O_2 and N_2 Gas Permselectivity of Alternating Copoly(vinylidene cyanide–vinyl acetate)

HISAO HACHISUKA, HITOSHI KITO, YOSHIHARU TSUJITA,* AKIRA TAKIZAWA, and TAKATOSHI KINOSHITA, *Department of Materials Science and Engineering, Polymeric Materials Course, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan*

Synopsis

The sorption and permeation of oxygen and nitrogen in and through alternating copoly(vinylidene cyanide–vinyl acetate) [copoly(VDCN–VAc)] ($T_g = 176°C$) membranes annealed for different periods just below T_g, 160°C, were investigated over the pressure range from 100 to 1000 cmHg. The dual-mode sorption and mobility models were used to analyze the results. A sub-T_g annealing of copoly(VDCN–VAc) caused a slight decrease in the amount of sorption in the membranes. This decrease in the amount of oxygen and nitrogen sorption can be attributed to a decrease in the Langmuir sorption capacity term, C'_H, with increasing sub-T_g annealing period. The densification of copoly(VDCN–VAc) membranes caused simultaneously by the annealing remarkably reduced diffusion coefficients for both gases. The reduction in diffusion coefficients of Langmuir mode, D_H, for both gases was found to be larger than that of Henry's law mode, D_D. Furthermore, permselectivity of oxygen to nitrogen, the ratio of permeability coefficient of oxygen to nitrogen ($\bar{P}O_2/\bar{P}N_2$), reached to 11.8 for the copoly(VDCN–VAc) annealed for 30 h. Evidently the reduction of D_H and D_D for nitrogen with increasing annealing period was much larger than that for oxygen.

INTRODUCTION

Oxygen and nitrogen separation characteristics of polymer membranes have been studied extensively over the years to apply to the medical and combustible uses. Poly(dimethyl siloxane) and its derivatives[1,2] have been reported to have a high oxygen permeability owing to their high diffusion, and have relatively low permselectivity of oxygen to nitrogen and poor thin film formability. On the other hand, glassy polymers have, in general, a high permselectivity of oxygen to nitrogen and are also interested in a thinner film formability and heat-stable property, even though the magnitude of the permeability coefficient is comparatively low.

In the previous study,[3] the gas permeabilities through polystyrene were strongly dependent on their thermal history such as quenching from their melt, since an unrelaxed volume, which is a main factor to determine permeability of glassy polymers, could vary by such a thermal treatment. We have also shown the changes in sorption properties of the alternating copoly(vinylidene cyanide–vinyl acetate) [copoly(VDCN–VAc)] sub-T_g an-

---

nealed for various periods and have quantitatively correlated the changes in the amount of sorption with the enthalpy relaxation of the polymer annealed.[4] These results imply that the thermal treatment of glassy polymers can produce various glassy structures, giving rise to considerable changes in permeability coefficient and/or permselectivity of glassy polymers.

In this paper, we report on the influence of the sub-T_g annealing of the copoly(VDCN–VAc) membranes on their permeabilities of oxygen and nitrogen. Furthermore, based on the dual-mode sorption and mobility models, the separation characteristics of the copoly(VDCN–VAc) membranes are also discussed.

EXPERIMENTAL

Materials

A powder of the copoly(VDCN–VAc) was kindly supplied from Mitsubishi Petrochemical Co., Ltd., and dried under reduced pressure for 24 h at room temperature before membranes preparation. The copoly(VDCN–VAc) membranes were prepared by casting on petri dish from 1% dimethyl formamide solution at 60°C and the residual solvent was removed by immersion into 1 : 1 mixture of acetone and methanol. The membranes obtained were dried completely under vacuum at room temperature till a weight decrease was not observed at all. Annealing of the membranes was performed as follows. As cast membranes ($T_g = 176°C$) were annealed just below T_g, 160°C, for various periods and slowly cooled to room temperature. A density of the copoly(VDCN–VAc) annealed for various periods was determined at 25°C as usual by using the mixed solvent of n-hexane and carbon tetrachloride. X-ray diffraction and thermal analyses showed that the as-cast and annealed membranes were completely amorphous.

