

Gas Transport in Poly[bis(trifluoroethoxy)phosphazene]

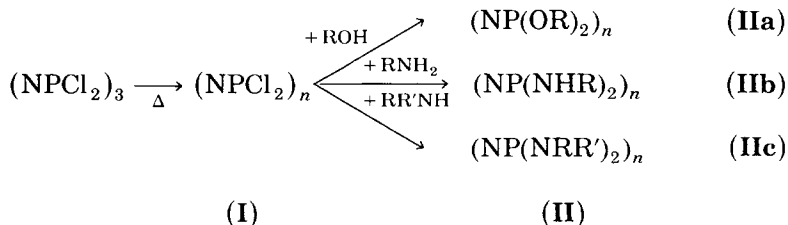
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Synopsis

The gas transport parameters of 14 gases in poly[bis(trifluoroethoxy)phosphazene] were determined at temperatures ranging from about 12 to 45°C by the time-lag method. The phosphazene polymer demonstrated a high diffusivity; rather high crystallinity was expected, though. The permeation data determined were between polydimethylsiloxane and low-density polyethylene. The most interesting characteristic shown over the course of experimentation is that poly[bis(trifluoroethoxy)phosphazene] has significantly high solubility for CO₂, as compared to other gases. The polar side groups—i.e., the electron-withdrawing trifluoroethoxy parts—which should contribute specific interaction with CO₂, were shown to be stronger than their interaction with the polar N₂O molecule. The sorption behavior is compared with those of other rubbery polymers, while phosphazene polymer characteristics are also discussed.

INTRODUCTION

The study of phosphazene polymers continues to be a vital research interest from the standpoint of fundamental research and technological development.¹ Allcock and Kugel first discovered that essentially linear polydichlorophosphazene (I) can be obtained by limiting the polymerization reaction, and thus can be used as a substrate in order to prepare a wide range of polyorganophosphazene (II) by reacting with nucleophiles such as alkoxides, aryloxides, and amines.² In the period since Allcock et al.'s work, many polyalkoxyphosphazenes and polyaryloxyphosphazenes (IIa) have been prepared and studied because of the interesting structures and properties they contain, such as these: elastic, film-forming, and biologically compatible.¹



Gas transport behavior in polyalkoxyphosphazene films is a very worthwhile research area in polyphosphazene chemistry. Bittirova et al. have reported the permeabilities of three gases, O₂, N₂, and Ar, in polydioctyloxyphosphazene³; additionally, many patents exist on various phos-

phazene polymers. A review of the literatures indicates that the phosphazene polymers have significantly high gas permeabilities, next to those of polyacetylenes with bulky substituents^{4,5} and polydimethylsiloxane (PDMS).⁶⁻⁸ Thus far, no detailed work on diffusion and solubility coefficients has been reported, and there has been no systematic study performed on the correlation between gas transport parameters and their chemical structures or physical properties.

It is well known that permeation of gases through polymers occurs by a solution-diffusion mechanism, and gas transport in rubbery polymers is relatively easy to understand compared to that in glassy polymers.⁹ The permeability coefficient P , which is derived experimentally from the steady state of gas permeation, is the product of the mean diffusion \bar{D} and the solubility \bar{S} coefficients. When the concentration of sorbed gas is sufficiently low, the sorption isotherm of a gas in a rubber is linear; that is, the solubility coefficient S is constant, and the diffusion coefficient is usually assumed to be constant, D . Therefore, P is written by

$$P = D \times S \quad (1)$$

In such a case, D is easily obtained from the diffusional time lag θ by^{9,10}

$$D = l^2/6\theta \quad (2)$$

where l is the film thickness. Therefore, eq. (1) is used to calculate S from two other parameters obtained from the time-lag method.^{9,10} These transport parameters obtained from the method should be deeply related to the chemical and physical properties of the polymer. Recently, several series of related polymers have been studied from this point of view.^{7,8,11-15} However, it continues to be a difficult problem to make clear the relationship between chemical structure or other properties and gas transport property. The objective of this study is to better understand the relationship between gas permeability and the structure of rubbery phosphazene polymers. For the purpose of the study, poly[bis(trifluoroethoxy)phosphazene] (PTFEP), which is commercially available, was chosen as an initial sample; transport parameters were determined for a number of gases, and a comparison was made with three other rubbery polymers, such as PDMS, low-density polyethylene (LDPE), and natural rubber (NR).

