the diamine residues strongly affect the gas permeabilities and permselectivities of the HQDPA-based polyetherimides. The gas permeability of the polyetherimide progressively increases with an increase in the number of the methyl side groups. Both the gas permeability and permselectivity of the polyetherimides with methyl side groups are higher than those of HQDPA-MDA. The polyetherimide prepared from 3,3'-dimethyl 4,4'-methylene dianiline (DMMDA1) possesses both higher permeability and permselectivity than the polyetherimides prepared from 2,2'-dimethyl 4,4'-methylene dianiline (DMMDA2). However, two of the polyetherimides prepared from

2,2',3,3'-tetramethyl 4,4'-methylene dianiline (TMMDA1) or 2,2',5,5'-tetramethyl 4,4'-methylene dianiline (TMMDA2) possess almost the same gas permeability and permselectivity.

## INTRODUCTION

As membrane materials for gas separation, aromatic polyetherimides have attracted much attention because of their excellent gas separation performance, high mechanical strength, and excellent chemical and thermal stability. Moreover, their processability is better than that of the traditional polyimides such as those prepared from pyromellitic dianhydride (PMDA) or 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) [1–6]. It is very important to have a good understanding of the relationship between the gas permeation and the chemical structure of the polyetherimides to optimize the molecular design of polyetherimide membrane materials for gas separation. Hence, it is necessary to systematically investigate the effect of the chemical structures on the gas permeation through the polyetherimide membranes. Eastmond and his coworkers investigated the gas permeation of various polyetherimides containing Bisphenol A derivative units, and the results indicate that the structure of double ether dianhydrides and diamines strongly affects the permeabilities and permselectivities [4–6]. In previous papers we reported the relationship between the chemical structure and the gas permeation through polyetherimides prepared from HQDPA and various bridged diamines or phenylene diamines with various substitutes [7, 8], and they indicated that the structure of the polyetherimides, especially those with substitutes on the benzene ring, has a strong effect on their gas permeabilities and permselectivities. Furthermore, Lancsam and Tanaka reported that the chemical structures and numbers of substituents on the diamine residues strongly affect the gas permeabilities and permselectivities of the 6FDA-based polyimides [9, 10]. However, there are few reports on the relationship between the position of substituents and gas permeation through polyimide membranes [11].

In this study we purposely synthesized a series of polyetherimides from HQDPA and various (methene dianiline)s with a methyl group substituent for systematically investigating the effect of the numbers and positions of substituted groups of the diamine residues on the gas permeation of the polyetherimides.

## EXPERIMENTAL

### Materials

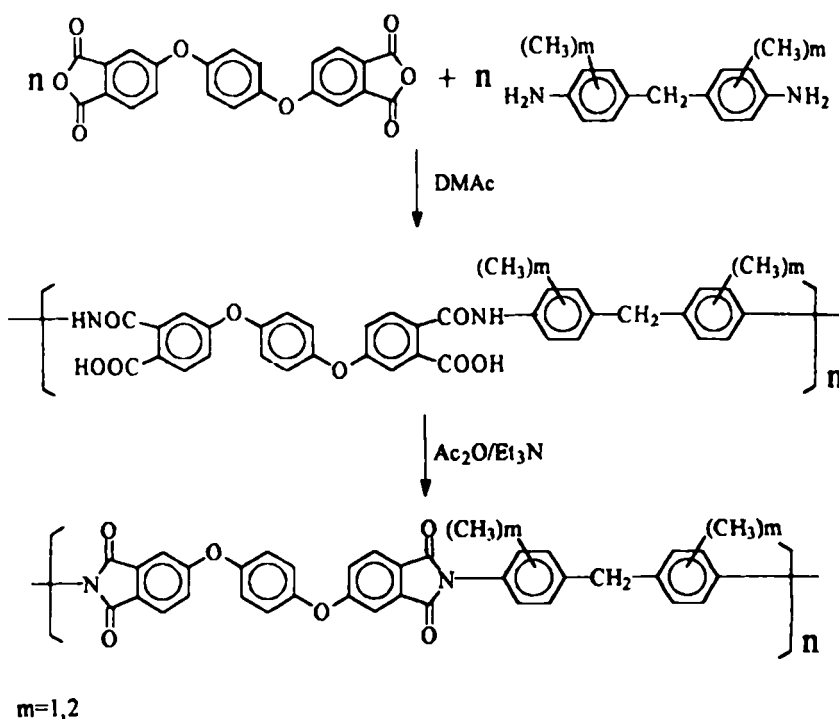
The diamines used for this study were 3,3'-dimethyl 4,4'-methylene dianiline (DMMDA1), 2,2'-dimethyl 4,4'-methylene dianiline (DMMDA2), 2,2',3,3'-tetramethyl 4,4'-methylene dianiline (TMMDA1), and 2,2',5,5'-tetramethyl 4,4'-methylene dianiline (TMMDA2). HQDPA and the diamines were all prepared in our laboratory. All the monomers were purified by recrystallization before use in polymerization. The solvent dimethylacetamide (DMAc) was dried at 30°C with a 4-Å molecular sieve for 1 week, followed by distillation under a nitrogen atmosphere. The purity of the gases used for permeation experiments was more than 99.95%.

