# Gas Transport in Poly(alkoxyphosphazenes)

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## SYNOPSIS

The permeability of four structurally related poly(alkoxyphosphazenes), three isomers of poly(dibutoxyphosphazenes) (PBuP), and poly(di-neopentyloxyphosphazene) (Pneo-PeP), to 13 gases has been determined by the time-lag method. Systematic variations in chemical structure have shown a large effect of side chains on permeabilities and perm-selectivities. The permeability of poly(di-$n$-butoxyphosphazene) (Pn-BuP) is of the order of $10^{-8}$ cm$^3$ (STP) cm/(cm$^2$ s cmHg) for many gases, and the value for a large gas is higher than that for a smaller one. For small gases such as He and H$_2$, poly(di-sec-butoxyphosphazene) (Ps-BuP) is as permeable as Pn-BuP, but its diffusivities for larger gases such as Xe and C$_3$H$_8$ are about one order lower than those of Pn-BuP. While the permselectivity of Pn-BuP is determined by the solubility, that of Ps-BuP depends on both the diffusivity and solubility factors. The property of poly(diisobutoxyphosphazene) (Pi-BuP) is intermediate between them. These polymers are constitutionally identical, and the only difference is the arrangements of carbons in the side groups. As the side chains become bulky, the permeability decreases, whereas the permselectivity increases. Further decreases of diffusivity and then permeability are observed for Pneo-PeP, whose side groups have one more methyl group than does Pi-BuP. But the solubility data are not much different from other three polymers and the diffusivity factor becomes more significant in permselectivity. The diffusivity depends on the polymer structure much more than does the solubility. The relationships between chemical structure and gas diffusivity and solubility are discussed.

## INTRODUCTION

Since the first syntheses of un-cross-linked poly(organophosphazenes),[1] they have been studied intensively because of a wide range of physical and chemical properties from the standpoints of not only fundamental research but also of applications.[2-4] A variety of polymers can be derived with relative ease, and this is another reason why a lot of attention has been paid to phosphazene polymers. Basically, phosphazene polymer has a flexible main chain and many of them are rubbers.[1,2] By introducing different kinds of side groups, however, physical and chemical properties, such as $T_g$, stability, and hydrophilicity, change widely.[2-4] Gas transport property is also expected to be affected greatly by the structure and the nature of the side groups. But no systematic

studies have been done on the effects of side chains, such as chain length, bulkiness, and stiffness, on the diffusivity and solubility of gases in phosphazene polymers. Recently, we have started research on gas transport properties of phosphazene polymers in order to generate information on the structure-gas transport relationships.

In the previous papers,[5,6] gas transport in poly[bis(trifluoroethoxy)phosphazene] (PTFEP) has been studied extensively both below and above the mesomorphic transition temperature $T(1)$ of the crystalline phase. Probably this is the most well-studied phosphazene polymer because of the $T(1)$ transition and the corresponding changes of several properties.[7-11] Our previous studies also revealed a few interesting characteristics of PTFEP: This polymer has specifically high solubility for CO$_2$ because of its polar trifluoroethoxy groups.[5] It shows a noticeable change of gas transport parameters together with hystereses at the transition of its crystals.[6] With both permeability and solubility data of CO$_2$ above and below $T(1)$, the diffusivity in the

mesophase was determined. It was suggested that the mobility of the side groups plays an important role on gas solution and diffusion in PTFEP. But in order to understand and improve gas transport properties of phosphazene polymer, further investigation is necessary. In this study, three kinds of poly(dibutoxyphosphazenes) (PBuP) and poly(dineopentyloxyphosphazene) (Pneo-PeP) were prepared and their gas transport behaviors were examined. The repeat units of PBuP have the same number of atoms, that is, the side groups are the isomers and they differ in the relative positions of methyl or methylene groups to each other. Pneo-PeP has one more carbon in each side group than does PBuP. The objective of the present study is to investigate how much the structure of the side chains affects gas transport properties.

## EXPERIMENTAL

### Materials

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ was obtained from Johoku Chemical Co. and was purified by vacuum sublimation. All organic solvents and reagents were reagent grade. Tetrahydrofuran (THF), which was used as a reaction solvent, was distilled from sodium, stored over sodium, and distilled from lithium aluminum hydride before use. $n$- and sec-Butyl, isobutyl, and neopentyl alcohols were distilled from calcium chloride before use. Organic solvents used for purification of polymers were not purified. All gases were at least greater than 99.9% pure and were used without further purification.

Poly(dichlorophosphazene) $(NPCl_2)_n$ was prepared by the thermal polymerization of $(NPCl_2)_3$ at 250–270°C in sealed glass tubes by the method described in the literature.[1] The conversion of $(NPCl_2)_3$ was approximately 70–95%, and the residual was recovered by vacuum sublimation.