EXPERIMENTAL

As noted above, permeation measurements were performed by the high-vacuum time-lag method.^{13,14} However, for the purposes of this study, a new experimental apparatus was constructed in order to determine short time lags with precision. All of the tubing, connections, and valves, and the permeation cell itself were made of stainless steel, while the downstream pressure was monitored with an MKS Baratron 317HA-type pressure transducer; fast response time is 1 s. The pressure transducer was directly attached to the permeation cell with a 1-in. diameter tube. Both the permeation cell and the

pressure transducer were placed in an air bath, thermostatically controlled within the precision $\pm 0.1^\circ\text{C}$.

Another Baratron pressure transducer 227A type was put into place in order to monitor the pressure of the upstream side. The two pressure transducers were connected with a microcomputer (PC-9801F, NEC), via an AD converter (AB98-05, ADTEC). The microcomputer was set to record the experimental data and also to obtain the transport parameters by means of our laboratory-designed software, programmed for us by Tsukuba Rikaseiki Co., Ltd. The permeation measurements for PDMS and LDPE were also compiled by the microcomputer system; details on these aspects of the test apparatus will be reported elsewhere.

The sample film of PTFEP, kindly supplied from Nippon Soda Co., Ltd., was prepared as follows: A solution of around 15% tetrahydrofuran of the polymer was made; a film was then cast onto a glass plate floating on mercury, and was kept at room temperature for several days. The remaining solvent was removed under vacuum, and the film molded under compression at about 15 MPa and 150°C ; finally, the molding apparatus was water-cooled after a 30-min wait.

The literature indicates that the crystalline form of PTFEP would be modified to γ -form during the treatment;¹⁶ however, no currently available data indicates how to determine the crystallinity of PTFEP. For the first time, during the course of this procedure, the crystallinity was estimated to be about 0.60 by wide-angle X-ray spectroscopy.¹⁷ The film thickness was $117.6\ \mu\text{m}$ and the density, determined by a floating method with a KI aq solution was $1.707\ \text{g}/\text{cm}^3$ at 25°C , while the glass transition temperature (T_g) of PTFEP was -82°C , determined by differential scanning calorimetry with a Dupont 9900 thermal analyzer, and which was in agreement with the literature values.^{1,18}

As reported previously,¹⁹ the film of LDPE (Rexlon), from Nippon Petrochemical Co., Ltd., was prepared by a Haake Transfermix. The thickness was $212.1\ \mu\text{m}$ and the density, determined by the use of an isopropanol-water solution, was $0.918\ \text{g}/\text{cm}^3$ at 25°C , from which the crystallinity was estimated as 0.45 with the assumption of additivity of density.²⁰

Polydimethylsiloxane film of $108.1\ \mu\text{m}$ thickness was kindly supplied from ShinEtsu Chemical Co., Ltd.

RESULTS AND DISCUSSION

The temperature dependence of P in PTFEP is presented in the Arrhenius plots for noble gases at temperatures between about 12 and 45°C in Figure 1. To estimate D and S , eqs. (1) and (2) were used. The rationale for this choice was our demonstration that the plasticization effect of CO_2 , one of the most soluble gases, is negligible for a few glassy polymers below 1 atm.^{21,22} Therefore, D and S are expected to be constant under the present experimental conditions, and, further, no pressure dependence was observed for P during our measurements. The temperature dependence of D and S are presented in Figures 2 and 3, respectively; additionally, a linear relationship was obtained for every gas measured in this study. The straight lines in Figures 2 and 3 show no transition in the rubbery state of PTFEP at this temperature range.

