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Gas Permeability and Selectivity of Poly(Organophosphazene) Membranes

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Abstract

The gas permeabilities and selectivities were determined for some poly(organophosphazene) membranes. It was found that $[NP(OC_6H_2Et\text{-}p)_2]_n$ had the highest selectivity for nitrogen or hydrogen, and $[NP(OCH_2CF_3)_2]_n$ had the highest selectivity for carbon dioxide or helium gas. Selectivity was not dependent on the glass transition temperatures and dielectric constants of the membranes. Increasing the gas permeability tended to accompany an increasing dielectric constant. The activation energy of gas permeability for some membranes was measured at various temperatures. The results showed that the magnitude of the activation energy was not related to the covalent radii or dielectric constant of such gases as H_2, N_2, O_2, CO_2, and He.

INTRODUCTION

Gas permeabilities and separations have been investigated by many researchers by using various organic polymer membranes, but there have been few paper about gas permeabilities and separations with inorganic polymer membranes. The study of gas permeabilities and separations of poly(organophosphazenes) membranes such as $(NPR_2)_n$ or $(NPR^1R^2)_n$ has been especially interesting to industrial and academic research. As for gas separation by poly(organophosphazenes) membranes of inorganic polymers, Bittirova (*1*) reported the gas permeabilities of O_2, N_2 and Ar by using $[NP(OC_8H_{17})_2]_n$ transparent elastic films. The permeabilities to O_2, N_2 and Ar were 12.84×10^{-7}, 5.25×10^{-7}, and 11.88×10^{-7} $cm^3 \cdot cm/cm^2 \cdot s \cdot atm$, respectively.

Kajiwara (*2*) described that for 10 kinds of poly(organophosphazenes) prepared, the membrane having the formula $[NP(OC_6H_4Cl\text{-}p)_2]_n$ had the highest selectivity for O_2/N_2: 3. Recently, McCaffrey (*3*) reported the gas transport behavior and membrane microstructure of poly(phenoxyphosphazenes).

The objective of this study was to determine the permeability of H_2, CO_2 and He gases and the selectivities of N_2 to O_2, H_2, and CO_2; CO_2 to H_2, O_2, and N_2; H_2 to O_2, N_2, CO_2, and He; and He to H_2, N_2, O_2, and CO_2.

EXPERIMENTAL

Preparation of Hexachlorocyclotriphosphazene $(NPCl_2)_3$ and Poly(Dichlorophosphazene) $(NPCl_2)_n$

$(NPCl_2)_3$ was synthesized by the method of Saito (*4*) and was prepared from the reaction of 500 g phosphorus pentachloride (PCl_5) and 200 g ammonium chloride (NH_4Cl) by using 1500 mL tetrachloroethane. Pure $(NPCl_2)_3$ (mp 112°C) was obtained by repeated vacuum distillation.

Linear poly(dichlorophosphazene) $(NPCl_2)_n$ was prepared by the method of Kajiwara (*5*): 5 g $(NPCl_2)_3$ and 0.1 g sodium dibutyldithiocarbamate were placed in a three-necked flask equipped with a stirrer and a condenser, which was then evacuated to 10 torr for 1 h. Then, 5 g *o*-dichlorobenzene was added to the flask, and the mixture was heated to 190°C for 24 h in a flow of dry nitrogen. After the reaction was completed, the polymer–oligomer mixture was dissolved in 200 mL dry tetrahydrofuran (THF). To remove the oligomer, the THF solution was added to 500 mL *n*-heptane. After $(NPCl_2)_n$ precipitated, the precipitate was separated by decantation, followed by dissolution in THF and reprecipitation. This purification procedure was repeated several times, and the purified $(NPCl_2)_n$ was then dissolved in 100 mL THF.

Preparation of Poly(Organophosphazenes) $(NPR_2)_n$

Various poly(organophosphazenes) $(NPR_2)_n$ were formed by using nucleophilic reagents such as alkoxide, phenoxide, and amine compounds via a modified method due to Allcock (*6*). The preparations of typical poly(organophosphazenes) were as follows.

