

THE GAS TRANSPORT BEHAVIOR IN AROMATIC POLYESTER MEMBRANES

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ABSTRACT

Six aromatic polyesters were prepared for gas separation membranes, and their permeation properties for hydrogen, oxygen, nitrogen, carbon dioxide, and methane were measured at 30°C and 1 atmosphere by low pressure manometric method. The correlation between the gas transport behavior and molecular structure of aromatic polyester membrane is discussed. These data are interpreted qualitatively in terms of the calculated packing density, gas-polymer interaction, concentration of aryl bromine on backbone, and effect of silane group on main chain of polymer.

INTRODUCTION

The synthesis of polymer specially designed for use as gas separation membrane has become an active area of research in recent years^[1,2]. More and more investigations have been focused on how to improve the gas permeability and permselectivity of membrane. So, it is important to study the correlation between the gas transport behavior and molecular structure of the polymer. There are many kinds of materials which have been accepted for this research, such as polysiloxane^[3], polyimide^[4], and polyester^[5,6], etc.

Poly (phenolphthalein phthalate) has been reported showing excellent gas transport properties^[5,6]. In the present paper, six polyesters from phenolphthalein and tetrabromo-phenolphthalein with bis (p-chlorocarbonylphenyl) dimethylsilane, 4, 4'-biphenyl dicarboxylic chloride, and phthaloyl chloride were prepared for membranes and their gas transport properties were determined. Attention has been paid to investigate that how the molecular structure influences on gas permeation properties in aromatic polyester membranes.

EXPERIMENTAL

Materials

Bis (p-chlorocarbonylphenyl) dimethylsilane was prepared from p-bromotoluene and dichlorodimethylsilane by modification method of Speck and Kovacs^[7,8], including three steps: Grignard reaction in ether, oxidation by potassium permanganate in pyridine and water, and acrylation by thionyl chloride. The resultant compound was recrystallized in petroleum ether, and overall yield is 26.2% of dichlorodimethylsilane, m.p. 69–71°C. Its characteristic of ¹H NMR is:

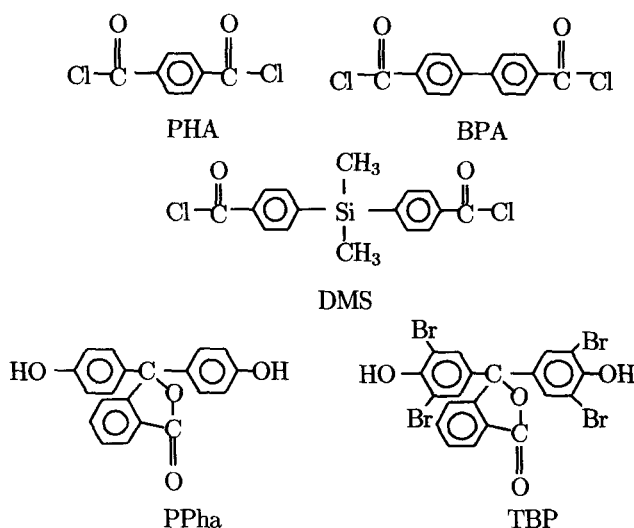
¹H NMR (in CDCl₃ solution): $\delta = 0.6$ (s, methyl), 7.5–8.1 (m, phenylene).

Terephthaloyl chloride and biphenyl dicarbonyl chloride were prepared from terephthalic acid and biphenyl dicarboxylic acid with thionyl chloride, respectively.

Reagent-grade phenolphthalein, tetrabromophenolphthalein, and organic solvents are used without further purification. Gases used in experiment are hydrogen, oxygen, nitrogen, carbon dioxide, and methane, with the purity above 99%.

The method of polycondensation in solution of 1,2-dichloroethane, reported by Morgen^[9], was adopted. The polymer was precipitated in petroleum ether, and washed by methanol and water. The polymer was purified by dissolving in methylene chloride, then precipitated in petroleum ether. The resultant polymer was dried under vacuum at 50°C over night. The molecular structures of monomers are shown in Table 1.