O_2 and N_2 used in permeation and sorption measurements were at least greater than 99.9% purity and used without further purification.

Methods

The membranes placed in a permeation cell sealed with an O-ring were degassed for 24 h at 10^{-4} mmHg in a permeation apparatus. A permeation measurement is followed by a Rouse type method: evacuation of the downstream side of the membranes up to about 10^{-4} mmHg, introduction of a differential pressure of permeant gas to the upstream side, and monitoring the permeated gas pressure in the downstream side by using MKS-Baratron pressure transducer (227 AA). Permeability coefficient $\bar{P}$ was calculated by a steady-state gas permeation rate.

Sorption measurements were carried out by using a gravimetric sorption apparatus with Cahn Electromicrobalance 2000 manufactured by Cahn Instruments, Inc. (Cerritos, Calif.). After a sufficient drying up the membranes under about 10^{-4} mmHg, a weight increase due to sorption of gas in the membranes under a fixed pressure was recorded and the net amount sorbed was corrected using a buoyancy contribution.

RESULTS AND DISCUSSION

Figure 1 shows the sorption isotherms at 25°C for O$_2$ and N$_2$ of the copoly(VDCN–VAc) annealed for various periods. The amount of sorption for O$_2$ and N$_2$ decreased over an entire pressure range studied with increasing annealing period. This result is understandable in terms of a density change of the copoly(VDCN–VAc) by the annealing as described later. We have already shown that the amount of CO$_2$ sorption in the copoly(VDCN–VAc) membranes decreased with increasing annealing period, and evidently the reduction in a Langmuir sorption capacity term, C_H', was resulted from enthalpy relaxation and/or densification during the isothermal annealing.[4] It can similarly say that the decrease in the amount of sorption for O$_2$ and N$_2$ as seen from Figure 1 is also attributable to the densification in the copoly(VDCN–VAc) on the annealing. The values of density at 25°C of the annealed copoly(VDCN–VAc) were 1.212, 1.217, 1.220 (g/cc) for as cast, 5 h annealing and 15 h annealing samples, respectively.

It is found that each isotherm could be described well by the dual-mode sorption model which is represented by following equation[5, 6]:

$$C = C_D + C_H = k_D p + \frac{C_H' b p}{(1 + bp)} \tag{1}$$

where C is total penetrant concentration, C_D is concentration due to Henry's law contribution, C_H is concentration of penetrant held in "microvoid" or Langmuir contribution, k_D is Henry's law constant, p is pressure of penetrant at equilibrium, b is affinity constant of penetrant for the Langmuir site, and
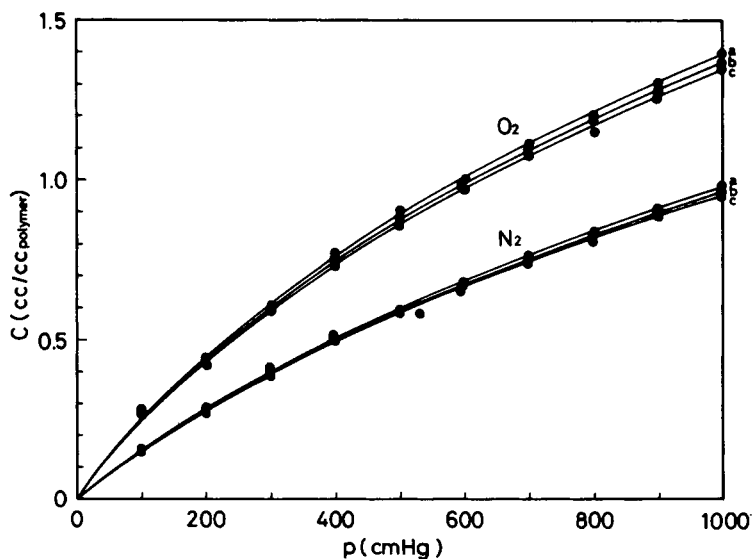

Fig. 1. Sorption isotherms at 25°C of the copoly(VDCN–VAc) membranes annealed for various periods at 160°C: (a) as cast; (b) 5 h annealing; (c) 15 h annealing.