(*1*) *Synthesis of* $[NP(OCH_2CF_3)_2]_n$

A solution of sodium trifluoroethoxide was prepared by the addition of sodium (6 g) to 2,2,2-trifluoroethanol (25 g) in dry THF (200 mL). The reaction mixture was added dropwise to a stirred solution of $(NPCl_2)_n$ dissolved in THF. The reaction was exothermic, and the mixture was heated to keep the solvent boiling for 20 h. At the end of the reaction, the mixture was cooled and acidified with dilute hydrochloric acid, and benzene was added to coagulate the polymer. After isolation of the polymer by filtration, it was washed with a large excess of water to remove salts and then precipitated from THF into benzene to remove oligomer and low-molecular-weight polymers. The polymer was then exhaustively dried under vacuum.

(2) *Synthesis of* $[NP(NEt_2)(NHBu\text{-}n)]_n$

A solution of $(NPCl_2)_n$ (20 g) dissolved in THF was added dropwise over 2 h to a stirred solution of diethylamine (21.2 g) in 100 mL THF. The reaction was allowed to proceed at 25°C for 24 h. Then *n*-butylamine (15 g) and triethylamine (20 g) dissolved in 50 mL THF were added dropwise over 2 h. The reaction mixture was allowed to remain at 25°C for 24 h. The mixture was then filtered to remove amine salts, and the polymer was precipitated from the filtrate by addition to heptane. Purification was effected by precipitation of the polymer three times from solution in dilute aqueous sulfuric acid into dilute acetic acid in ethanol or methanol which contained a trace of triethylamine. The polymer was then dried under vacuum over P_2O_5.

Preparation of Poly(Organophosphazene) Membranes

Some 5 or 10 g $(NPR_2)_n$ was dissolved in 100 mL THF, and the solution was filtered through a glass filter. The filtered solution was added to a Petri dish, and a protective covering was put over it. The Petri dish was kept at room temperature, and the solvent was slowly evaporated over several hours until a film was formed in the presence of solvent at room temperature. The films thus prepared were dried at reduced pressure at 50°C for 10 h.

Measurement of Oxygen Permeability of Poly(Organophosphazene) Membranes

The oxygen, nitrogen, hydrogen, carbon dioxide, and helium permeabilities of $(NPR_2)_n$ membranes were determined by using an instrument manufactured by Yanagimoto Co. The dimensions of the $(NPR_2)_n$ membranes were 8 cm × 8 cm × 15–120 μm, and the gas permeability of some membranes was determined over the temperature range 20 to 100°C.

Measurement of Glass Transition Temperatures and Dielectric Constants of Poly(Organophosphazenes)

Each sample was molded into a disk about 0.6 mm thick. An inductive-ratio-arm bridge (Ando Electric Co. TR-10) was employed in the frequency range from 30 to 10^6 Hz. These results were reported by Murakami et al. (*8*).

RESULTS AND DISCUSSION

Comparison of Oxygen, Nitrogen, Hydrogen, Carbon Dioxide, and Helium Gas Permeability Values for Poly(Organophosphazene) Membranes

Hydrogen, nitrogen, oxygen, carbon dioxide, and helium gas permeabilities determined for $(NPR_2)_n$ membranes are summarized in Table 1. The membrane having the highest permeability for hydrogen, nitrogen, oxygen, carbon dioxide, and helium is poly(*n*-propylaminophosphazene) $[NP(NHPr\text{-}n)_2]_n$. Kajiwara (7) reported that poly(organophosphazene) membranes with high oxygen permeability values exhibit high nitrogen permeability values. In order to separate carbon dioxide and nitrogen gas from air, or hydrogen and helium gas from natural gas by using the poly(organophosphazene) membranes prepared in this study, the relationship between carbon dioxide and oxygen, nitrogen, and hydrogen (instead of water) of the gas permeabilities and selectivities were evaluated with the data shown in Table 1. The results obtained are discussed in the next section.

Nitrogen and Carbon Dioxide Gas Permeability and Selectivity

The relationship between nitrogen and oxygen, hydrogen, and carbon dioxide, or between carbon dioxide and hydrogen, oxygen, and nitrogen of the gas permeabilities and selectivities were determined with the data shown in Table 1 in order to separate carbon dioxide or nitrogen gas in air. The results are given in Figs. 1 and 2.

