Gas Permeability in an Aromatic Polyester

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ABSTRACT: A series of copolymers of phenolphthalein with 4,4'-biphenyl dicarbonyl chloride and bis[*p*-(chlorocarbonyl)phenyl]dimethylsilane were synthesized, and their flexible films were cast readily. The gas transport properties for hydrogen, oxygen, nitrogen, carbon dioxide, and methane in membranes were measured by a low pressure method at 30 °C and 1 atm. As the solubility–diffusion process analysis, how the molar content of the silane segment on the polymer backbone affects the behavior of gas transport through an aromatic polyester was studied. It is sure that the packing density is an important factor for determining the gas diffusivity in a polymer. With the increasing molar content of the silane segment, the packing density reduces and the gas diffusivity in the aromatic polyester increases. Contrary to that, gas solubility reduces. Meanwhile, both diffusivity selectivity and solubility selectivity decrease. The result is that gas permeability rises and permselectivity for hydrogen over nitrogen, oxygen over nitrogen, and carbon dioxide over methane in a membrane of an aromatic polyester reduces with the introduction of a silane segment on the polymer backbone. The correlation between the concentration of the carbonyl group and the gas solubility selectivity is discussed in this paper. At the end, we compare the gas transport properties of those aromatic polyesters with common commercial polymer materials used as the separation membrane.

Introduction

Recent intensified research for better gas-separation membrane and permeation barrier materials has led to the discovery of many polymers exhibiting extraordinary transport properties.[1-4] So, it is important to explain how the molecular structure of the polymer material affects the gas transport property in it. In this paper, our interest is in the correlation between the chemical structure of the polymer and the gas transport property, such factors as gas permeability and permselectivity, for further research that will lead to the preparation of better material.

One of the polymers, which is found to exhibit the gas transport property superior to commercial materials, is the aromatic polyester polycondensed from phenolphthalein and phthalic acid.[5-10] To improve its permeation behavior, a series of aromatic polyesters from phenolphthalein, whose molecular structures are almost the same as polyphthalate except containing various molar contents of the silane segment on their backbones, were synthesized. By a method of gas molecule penetration through the polymer membrane, we researched seriously the influence of the silane segment on the gas transport properties in aromatic polyesters, whose chemical natures are essentially the same.

The gas permeation properties could be determined by the instrument of low pressure method, and gas permeability J [cm^3(STP)/(cm^2 s cmHg)] would be calculated directly. Then the gas permeation coefficient P [cm^3(STP) cm/(cm^2 s cmHg)] can be decided by the following formula:

$$P = JL$$

where L [cm] is the thickness of the film. According to the solubility–diffusion mechanism, the permeability of a polymer film to gases when the downstream pressure is zero can be written as[4]

$$P = (c/p)\frac{\int_0^c D(c')\,\mathrm{d}c'}{c} = [S][D]$$

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

where c is the solubility of gas in the 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, $N = D(c')(\mathrm{d}c'/\mathrm{d}x)$ (cm^2/s).

The intrinsic permselectivity of the polymer to a pair of gases, a and b, without reference to any special model, can be represented by

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

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

Diffusivity is determinted by the time-lag method[11,12] and defined by correlation;[13,14]

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

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

Experimental Section

Monomers. All chemical reagents and organic solvents were purchased commercially in China and were used without further

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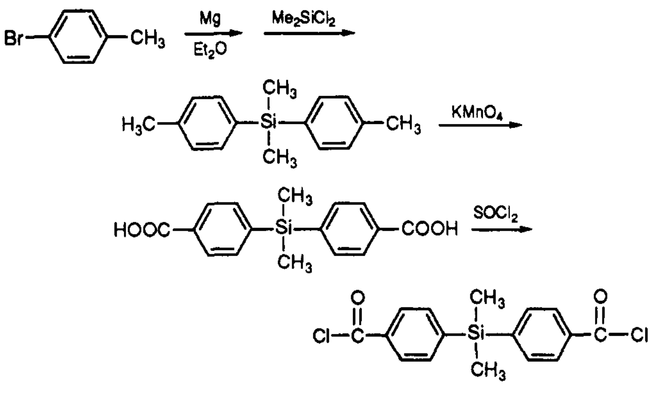
purification. Hydrogen, oxygen, nitrogen, carbon dioxide, and methane were used in this experiment, and all their purities are greater than 99.9%.