The procedure described in the literature was followed for preparation of poly(alkoxyphosphazenes).[1] A typical procedure is as follows: A solution of $(PNCl_2)_n$ (2.49 g) in dry THF (125 mL) was filtered through a glass filter to remove insoluble materials. At room temperature, the solution was added to a stirred solution of potassium sec-butoxide prepared from potassium (2.35 g) and sec-butyl alcohol (14.34 g) in THF (100 mL). The reaction mixture was warmed up to about 50°C, and stirring was continued for a couple of days. The mixture was allowed to cool to room temperature and neutralized with concentrated hydrochloric acid. The solvent was party evaporated, and the concentrated solution was poured into water to remove potassium chloride. The polymer was dissolved in THF and precipitated into methanol–water (9 : 1 by volume) solution twice, and the precipitate (2.94 g) was dried under vacuum. Poly(di-sec-butoxyphosphazene) (Ps-BuP) was a colorless, rubbery material. The polymer was soluble in THF, benzene, toluene, and chloroform but insoluble in water, methanol, ethanol, and diethylether. The IR spectrum of the film cast on the KBr plate gave a negligible spectrum of a hydroxyl group to indicate almost a complete substitution reaction.

The molecular weight, $T_g$, and density of each polymer are summarized in Table I. No other transitions were observed for any polymers in this study

**Table I   Properties of Phosphazene Polymers Studied**

| Polymer | Pn-BuP | Pi-BuP | Ps-BuP | Pneo-PeP |
|---|---|---|---|---|
| Structure | $OCH_2CH_2CH_2CH_3$ <br> $+P=N+_n$ <br> $OCH_2CH_2CH_2CH_3$ | $CH_3$ <br> $OCH_2CHCH_3$ <br> $+P=N+_n$ <br> $OCH_2CHCH_3$ <br> $CH_3$ | $CH_3$ <br> $OCHCH_2CH_3$ <br> $+P=N+_n$ <br> $OCHCH_2CH_3$ <br> $CH_3$ | $CH_3$ <br> $OCH_2CCH_3$ <br> $CH_3$ <br> $+P=N+_n$ <br> $CH_3$ <br> $OCH_2CCH_3$ <br> $CH_3$ |
| $T_g$ (°C) | −108 | −95 | −91 | −92 |
| $d^{25}$ (g/cm³) | 1.047 | 1.055 | 1.104 | 1.032 |
| $M_w$ | > 300,000 | > 550,000 | > 550,000 | > 510,000 |

by DSC at the temperature range from −150 to 100°C.

## Film Preparation

The THF solution (30 mL) of poly(diisobutoxy-phosphazene) (Pi-BuP) (1.5 g) was cast on a glass plate floated on mercury and was allowed to air dry at room temperature for a few days. The film was immersed in distilled water to remove it from a glass plate. It was dried under vacuum at about 30–60°C for a few days before permeation measurements. The specimen for permeation measurements was cut off the film, and its average thickness was 145.2 μm.

Three other poly(alkoxyphosphazenes) were also cast from their THF or benzene solutions, and the film thicknesses were between 160.1 and 254.5 μm.

## Apparatus and Procedures

Gel permeation chromatography (GPC) was accomplished with about a 0.5% THF solution by the use of a Shimazu 830 liquid chromatograph. The instrument was calibrated with polystyrene standards, and the molecular weights determined here were only approximate. Infrared (IR) spectra were obtained by a Model A-3 IR spectrometer of Japan Spectroscopic Co., Ltd. The glass transition temperature $T_g$ was determined by differential scanning calorimetry (DSC) with the heating rate of 20 K/min on a DuPont 9900 thermal analyzer. The density was determined by a density–gradient column using KI aq solution at 25.0°C. Permeation measurements were made using facilities and procedures described previously.[5]

## RESULTS AND DISCUSSION

The Arrhenius plots of permeability coefficients $P$ for noble gases in poly(di-$n$-butoxyphosphazene (Pn-BuP) are shown in Figure 1. There are no
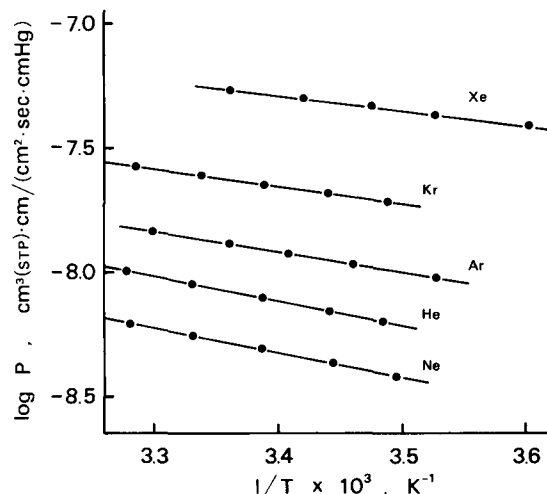


**Figure 1**   Arrhenius plot of the permeability coefficients for noble gases in poly(di-$n$-butoxyphosphazene) (Pn-BuP).

breaks in the range of experimental temperature as expected from the results of DSC measurements. But gas dependence of the permeabilities shown in Figure 1 is interesting. The permeabilities of Xe, Kr, and even Ar are higher than that of He. Except Ne, the larger the size of penetrant molecule, the higher the permeability. The $P$ values at 25°C in Pn-BuP are summarized in Table II for noble gases and in the Appendix for other gases with the activation energy for permeation, $E_p$. The tables show that the permeabilities of many gases are of the order of $10^{-8}$ cm$^3$ (STP) cm/(cm$^2$ s cmHg) and those of He, Ne, and N$_2$ are of the order of $10^{-9}$ at 25°C. To our knowledge, Pn-BuP has the highest permeability in phosphazene polymers, which is comparable to the data of poly(dioctyloxyphosphazene).[12]