It was found from Figs. 1 and 2 that there is a linear relationship between nitrogen and the summation of the gas permeabilities of oxygen, hydrogen, and carbon dioxide, but there is no relationship between carbon dioxide gas permeability and the summation of the gas permeabilities of hydrogen, nitrogen, and oxygen. The selectivities α and β compared with the poly(dimethylsiloxane) membrane are given in Table 2.

Table 2 shows that the membrane having the highest selectivity in the case of nitrogen gas separation in air is poly(bis-*p*-ethylphenoxyphosphazene) $[NP(OC_6H_4Et\text{-}p)_2]_n$. Its selectivity is about 7 times that of poly(dimethylsiloxane). On the other hand, poly(bis-trifluoroethoxyphosphazene) $[NP(OCH_2CF_3)_2]_n$ has the highest selectivity for carbon dioxide separation, with a selectivity about 35 times greater than that of poly(dimethylsiloxane).

Hydrogen and Helium Gas Permeability and Selectivity

To obtain basic data on the separation or recovery of hydrogen and helium gas in natural gas, the relationship between hydrogen to the sum-

TABLE 1

H_2, N_2, O_2, CO_2, and He Gas Permeability for Poly(Organophosphazene) Membranes

No.	$(NPR^1R^2)_n$		Temperature	Permeability $cc(STP) \cdot cm/cm^2 \cdot s \cdot cmHg$				
	R^1	R^2	(°C)	H_2	N_2	O_2	CO_2	He
1	OCH_2CF_3		27	67.1×10^{-8}	16.2×10^{-8}	20×10^{-8}	78.8×10^{-6}	89.1×10^{-8}
2	OPhEt-*p*		24	32.3×10^{-10}	37×10^{-10}	11.6×10^{-10}	45.7×10^{-10}	20.1×10^{-10}
3	OPh		25	19.9×10^{-9}	56.5×10^{-9}	75.5×10^{-9}	36×10^{-8}	86.5×10^{-8}
4	$OPhCF_3$-*m*		20	11.6×10^{-5}	13.5×10^{-5}	11.8×10^{-5}	11.7×10^{-5}	82.6×10^{-5}
5	$OPhCH_3$-*m*		25	37.2×10^{-8}	51×10^{-7}	76×10^{-7}	11.6×10^{-5}	82.6×10^{-6}
6	$OPhCH_3$-*p*		20		18.3×10^{-9}	34.1×10^{-9}	40.3×10^{-9}	11×10^{-6}
7	HNPr-*n*		26	84×10^{-8}				
			28	28.3×10^{-5}	18.6×10^{-5}	13.6×10^{-5}	18.2×10^{-5}	17.2×10^{-8}
8	HNPr-*n*	Et_2N	76		21.7×10^{-5}	14.7×10^{-5}	16.2×10^{-5}	
9	OPhCl-*p*		24		27.4×10^{-9}	79.7×10^{-9}	48.6×10^{-9}	30×10^{-9}

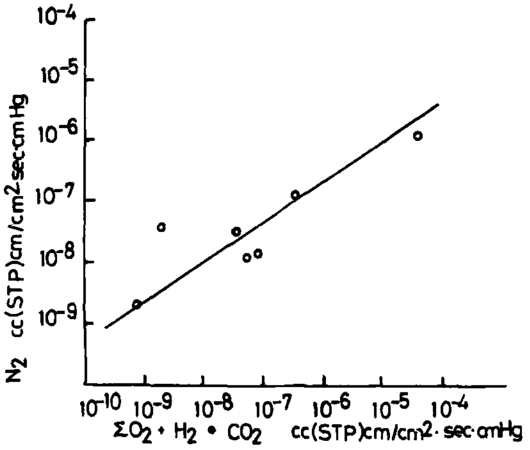

FIG. 1. The relationship between N_2 and $\Sigma O_2 + H_2 + CO_2$ permeability.

mation of O_2, N_2, CO_2, and He, or of He to O_2, N_2, CO_2, and H_2 gas permeabilities were calculated with the data of Table 1. The results are shown in Figs. 3 and 4, respectively. It was found that there is a nonlinear relationship between hydrogen or helium and the summation of each gas permeability. It is important to gas separation techniques using membranes that the selectivity and gas permeability rates have the highest values possible. The calculated selectivity values α are summarized in Table 2.

