Gas transport properties of cured polyalkoxysilylbutadiene

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The gas solubility and permeability of various cured polyalkoxysilylbutadiene films were studied. The alkoxysilyl groups of this polymer react and crosslink by curing in the presence of saturated water vapour around 100°C. The permeability coefficients of loosely cured polyalkoxysilylbutadiene films varied considerably with the bulkiness of the alkoxy groups and crosslinking density and were high compared with polybutadiene, which composes the main chain. The cured polytriisopropoxysilylbutadiene showed the highest O_2 gas permeability coefficient of various polyalkoxysilylbutadiene films. The high gas permeability of the cured polyalkoxysilylbutadienes, which is comparable to polydimethylsiloxane, is attributed to the fact that gas diffusivity is enhanced by the increasing mobility of unreacted alkoxy groups, since solubility is almost independent of the species of alkoxysilyl group. This enhancement of mobility might be attributed to local coarse structure, in other words local increased free volume near –Si–O–Si– or –Si–OH formed by the release of alkylalcohol during curing. The selectivities, i.e. permeability coefficient ratios of O_2 to N_2 of various cured polyalkoxysilylbutadiene films ranged from 2 to 4.

(Keywords: polyalkoxysilylbutadiene; crosslinking; permeation; sorption; diffusion; permselectivity)

INTRODUCTION

Oxygen and nitrogen separation characteristics of polymer films have been a subject of interest in the field of gas separation for many years because of their potential uses in medicine and combustion. Various polymers, including silicone rubber, have been reported as gas permeable films[1-10]. Rubbery polydimethylsiloxane and its derivatives[1,2] have been reported to have high O_2 gas permeability coefficients. Glassy poly(1-trimethylsilyl-1-propyne)[3-8] is also noted as a polymer film showing the highest permeability coefficient $\bar{P}$ to oxygen among polymer films developed: O_2 gas permeability coefficient $\bar{P}_{O_2} = 4.0 \times 10^{-7} cm^3$(s.t.p.) $cm\, cm^{-2}\, s^{-1}\, cmHg^{-1}$†. The permeability of the former is enhanced mainly owing to active segmental motion and/or much free volume based on the high flexibility of the siloxane bond. The permeability of the latter is enhanced mainly by a large unrelaxed volume in the glassy polymer[8]. Thus the free volume of these polymer films plays an important role in permeability and diffusion coefficients. Enhancement of gas diffusivity governed by the free volume of polymer films is an effective method for improving gas permeability.

The present paper reports on the gas sorption and permeation of polyalkoxysilylbutadiene films with various types of trialkoxysilyl groups introduced as the side chain of polybutadiene (PB). These groups, which possess large bulkiness, bring about an increase of free volume due to the formation of loose crosslinking between butadiene segments. The alkoxy groups in the side chain can be made to react and crosslink by curing in the presence of water and thus membrane structure is expected to be regulated by cure period and/or cure temperature.

Sorption and permeation mechanisms in and through loosely cured rubbery polyalkoxysilylbutadiene films are clarified for various gases. The influence of alkoxysilyl groups on gas selectivity is also discussed.

EXPERIMENTAL

Materials

Various types of polyalkoxysilylbutadienes[11] were polymerized from the monomer, which was manufactured at Nissan Chemical Industries Ltd. *Cis* content of the samples is 70–80%. Alkoxysilyl groups introduced as the side chain of PB were as follows: trimethoxysilyl, dimethyl iso-propoxysilyl, methyl diiso-propoxysilyl, triiso-propoxysilyl and tritert-butoxysilyl groups. Abbreviations used for these polymers are shown in *Table 1*. It is difficult to prepare measurable films without any support, except for tri-PtBOSB. A cure reaction was carried out to improve film formability. The cured films were prepared by exposing films to saturated water vapour at different temperatures for various periods in the course of casting from 10% THF solution in a Teflon petri dish, since these polymers are hydrophobic and the reaction does not proceed homogeneously in the films after casting. All films used for permeation measurements were prepared by using Duragard (0.2 μm × 0.02 μm, pore density 0.38) as support film.