For a rubbery polymer, the diffusion coefficient $D$ can be obtained from a time lag, $\theta$, by eq. (1) and the solubility coefficient $S$ is calculated from the ratio of $P$ to $D$ by eq. (2) when the solubility is low enough to be within the limit of Henry's law[13]:

**Table II   Gas Transport Parameters for Noble Gases in Poly(di-$n$-butoxyphosphazene (Pn-BuP)**

| Gas | $P$ (25°C) × $10^8$ | $E_p$ | $D$ (25°C) × $10^7$ | $E_d$ | $S$ (25°C) × $10^4$ | $\Delta H_s$ |
|-----|-----|-----|-----|-----|-----|-----|
| He | 0.847 | 4.45 | 268 | 2.52 | 3.16 | 1.93 |
| Ne | 0.524 | 4.49 | 122 | 3.18 | 4.28 | 1.31 |
| Ar | 1.30 | 3.67 | 44.7 | 4.03 | 29.2 | −0.36 |
| Kr | 2.36 | 3.18 | 28.7 | 4.52 | 82.4 | −1.34 |
| Xe | 5.48 | 2.86 | 18.2 | 5.43 | 301 | −2.57 |

Units: $P$ is in cm$^3$ (STP) cm/(cm$^2$ s cmHg), $D$ is in cm$^2$/s, $S$ is in cm$^3$ (STP)/[cm$^3$(polymer) cmHg], $E_p$, $E_d$, and $\Delta H_s$ are in kcal/mol.

$$D = l^2/6\theta \tag{1}$$

$$S = P/D \tag{2}$$

where "$l$" is the film thickness. The temperature dependencies of $D$ and $S$ in Pn-BuP are shown in Figures 2 and 3 for noble gases. The parameters for the diffusivity and the solubility are also summarized in Table II. Figures 2 and 3 show the usual characteristics. The $D$ values for small gases are higher than those for larger ones, because the smaller gases need less space to go through a polymer matrix. On the other hand, the $S$ value of a larger gas is higher than that of a smaller one because the former is more condensable and interacts more strongly with a polymer than does the latter.

In a "solution–diffusion" mechanism, the diffusion process is the rate-determining process and determines permselectivity in many cases. But in the case of polymers with high gas diffusivity, such as silicone rubber, the gas dependence of the diffusivity is not very much but $S$ varies with gases more strongly than does $D$.[5,14] This tendency is also observed in gas solution and diffusion in Pn-BuP. Figure 2 shows, by comparing the many polymers,[15] that the $D$ value of each gas is rather high and the difference between He and Xe, for example, is about one and one-half orders. On the other hand, the solubility for Xe is about two orders (95 times) higher than that of He. As a result, the Xe permeability is higher than is the He permeability in Pn-BuP, that is, gas permeability in Pn-BuP depends on the solubility factor more than on the diffusivity or mobility
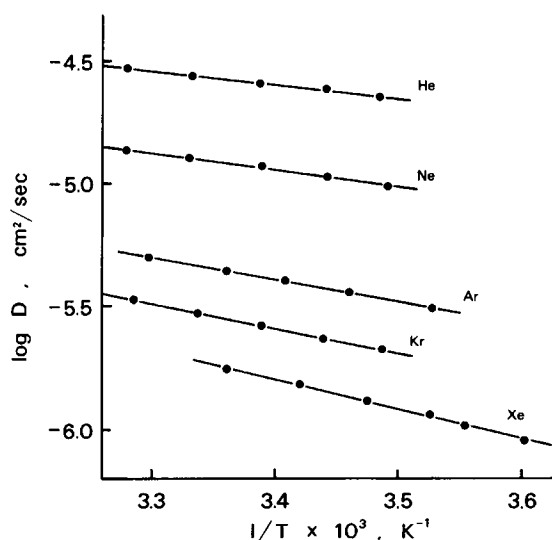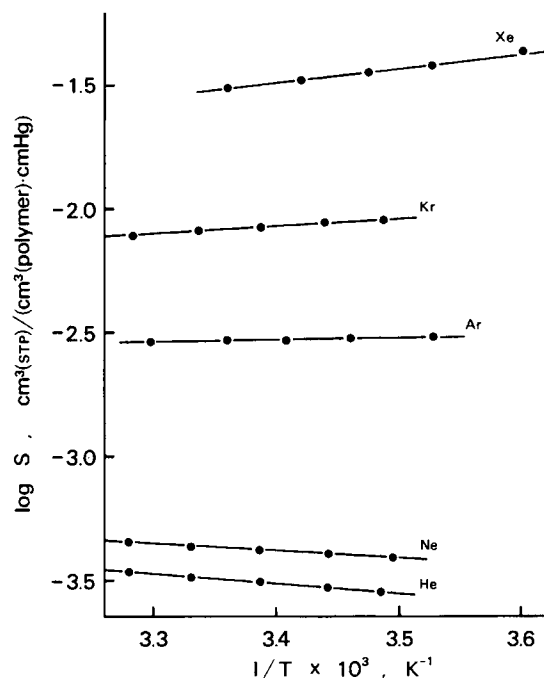


**Figure 3** van't Hoff plot of the solubility coefficients for noble gases in poly(di-$n$-butoxyphosphazene) (Pn-BuP).

factor. The $E_p$ value of $C_3H_8$ in Pn-BuP is positive because the increase in diffusivity is greater than is the decrease of the solubility as the temperature is raised. But the opposite has been found for several silicone polymers, whose selectivities are controlled by the ratio of solubilities.[14] This trend has not yet been reported for other polymers than silicon-containing polymers,[15,16] and it should be investigated for phosphazene polymer-gas systems.