Table 1 The molecular structure of monomers in polyesters synthesis



The membranes were cast from 1 wt. % of polymer in methylene chloride solution

on a flat glass plate in a controlled dust-free environment at room temperature. The membrane thickness is about 70 μm . Then, they were dried completely under vacuum at 50°C for 10 hours before measurement of gas permeation properties.

Table 2 The pertinent physical properties of aromatic polyester

Polymer	Density (g/cm ³)	Packing density 1/ V_f	Conc. of aryl bromine (g/cm ³)	Conc. of carbonyl group (g/cm ³)
PHA-PPha	1.30	2.82	0	0.38
PHA-TBP	1.74	2.77	0	0.32
BPA-PPha	1.27	2.81	0	0.25
BPA-TBP	1.66	2.78	0.72	0.30
DMS-PPha	1.09	2.07	0.62	0.26
DMS-TBP	1.54	2.34	0.54	0.23

The density of the films was measured at 30°C by the density gradient column method using 1, 1, 2, 2-tetrabromoethane and n-hexane. The glassy transition temperature was determined by SR-1C DSC instrument, but it is difficult to determine accurately the glassy transition temperature for aromatic polyester. These data are listed in Table 2.

Measurement of gas permeability and background

The gas permeability J in membrane was determined by K-315-N Gas Permeability Apparatus (Rikaseiki Co., Japan). The gas permeation coefficient P can be calculated by formulae:

$$P = J \times L$$

where L is the thickness of film. According to the solubility-diffusion mechanism, the permeability of a polymer film to gases when the downstream pressure is negligible can be written as^[10]:

$$P = (c/p) \frac{\int_0^c D(c') dc'}{c} = [S] \times [D]$$

$$= [\text{apparent solubility coefficient}] \times [\text{concentration-averaged diffusivity}]$$

where c is the solubility of gas in polymer [cm^3 (STP)/ cm^3 polymer], p is the upstream gas pressure (atm), and $D(c')$ is the apparent concentration-dependent diffusivity of the gas as in Fick's First Law, $N = D(c') \times (dc'/dx)$ ($\text{cm}^2/\text{sec.}$).

The intrinsic permselectivity of the polymer to a pair of gases, a and b , without

reference of any special model, can be represented by:

$$\alpha = P_a/P_b = [S_a]/[S_b] \times [D_a]/[D_b]$$

where $[S_a]/[S_b]$ and $[D_a]/[D_b]$ are defined as solubility selectivity and diffusivity selectivity, respectively.

Diffusivity is determined by time-lag method¹¹, and defined by the relation^[12]:

$$D = L^2/6\theta$$

where θ is the gas diffusion lag-time. The value measured is approximately equal to concentration-averaged diffusivity, and gas permeability/concentration-averaged diffusivity is considered as apparent solubility coefficient.

RESULT AND DISCUSSION

The gas permeability in membrane of aromatic polyester is determined by low pressure manometric method at 30°C and 1 atmosphere. The gas permeation coefficients of hydrogen, oxygen, nitrogen, carbon dioxide, and methane, and separation coefficients for hydrogen over nitrogen, oxygen over nitrogen, and carbon dioxide over methane are shown in Table 3. The gas diffusion coefficients and solubility coefficients of oxygen, nitrogen, carbon dioxide, and methane, as well as diffusivity selectivities and solubility selectivity of oxygen over nitrogen and carbon dioxide over methane are shown in Table 4.

Table 3 The gas permeation coefficients in aromatic polyester
membranes at 30°C and 101325 Pa (1 atm.)