O_2, N_2, CO_2 and CH_4 used in this study are at least 99.9% pure and used without further purification.

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† 1 cmHg ≈ 1.3 kPa

Table 1 Cure conditions of various polyalkoxysilylbutadienes

Alkoxysilyl group	Abbreviation	T_g (°C)^a	Cure temp. (°C)	Cure period (h)	T_g (°C)^b
$-Si(OCH_3)_3$	Tri-PMOSB	-63	100	10	-45
$-Si(OC(CH_3)_3)_3$	Tri-PtBOSB	-55	$-$	$-$	$-$
$-Si(OCH(CH_3)_2)_3$	Tri-PiPOSB	-57	100	18	-48
$\begin{array}{c} CH_3 \\ -Si(OCH(CH_3)_2)_2 \end{array}$	Di-PiPOSB	-69	100	15	-55
$\begin{array}{c} (CH_3)_2 \\ -Si(OCH(CH_3)_2) \\ CH_3 \end{array}$	Mono-PiPOSB	-76	100	15	17

^{a} T_g of non-cured sample
^{b} T_g of cured sample

Method

Differential scanning calorimetry (d.s.c.) measurements were made using SSC 560 apparatus (Seiko Electronics Co. Ltd). D.s.c. thermograms were obtained at a heating rate of 15°C min^{-1} from -100 to 100°C in an atmosphere of dry N_2. The glass transition temperature, T_g, was determined as the onset temperature varying from the heat capacity in the glassy state to that in the rubbery state.

Fourier transform infrared FTi.r. spectroscopy measurements of various cured polyalkoxysilylbutadienes were made at 25°C with a Nicolet 5DX FTi.r. spectrometer.

The film held in a permeation cell sealed with a Teflon plate was degassed for 24 h under 10^{-4} mmHg in a permeation apparatus and a permeation measurement at 25°C was made as follows: the downstream side of the film was evacuated to $\approx 10^{-4}$ mmHg, permeant gas of differential pressure was introduced to the upstream side, and the permeated gas pressure in the downstream side was monitored using an MKS-Baratron pressure transducer (227AA). The permeability coefficient was evaluated from a permeation area corrected by the pore density of the support film, the thickness of film which contains the support film and the gas permeation rate in steady state.

Sorption measurements were made at 25°C by using a gravimetric sorption apparatus with electromicrobalance 2000 (Cahn Instruments Inc.). After sufficient drying of the films under about 10^{-4} mmHg, the net sorption amount of gas sorbed in the film at a fixed pressure was corrected by subtracting a buoyancy contribution.