The temperature dependences of $P$, $D$, and $S$ for noble gases in Ps-BuP are shown in Figures 4–6,
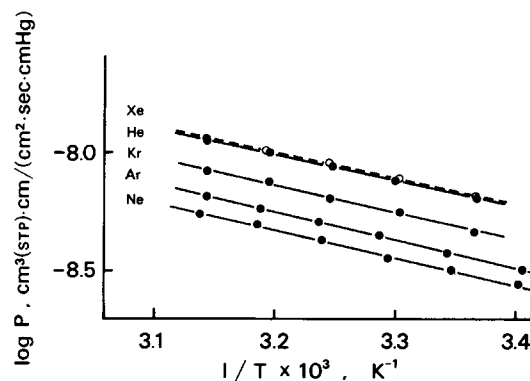


**Figure 2** Arrhenius plot of the diffusion coefficients for noble gases in poly(di-$n$-butoxyphosphazene) (Pn-BuP).



**Figure 4** Arrhenius plot of the permeability coefficients for noble gases in poly(di-$sec$-butoxyphosphazene) (Ps-BuP).
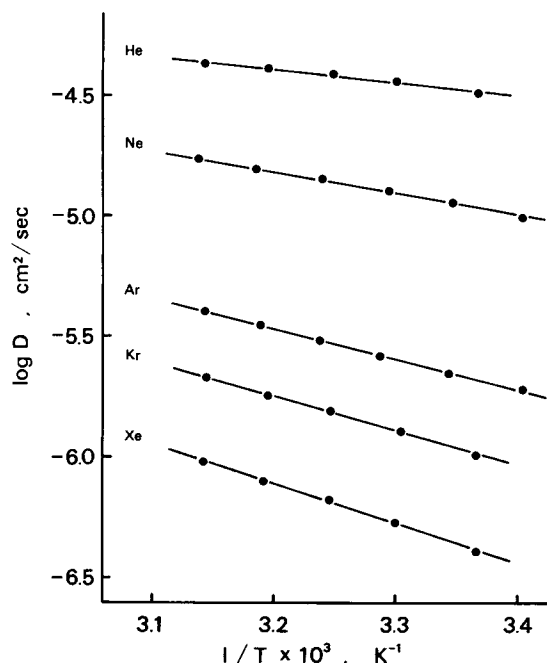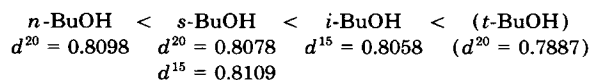
**Figure 5** Arrhenius plot of the diffusion coefficients for noble gases in poly(di-sec-butoxyphosphazene) (Ps-BuP).

respectively. Compared to the data of Pn-BuP, the permeabilities of Kr and Xe decreased significantly. The decrease in $P$ can be contributed to that in $D$ as the difference in gas solubility is small between Ps-BuP and Pn-BuP. On the other hand, the $P$ value for He is comparable to that of Pn-BuP. From Figures 2 and 5, it is evident that Ps-BuP shows a larger gas dependence of $D$ than that for Pn-BuP and the diffusivity of He is 80 times higher than that of Xe for Ps-BuP. The $S$ value depends on gas less than does $D$, and the solubility of Xe is about 80 times larger than that of He, which is the same extent for Pn-BuP. In this way, the permeability of Xe is almost the same as that of He for Ps-BuP. In Table III, the transport parameters are listed for noble gases.

The gas transport property of Pi-BuP was the intermediate between Pn-BuP and Ps-BuP. The transport parameters in Pi-BuP are listed in Tables IV for noble gases and in the Appendix for other gases.

The side groups of PBuP are derived from corresponding alcohols. From their densities,[17] the bulkiness of the alcohols are anticipated to be in the following order:

$$n\text{-BuOH} \ < \ s\text{-BuOH} \ < \ i\text{-BuOH} \ < \ (t\text{-BuOH})$$
$$d^{20} = 0.8098 \quad d^{20} = 0.8078 \quad d^{15} = 0.8058 \quad (d^{20} = 0.7887)$$
$$d^{15} = 0.8109$$

where $d^t$ (g/cm$^3$) is the density at the temperature $t$ (°C). The densities of PBuP in Table I do not correspond to this but roughly show the opposite order:

$$\text{Ps-BuP} \ < \ \text{Pi-BuP} \ < \ \text{Pn-BuP}$$

Probably, the order of the polymer densities is due to the combination of the flexibility of the main chain and the structure or the rigidity of the side chains, which has not been investigated in detail. Therefore, the effective bulkiness of the side chains are expected to increase in this order as the result of the combination. As presented in the preceding paragraphs, the gas permeabilities of PBuP increase in the same order. It is reasonable that gas diffusivity increases with decreasing the polymer density, which is expected to be related to the packing of polymer chains.[13]