Polymer	$P_{H_2}^*$	P_{CO_2}	P_{O_2}	P_{CH_4}	P_{N_2}	P_{H_2}/P_{N_2}	P_{O_2}/P_{N_2}	P_{CO_2}/P_{CH_4}
PHA-PPha	10.6	9.06	1.62	0.37	0.39	27.2	4.15	24.5
PHA-TBP	17.6	11.8	2.39	0.41	0.57	30.5	4.19	28.8
BPA-PPha	10.4	6.91	1.60	0.28	0.36	28.5	4.35	24.7
BPA-TBP	16.8	14.0	2.53	0.46	0.48	34.7	5.23	30.4
DMS-PPha	27.1	22.2	5.54	1.37	1.29	19.5	3.98	16.2
DMS-TBP	19.0	15.6	3.02	0.74	0.62	30.6	4.87	21.1

* Unit: 1 barrer = 10^{-10} [cm³ (STP) · cm/cm² · s · cmHg].

For gas transport through glassy polymer, gas solubility process is very important. From solubility data in Table 4, it indicates that the gas solubility in these aromatic polyesters decreases for one gas sample as shown:

BPA-TBP > PHA-TBP > PHA-PPha > BPA-PPha > DMS-TBP > DMS-PPha
It means that the gas solubility is affected obviously by two factors except small molecule property: mass concentration of carbonyl group and aryl bromine content on backbone in polymer^[13], for which these two series of data are listed in Table 2. In comparison of the gas solubility in three polymers prepared from phenolphthalein, we can find that solubility rises with increasing mass concentration of carbonyl group on polymer backbone. For polymer from the same acid chloride, the solubility in polymer from tetrabromo phenolphthalein is greater than that from phenolphthalein. The gas solubility in polymer from PHA and BPA is greater than that from DMS polymer, because mass concentration of carbonyl group and aryl bromine in aromatic polyester decrease when silane group is introduced into polymer backbone.

Table 4 The gas diffusion coefficients, and solubility coefficients, diffusivity selectivity, and solubility selectivity in membrane of aromatic polyester at 30°C and 101325 Pa (1 atm.)

Polymer	$D_{O_2}^*$	D_{O_2}/D_{N_2}	$S_{O_2}^{**}$	S_{O_2}/S_{N_2}	D_{CO_2}	D_{CO_2}/D_{CH_4}	S_{CO_2}	S_{CO_2}/S_{CH_4}
PHA-PPha	5.14	2.04	31.4	19.2	1.83	0.84	496	44.1
PHA-TBP	6.22	1.43	38.5	40.0	1.67	0.98	705	41.9
BPA-PPha	6.94	4.64	23.1	7.84	6.91	1.54	100	18.2
BPA-TBP	2.96	0.86	85.6	55.9	1.12	0.57	1240	80.3
DMS-PPha	222	92.8	2.49	1.39	117	32.7	19.0	4.19
DMS-TBP	24.1	12.3	7.89	5.06	18.2	8.20	85.5	9.02

* Unit: 10^{-8} [cm²/s] ** Unit: 10^{-4} [cm³/cm³·cmHg]

According to Chern’s theory, on the basis of packing density consideration alone, the diffusivity of a given gas in a polymer with larger packing density is expected to be lower than that in a polymer with a smaller packing density^[5,6]. A parameter to represent the packing density $1/V_f$ of a glassy polymer is defined as^[5,6]:

$$1/V_f = V/(V - V_W)$$

where V is the molar volume of the structure unit. The van der Waals volume V_W is calculated by group-contribution method. For DMS polymers, the contribution value of silicon atom is defined as 10, which is almost the same as that of sulfur atom^[14] since the value of silicon atom can not be found in the literature. Because the value of $(V - V_W)$ is bigger than 200, it is considered that the deviation of calculation is not much. The data are listed in Table 2. The packing density of polymer is correlated closely with the gas diffusivity, and it will be mentioned later.