### Synthesis of Polyetherimides

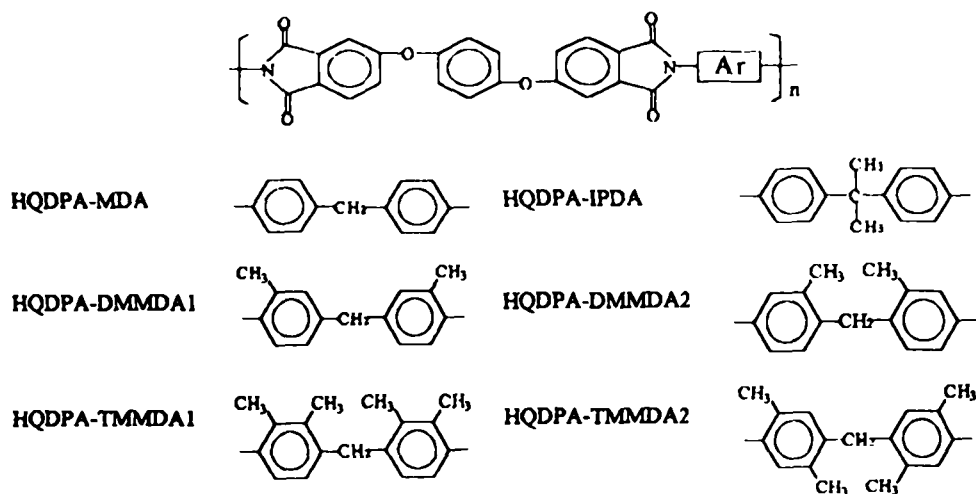
All the polyetherimides were synthesized according to a two-step procedure (Scheme 1). Polyetheramic acid precursors were prepared by solution condensation of an aromatic dianhydride with a stoichiometrical amount of an aromatic diamine in DMAc at room temperature, then chemically imidized with an equimolecular mixture of acetic anhydride and triethylamine at room temperature for 2 days. The viscous solution was poured into a blender with a 5-fold volume of ethanol. The resulting pale yellow powder was filtered and washed in refluxing ethanol with stirring for 30 minutes. It was washed 3 times and then dried at 100°C for 24 hours. The polyetherimide yields were essentially quantitative, and their inherent viscosities were not less than 0.80 dL/g in all cases.