When a methine hydrogen in Pi-BuP is replaced by a methyl group, the side group becomes bulkier and further change was observed for Pneo-PeP in line with the tendency mentioned before; that is, the $P$ value is larger for a smaller gas than for a larger one, which is opposite to the case of Pn-BuP but is an usual trend seen for many other polymers.[15] The transport parameters of noble gases in Pneo-PeP are listed in Table V and those of other gases in Tables A.I–A.IV in the Appendix. The permeation property of Pneo-PeP is close to that of polybutadiene.[15]
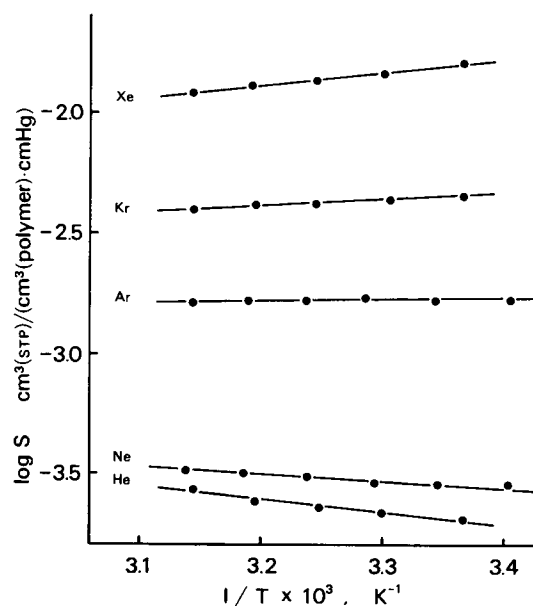


**Figure 6** van't Hoff plot of the solubility coefficients for noble gases in poly(di-sec-butoxyphosphazene) (Ps-BuP).

**Table III  Gas Transport Parameters for Noble Gases in Poly(di-*sec*-butoxyphosphazene (Ps-BuP)**

| Gas | $P$ (25°C) $\times 10^8$ | $E_p$ | $D$ (25°C) $\times 10^7$ | $E_d$ | $S$ (25°C) $\times 10^4$ | $\Delta H_s$ |
|-----|-----|-----|-----|-----|-----|-----|
| He | 0.671 | 4.80 | 334 | 2.35 | 2.01 | 2.45 |
| Ne | 0.311 | 5.29 | 112 | 3.88 | 2.80 | 1.41 |
| Ar | 0.368 | 5.43 | 21.6 | 5.74 | 17.1 | -0.31 |
| Kr | 0.486 | 5.15 | 10.7 | 6.46 | 45.3 | -1.31 |
| Xe | 0.679 | 4.97 | 4.32 | 7.53 | 157 | -2.56 |

Units: See footnote to Table II.

**Table IV  Gas Transport Parameters for Noble Gases in Poly(diisobutoxyphosphazene) (Pi-BuP)**

| Gas | $P$ (25°C) $\times 10^8$ | $E_p$ | $D$ (25°C) $\times 10^7$ | $E_d$ | $S$ (25°C) $\times 10^4$ | $\Delta H_s$ |
|-----|-----|-----|-----|-----|-----|-----|
| He | 1.06 | 4.43 | 437 | 1.99 | 2.40 | 2.44 |
| Ne | 0.568 | 4.62 | 161 | 3.04 | 3.52 | 1.58 |
| Ar | 0.821 | 4.74 | 39.7 | 5.17 | 20.7 | -0.43 |
| Kr | 1.18 | 4.44 | 21.5 | 5.69 | 48.7 | -1.25 |
| Xe | 1.96 | 4.19 | 9.79 | 6.76 | 197 | -2.57 |

Units: See footnote to Table II.

Table VI lists the ideal separation factor as the ratio of permeabilities for three gas pairs. The separation factor increases as the side chains become bulky, which is the same trend seen in the decrease of the diffusivity; that is, as the side groups increase bulkiness, the diffusivity decreases and the contribution of the diffusivity factor becomes more significant. The permselectivity is due primarily to differences in the gas diffusivities in the polymers.

In the previous paragraphs, it was shown that gas permeability in phosphazene polymers decreases and permselectivity increases as the side chain becomes branched or bulky. But the effect of the structural change depends on the size of a penetrant, which is again demonstrated for $H_2$, $O_2$, and $C_3H_8$ in Table VII. All transport coefficients for $H_2$ in three PBuP are very close to each other. But the $P$ value of $C_3H_8$ in Pn-BuP is 16 times larger than that of Ps-BuP because of the diffusivity that is about nine times higher than that of Ps-BuP.