Bis[p-(chlorocarbonyl)phenyl]dimethylsilane was synthesized from p-bromotoluene and dichlorodimethylsilane by a modified method of Speck and Kovacs.[15-18] The methods for preparation of bis[p-(chlorocarbonyl)phenyl]dimethylsilane are shown as the following reaction:



and its detail steps follow.

p-Toluene (28.2 g) in 15 mL of absolute ether was added dropwise to a mixture of 10.0 g of dichlorodimethylsilane, 4.5 g of magnesium, and 35 mL of absolute ether to maintain the mixture refluxing under nitrogen atmosphere, and the reaction was initiated by iodomethane or iodine. Then the mixture was refluxed for an additional 2 h. After ether was evaporated completely, the mixture was kept at 180 °C for 10 h and then was poured into 50 mL of water. The aqueous solution was extracted three times by ether, and the merged ether solution was dried by magnesium sulfate. After evaporation of the ether, bis(p-tolyl)dimethylsilane was collected at 125–135 °C/0.1 mmHg. The product yield was 14.1 g.

Bis(p-tolyl)dimethylsilane (14.1 g) was dissolved in 90 mL of pyridine and 45 mL of water, and then 55 g of potassium permanganate was added several times at 60 °C to keep the solution refluxing. The mixture was refluxed for an additional 2 h and then cooled to room temperature. The mixture was separated by filtration, and the solid was washed two times with pyridine. In an ice bath, bis[p-carboxylphenyl]dimethylsilane was precipitated by hydrochloric acid from the above filtrate and then collected by filtration. The white compound was purified by dissolving in sodium carbonate aqueous solution and precipitating by hydrochloric acid. Completely dried solid was dissolved in absolute ether, and undissolved material was removed by filtration. The filtrate was concentrated until solid appeared in solution; then an equal volume of petroleum ether was added. White crystals (8.4 g) were collected at 0 °C, mp 279–285 °C.

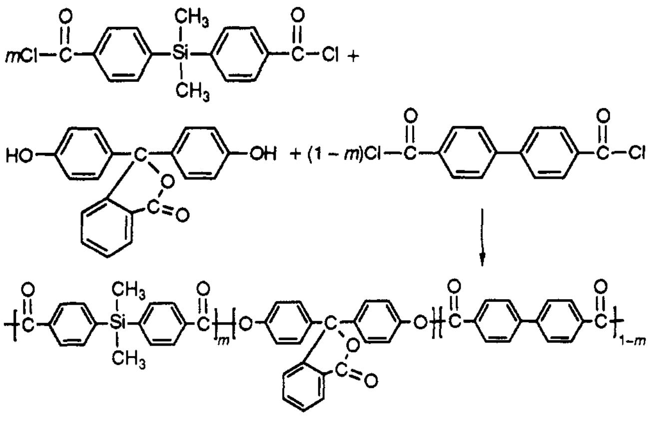
Bis[p-carboxyphenyl]dimethylsilane (2.0 g) was added to 25 mL of thionyl chloride, and the mixture was refluxed for 1 h. After excess thionyl chloride was completely evaported, the remainder was recrystallized in petroleum ether. The resultant yield of the white compound of bis[p-(chlorocarbonyl)phenyl]dimethylsilane was 1.6 g, mp 69–71 °C.

The overall yield was 26.2% of the dichlorodimethylsilane effect. The characteristics of ^{1}H NMR for bis[p-(chlorocarbonyl)phenyl]dimethylsilane are as follows: ^{1}H NMR (in $CDCl_3$ solution) δ 0.6 (s, methyl), 7.5–8.1 (m, phenylene).