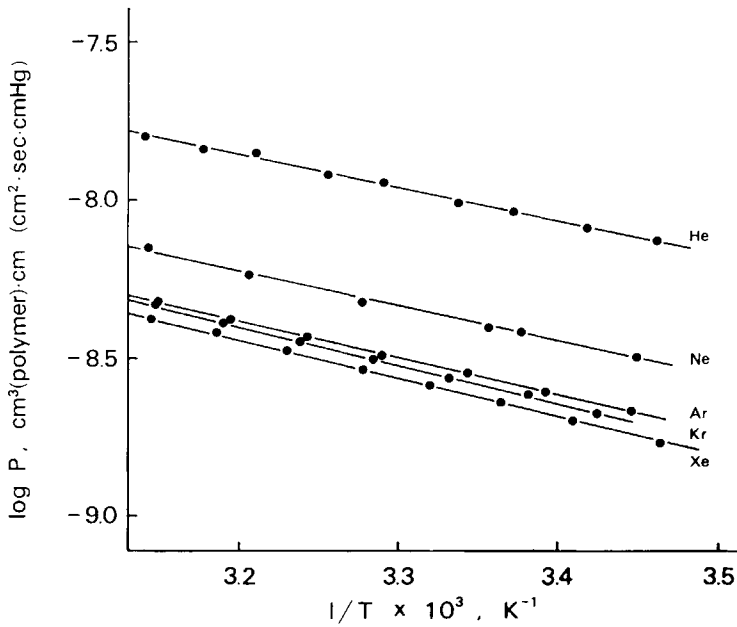


Fig. 1. Arrhenius plot of the permeability coefficients for the noble gases in poly[bis(trifluoroethoxy)phosphazene].

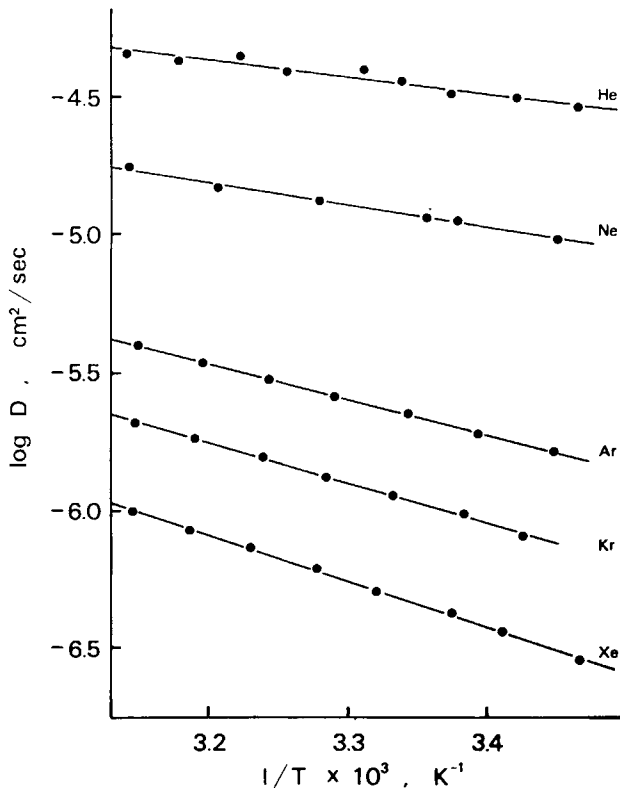


Fig. 2. Arrhenius plot of the diffusion coefficients for the noble gases in poly[bis(trifluoroethoxy)phosphazene].