The present result corresponds well to the discussion in the comprehensive study on silicone polymers by Shah et al.[14] They concluded that the substitution of bulkier functional groups in the side chains of silicone polymers decreases substantially the gas permeability by decreasing the diffusivity of the penetrant. But it should be noted again that the number of functional groups are the same in three PBuP of this study. The side groups are isomers, and the displacement of the methyl group is the only difference. The structural arrangement of side groups seems very important in the transport of gases through phosphazene polymers. So far, the primary effect of the structure is expected to alter the distribution of the free volume. The amount of the free volume might be changed more or less as

**Table V  Gas Transport Parameters for Noble Gases in Poly(di-neopentyloxyphosphazene) (Pneo-PeP)**

| Gas | $P$ (25°C) $\times 10^8$ | $E_p$ | $D$ (25°C) $\times 10^7$ | $E_d$ | $S$ (25°C) $\times 10^4$ | $\Delta H_s$ |
|-----|-----|-----|-----|-----|-----|-----|
| He | 0.602 | 4.87 | 256 | 2.51 | 2.36 | 2.36 |
| Ne | 0.240 | 4.96 | 69.2 | 4.25 | 3.47 | 0.71 |
| Ar | 0.120 | 6.71 | 5.79 | 7.12 | 20.8 | -0.41 |
| Kr | 0.0942 | 6.94 | 1.65 | 9.33 | 57.1 | -2.39 |

Units: See footnote to Table II.

**Table VI   Ratios of Permeability Coefficients for Three Gas Pairs in Phosphazene Polymers at 25°C**

| Polymer | Ideal Separation Factor $\alpha$ | | |
|---|---|---|---|
| | $P(O_2)/$ $P(N_2)$ | $P(CO_2)/$ $P(CH_4)$ | $P(CH_4)/$ $P(He)$ |
| Pn-BuP | 2.29 | 3.30 | 2.31 |
| Pi-BuP | 2.73 | 4.00 | 0.931 |
| Ps-BuP | 3.04 | 4.53 | 0.583 |
| Pneo-PeP | 4.45 | 6.48 | 0.125 |

suggested by the density data and the glass transition temperatures. But a significant decrease of the free volume is unlikely because change in the amount must affect the transport parameters of smaller molecules as well as the larger ones, which is not the case in this study. The introduction of one carbon element might lead to a decrease in both the amount and the distribution of the free volume and cause further change in gas permeability. But the difference between Pneo-PeP and PBuP in the free volume is not known yet.

It is well known that the nature of a penetrant gas affects the diffusivity in polymers.[13] A good correlation between the activation energy of diffusion ($E_d$) and the molecular diameter $d$ can be obtained for a given polymer. But the correlation varies with polymers because it reflects the nature of a polymer. It was examined for noble gases and methane in four phosphazene polymers. For all polymers, $E_d$ increases monotonically from He to Xe with the in-
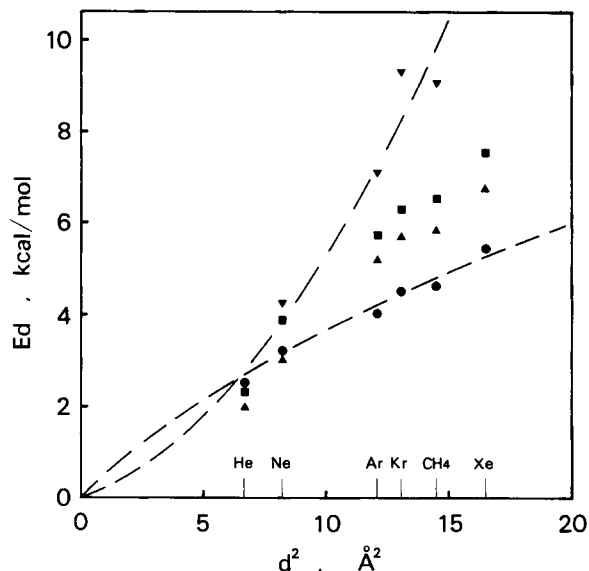


**Figure 7**   Activation energies for diffusion for noble gases and methane in Pn-BuP (●), Pi-BuP (▲), Ps-BuP (■), and Pneo-PeP (▼) vs. $d^2$ (the molecular diameters).

crease in $d$ and the results of $E_d$ against $d^2$ are shown in Figure 7. The plot is concave to the $d^2$ axis for Pn-BuP, which has the highest gas diffusivity in four polymers. For a linear relationship between $E_d$ and $d^n$, the number of the power of $d$ should be between 1 and 2. On the other hand, the correlations in Figure 7 are almost linear for Pi-BuP and Ps-BuP, while an upward curvature is obtained in the case of Pneo-PeP, which has the lowest diffusivity. In a linear relation between $E_d$ and $d^n$, the number of power increases as the diffusivity of a polymer

**Table VII   Comparison of the Permeation, Diffusion, and Solubility Coefficients for $H_2$, $O_2$, and $C_3H_8$ in Phosphazene Polymers at 25°C**

| Polymer | Pn-BuP | Pi-BuP | Ps-BuP | Pneo-PeP |
|---|---|---|---|---|
| $H_2$ | | | | |
| $P$ (25°C) × $10^8$ | 1.70 | 1.67 | 0.950 | 0.657 |
| $D$ (25°C) × $10^7$ | 183 | 262 | 180 | 108 |
| $S$ (25°C) × $10^4$ | 9.29 | 6.35 | 5.29 | 6.10 |
| $O_2$ | | | | |
| $P$ (25°C) × $10^8$ | 1.28 | 0.866 | 0.407 | 0.154 |
| $D$ (25°C) × $10^7$ | 51.0 | 47.8 | 27.8 | 8.40 |
| $S$ (25°C) × $10^4$ | 25.1 | 18.1 | 14.6 | 18.3 |
| $C_3H_8$ | | | | |
| $P$ (25°C) × $10^8$ | 10.0 | 2.24 | 0.616 | — |
| $D$ (25°C) × $10^7$ | 10.6 | 3.60 | 1.21 | — |
| $S$ (25°C) × $10^4$ | 945 | 622 | 511 | — |

