

Oxygen-permselectivity in new type polyorganosiloxanes with carboxyl group on the side chain

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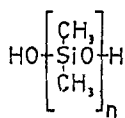
SUMMARY

Oxygen-permselectivity through polyorganosiloxanes with carboxyl group on the side chain is discussed in terms of the differences between the O_2 , N_2 diffusion coefficients or their solubility coefficients. The oxygen-selectivity increases from 2 to 5 with the increase in the carboxyl component of the side chain. Especially the selectivity in the diffusion coefficient is found to more contribute to the oxygen-permselectivity in comparison with that of the solubility coefficient. But the permeation coefficient decreases with the permselectivity.

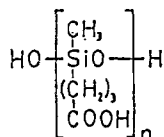
INTRODUCTION

Poly(dimethylsiloxane) membrane generally indicates a high oxygen permeability for its flexible main chain, but the low permselectivity.(1) On the other hand, polymer membranes with a functional group such as carboxyl or pyridyl on the side chain exhibit relatively high oxygen permselectivity but low permeability.(2) Therefore, new type polyorganosiloxanes with carboxyl group on the side chain would be interesting as an oxygen-permselective membrane. The polyorganosiloxanes with the T_g below room temperature are also very valuable for allowing to analyze the gas permeability according to the simple permeation theory of a solubility based on Henry's law and a diffusion based on Fick's law. There are a few reports in connection with the polyorganosiloxanes with carboxyl groups on the side chain.(3,4,5) They, however, are restricted to only a discussion on the novel syntheses, the thermal, and the mechanical properties. In this paper, the effect of O_2 , N_2 diffusion and solubility coefficients on the oxygen permselectivity was systematically described in their polymer membranes. The oxygen selectivity was found to be mainly affected by the difference between O_2 and N_2 diffusion coefficients. The oxygen selectivity decreases with increasing a permeation coefficient similar to the relationship between the selectivity and the permeability in general polymer membranes.

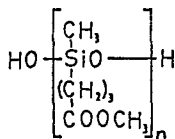
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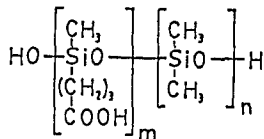
PDMS



PCPMS



PMCPMS



PDMS/PCPMS

EXPERIMENTAL

Materials Poly(dimethylsiloxane)(PDMS) membrane ($T_g = -123^\circ$) was prepared by using room temperature vulcanizing silicone rubber (KE-103, Shinetsu Silicone Inc.). Poly[(3-carboxypropyl)methylsiloxane](PCPMS), poly[dimethylsiloxane-co-(3-carboxypropyl)methylsiloxane](PDMS/PCPMS, mole ratio; 3/2), and poly[(3-methoxycarbonylpropyl)methylsiloxane](PMCPMS) were synthesized as in previous reports.(3,4,5) These polymers are listed in Scheme. PCPMS, PDMS/PCPMS were cross-linked with ethylene glycol (content: 5 wt%) and PMCPMS was cross-linked with benzoyl peroxide (content: 1 wt%) for the preparation of their membranes ($T_g = -25^\circ\text{C}$ for PCPMS; -45°C for PDMS/PCPMS; -75°C for PMCPMS).

Permeability Measurement Oxygen permeation coefficients were measured at 20, 25, 30, and 35°C with a low-vacuum permeation apparatus in the chamber with stable thermostating (Rika Seiki Inc. Gas permeation apparatus K-315 N-01). The pressure on the upstream side is maintained essentially constant. The pressures on the upstream and downstream side are detected using a Baratron absolute pressure gauge (MKS Instruments Inc.). Nitrogen permeation coefficients are separately measured by the same procedure as for oxygen. After the membranes were dried in vacuo at 80°C over a day, they were set in the apparatus and kept in vacuo at 45°C over three days before the measurement to remove the last traces of the sorbed gaseous molecules such as water and to exclude gas leakage. The attention has to be especially paid to the measurement of PCPMS membrane. The permeation coefficient, P , was calculated from the slope of the steady-state straight line of the permeation curve. The time lag, θ , was measured from the crossing point of the steady-state straight line and the abscissa on the permeation curve. The diffusion coefficient (D) was calculated from time-lag (θ) ($D = L^2/6\theta$, L ; thickness of the membrane), and the division of P by D yields the solubility coefficient (S) ($P = D \times S$).