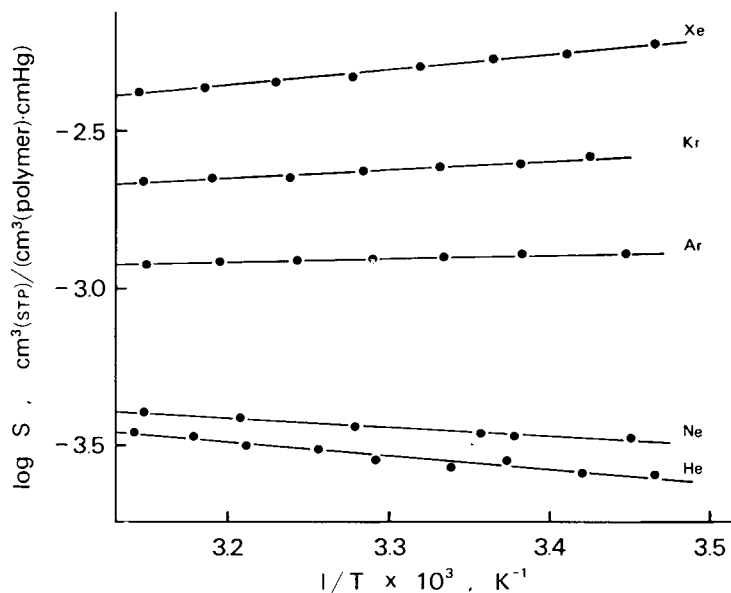


Fig. 3. Van't Hoff plot of the solubility coefficients for the noble gases in poly[bis(trifluoroethoxy)phosphazene].

In Table I, the transport parameters at 25°C, and their activation energies, E_p and E_d , and the heat of solution, ΔH_s , are listed for noble gases.

The data of other gases are shown in Tables II and III, while Table IV lists the transport parameters in other rubbery polymers for O_2 and N_2 . A comparison of Tables II and IV demonstrates that PTFEP is highly gas permeable. Although the permeability of PTFEP does not reach PDMS, it is more than 1 order higher than that of LDPE, and about 50% higher than that of NR. The P value falls between that of PDMS and LDPE, and is shown to be caused by the high diffusivity of PTFEP since S is comparable to that of NR, and only a few times larger than that of LDPE. A similar tendency was observed for all gases except CO_2 . As noted above, P is the product of D and S ; hence, gas transport in PTFEP should be discussed separately in terms of diffusivity and solubility.

TABLE I
Gas Transport Parameters for Noble Gases in Poly [bis(trifluoroethoxy)phosphazene]
at 25°C^a

Gas	P	E_p	D	E_d	S	ΔH_s
He	9.456×10^{-9}	4.71	3.430×10^{-5}	2.67	2.757×10^{-4}	2.04
Ne	4.197×10^{-9}	5.00	4.385×10^{-5}	3.65	3.620×10^{-4}	1.35
Ar	2.731×10^{-9}	5.24	2.161×10^{-6}	5.81	1.263×10^{-3}	-0.57
Kr	2.576×10^{-9}	5.45	1.052×10^{-6}	6.69	2.448×10^{-3}	-1.24
Xe	2.334×10^{-9}	5.50	4.460×10^{-7}	7.71	5.233×10^{-3}	-2.21

^aUnits: P [$cm^3(STP) \cdot cm / (cm^2 \cdot s \cdot cmHg)$], E_p (kcal/mol), D (cm^2/s), E_d (kcal/mol), S [$cm^3(STP)/(cm^3(polymer) \cdot cmHg)$], and ΔH_s (kcal/mol).

TABLE II
Gas Transport Parameters for Di- and Triatomic Molecules in
Poly[bis(trifluoroethoxy)phosphazene] at 25°C^a

Gas	P	E_p	D	E_d	S	ΔH_s
H ₂	6.319×10^{-9}	5.14	1.618×10^{-5}	3.97	3.903×10^{-4}	1.17
O ₂	3.544×10^{-9}	4.88	2.783×10^{-6}	5.36	1.273×10^{-3}	-0.48
N ₂	1.472×10^{-9}	5.81	1.715×10^{-6}	6.19	8.580×10^{-4}	-0.12
CO ₂	1.963×10^{-8}	2.89	1.266×10^{-6}	6.51	1.550×10^{-2}	-3.62
N ₂ O	2.160×10^{-8}	2.81	1.342×10^{-6}	6.32	1.609×10^{-2}	-3.51

^aUnits: P [cm³(STP) · cm/(cm² · s · cmHg)], E_p (kcal/mol), D (cm²/s), E_d (kcal/mol), S [cm³(STP)/(cm³(polymer) · cmHg)], and ΔH_s (kcal/mol).