Units: see footnote to Table II.

decreases. This is a consistent tendency observed in a paper by Ash et al.[18] and also reported in our previous paper.[5]

Although several diffusion models suggest different correlations between $E_d$ and $d$ for a given polymer,[19-23] they usually include two kinds of parameters that represent the nature of polymer. One of them is the distance parameter such as segment length, jump length, and interchain distance, and the other is the energy parameter, such as cohesive energy density and Lennard–Jones force constant. Because the polymers studied here are chemically related to each other, the differences in energy parameters are expected to be small between them. Further, the common conformational structure of the main chains is well known.[2] The bulkiness of side chains must increase a certain distance parameter. It can be the polymer molecule diameter in the model of Brandt[20] or the temperature dependence of the equilibrium interchain separation in the model of Pace and Datyner.[23]

The linear relationships between the solubility at 25°C and the Lennard–Jones force constant of the gases are shown in Figure 8 for Pn-BuP and Ps-BuP. The plots for Pi-BuP and Pneo-PeP were between those of Pn-BuP and Ps-BuP and paralleled them. This result is plausible considering the chemical structures of them and that gas solubility is determined by the interaction between a polymer and a gas. The dashed lines in Figure 8 show the rela-
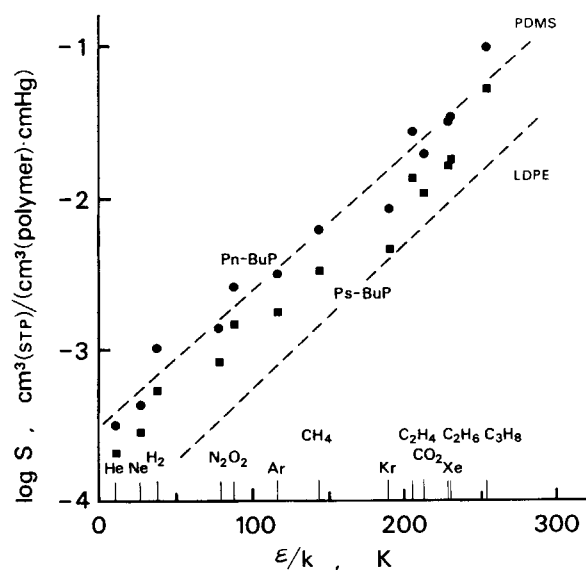
tionships for low-density polyethylene (LDPE) and polydimethylsiloxane (PDMS). They parallel the results of this study. In our previous paper, the relationship for PTFEP is found to be different from those for LDPE and PDMS and we discussed that the nature of the main chain might be the reason.[5] But the present study clearly shows that the plot of PTFEP does not parallel those of LDPE and PDMS because of its polar side groups and the gas solubility property can be changed by the nature of side groups of phosphazene polymers. The fewer polar side groups in three PBuP and Pneo-PeP cause their solubility behaviors that are similar to those of LDPE and PDMS and, therefore, to those of nonpolar organic liquids.[24]

## CONCLUSIONS

It was shown that gas permeability can be altered widely by the structural variation of the side groups of poly(alkoxyphosphazene). The substitution of the $n$-butyl group for $sec$-butyl group resulted in the decrease of permeabilities and the permeabilities of large gases such as Xe and $C_3H_8$ for Pn-BuP were about one order higher than those for Ps-BuP. Variation in the permeabilities are due mainly to changes in the diffusivities. But the permeabilities for small gases such as He and $H_2$ were not affected. It was suggested that the structural change of side groups in this study, that is, the regioisomerical change, affects the distribution of the free volume more than it does the amount of it.

A general trend that an increase in permeability is attended by a decrease in permselectivity was also observed in this study. The permselectivities in the polymers also seemed to be primarily affected by changes in the diffusivities or the diffusivity selectivities. The variation in the diffusion properties were seen in the relationships between the activation energies for diffusion and the molecular diameters of penetrants. On the other hand, the solution properties were not affected very much, which was understood easily because the polymers were chemically quite similar to each other.



**Figure 8** The solubility coefficients for 13 gases at 25°C in Pn-BuP (●) and Ps-BuP (■) vs. the Lennard–Jones force constants $\epsilon/k$. Dashed lines are the data of PDMS and LDPE.[5]

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# APPENDIX

**Table A.1   Gas Transport Parameters for Hydrogen, Oxygen, Nitrogen, Carbon Dioxide, and Hydrocarbon Gases in Poly(di-$n$-butoxyphosphazene) (Pn-BuP)**

| Gas | $P$ (25°C) $\times$ 10$^8$ | $E_p$ | $D$ (25°C) $\times$ 10$^7$ | $E_d$ | $S$ (25°C) $\times$ 10$^4$ | $\Delta H_s$ |
|---|---|---|---|---|---|---|
| H$_2$ | 1.70 | 4.53 | 183 | 2.93 | 9.29 | 1.60 |
| O$_2$ | 1.28 | 3.62 | 51.0 | 4.06 | 25.1 | −0.44 |
| N$_2$ | 0.558 | 4.33 | 40.6 | 3.99 | 13.7 | 0.83 |
| CO$_2$ | 6.47 | 1.79 | 35.4 | 4.44 | 183 | −2.65 |
| CH$_4$ | 1.96 | 3.50 | 32.9 | 4.62 | 59.6 | −1.12 |
| C$_2$H$_6$ | 5.70 | 2.08 | 17.5 | 4.95 | 326 | −2.87 |
| C$_2$H$_4$ | 5.82 | 2.25 | 22.2 | 4.87 | 263 | −2.62 |
| C$_3$H$_8$ | 10.0 | 1.16 | 10.6 | 5.21 | 945 | −4.05 |