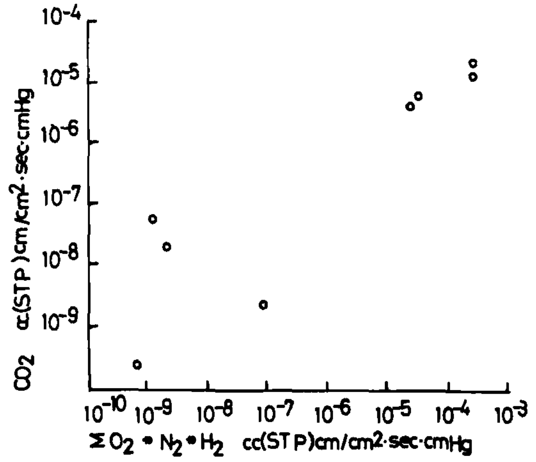

FIG. 2. The relationship between CO_2 and $\Sigma O_2 + N_2 + H_2$ permeability.

TABLE 2
Selectivities α and β Compared for the $(Me_2SiO)_n$ Membrane

		Selectivity							
		$N_2/\Sigma H_2 + O_2 + CO_2$		$CO_2/\Sigma H_2 + N_2 + O_2$		$H_2/\Sigma N_2 + O_2 + CO_2 + He$		$He/\Sigma H_2 + N_2 + O_2 + CO_2$	
No.	$(NPR_2)_n$, R	α	β	α	β	α	β	α	β
1	OCH_2CF_3	0.002	0.33	76.28	34.8	0.28	1.75	0.16	1.78
2	OPhEt-*p*	0.4	6.83	0.57	0.3	0.78	4.88	0.24	2.67
3	OPh	0.18	3	0.11	0.15	0.01	0.06	0.16	1.78
4	$OPhCF_3$-*m*	0.23	3.8	0.32	0.15	0.61	3.81	0.61	6.78
5	$OPhCH_3$-*m*	0.09	1.5	0.23	0.11	0.09	0.56	1.09	12.11
6	$OPhCH_3$-*p*	0.002	0.33	0.05	0.02	0.42	2.63	0.22	2.41
7	HNPr-*n*	0.31	5.2	0.20	0.09				

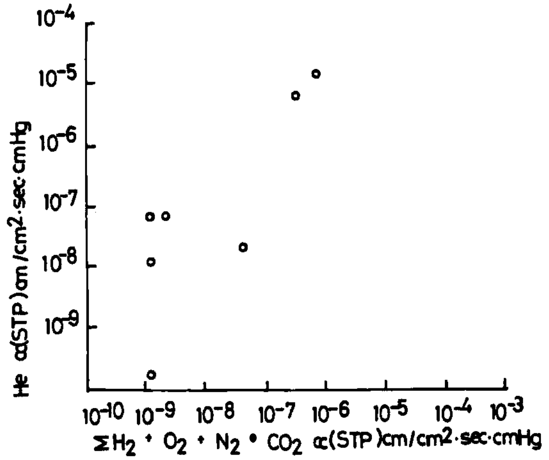

FIG. 3. The relationship between He and $\Sigma H_2 + O_2 + N_2 + CO_2$ permeability.

It is difficult to find a membrane that has a selectivity larger than 1 in the case of hydrogen separation.

The poly(bis-*p*-ethylphenoxyphosphazene) membrane has about 5 times the selectivity of the poly(dimethylsiloxane) membrane for hydrogen separation. The poly(bis-trifluoroethoxyphosphazene) has about 12 times the selectivity of the poly(dimethylsiloxane) membrane for helium.