TABLE III
Gas Transport Parameters for Hydrocarbon Gases in Poly[bis(trifluoroethoxy)phosphazene]
at 25°C^a

Gas	P	E_p	D	E_d	S	ΔH_s
CH ₄	1.903×10^{-9}	5.58	1.130×10^{-6}	6.62	1.683×10^{-3}	-1.04
C ₂ H ₆	1.965×10^{-9}	5.26	3.611×10^{-7}	7.99	5.442×10^{-3}	-2.73
C ₂ H ₄	3.581×10^{-9}	4.52	5.911×10^{-7}	7.52	6.058×10^{-3}	-3.00
C ₃ H ₈	1.670×10^{-9}	4.94	1.291×10^{-7}	8.94	1.293×10^{-2}	-4.00

^aUnits: P [cm³(STP) · cm/(cm² · s · cmHg)], E_p (kcal/mol), D (cm²/s), E_d (kcal/mol), S [cm³(STP)/(cm³(polymer) · cmHg)], and ΔH_s (kcal/mol).

Many experiments have tried to relate gas diffusivity to thermal expansivity, free volumes, density, and so on;^{9,11,12} we, however, have shown that E_d clearly can be related to expansivity in a series of polymers which have the same main structure.^{13,14} But the polymers compared here are very different from each other: PTFEP and LDPE are crystalline rubbers, and PDMS and NR are amorphous, yet crosslinked. Furthermore, the main chains of PTFEP and PDMS consist of inorganic elements. Their physical properties T_g , the density at 25°C (d_{25}), and the coefficient of thermal expansion (α), are all listed in Table V in order to compare these polymers with the diffusivity data listed for Ar 25°C in them. As was expected, Table V shows that E_d becomes smaller as D increases, but no other reasonable correlation can be seen.

TABLE IV
Gas Transport Parameters for O₂ and N₂ in PDMS, NR, and LDPE at 25°C^a

Polymer	Gas	P	E_p	D	E_d	S	ΔH_s
PDMS	O ₂	5.840×10^{-8}	2.06	1.948×10^{-5}	2.45	2.998×10^{-3}	-0.39
	N ₂	2.699×10^{-8}	2.68	1.624×10^{-5}	2.67	1.662×10^{-3}	0.011
NR ^b	O ₂	2.4×10^{-9}	7.5	1.6×10^{-6}	8.3	1.5×10^{-3}	-0.8
	N ₂	8.1×10^{-10}	8.8	1.1×10^{-6}	8.7	7.4×10^{-4}	0.1
LDPE	O ₂	2.713×10^{-10}	9.64	4.729×10^{-7}	9.10	5.737×10^{-4}	0.54
	N ₂	8.590×10^{-11}	11.05	2.979×10^{-7}	10.42	2.884×10^{-4}	0.63

^aUnits: P [cm³(STP) · cm/(cm² · s · cmHg)], E_p (kcal/mol), D (cm²/s), E_d (kcal/mol), S [cm³(STP)/(cm³(polymer) · cmHg)], and ΔH_s (kcal/mol).

^bRef. 22.

TABLE V
Some Physical Properties of PTFEP, PDMS, NR, and LDPE

Polymer	T_g (K)	d_{25} (g/cm ³)	α ($\times 10^{-4}$ /deg)	Ar ^a	
				D	E_d
PTFEP	191	1.707	2.48 ^b	2.161×10^{-6}	5.81
PDMS	146 ^c	0.970 ^d	9.07 ^d	1.744×10^{-5}	2.47
NR	200 ^e	0.913 ^f	6.54 ^f	1.4×10^{-6g}	8.3 ^g
LDPE	148 ^e	0.918	8.22-7.68 ^h	3.510×10^{-7}	9.80

^aUnits: D (cm²/s) and E_d (kcal/mol).

^bRef. 24.

^cRef. 25.

^dRef. 26.

^eRef. 27.

^fRef. 28.

^gRef. 23.

^hRef. 19.