Units: $P$ is in cm$^3$ (STP) cm/(cm$^2$ s cmHg), $D$ is in cm$^2$/s, $S$ is in cm$^3$ (STP)/[cm$^3$ (polymer) cmHg], $E_p$, $E_d$, and $\Delta H_s$ are in kcal/mol.

**Table A.2   Gas Transport Parameters for Hydrogen, Oxygen, Nitrogen, Carbon Dioxide, and Hydrocarbon Gases in Poly(diisobutoxyphosphazene) (Pi-BuP)**

| Gas | $P$ (25°C) $\times$ 10$^8$ | $E_p$ | $D$ (25°C) $\times$ 10$^7$ | $E_d$ | $S$ (25°C) $\times$ 10$^4$ | $\Delta H_s$ |
|---|---|---|---|---|---|---|
| H$_2$ | 1.67 | 4.49 | 262 | 3.19 | 6.35 | 1.30 |
| O$_2$ | 0.866 | 4.49 | 47.8 | 4.83 | 18.1 | −0.34 |
| N$_2$ | 0.317 | 5.25 | 32.9 | 5.13 | 9.63 | 0.12 |
| CO$_2$ | 3.95 | 2.45 | 30.4 | 5.39 | 130 | −2.94 |
| CH$_4$ | 0.987 | 4.64 | 24.4 | 5.85 | 40.4 | −1.21 |
| C$_2$H$_6$ | 1.93 | 3.79 | 8.90 | 6.77 | 217 | −2.98 |
| C$_2$H$_4$ | 2.25 | 3.47 | 13.6 | 6.27 | 166 | −2.80 |
| C$_3$H$_8$ | 2.24 | 3.48 | 3.60 | 7.52 | 622 | −4.04 |

Units: see footnote to Table A.1.

**Table A.3    Gas Transport Parameters for Hydrogen, Oxygen, Nitrogen, Carbon Dioxide, and Hydrocarbon Gases in Poly(di-sec-butoxyphosphazene) (Ps-BuP)**

| Gas | $P$ (25°C) $\times 10^8$ | $E_p$ | $D$ (25°C) $\times 10^7$ | $E_d$ | $S$ (25°C) $\times 10^4$ | $\Delta H_s$ |
|---|---|---|---|---|---|---|
| $H_2$ | 0.950 | 5.17 | 180 | 3.32 | 5.29 | 1.85 |
| $O_2$ | 0.407 | 4.98 | 27.8 | 5.24 | 14.6 | −0.26 |
| $N_2$ | 0.134 | 6.12 | 16.7 | 5.97 | 8.02 | 0.15 |
| $CO_2$ | 1.77 | 3.25 | 17.1 | 5.94 | 104 | −2.69 |
| $CH_4$ | 0.391 | 5.49 | 11.9 | 6.53 | 32.8 | −1.04 |
| $C_2H_6$ | 0.622 | 4.77 | 3.61 | 7.69 | 172 | −2.92 |
| $C_2H_4$ | 0.753 | 4.67 | 5.74 | 7.27 | 131 | −2.60 |
| $C_3H_8$ | 0.616 | 4.38 | 1.21 | 8.59 | 511 | −4.21 |

Units: see footnote to Table A.1.

**Table A.4    Gas Transport Parameters for Hydrogen, Oxygen, Nitrogen, Carbon Dioxide, and Hydrocarbon Gases in Poly(di-neopentyloxyphosphazene) (Pneo-PeP)**

| Gas | $P$ (25°C) $\times 10^8$ | $E_p$ | $D$ (25°C) $\times 10^7$ | $E_d$ | $S$ (25°C) $\times 10^4$ | $\Delta H_s$ |
|---|---|---|---|---|---|---|
| $H_2$ | 0.657 | 5.05 | 108 | 4.04 | 6.10 | 1.01 |
| $O_2$ | 0.154 | 5.84 | 8.40 | 6.82 | 18.3 | −0.98 |
| $N_2$ | 0.0346 | 7.27 | 3.36 | 8.07 | 10.3 | −0.80 |
| $CO_2$ | 0.487 | 4.54 | 3.98 | 7.59 | 122 | −3.05 |
| $CH_4$ | 0.0751 | 7.27 | 1.82 | 9.07 | 41.3 | −1.80 |
| $C_2H_6$ | 0.0460 | 7.82 | 0.193 | 12.1 | 238 | −4.27 |
| $C_2H_4$ | 0.0738 | 7.39 | 0.478 | 10.4 | 154 | −3.05 |

Units: see footnote to Table A.1.