The chemical structure of the resultant compound was confirmed by ^{1}H NMR spectra.

4,4′-Biphenyl dicarbonyl chloride was prepared from 4,4′-biphenyldicarboxylic acid with thionyl chloride by refluxing for 12 h. After excess thionyl chloride was completely evaporated, the resultant compound was recrystallized in petroleum ether.

Polycondensation. The polycondensation procedures reported by Morgan[19] were used, and its reaction proceeded as follows:



m: 0, 0.25, 0.50, 0.75, 1.00

An ice-cooled 25-mL 0.8 N solution of acid chloride in 1,2-dichloroethane was added dropwise to a 25-mL solution of 0.8 N phenolphthalein and 0.8 N triethylamine in 1,2-dichloroethane for 1 h. The mixture was kept at room temperature for 1 h.

An additional 50 mL of 1,2-dichloroethane was added to dilute it. The polymer was precipitated in 250 mL petroleum ether and then recovered by filtration. The polymer was purified by dissolving it in methylene chloride and pouring the filtrate into a large volume of petroleum ether. The resultant precipitate was filtered and dried completely under vacuum at 50 °C for 10 h.

The molar content of bis[p-(chlorocarbonyl)phenyl]dimethylsilane in the polymer is listed in Table I. The density of the sample was determined by way of a mixture of organic solvents; those data are useful for calculating the packing density of a polymer. The glassy transition temperature is not obvious to measure by DSC and impossible to show in the paper.

Preparation of the Membrane and Gas Permeability Measurement. The membrane was cast from 1.0 wt % methylene chloride solution onto a flat glass plate in a controlled dust-free environment at room temperature. It takes about 24 h, and the membrane thickness is about 70 μm. Then the membrane was completely dried under vacuum at 50 °C overnight.

The gas permeation properties in a membrane of the aromatic polyester were determined by a K-315-N gas permeability apparatus (Rikaseiki Co., Japan).

Results and Discussion

The resulant polymers are white solids and dissolve in ordinary organic solvents, such as methylene chloride, chloroform, etc. In Table II, the density, mass concentration of the carbonyl group, and packing density $1/V_f$ of the aromatic polyester are listed. The densities decrease with increasing molar content of the silane segment in them. A parameter of packing density for a glass polymer is defined[5-8]

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

where V is the molar volume of the structure unit. The van der Waals volume V_w is calculated by a group-contribution method.[20,21] The contribution value of the silicon atom, which cannot be found in the literature, is defined as 10, that is, approximately the value of the sulfur atom. We consider that the derivation is not high for a value of $(V - V_w) > 200$. In comparison of this series of polymer, the packing density reduces with the increasing molar content of the silane segment in the polymer, and four kinds of polymers with the 4,4′-biphenyl dicarbonyl segment on their backbones do not have very different packing densities, but the polymer with the 100% bis[p-carbonylphenyl]dimethylsilane segment, whose value is much lower. The packing density correlates closely with the gas diffusivity in glassy polymers,[5-8] and we will mention that later.

Table I. Molar Content of Bis[*p*-(chlorocarbonyl)phenyl]dimethylsilane Monomer in Polymer

polymer	no. 1	no. 2	no. 3	no. 4	no. 5
content (percent)	0.0	25.0	50.0	75.0	100

Table II. Some Pertinent Properties of Aromatic Polyesters

polymer	density (g/cm^3)	density of the carbonyl group (g/cm^3)	$1/V_f$
no. 1	1.27	0.317	2.84
no. 2	1.26	0.309	2.80
no. 3	1.25	0.298	2.78
no. 4	1.23	0.286	2.75
no. 5	1.09	0.257	2.31