For these six aromatic polyesters, it is clearly illustrated in Fig. 1 what the correlation between the gas diffusivity and packing density is. The gas diffusivity in DMS polymers is much higher than that of PHA and BPA polymers. It means that the diffusivity is obviously influenced by silane group on main chain of polymer. The effect of silane group on the gas diffusivity in polymer can be reflected by the value of packing density. The smaller packing density of silicon-containing polymers corresponds to looser packing and is easier for gas transport by diffusion process through polymer than others. The other reason for the improvement of diffusivity when silane group is introduced into aromatic polymer, we consider, is that limit of movement for stiff aromatic polymer main chain is reduced^[15].

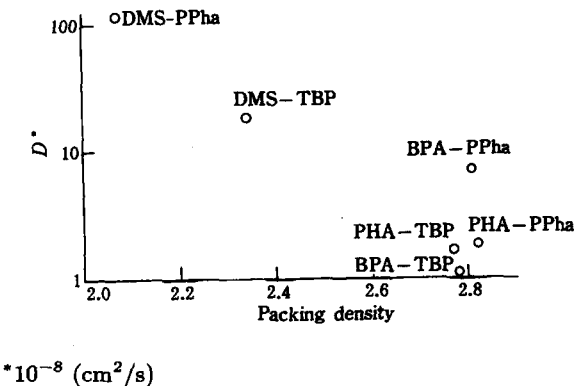
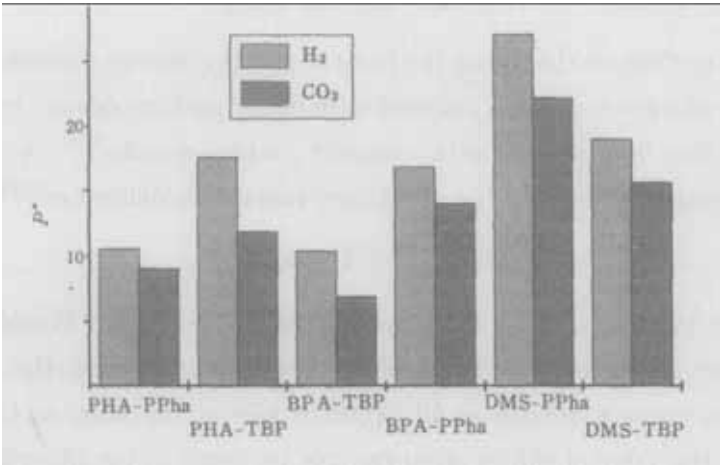


Fig. 1 Correlation between packing density and the gas diffusion coefficient of carbon dioxide in aromatic polyesters at 30°C and 101325 Pa (1 atm.)



* barrer

Fig. 2 Comparison of permeability of hydrogen, and carbon dioxide in membrane of aromatic polyesters at 30°C and 101325 Pa (1 atm.)

Besides the effect of silane group in polymer, aryl bromine on polymer backbone is also another important factor for the gas diffusivity in aromatic polyesters. The diffusivity in tetrabromo phenolphthalein polymer is lower than that in phenolphthalein polymer.

The gas permeability of hydrogen and carbon dioxide in these polymers are compared in Fig. 2, and the results of other gas are roughly the same. We can conclude that the gas permeability in PHA and BPA polymers rises when aryl bromine is introduced into their main chain, but for polymer containing silane group, permeability in DMS-PPha is higher than that of DMS-TBP. Because of similar structure of polymers, the different result of polymers can be considered as both the effects of mass concentration of carbonyl group and aryl bromine, and silane group on gas permeability in polymer. In silicon-containing polymer, the diffusion procedure is more important because of the effect of silane group, but the solubility procedure is more important in non-silicon containing aromatic polyesters, as effect of functional groups for carbonyl group and aryl bromine in polymers.