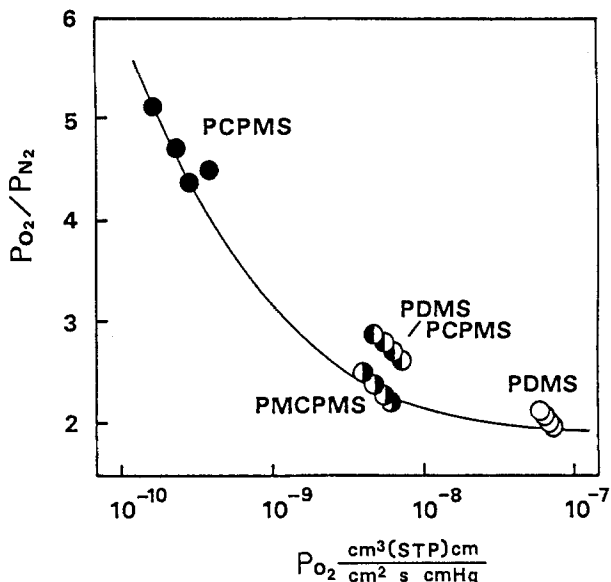


Figure 1 Relationship between the oxygen permeation coefficient and the ratio of the oxygen and the nitrogen permeation coefficients (measuring temperatures: 20, 25, 30, and 35°C in order of the low permeability coefficient in respective membranes).

RESULTS AND DISCUSSION

Oxygen and nitrogen permeation coefficients through the PDMS, PCPMS, PDMS/PCPMS, and PMCPMS membranes with a rubbery state at room temperature (T_g : see Experimental) are measured and the ratios of those coefficients are plotted against the oxygen permeation coefficients in Figure 1. The four plots of the respective membranes are corresponding to the cases of the four measuring temperatures (20, 25, 30, and 35°C in order of the low permeability coefficient). The oxygen selectivities increase with a decrease of the permeability coefficients, which are observed in general polymer membranes. Although the PCPMS membrane is a rubbery state at the measuring temperatures, the oxygen permeation coefficients are small to be the order of 10^{-10} [$\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s cmHg}$] and the oxygen selectivity is high (the ratio of the permeation coefficients is over 5 at 20 °C) in comparison with a general polymer membrane. The oxygen permeation coefficients of the polyethylene(2) with the T_g below room temperature or the passive liquid membrane(6) impregnated with glycerol are also the order of 10^{-10} [$\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s cmHg}$], respectively. These mean that the permeation coefficient of PCPMS membrane does not deviate so much from the values of rubbery polymer membranes. And both of the oxygen permeation coefficients and the selectivities of the PDMS/PCPMS and PMCPMS membranes are similar to a general polymer membrane.(2) The PDMS/PCPMS and

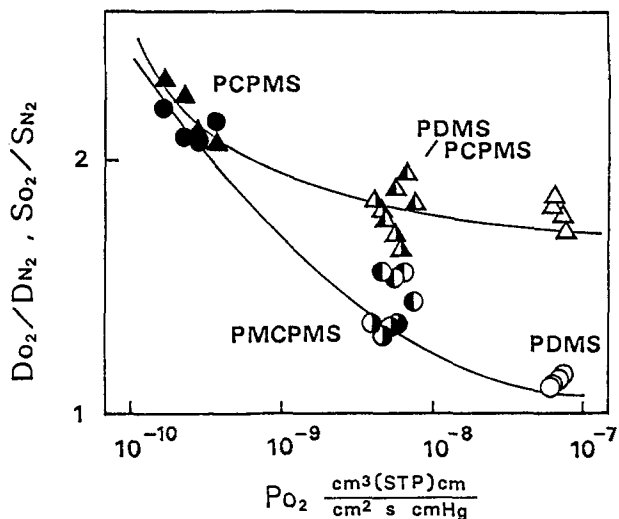


Figure 2 Relationship between the oxygen permeation coefficient and the ratios of the diffusion (: circle) and the solubility (: triangle) coefficients of oxygen and nitrogen (measuring temperatures: 20, 25, 30, and 35°C in order of the low permeability coefficient in respective membranes).

PMCPMS have a siloxane bond as the main chain and a carboxyl group as the side chain. Their chemical structures resemble the PCPMS. However, the oxygen selectivities are smaller and the permeabilities are larger than those of the PCPMS membrane. These differences are elucidated due to the following discussions.