RESULTS AND DISCUSSION

Cure reaction

The structural change of cured polyalkoxysilylbutadiene was examined by FTi.r. spectroscopy. A typical example of FTi.r. spectra of tri-PiPOSB cured under various conditions is shown in *Figure 1*. The solid lines A and B show, respectively, the spectra of non-cured tri-PiPOSB and tri-PiPOSB cured in saturated water vapour at 100°C for 18 h. The intensities of bands 2 and 3 near 2960 cm^{-1} and 1380 cm^{-1}, respectively, which are assigned to the vibration of $-Si-O-$ in $-Si-OCH(CH_3)_2$, decreased considerably after the cure reaction. On the contrary, the intensity of band 1, assigned to the vibration of $-Si-OH$, near 3300 cm^{-1} and band 4, assigned to the stretching vibration of $-SiOH$ or $-Si-O-Si-$, near 1000–1300 cm^{-1} increased after the reaction. The formation of the siloxane bond, $-Si-O-Si-$, was also confirmed by the fact that the cured sample was not dissolved in THF solution again. Similar cure reactions were also observed
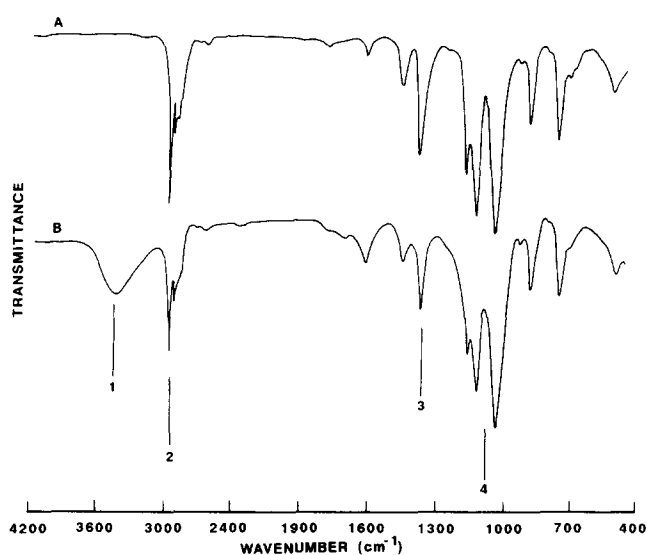
Figure 1 FTi.r. absorption spectra of tri-PiPOSB: A, non-cured; B, cured at 100°C for 18 h
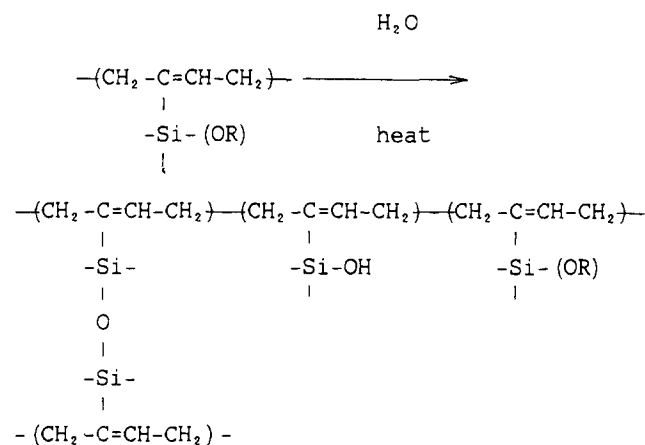
Scheme 1 Cure reaction of polyalkoxysilylbutadiene in saturated water vapour (R = alkyl group)

for another polyalkoxysilylbutadiene. The reactivity of the various polyalkoxysilylbutadienes was influenced by the bulkiness of the side chain as shown in *Table 1*.

On the basis of these facts *Scheme 1* is proposed as the cure reaction of polyalkoxysilylbutadiene in saturated water vapour. Some alkoxysilyl groups were reacted to $-SiOH$ and $-Si-O-Si-$, which plays a role in crosslinking butadiene backbones. As a result of a cure reaction, the mobility of unreacted alkoxy groups may be enhanced by the local coarse structure near $-Si-O-Si-$ or $-SiOH$ formed by releasing alkylalcohol during curing, since the mobility of bulky alkoxy groups may be depressed by