Table III. Gas Permeation Coefficients and Separation Coefficients in Membranes of Aromatic Polyesters at 30 °C and 1 atm

	polymer				
	no. 1	no. 2	no. 3	no. 4	no. 5
P_{H_2}[a]	10.4	11.7	14.1	19.8	27.1
P_{CO_2}	6.91	9.08	11.7	12.6	22.2
P_{O_2}	1.60	1.63	2.49	2.83	5.54
P_{CH_4}	0.365	0.372	0.594	0.693	1.39
P_{N_2}	0.282	0.427	0.637	0.705	1.37
P_{H_2}/P_{N_2}	28.5	31.4	23.7	28.6	19.5
P_{O_2}/P_{N_2}	4.38	4.38	4.19	4.08	3.98
P_{CO_2}/P_{CH_4}	24.5	21.3	18.4	17.9	16.2

[a] Unit: 1 bar = 10^{-10} cm^3(STP) cm/(cm^2 s cmHg).

Table IV. Gas Diffusivity, Diffusivity Selectivity, Solubility, and Solubility Selectivity for Oxygen, Nitrogen, Carbon Dioxide, and Methane in Membranes of Aromatic Polyesters at 30 °C and 1 atm

	polymer				
	no. 1	no. 2	no. 3	no. 4	no. 5
D_{O_2}[a]	12.8	28.9	81.7	105	222
D_{O_2}/D_{N_2}	2.60	2.55	2.49	2.47	2.22
S_{O_2}[b]	12.5	5.64	3.05	2.70	2.49
S_{O_2}/S_{N_2}	1.59	1.68	1.69	1.66	1.79
D_{CO_2}	6.91	16.1	36.1	52.0	117
D_{CO_2}/D_{CH_4}	4.49	4.17	3.61	3.67	3.58
S_{CO_2}	100	56.5	32.4	24.2	19.0
S_{CO_2}/S_{CH_4}	5.49	5.14	5.08	4.88	4.53

[a] Unit: 10^{-8} cm^2/s. [b] Unit: 10^{-4} cm^3/(cm^3 cmHg).

The gas permeabilities in the membrane of the aromatic polyester were determined by a low pressure method at 30 °C and 1 atm. The permeation coefficients of hydrogen, oxygen, nitrogen, carbon dioxide, and methane and separation coefficients of hydrogen over nitrogen, oxygen over methane, and carbon dioxide over methane are summarized in Table III. The gas diffusion coefficients, solubility coefficients, diffusivity selectivity, and solubility selectivity of oxygen, nitrogen, carbon dioxide, and methane are listed in Table IV. For hydrogen, it is too high to determine its gas diffusivity by the time-lag method used with the *K*-315-N permeability apparatus.

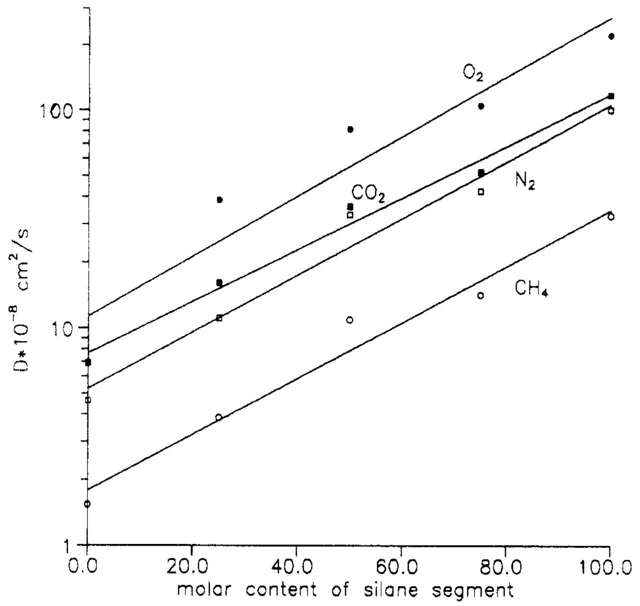


Figure 1. Correlation between the gas diffusion coefficient and molar content of the silane segment in the aromatic polyester at 30 °C and 1 atm.