### Preparation and Characterization of Membrane

The molecular structures of the polyetherimides are shown in Scheme 2. The dense membranes used for testing were prepared by solution casting on a glass plate from 15 wt% solutions in DMAc. The freshly cast membranes were heated at about 40–50°C, 100°C, and 250°C each for 6 hours. After being cooled to below 50°C, the polyetherimide membranes were removed from the glass plate by stripping in a hot water bath and then dried in a vacuum oven at 150°C for 1 week. The polyetherimide membranes thus obtained were generally about 0.0025 cm in thickness. The



SCHEME 1. Synthesis of HQDPA-based polyetherimides.



SCHEME 2. Structure of the HQDPA-based polyetherimides studied.

membranes were characterized according to the procedure described in previous papers [10, 11]. The permeability coefficients to  $H_2$ ,  $CO_2$ ,  $O_2$ ,  $N_2$ , and  $CH_4$  were measured under 7 atm and within a temperature range from 30 to 150°C [10, 11].

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Polyetherimides

Aromatic polyetherimide may be synthesized by many approaches such as a one-step or a two-step procedure from an aromatic ether dianhydride with an aromatic diamine, polymerization of a diisocyanate with an aromatic ether dianhydride, and aromatic nucleophilic displacement polymerization from bis(nitrophthalimide)s or bis(chlorophthalimide) with diols [12]. The general reaction of a diamine with a dianhydride, followed by chemical imidization, is widely used for preparing soluble polyimide [6, 12, 13]. This approach has been used for preparing HQDPA-based polyetherimides, HQDPA-DMMDAs and HQDPA-TMMDAs, which are soluble in some organic solvents such as DMAc, *N,N'*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), and chloroform. However, when thermal imidization is adopted, the polyetherimides obtained are not soluble in DMAc, DMF, NMP, and chloroform, but are only soluble in chlorophenol and cresol. It is more convenient to prepare hollow fibers for gas separation from polyetherimides solution in DMAc or DMF or NMP than in chlorophenol or cresol. Indeed, we have successfully prepared high performance hollow fibers for gas separation from HQDPA-based polyetherimides obtained by the chemical imidization procedure, so the method of chemical imidization was adopted in this work.

Some physical properties of the HQDPA-based polyetherimides are listed in Table 1. The wide-angle-x-ray diffraction (WAXD) curves of all the polyetherimides are broad and without obvious peak features, indicating that the polyetherimides were amorphous. The average interchain spacing distances (*d*-spacing) of the poly-

TABLE 1. Properties of HQDPA-Based Polyetherimides

Polyetherimide	Glass transition temperature $T_g$ , °C	Sub- $T_g$ , °C	Density $\rho$ , g/cm <sup>3</sup>	$d$ -Spacing, nm	Special free volume SFV, cm <sup>3</sup> /g
HQDPA-MDA	254	123	1.356	0.50	0.088
HQDPA-IPDA	264	130	1.298	0.53	0.094
HQDPA-DMMDA1	268	146	1.296	0.52	0.093
HQDPA-DMMDA2	264	143	1.301	0.52	0.090
HQDPA-TMMDA1	277	146	1.266	0.53	0.095
HQDPA-TMMDA2	278	146	1.264	0.53	0.095

etherimides were calculated from WAXD results with Barge's equation,  $n\lambda = 2d \sin \theta$ . The special free volumes of the polyetherimides were calculated by

$$\text{SFV} = M/\rho - 1.3V_w \quad (1)$$

where SFV is the special free volume of polyetherimide,  $M$  is the molecular weight of the repeat unit,  $\rho$  is the density of polyetherimide at 25°C, and  $V_w$  is van der Waals volume calculated by the group contribution method reported by Lee and Bondi [14, 15]. Glass transition temperature ( $T_g$ ) and sub- $T_g$  transition were measured by dynamic mechanical analysis (DMA).