the steric hindrance among side chains in the unreacted state. Such a local structure change is expected to improve membrane functions. Furthermore, the crosslinked structure formed by the above reaction provided the mechanical strength for various measurements studied here. The film itself can be regulated from rubbery to glassy state by altering the cure condition. For example, the glass transition temperature, T_g, of non-cured tri-PMOSB is $-63°C$, whereas the T_g of cured tri-PMOSB varies from -50 to $30°C$ on raising the cure temperature from 30 to 110°C, with the cure period remaining constant at 5 h. In this study, only loosely cured rubbery polymer was used for sorption and permeation measurements. The crosslinking density of films obtained cannot be clearly determined from i.r. spectroscopy at present since band 4 of $-Si-O-Si-$ overlaps with the bands of $-SiOH$. T_g was, therefore, used as a measure of crosslinking density in this study: higher T_g indicates higher crosslinking density. *Table 1* lists the T_g values of various cured polyalkoxysilylbutadienes together with the cure conditions.
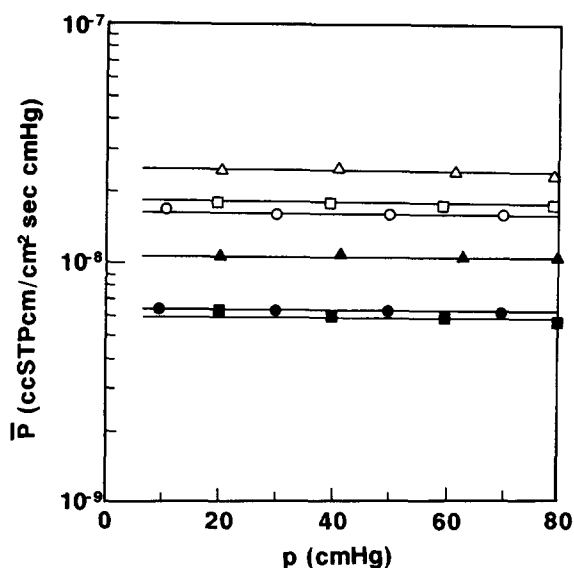

Figure 2 Pressure dependence of O_2 (open symbols) and N_2 (filled symbols) gas permeability coefficient of various cured polytrialkoxysilylbutadienes: ○, ●, tri-PMOSB; △, ▲, tri-PiPOSB; □, ■, tri-PtBOSB

Permeation

Figure 2 shows the pressure dependence of O_2 and N_2 gas permeability coefficients for tri-PMOSB, tri-PiPOSB and tri-PtBOSB. A pressure dependence of permeability coefficients is not observed since these films are in the rubbery state at 25°C. The values of the permeability coefficients of these films are larger than those of PB[12], which composes the main chain ($\bar{P}_{O_2} = 1.9 \times 10^{-9}$ cm^3(s.t.p) cm cm^{-2} s^{-1} $cmHg^{-1}$). Furthermore, the permeability coefficient varies notably with the species of alkoxysilyl group. The permeability coefficient of tri-PiPOSB is the largest of the three samples, comparable with the permeability coefficient of polydimethylsiloxane. The diffusion of penetrant through rubbery polymer films is in general explained by penetrant size, volume fraction of penetrant and free volume of rubbery polymer films[13-15]. In this study, the volume fraction of penetrant is negligible because of the low solubility of penetrant, as mentioned below. Therefore, the high gas permeability of these loosely cured films might be attributable to the increase of free volume based on the enhancement of the mobility of unreacted alkoxy groups, reflecting local coarse structure near $-Si-O-Si-$ and $-SiOH$ as mentioned above. The degree of local course structure is likely to differ with the bulkiness of alkoxy groups. Note that the cured tri-PiPOSB film has much more free volume caused by the enhancement of mobility of the side chain region between the loosely cured polyalkoxysilylbutadienes studied here.

The contribution of the number of iso-propoxy groups attached to the silyl group to gas permeation was investigated. We synthesized polymethyl iso-propoxysilylbutadienes containing mono- or di-iso-propoxy groups and di- or mono-methyl groups, respectively, attached to the silyl group and called them mono-PiPOSB and di-PiPOSB, respectively.