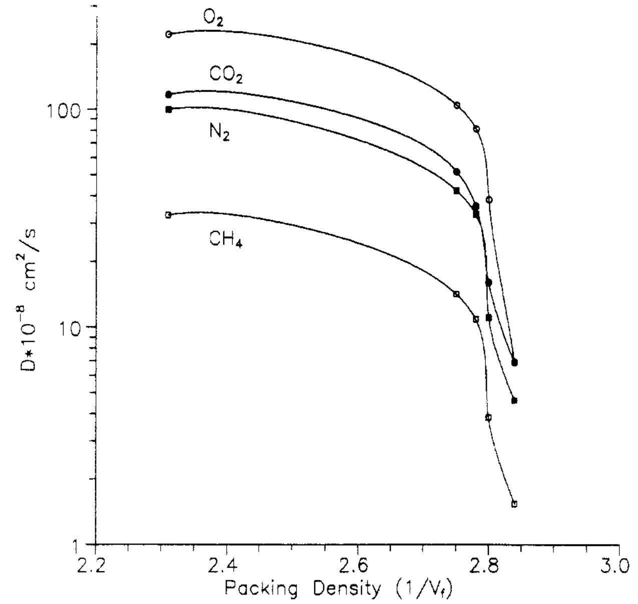


Figure 2. Correlation between the gas diffusion coefficient and packing density in the aromatic polyester at 30 °C and 1 atm.

The effect of polymer chemical structure on the gas transport property will be discussed, especially the influence of the silane segment on the polymer backbone. For a glassy polymer, a given gas penetrates through it by two processes: solubility and diffusion. First, we focus on the gas diffusion step. In Figure 1, it is clearly illustrated that the gas diffusivity rises with increasing content of the silane segment in the polyester. It means that the content of the silane segment on the polymer main chain is an important factor for determining the change of the gas diffusive property. In our other paper,[22,23] we have studied the effect of the silane segment on the gas transport through the membrane of a silicon-containing aromatic polyamide. Because the backbone of an aromatic polymer is rigid, introduction of a flexible silane segment on the polymer main chain may improve its gas diffusivity in the polymer. In other words, it indicates that the gas diffusion coefficient depends on the content of the silane segment for this series of aromatic polyesters.

As in Chern's theory, on the basis of packing density considerations alone, the diffusivity of a given gas in a polymer with a large packing density, which corresponds a higher packing, is expected to be lower than that in a polymer with a small packing density.[5-8] The correlation between gas diffusivity and packing density is shown in Figure 2. For aromatic polyesters in this paper, we know that they have roughly the same packing densities and their values rise with the decreasing content of the silane segment, except the sample with 100% molar content of the silane segment. So, the gas diffusivity rises with the increasing content of the silane segment, and meanwhile, decreasing packing density.

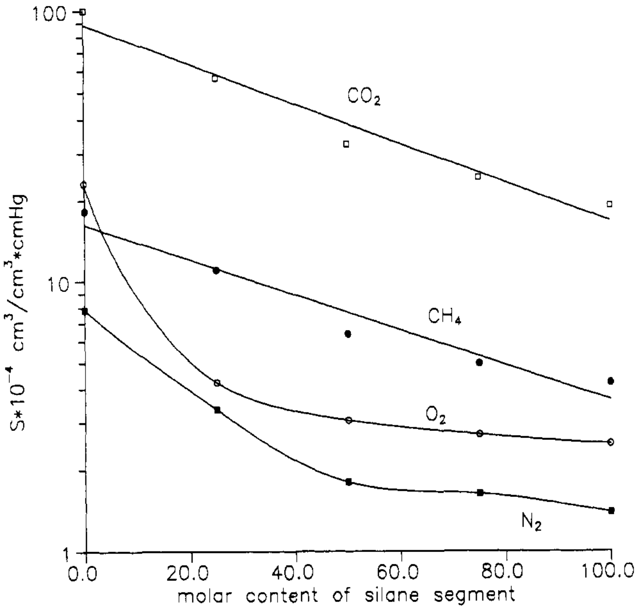


Figure 3. Correlation between the gas solubility coefficient and molar content of the silane segment in the aromatic polyester at 30 °C and 1 atm.