### Structure and the Gas Permeability and Permselectivity

The sub- $T_g$  transition is determined by the local mobility of polymer chains and/or substituents. Both methyl substituents on the ortho positions of the C–N bond and those on the ortho positions of the C(CH<sub>2</sub>)–C(benzene ring) bond of polyetherimides restrict the local mobility of the polyetherimide chains. The efficiency of the former in restricting the local mobility of the polyetherimide chains is higher than that of the latter. Consequently, the local mobility of HQDPA-DMMDA1 chains with two methyl groups on the ortho positions of the C–N bond is lower than that of HQDPA-DMMDA2 chains with two methyl groups in the ortho positions of the C(CH<sub>2</sub>)–C(benzene ring) bond. Moreover, the local mobility of two methyl groups on the ortho positions of the C–N bond is expected to be lower than that on the C(CH<sub>2</sub>)–C(benzene ring) bond ortho-positions, resulting in HQDPA-DMMDA1 having a higher sub- $T_g$  transition than HQDPA-DMMDA2. As shown in Table 1, this hypothesis is supported by the experimental results.

Furthermore, both the substituted methyl groups on the ortho positions of the C–N bond and those on the ortho positions of the C(CH<sub>2</sub>)–C(benzene ring) bond of polyetherimides restrict the chain packing of the polyetherimides, while the effect of the former is even efficient than that of the latter. This will make the special free volume of HQDPA-DMMDA1 higher than that of HQDPA-DMMDA2, and the average interchain spacing distance of the former will be larger than that of the latter.

Gas permeation through a homogeneous polymer membrane depends on the fact that the penetrant must experience a series of diffusional jumps as it permeates

TABLE 2. Permeability Coefficients<sup>a</sup> of the HQDPA-Based Polyetherimides at 30 and 100°C

Polyetherimide	Temperature,		$P_{H_2}$	$P_{CO_2}$	$P_{O_2}$	$P_{N_2}$	$P_{CH_4}$
	°C						
HQDPA-MDA	30		5.08	1.22	0.242	0.0355	0.0222
	100		14.4	3.19	0.970	0.175	0.136
HQDPA-IPDA	30		9.33	2.65	0.586	0.104	0.0692
	100		24.9	6.47	1.68	0.431	0.331
HQDPA-DMMDA1	30		7.83	1.66	0.358	0.0357	0.0209
	100		19.3	3.55	1.13	0.161	0.117
HQDPA-DMMDA2	30		6.83	1.51	0.317	0.0357	0.0209
	100		18.3	3.63	1.04	0.168	0.129
HQDPA-TMMDA1	30		14.2	2.26	0.668	0.0631	0.0404
	100		32.4	4.81	1.73	0.273	0.203
HQDPA-TMMDA2	30		13.9	2.28	0.678	0.0634	0.0399
	100		32.5	4.79	1.78	0.278	0.208

<sup>a</sup>Unit:  $10^{-10} \text{ cm}^3 \text{ (STP)} \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ .

across the polymer membrane. These jumps are mainly controlled by the special free volume and the local mobility of polymer chains and/or substituents [16–18]. Increasing the special free volume or raising the local mobility of the polymer chains and/or substituents will lead to an increase in gas permeability and a decrease in permselectivity for gas pairs [18]. It can be seen from the data listed in Tables 2 and 3 that both the gas permeability and permselectivity of HQDPA-DMMDA1 are

TABLE 3. Permselectivity Coefficients of the HQDPA-Based Polyetherimides at 30 and 100°C

Polyetherimide	Temperature, °C	Permselectivity Coefficients					
		$P_{H_2}/P_{CH_4}$	$P_{H_2}/P_{N_2}$	$P_{CO_2}/P_{CH_4}$	$P_{CO_2}/P_{N_2}$	$P_{O_2}/P_{N_2}$	$P_{N_2}/P_{CH_4}$
HQDPA-MDA	30	229	143	54.9	34.4	6.8	1.6
	100	106	82.3	23.5	18.2	5.5	1.3
HQDPA-IPDA	30	135	89.7	38.3	25.5	5.7	1.5
	100	75.2	57.8	19.5	15.0	3.9	1.3
HQDPA-DMMDA1	30	375	219	79.4	46.5	10	1.7
	100	165	120	30.3	22.0	7.0	1.4
HQDPA-DMMDA2	30	313	191	69.3	42.3	8.9	1.6
	100	142	109	28.1	21.6	6.2	1.3
HQDPA-TMMDA1	30	351	225	56.6	35.8	10.6	1.6
	100	160	119	23.7	17.6	6.3	1.3
HQDPA-TMMDA2	30	349	220	57.1	36.0	10.7	1.6
	100	157	117	23.0	17.2	6.4	1.3