Figure 3 shows the pressure dependence of the permeability coefficient of mono-, di- and tri-PiPOSB films for O_2, N_2, CO_2 and CH_4 gases at 25°C. A pressure dependence of permeability coefficient to various gases was not observed, as in *Figure 2*, reflecting the rubbery state of the films. The permeability coefficient of O_2 for mono-PiPOSB is lower than that for PB, but the other two films show higher permeability coefficients. The permeability coefficient to each gas increases with an increase in the number of the iso-propoxy groups
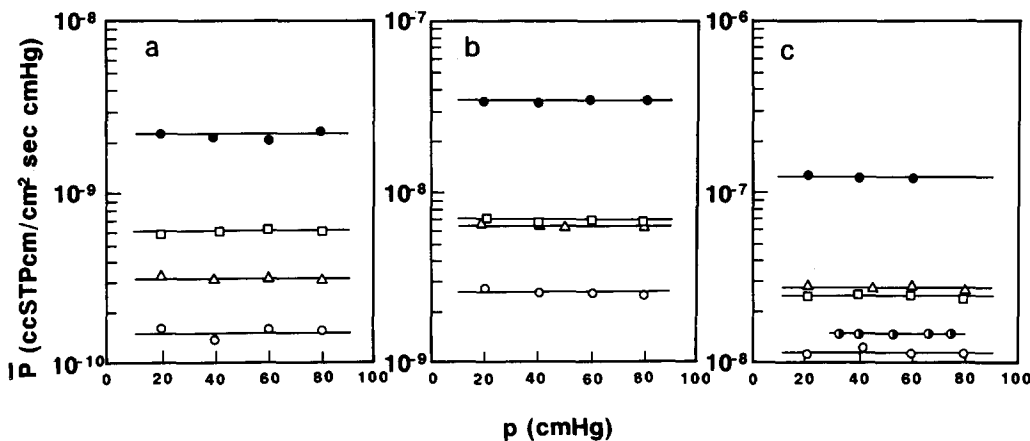

Figure 3 Pressure dependence of permeability coefficient of various cured polyalkoxysilylbutadienes to various gases: (a) mono-PiPOSB; (b) di-PiPOSB; (c) tri-PiPOSB. ●, CO_2; □, O_2; △, CH_4; ○, N_2. ◐, CO_2 for Tri-PiPOSB with $T_g \approx 52°C$
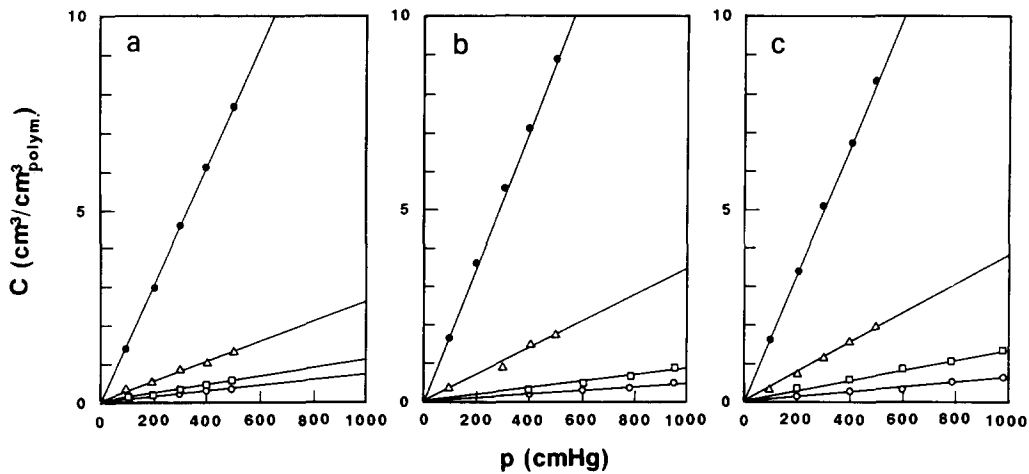
Figure 4 Sorption isotherms of (●) CO_2, (□) O_2, (△) CH_4 and (○) N_2 gases in various cured polyalkoxysilylbutadienes: (a) mono-PiPOSB; (b) di-PiPOSB; (c) tri-PiPOSB