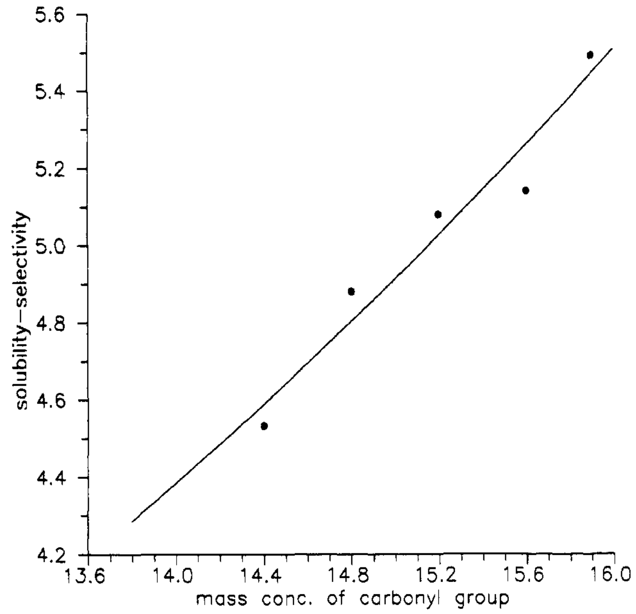


Figure 4. Correlation between the gas solubility selectivity and mass density of the carbonyl group in the aromatic polyester at 30 °C and 1 atm.

Then, the gas solubility is the other elementary factor for the gas transport behavior, in addition to diffusivity. It is found in Figure 3 that the gas solubility reduces with the increasing content of the silane segment on the polymer main chain. In Koros' and our papers, the concentration of the carbonyl group, as a functional group, is an important factor for determining the gas solubility in polymers and organic compounds, especially a condensed gas such as carbon dioxide.[24,25] The correlation between the mass concentration of the carbonyl group in this series of aromatic polyesters and the solubility selectivity of carbon dioxide over methane is plotted in Figure 4. It is sure from data in Table II and Figure 4 that as the density of the carbonyl group in the polymer reduces with the increasing content of the silane segment, solubility decreases.

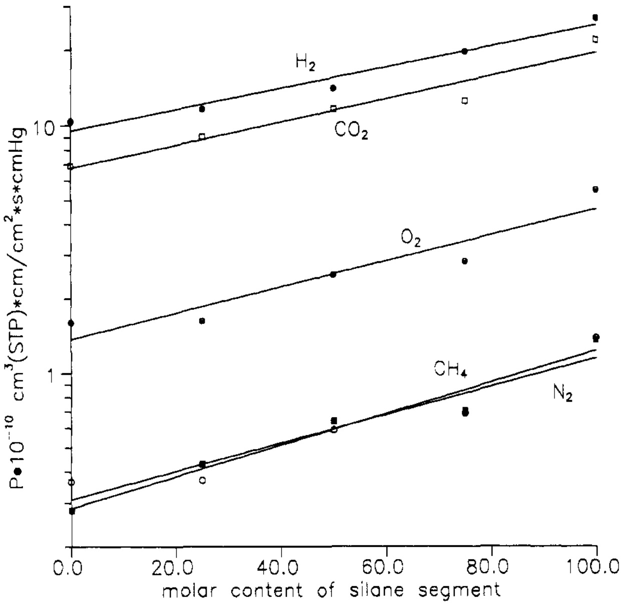


Figure 5. Correlation between the gas permeation coefficient and molar content of the silane segment in the aromatic polyester at 30 °C and 1 atm.