higher than those of HQDPA-DMMDA2. For example, compared with HQDPA-DMMDA2, the permeability coefficients of HQDPA-DMMDA1 to  $H_2$ ,  $CO_2$ , and  $O_2$  are increased by 15, 10, and 13% at 30°C, respectively, and the permselectivities for gas pairs  $H_2/CH_4$ ,  $H_2/N_2$ ,  $CO_2/CH_4$ , and  $O_2/N_2$  are increased by 20, 15, 15, and 12% at 30°C, respectively. This evidently indicates that HQDPA-based polyetherimides which have both low chain packing (or large free volume) and low local mobility of polymer chains and/or substituents will possess both high permeability and high permselectivity.

From the data listed in Table 1, it is seen that the special free volumes of both the two HQDPA-DMMDAs are larger than that of HQDPA-MDA, and the local mobility of polymer chains and/or substituents of the former is lower than that of the latter, namely, the sub- $T_g$  transitions of the two HQDPA-DMMDAs are higher than that of HQDPA-MDA, which results in the higher permeabilities and higher permselectivities of the two HQDPA-DMMDAs than those of HQDPA-MDA. For example, as compared with HQDPA-MDA, the permeability coefficients of HQDPA-DMMDA1 to  $H_2$ ,  $CO_2$ , and  $O_2$  are increased by 54, 36, and 48% at 30°C, respectively, and the permselectivities for gas pairs  $H_2/CH_4$ ,  $H_2/N_2$ ,  $CO_2/CH_4$ , and  $O_2/N_2$  are increased by 64, 53, 45, and 47% at 30°C, respectively (Table 2).

Both DMMDAs and IPDA are isomers. Their molecular structures differ only in the positions of the substituted methyl group. The methyl groups in IPDA possess a higher ability to restrict the chain packing of polyetherimide than do those in DMMDAs, while the methyl groups in DMMDAs, particularly in DMMDA1, have a higher ability to restrict the chain segmental movement of polyetherimide than do those in IPDA. Therefore, the special free volume of HQDPA-IPDA is larger than those of HQDPA-DMMDAs, and the local mobility of polymer chains and/or substituents of HQDPA-IPDA is also higher than that of HQDPA-DMMDAs. This makes the gas permeabilities of the two HQDPA-DMMDAs lower than that of HQDPA-IPDA, but the permselectivities higher than that of HQDPA-IPDA. The above discussion indicates that the gas permeability and the permselectivity of polyetherimide can be increased by controlling the molecular structure through the type and number of substituents and the substitute position.

The substitution of methyl groups on 2,2' or 5,5' positions of benzene rings of DMMDA1 to form TMMDA1 and TMMDA2 causes an increase in the sub- $T_g$  transition and a decrease in density of polyetherimides compared with HQDPA-DMMDA1. In other words, HQDPA-TMMDAs have larger special free volumes (or longer average interchain spacing distances) and lower local mobility of polymer chains and/or substituents than HQDPA-DMMDA1. The gas permeability of HQDPA-TMMDAs is much higher than that of the two HQDPA-DMMDAs due to the differences in the special free volumes. For example, compared with HQDPA-DMMDA1, the permeability coefficients of HQDPA-TMMDA1 to  $H_2$ ,  $CO_2$ ,  $O_2$ ,  $N_2$ , and  $CH_4$  are increased by 79, 37, 87, 76, and 90% at 30°C, respectively, and compared with HQDPA-DMMDA2, the permeability coefficients are increased by 105, 50, 110, 76, and 90% at 30°C, respectively. This case seems to indicate that special free volumes play a dominant role in determining the gas permeability as compared with subtle differences in the local mobility of polymer chains and/or substituents. It can be seen from the data listed in Table 3 that the permselectivities of the two HQDPA-TMMDAs for gas pairs  $H_2/CH_4$ ,  $H_2/N_2$ , and  $O_2/N_2$  are higher