Table 2 Transport properties of various cured polyalkoxysilylbutadienes

	$10^9 \bar{P}$ (cm^3(s.t.p.)cm cm^{-2} s^{-1} cmHg^{-1})			$10^7 \bar{D}$ (cm^2 s^{-1})			$10^3 S$ (cm^3(s.t.p.)cm^{-3} cmHg^{-1})		
	Mono-PiPOSB	Di-PiPOSB	Tri-PiPOSB	Mono-PiPOSB	Di-PiPOSB	Tri-PiPOSB	Mono-PiPOSB	Di-PiPOSB	Tri-PiPOSB
O_2	0.60	6.92	24.7	5.50	77.7	180	1.09	0.89	1.37
N_2	0.15	2.54	10.9	2.05	63.5	140	0.73	0.40	0.78
CO_2	2.32	34.5	123	1.46	19.2	72.8	15.9	18.0	16.9
CH_4	0.31	6.32	26.3	1.03	18.4	64.1	2.98	3.43	4.10

together with a lowering of T_g. The permeability of these films can be decreased by increasing crosslinking density or T_g. For example, the permeability coefficient of tri-PiPOSB, which has higher T_g ($\approx 52°C$), obtained by cure for 50 h at 120°C for CO_2 was decreased by about one order of magnitude, as shown in *Figure 3*. This suggests that the mobility of side chains is depressed by an increase in crosslinking density or T_g. It is interesting that the order of permeability coefficients of O_2 and CH_4 gases is different in mono- and tri-PiPOSB films. The permeability coefficient of O_2 is higher than that of CH_4 in mono-PiPOSB, but that of O_2 is lower than that of CH_4 in tri-PiPOSB, as shown in *Figure 3*. The cause will be discussed in detail below.

Gas sorption and diffusion were studied as described below to clarify the permeation mechanism.

Sorption and diffusion

Figure 4 shows the sorption isotherms of O_2, N_2, CO_2 and CH_4 gases in mono-, di- and tri-PiPOSB films at 25°C. The amount of sorption of each gas is proportional to applied pressure, indicating Henry's mode sorption, and the solubility coefficient (S) is obtained from the slope of the isotherms. The solubility coefficient of each PiPOSB varied with the species of gas, indicating different affinities of gases to polymer. It is known that $\log S$ versus ε/k, or $\log(Sp_c)$ versus $(T_c/T)^2$ (Reference 16) is a linear relationship, where ε, p_c and T_c are the Lennard–Jones potential well depth, critical pressure and temperature of penetrant, respectively. *Figure 5* shows a plot of $\log S$ versus ε/k for various cured polyalkoxysilyl-butadienes. There is a good linear relationship between $\log S$ and ε/k. This relationship is better than that of $\log(Sp_c)$ versus $(T_c/T)^2$. Therefore, the solubility coefficient is almost independent of side chain structure and the solubility coefficients of these samples are nearly equivalent
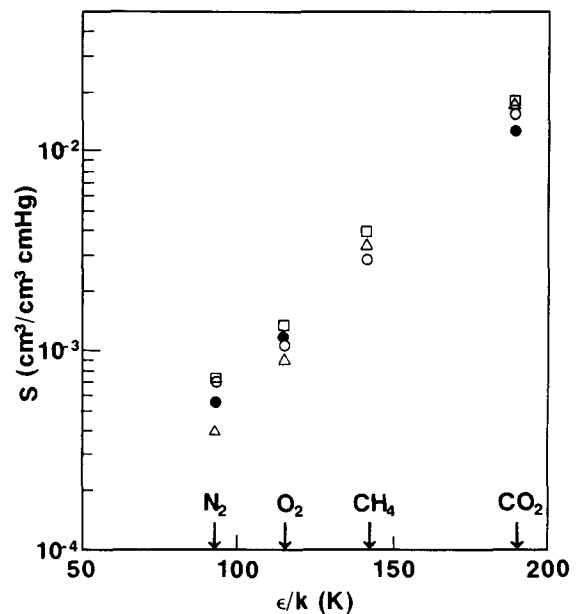

Figure 5 Correlation of solubility coefficient of various cured poly-alkoxysilylbutadienes and PB[12] with Lennard–Jones potential well depth of the gas: ●, PB; ○, mono-PiPOSB; △, di-PiPOSB; □, tri-PiPOSB

to those of PB. It is suggested that variation of alkoxysilyl group does not influence considerably solubility of gases.