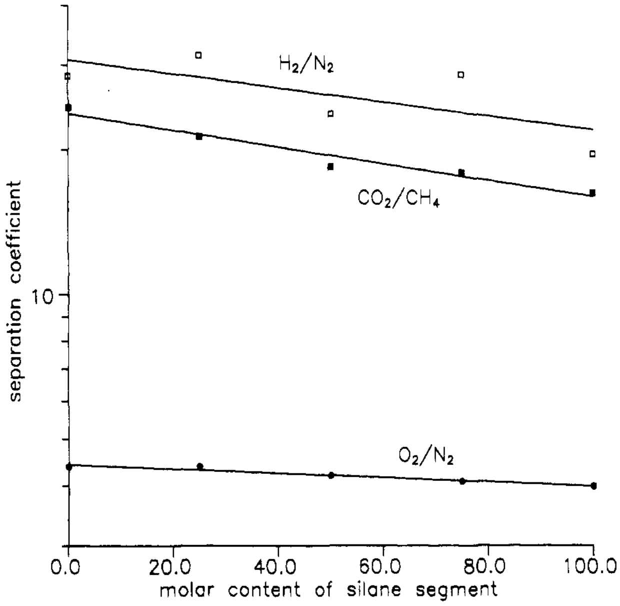


Figure 6. Correlation between the gas separation coefficient and molar content of the silane segment in the aromatic polyester at 30 °C and 1 atm.

The gas permeation coefficient is the product of the gas diffusion coefficient and solubility coefficient. Even though there are different developments of the gas diffusivity and solubility, the result is that gas permeability rises with the increasing content of the silane segment in the polymer. It means that a gas molecule penetrates through the membrane more quickly with introduction of a silane segment on the polymer main chain, as shown in Figure 5.

The gas permselectivity in the polymer reduces with the increasing content of the silane segment, and the relationship is shown in Figure 6. For carbon dioxide over methane, its solubility selectivity reduces with the decreasing mass density of the functional group, which is the carbonyl group for the current aromatic polyester, as we have discussed above. It is easily understood that diffusivity selectivity decreases with the increasing gas diffusivity. The data are plotted and compared in Figure 7. It indicates that both the gas diffusivity selectivity and solubility selectivity for carbon dioxide over methane decrease with the increasing content of the silane segment.

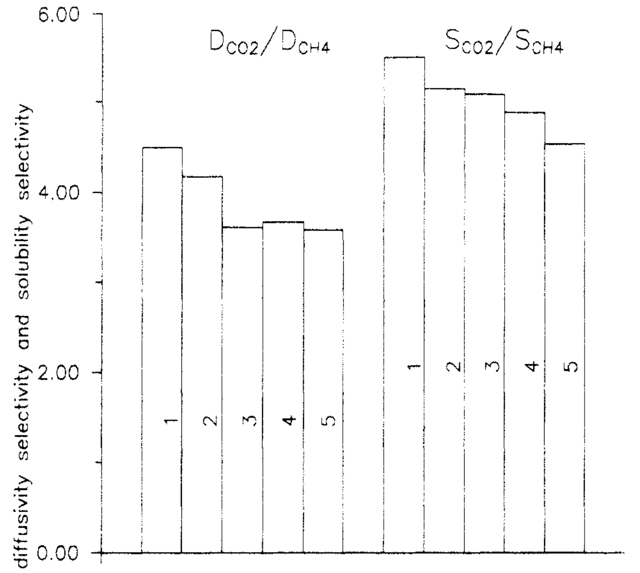


Figure 7. Comparison of gas diffusivity selectivity and solubility selectivity for carbon dioxide over methane in the aromatic polyester.

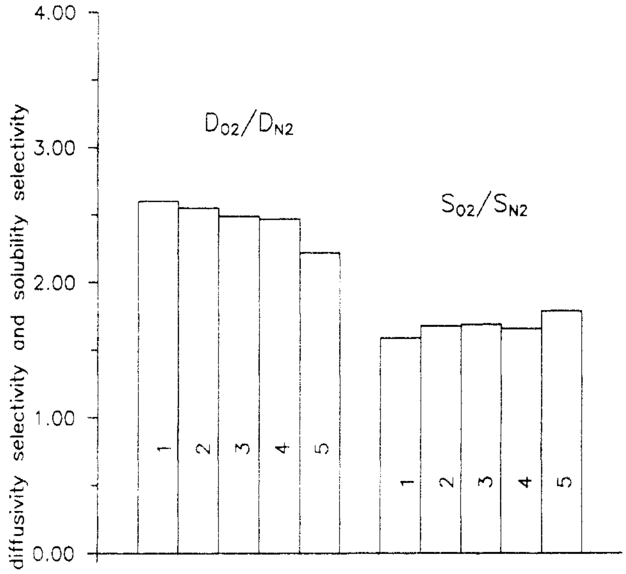


Figure 8. Comparison of gas diffusivity selectivity and solubility selectivity for oxygen over nitrogen in the aromatic polyester.