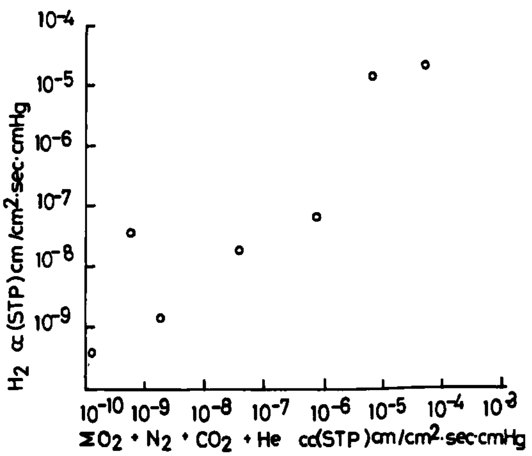

FIG. 4. The relationship between H_2 and $\Sigma O_2 + N_2 + CO_2 + He$ permeability.

The Relation between the Selectivity α and Gas Permeability or Glass Transition Temperature and Dielectric Constant of Poly(Organophosphazene) Membranes

To understand the factors that affect the selectivity α, the relation between α and gas permeability or the glass transition temperature and the dielectric constant of poly(organophosphazene) membranes were determined from the data shown in Table 2 and the report by Murakami (*8*). The results obtained are given in Figs. 5 and 6, respectively.

Generally, selectivity α increased with decreasing gas permeability, and there was an approximately linear relationship. Also, gas permeability increased with increasing glass transition temperature. However, there is a random relationship between selectivity α and gas permeability or between selectivity and the glass transition temperature. On the other hand, the relationship between gas permeability and the dielectric constant (ε) of poly(organophosphazene) membranes is shown in Fig. 7. Gas permeability was related to the dielectric constants of the membranes in the paper by Kajiwara (*9*). However, the permeabilities of poly(organophosphazene) membranes under dry condition are not directly dependent on the dielectric constant, as shown in Fig. 7.

The relationship between the dielectric constants of H_2, N_2, O_2, CO_2, and He gas and their gas permeabilities for some poly(organophosphazene)

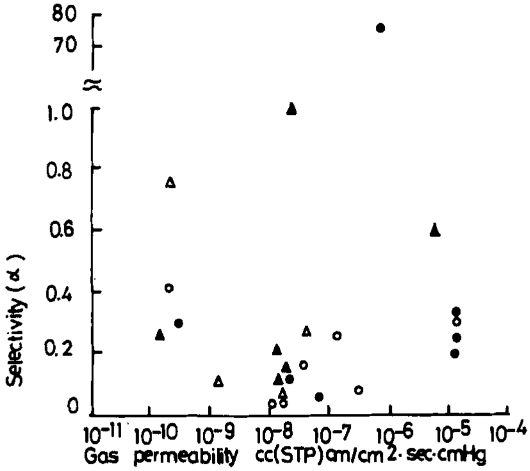

FIG. 5. The relationship between selectivity (α) and permeability: (○) N_2, (●) CO_2, (△) H_2, (▲) He.

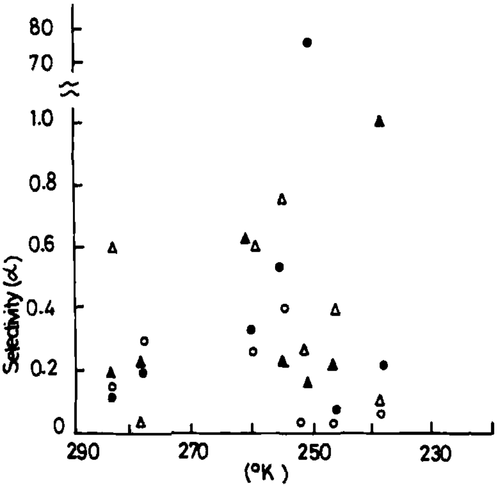

FIG. 6. The relationship between selectivity (α) and the glass transition temperature of the polymer: (○) N_2, (●) CO_2, (△) H_2, (▲) He.

membranes are summarized in Fig. 8. It was found that gas permeability is related to the dielectric constant for each gas. Gas permeability increases with decreasing dielectric constant. Helium, having the lowest dielectric constant, has the highest gas permeability, and it has no dependence on the kind of membrane.