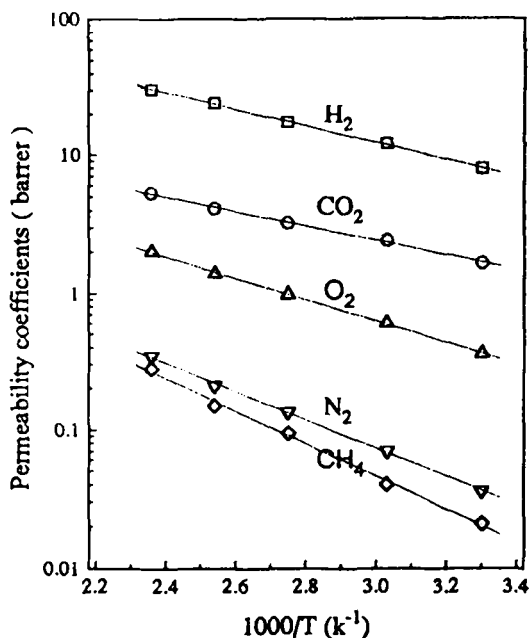


FIG. 1. Temperature dependence of the permeability coefficients of HQDPA-DMMDA1. 1 barrer =  $10^{-10}$  cm<sup>3</sup> (STP) · cm/cm<sup>2</sup> · s · cmHg.

than those of HQDPA-DMMDA2, which again indicates that the gas permeability and the permselectivity of polymers can be controlled by their molecular structure through the type, number, and position of the substitutes.

It should be pointed out that unlike the case of HQDPA-DMMDAs, the local mobility of polymer chains and/or substituents and the special free volumes (or average interchain spacing distances) of two isomeric polyetherimides, HQDPA-TMMDAs, are almost the same, and hence the gas permeability and permselectivity of the two isomeric polyetherimides are also almost the same.

The gas permeability coefficients of a representative polyetherimide, HQDPA-DMMDA1, to H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> are illustrated in the form of Arrhenius plots in Fig. 1. It is obvious that a linear relationship exists between the logarithm of the permeability coefficient ( $\log P$ ) and the reciprocal of the temperature ( $1/T$ ). It is also noticed from Tables 1 and 2 that the structure dependence of the gas permeability and permselectivity of polyetherimides is smaller at high temperatures than at low temperatures.

## CONCLUSION

A series of aromatic polyetherimides was prepared from 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride and (methylene dianiline)s with methyl side groups to investigate the influence of the structure of the diamines, particularly the number and position of the methyl substitutes on the gas permeation properties.

Not only the number but also the position of the methyl substituents on the residues of the methylene dianiline derivatives strongly affects the gas permeabilities and permselectivities of HQDPA-based polyetherimides. The gas permeability of the polyetherimide progressively increases with an increase in the number of methyl side groups. Both the gas permeability and permselectivity of the polyetherimides with methyl side groups on the benzene rings of diamine residues are higher than those of HQDPA-MDA. The gas permeability of the two polyetherimides HQDPA-DMMDAs is lower than that of HQDPA-IPDA, while the permselectivity is much higher than that of HQDPA-IPDA. Both gas permeability and permselectivity of polyetherimide HQDPA-DMMDA1 prepared from 3,3'-dimethyl 4,4'-methylene dianiline are higher than those of the polyetherimides HQDPA-DMMDA2 prepared from 2,2'-dimethyl 4,4'-methylene dianiline.

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