For oxygen over nitrogen, its diffusivity selectivity changes in the same way as that of carbon dioxide over methane, but its solubility selectivity changes not much and unstably because the physical properties of oxygen and nitrogen are much different from those of carbon dioxide and methane. The comparison of diffusivity selectivity and solubility selectivity for oxygen and nitrogen is shown in Figure 8. We think that there could be an effect for hydrogen over nitrogen similar to that for oxygen over nitrogen. So, the result is easily understood that the gas permselectivity decreases with the increasing content of the silane segment on the polymer backbone.

Permselectivities of carbon dioxide over methane are plotted in Figure 9 against the gas permeabilities of carbon dioxide for a representative group of commercial polymers often considered for this application. Among the common commercial polymers, one can see a general rule: polymers with higher selectivities usually have lower permeabilities.[26] All the current aromatic polyesters prepared in the paper fit for the curve in Figure 9, as shown. In other words, the relationship between permeability and permselectivity in these five aromatic polyesters is the same as that in applied glassy materials.

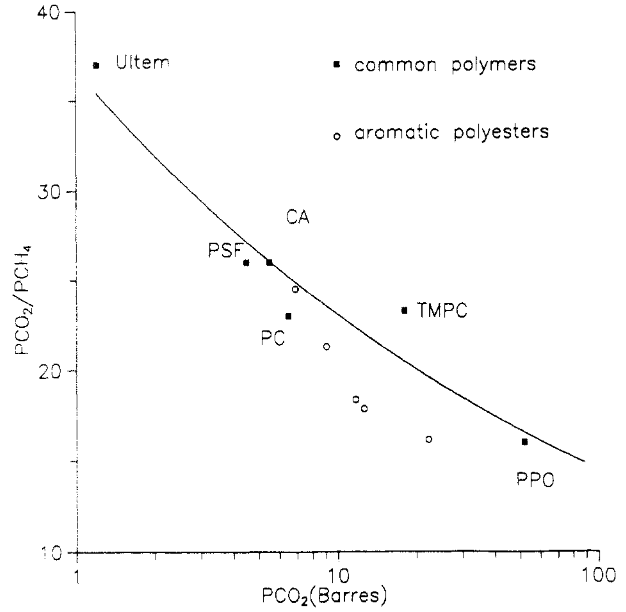


Figure 9. Correlation between the gas permeability and permselectivity for carbon dioxide over methane in common polymer materials used as the gas separation membrane and aromatic polyester prepared in this experiment.

Summary

Aromatic polyesters with various molar contents of silane segments were synthesized; their gas penetration behavior and pertinent physical properties were studied. From correlation between the chemical structure and gas transport property, we focus on the transport process of hydrogen, oxygen, nitrogen, carbon dioxide, and methane through the aromatic polyester as the solubility–diffusivity analysis. It indicates that with the increasing molar content of the silane segment, the gas diffusivity rises, but solubility reduces. It reveals that packing density, which correlates closely to the molar content of the silane segment on the aromatic polyester backbone, is an important factor for determining the gas diffusivity. Meanwhile, the gas solubility is dependent on the concentration of the carbonyl group in the polymer. The result is that the gas permeability increases, but selectivity decreases with the increasing content of the silane segment in the aromatic polyester. Compared with common commercial polymer materials used as the gas separation membrane, those aromatic polyesters have similar rules and fit the curve for the correlation between the gas permeability and permselectivity to the gases used in this experimental measurement.

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