In earlier papers,^{13,14} the E_d values were related to the molecular diameters of gases, but the relationship is not still clear; that relationship was examined in this study, also. In Figure 4, E_d for the various gases in PTFEP are plotted as a function of d^2 , where d is the molecular diameter of each gas. A linear relationship was seen between E_d and d^2 for this polymer. In Figure 5, E_d

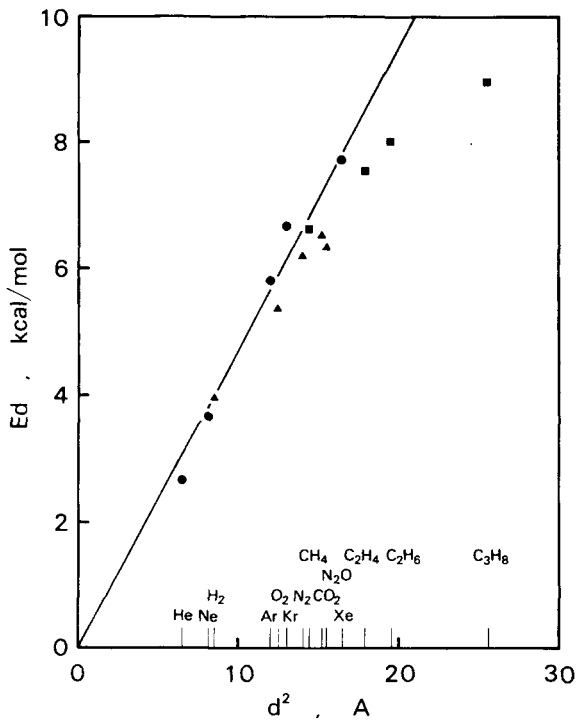


Fig. 4. Activation energies for diffusion for 14 gases in PTFEP vs. d^2 (the molecular diameters).

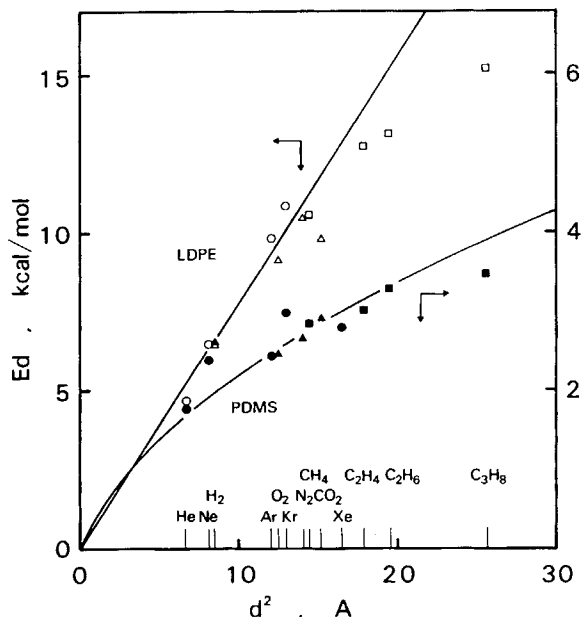


Fig. 5. Activation energies for diffusion for 13 gases in PDMS and LDPE vs. d^2 (the molecular diameters).

for LDPE was also linear to d^2 , but the data for PDMS showed a good linearity for d , not for d^2 . In every case, the correlation line was drawn for the E_d values of spherical molecules.²⁹ From the present and the previous results, it seems to be difficult to conclude a general relationship between E_d and the molecular diameter of a penetrant. In other words, it depends on certain properties of a polymer, which is related to the structure of each polymer.³⁰ It is possible that the power of the d value may not be required to be an integer for some gas-polymer systems.⁹ Further theoretical and phenomenological investigation will be necessary.

From microscopic observation, it was apparent that PTFEP had many spherical crystallines, and the crystallinity estimated was about 60% as mentioned in the Experimental section. As shown in Tables I-III, PTFEP shows rather high diffusion coefficients for gases, but the effect of crystallinity or crystalline form has not been considered in this discussion. It usually has been accepted that crystallinity reduces the diffusion coefficient.^{31,32} Therefore, much higher—possibly more than two times higher—diffusivity can be expected in the pure amorphous phase. The work to demonstrate this hypothesis is presently under way.