The diffusion coefficient ($\bar{D}$) is obtained from the permeability and solubility coefficients as follows:

$$\bar{P} = \bar{D}S$$

Table 2 lists the diffusion coefficients of mono-, di- and tri-PiPOSB of each gas together with the permeability and solubility coefficients. The permeability coefficient varied drastically with the number of iso-propoxy groups

as mentioned above and the diffusion coefficient of individual gases also varied corresponding to the trend of the permeability coefficient. This behaviour may also be caused by the variation of crosslinking density, bulkiness of side chain and difference of T_g of each sample. The diffusion and permeability coefficients increased drastically with the number of iso-propoxy groups, indicating that the bulky iso-propoxy group is able to accommodate much more free volume caused by loose crosslinking and its bulkiness between the butadiene segments. The ratio of the free volume fractions of di- and tri-PiPOSB to mono-PiPOSB was determined by applying the following equation[13]:

$$D_T = RTA_d \exp(-B_d/v_f) \qquad (1)$$

where D_T is the thermodynamic diffusion coefficient, R is the gas constant, T is the absolute temperature, v_f is the free volume fraction, and A_d and B_d are characteristic parameters based on the size and shape of the penetrant molecule. The value of A_d used was $5.3 \times 10^{-11} \, m^2 \, mol \, s^{-1} \, J^{-1}$, determined previously for the polyethylene/CO_2 system[14]. The ratio of free volume fractions was determined by using equation (1). The free volume fraction increases with increasing number of iso-propoxy groups. The ratio of free volume fractions of di- and tri-PiPOSB are 1.4 and 1.8, respectively. The difference may be attributed to the fact that free volume between the butadiene segments was formed more effectively by reflecting the differences of bulkiness of alkoxysilyl groups and crosslinking densities.

We now consider the influence of the increase of the diffusion coefficient with increasing number of iso-propoxy groups on the selectivity of O_2 to CH_4 as an example. The permeability coefficients of O_2 and CH_4, gases are of a different order in mono-, di- and tri-PiPOSB, as mentioned above. The cause of this behaviour can be attributed to the fact that the solubility coefficient ratio of O_2 to CH_4 gas is almost independent of the side-chain structure but the diffusion coefficient ratio of O_2 to CH_4 decreases with increasing number of iso-propoxy groups as shown in *Table 2*.

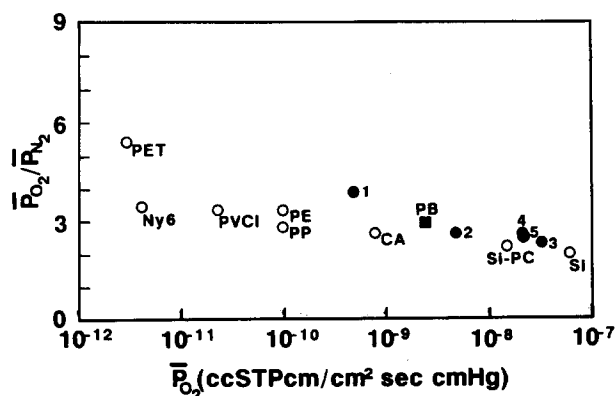*Figure 6* illustrates the plots of permselectivity of O_2 to N_2 *versus* O_2 permeability of cured polyalkoxysilyl-butadiene and many other polymer films[2,17]. It is obvious from this figure that the cured polyalkoxysilylbutadiene films, exhibit high O_2 permeability in comparison with the other polymer films. Selectivity of O_2 to N_2 of these films ranges from 2 to 4. The O_2 permeability coefficient of cured polyalkoxysilylbutadiene is comparable with that of polydimethylsiloxane.