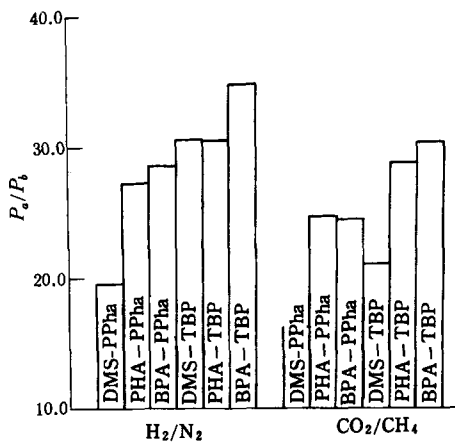


Fig. 3 Comparison of permselectivity of hydrogen/nitrogen, and carbon dioxide/methane in membrane of aromatic polyesters at 30°C and 101325 Pa (1 atm.)

The gas permselectivity for hydrogen over nitrogen and carbon dioxide over methane are shown in Fig. 3. It indicates that the gas permselectivity in polymers with aryl bromine are higher than those without bromine. According to literature, raising concentration of carbonyl group in polymer leads to favorable increasing in the solubility of carbon dioxide, because of polar interaction, relative to that of a nonpolar gas such as methane^[16]. In other words, the solubility selectivity of carbon

dioxide over methane would rise with increasing concentration of carbonyl group in polymer. The correlation for these aromatic polyesters is clearly shown in Fig. 4. In addition to carbonyl group on polymer backbone, it is found that aryl bromine is another functional group that has special effect with carbon dioxide because of polar interaction also. We can infer the relationship between gas solubility selectivity for carbon dioxide over methane and concentration of both carbonyl group and aryl bromine on polymer backbone. The value of gas selectivity is influenced obviously by solubility selectivity.

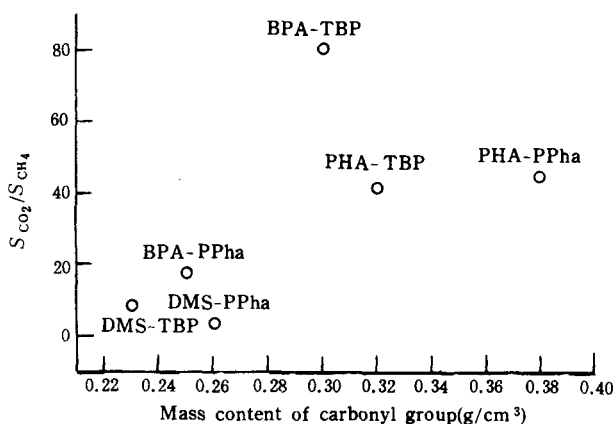


Fig. 4 Correlation between mass concentration of carbonyl group and gas solubility-selectivity of carbon dioxide/methane in membrane of aromatic polyester at 30°C and 101325 Pa (1atm.)

CONCLUSION

For non-silicon containing aromatic polyesters, the packing density of PHA-PPha is similar to that of BPA-PPha, and PHA-TBP is similar to BPA-TBP. The packing density of BPA-PPha and PHA-PPha both decreases with introduction of aryl bromine on their backbone. For silicon-containing polymers, their packing densities are much lower than those of PHA and BPA polymers, and the packing density of DMS-PPha is smaller than that of DMS-TBP. The packing density is closely correlated with the gas diffusivity in glassy polymer, which corresponding small packing density has higher diffusivity than polymer with large packing density. But the rule is unfit by check of phenolphthalein polymers against tetrobromophenol phthalein polymers from PHA and BPA. From similar molecular structure

of aromatic polyesters, it is found that silane group and aryl bromine are important factors for gas diffusion process in polymer. The gas solubility process correlates closely with two factors: (1) the concentration of carbonyl group and (2) content of aryl bromine on polymer backbone, because of polar interaction of gas-carbonyl group and aryl bromine. For polymers from PHA and BPA, the gas permeability and permselectivity are greater than those in polymers from phenolphthalein. But permeability in DMS-TBP is lower than in DMS-PPha, permselectivity is higher.

Keywords:

Aromatic polyester; Gas separation membrane; Gas permeability; Gas permselectivity

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