The solubilities of gases in a given polymer are usually correlated to the force parameters of gases, such as the Lennard-Jones force constant, the boiling point, and the critical temperature.^{7,9,20} The relationship between solubility at 25°C and the Lennard-Jones force constant, ϵ/k , are plotted in Figure 6, as has been done in the previous papers.^{13,14} PDMS and LDPE data are also plotted in Figure 7. Good linearity was obtained for each polymer, but the relationship is quite different between PTFEP and PDMS or LDPE. As a result, the gas solubility in PTFEP is closer to that of PDMS when the ϵ/k

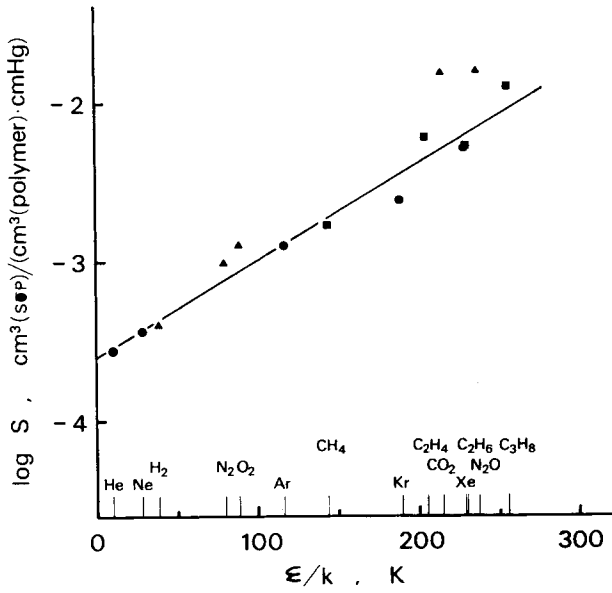


Fig. 6. The solubility coefficients for 14 gases at 25°C in PTFEP vs. The Lennard-Jones force constants ϵ/k .

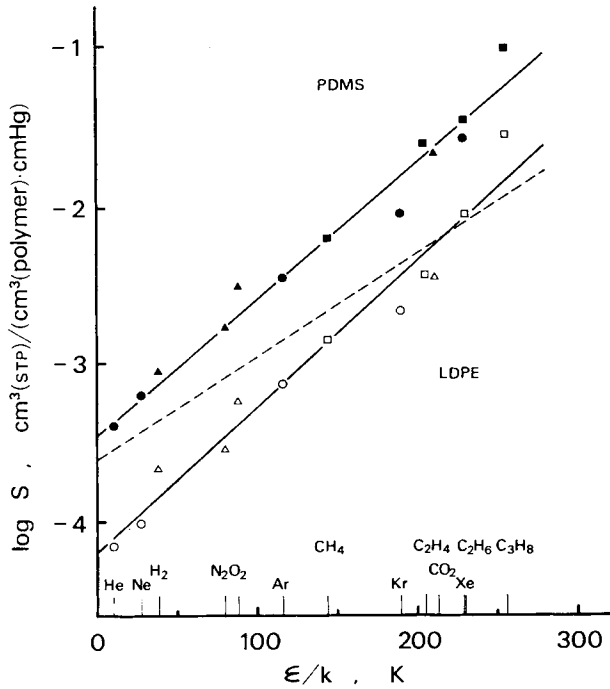


Fig. 7. The solubility coefficients for 13 gases at 25°C in PDMS and LDPE vs. the Lennard-Jones force constants ϵ/k . Dashed line is the data of PTFEP shown in Figure 6.

values are small, and it moves closer to that of LDPE as the ϵ/k values increase; clearly, this result is caused by the large difference of chemical properties of the polymer, PTFEP. Michaels and Bixler showed that the plot of LDPE parallels that of solubility in nonpolar liquids.²⁰ These results of PDMS show that the character of this polymer is similar to both LDPE and nonpolar liquids for the solution of gases, while, again, PTFEP's characteristics are markedly different from this grouping of polymers. Therefore, although the solution mechanism is not completely clear, the polarity of the phosphorous-nitrogen chain of phosphazene polymer must be the main reason of the difference indicated in Figures 6 and 7.