CONCLUSIONS

The permeability coefficients of loosely cured polyalkoxy-silylbutadiene films varied considerably with the bulkiness of the alkoxy groups and crosslinking density. The permeability coefficients were high compared with poly-butadiene, which composes the main chain. Cured tri-PiPOSB showed the highest O_2 permeability coefficient of various polyalkoxysilylbutadiene films. The high gas permeability of the cured polyalkoxysilylbutadienes was attributed to enhancement of gas diffusivity caused by the increase of free volume due to the bulkiness of the side chain and loose crosslinking, since solubility is almost independent of the species of alkoxysilyl group. The selectivities of O_2 to N_2 of various cured polyalkoxy-silylbutadiene films range from 2 to 4. Research into improved O_2 permeation characteristics will continue.

ACKNOWLEDGEMENTS

Figure 6 Plots of O_2 permselectivity *versus* O_2 permeability coefficient of various cured polyalkoxysilylbutadienes and other polymer membranes: 1, mono-PiPOSB; 2, di-PiPOSB; 3, tri-PiPOSB; 4, tri-PMOSB; 5, tri-PtBOSB; PET, PET, polyethyleneterephthalate; Ny6, Nylon6; PVCl, polyvinylchloride; CA, cellulose acetate; Si–PC, dimethyl siloxane–carbonate block copolymer; Si, polydimethylsiloxane

REFERENCES

1 Ward, III, W.J., Browall, W. R. and Sallemme, R. M. *J. Membrane Sci.* 1976, **1**, 99
2 Asakawa, S., Saito, Y., Kawahito, M., Itoh Y., Tsuchiya, S. and Sugata, K. *Natl. Tech. Rep.* 1983, **29**, 93
3 Masuda, T., Isobe, E., Higashimura, T. and Takada, K. *J. Am. Chem. Soc.* 1983, **105**, 7473
4 Takada, K., Matsuya, H., Masuda, T. and Higashimura, T. *J. Appl. Polym. Sci.* 1985, **30**, 1605
5 Masuda, T., Tang, B.-Z., Higashimura, T. and Yamaoka, H. *Macromolecules* 1985, **18**, 2369
6 Masuda, T., Tang, B.-Z. and Higashimura, T. *Macromolecules* 1986, **19**, 1459
7 Nakanishi, K., Odani, H., Kurata, M., Masuda, T. and Higashimura, T. *Polym. J.* 1987, **19**, 293
8 Ichiraku, Y., Stern, S. A. and Nakagawa, T. *J. Membrane Sci.* 1987, **34**, 5
9 Kawakami, Y., Aoki, T., Hisada, H., Yamamura, Y. and Yamashita, Y. *Polym. J.* 1985, **17**, 1159
10 Nakagawa, T., Saito, T., Saito, Y. and Asakawa, S. *Polym. Prepr. Jpn* 1985, **34**, 1885
11 Nakahama, S., Hirao, A., Takenaka, K. and Hattori, T. *Polym. Prepr. Jpn* 1986, **35**, 1644
12 van Amerongen, G. J. *J. Polym. Sci.* 1950, **5**, 307
13 Fujita, H. *Fortscher. Hochpolym. Forsch.* 1961, **3**, 1
14 Stern, S. A., Kulkarni, S. S. and Frisch, H. L. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 467
15 Stern, S. A., Sampat, S. R. and Kulkarni, S. S. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 2149
16 Shah, V. M., Hardy, B. J. and Stern, S. A. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 2033
17 Hachisuka, H., Tsujita, Y., Takizawa, A. and Kinoshita, T. *J. Appl. Polym. Sci.* 1988, **34**, 1333