The ratios (O_2/N_2) of the diffusion and the solubility coefficients in the four membranes are plotted against the oxygen permeation coefficients in Figure 2. The ratios of the diffusion coefficient greatly increase from 1 to 2 with a decrease in the oxygen permeation coefficient. The ratios of the solubility coefficient slightly increase with a decrease in the permeation coefficient but those are ca. 2 for the all membranes. The chemical structures of their polymers affect the ratio of the solubility of oxygen and nitrogen only a little. Thus, the difference in the diffusion mode greatly contributes to the oxygen-permselectivity (Figure 2).

Arrhenius plots of the diffusion coefficients of oxygen and nitrogen in the four membranes are given in Figure 3. Differences in the diffusion coefficients at respective membranes and temperatures can be clearly seen. The difference increases with an increase in carboxyl component of the side chain in PDMS, PDMS/PCPMS, and PCPMS membranes, that is, with a decrease in the diffusion coefficient. An inter- and intra-segment interaction based on hydrogen bond should cause dense network by the introduction of carboxyl group to PDMS, which results in the difference of oxygen- and nitrogen-diffusion coefficients. Activation energies for the

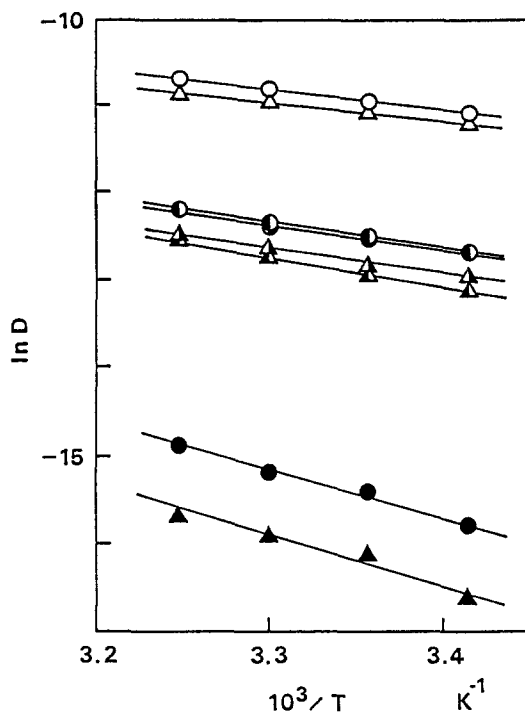


Figure 3 Arrhenius plots of the diffusion coefficients in the polymer membranes : PDMS, (○); PDMS/PCPMS, (◐); PMCPMS, (◑); PCPMS, (●); oxygen: circle; nitrogen: triangle.

Table 1 Oxygen Selective Permeation Parameters at 20°C and Activation Energies in Polyorganosiloxanes

Polymer	T _g	10 ¹⁰ P _{O₂} ^{a)}	P _{O₂} /P _{N₂}	10 ⁷ D _{O₂} ^{b)}	10 ³ S _{O₂} ^{c)}	ΔE _{O₂} ^{d)}
PDMS	-123	622	2.1	153	4.08	4.4
PMCPMS	-75	40.3	2.5	31.9	1.26	6.7
PDMS/PCPMS	-43	47.1	2.9	31.2	1.51	6.0
PCPMS	-25	1.65	5.1	1.43	1.16	10

a) [cm³(STP)cm/cm²scmHg], b) [cm²/s], c) [cm³(STP)/cm³cmHg],

d) [kcal/mol]

oxygen diffusions are listed in Table 1 with the oxygen permeation, the diffusion, and the solubility coefficients at 20°C. The energy for oxygen diffusion is larger in the case of the membrane with the lower diffusivity.

Consequently, even though such new type

polyorganosiloxanes with carboxyl group on the side chain are employed as an oxygen-permselective membrane, simultaneous improvement of the oxygen permeability and the selectivity are found to be too difficult because the oxygen-permselectivity is mainly governed by the difference between oxygen- and nitrogen-diffusion coefficients which increases with a decrease of the permeability, as discussed above. In poly(3-carboxypropylmethylsiloxane) membrane, the oxygen permeability coefficient is 1.7×10^{-10} [$\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s cmHg}$], and the oxygen-permselectivity against nitrogen is still high to be 5,1 at 20 °C in comparison with general polymers having the similar permeation coefficient. Such a polyorganosiloxane is interesting as an oxygen high permselective membrane.

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