Another interesting feature of Figure 6 is that the solubilities of CO₂ and N₂O in PTFEP deviate upward from the relationship. Similar results have been reported for the CO₂-fluorine-containing polymer systems, i.e., the solubility of CO₂ in poly(trifluoropropyl methyl siloxane)^{7,8} and that of poly(vinylidene fluoride)³³ are quite high, when compared with other gases. In those reports, the authors noted that the high solubility of CO₂ arises from the polar nature of the polymers, which include fluorine-containing parts. This study solidly confirms their findings. The CO₂ molecule is nonpolar as a whole, but local polarity is expected to exist, and the polarities of polymer and CO₂ should interact with each other.

The data on polar N₂O gas seems to support this expectation; however, the solubility of CO₂ is a somewhat higher than that of N₂O, although the ϵ/k value of CO₂ is smaller, signifying that the interaction between PTFEP and CO₂ is stronger. To find three research groups in such agreement with their results on three different polymers containing fluorine atoms is significant; thus, this discussion is expected to be generally valid. Therefore, the solubility, and then the permeability of a polymer, will be enhanced, at least for CO₂, by introducing fluorine atoms in the structure.

In order to further improve gas transport property of the phosphazene polymer, it is necessary to consider the characteristics in connection with its structure, even if it is a preliminary examination. The most important characteristic of phosphazene polymers is that the main chain contains inorganic elements, phosphorous atoms, similar to the silicones in polyorganosiloxane polymers. As Allcock mentioned in his review,¹ inorganic elements have relatively large covalent radii and the backbones of such elements move easily. Consequently, many of phosphazene and siloxane polymers are rubbers at ambient temperature. From the viewpoint of gas transport, this is an important feature because the polymers would be expected to have a great deal of free volume where gas diffusion occurs.

The conformation of the main chain is another characteristic of phosphazene polymer, with the *cis-trans* planar conformation appearing to be most plausible from a review of the literature.¹ Coupled with this distorted tetrahedral arrangement, the side groups of the phosphorous atom are directed exo, with respect to the chain axis. It is not a simple matter to say that the conformation is favorable to diffusion of the gases. However, when an appropriate side group is chosen, the side groups will work to increase the free volume, and gas permeability will be further improved.

As mentioned above, PTFEP has a large crystalline region, and, thus, gas diffusivity in the amorphous phase should be higher than it is in the present

data. If the polymer is partly modified by introducing another side group, the crystallinity will decrease because the symmetry in the structure is reduced, and the increases of both gas diffusivity and solubility will contribute to the increase of apparent permeability. A potential advantage of phosphazene polymer is that a variety of derivatives are easily prepared from a wide range of nucleophiles.

On the other hand, the local polarity between nitrogen and phosphorous atoms can be attributed to several properties of phosphazene polymers. Although its effects on gas transport properties are not completely clear, it seems that one characteristic of the solution of gases in PTFEP is due to this polarity. Further, it may increase the solubility of polar gases because of certain interactions. Clearly, there are many problems to be solved in examining the correlation between the structure of phosphazene polymers and their gas transport properties, and a systematic study of the use of several rubbery phosphazene polymers will be useful in solving some of these problems.

SUMMARY

The gas permeability of PTFEP was examined extensively by the use of the time-lag method. The transport property of PTFEP lies between that of PDMS and LDPE, but the solubility data in the polymer is quite different from both of them. The high solubility of CO₂ is an interesting characteristic because of the side groups that contain fluorine atoms. Considering its crystallinity, diffusivity in a pure amorphous polymer is expected to be very high. The use of phosphazene polymer is a good research tool, not only for the study of gas transport in polymers, but also as an aid in the development of new polymers.

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