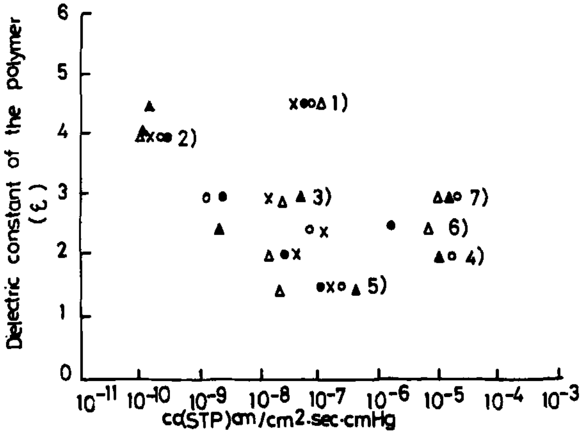

FIG. 7. The relationship between the dielectric constant of the polymer and permeability: (○) H_2, (●) CO_2, (△) He, (▲) O_2, (×) N_2.

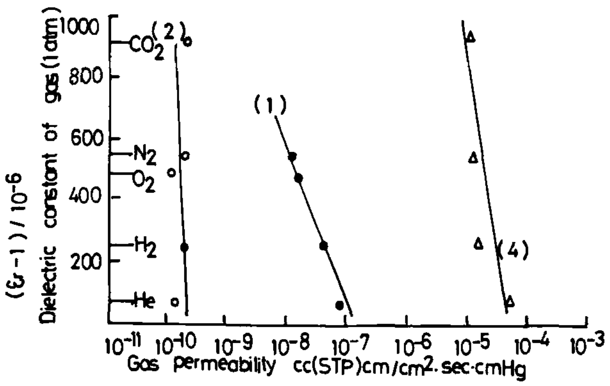

FIG. 8. The relationship between the dielectric constants of gases and the permeability of some membranes.

Activation Energy of Gas Permeability Using Poly(Organophosphazene) Membranes

H_2, N_2, O_2, CO_2, and He gas permeabilities at various temperatures were measured, and the Arrhenius plots are shown in Fig. 9. The calculated activation energies are summarized in Table 3. The covalent radii and dielectric constants of the gases are $H_2 < N_2 < O_2 < CO_2 <$ He and He $< H_2 < O_2 < N_2 < CO_2$, respectively.

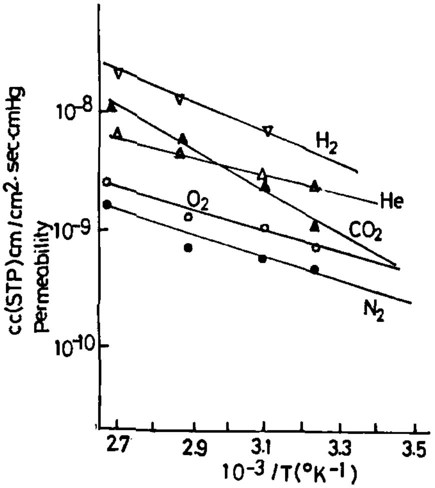

FIG. 9. Arrhenius plots of H_2, N_2, O_2, CO_2, and He gas permeability for $[NP(OC_6H_4CH_3\text{-}m)_2]_n$.

TABLE 3
Activation Energies for H_2, O_2, N_2, CO_2, and He Gas Permeabilities

$(NPR^1R^2)_n$		Activation energy (ΔE) (kcal/mol)				
R^1	R^2	H_2	N_2	O_2	CO_2	He
OC_6H_4Et-*p*	OC_6H_4Et-*p*	5.0	8.2	7.1	5.9	4.2
OC_6H_4Cl-*p*	OC_6H_4Cl-*p*	7.7	7.6	11.8	8.3	9.1
$OC_6H_4CH_3$-*m*	OC_6H_3Cl-*p*	5.6	3.4	3.5	6.8	2.1
HNPr-*n*	Et_2N	−7.6	−7.4	−7.5	−7.6	−7.4

The activation energies of the gas permeabilities of the membranes have no relationship to their covalent radii and dielectric constants. It is difficult to explain why a negative activation energy results from gas permeability when using $[NP(NHPr\text{-}n)(Et_2N)]_n$ and why the activation energy has no relationship to their covalent radii or dielectric constants.

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