TABLE I
Dual Sorption Parameters of Various Annealed Copoly (VDCN–VAc)s for O_2 and N_2 Gases

Time	Gas	C'_H [cc(STP)/cc]	$b \times 10^3$ (cmHg^{-1})	$k_D \times 10^4$ [cc(STP)/cc cmHg]
As cast	O_2	2.18	1.1	2.6
	N_2	1.74	0.8	2.0
5 h	O_2	2.12	1.1	2.6
	N_2	1.70	0.8	2.0
15 h	O_2	2.06	1.1	2.6
	N_2	1.66	0.8	2.0

C'_H is hole saturation constant of glassy polymers in the Langmuir sorption mode. C_H' is replaced by the following equation[7]:

$$C'_H = 22,400 \left[\frac{(V_g - V_l)}{V_g} \right] \frac{1}{V_p} \qquad (2)$$

where V_g and V_l are specific volume of polymer in a glassy state and a supercooled liquid state, respectivly, and V_p is molar volume of liquidlike penetrant. One can evaluate dual-mode sorption parameters by using isotherm's data and eq. (1) by the nonlinear least-squares method. The parameters obtained are tabulated in Table I.

The decrease in the amount of sorption for O_2 and N_2 in Figure 1 can be represented in terms of the changes in the dual-mode sorption parameters. As expected, the Langmuir hole saturation constant decreased with the increasing annealing period, whereas the values of the affinity constant and Henry's law constant for O_2 and N_2 did not vary. It is also found that the values of the C'_H of each membrane for O_2 are slightly larger than those for N_2. The ratio of C'_H for O_2 to that for N_2 is 1.25 and almost independent on the annealing period, indicative of the ratio of molar volume of N_2 to that of O_2. This indicates a relative unrelaxed volume $[(V_g - V_l)/V_g]$ of the copoly(VDCN–VAc) annealed for 15 h to be 0.26% irrespective of penetrant gas.[7]

Figure 2 shows the pressure dependence of permeability coefficients for O_2 and N_2 at 25°C through the copoly(VDCN–VAc) membranes annealed for various periods. The decreasing trend of permeability coefficients against pressure, which is a characteristic of a gas permeation through glassy polymers, was observed for both gases in Figure 2. It is confirmed that permeability coefficient in lower-pressure region decreases more remarkably than that in high-pressure region with increasing annealing period, as supposed by the dual-mode sorption model.

The pressure dependence of permeability coefficients can be analyzed by using the partial immobilized model represented by the following equation[8]:

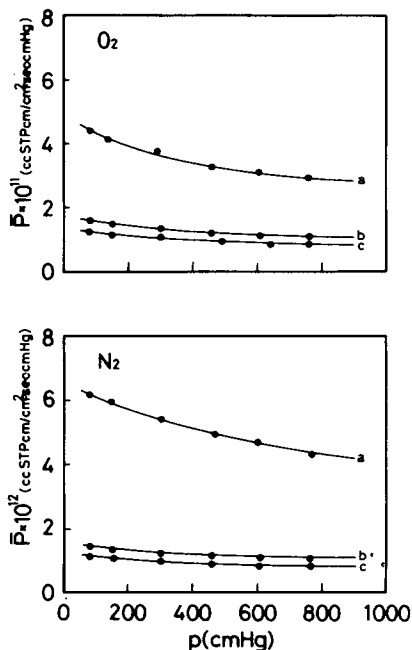$$\bar{P} = k_D D_D + \frac{C'_H b D_H}{(1 + bp)} \qquad (3)$$

Fig. 2. The pressure dependence of permeability coefficient at 25°C for O$_2$ (upper) and N$_2$ (lower) through the copoly(VDCN–VAc) membranes annealed for various periods at 160°C: (a) as cast; (b) 5 h annealing; (c) 15 h annealing.

which has been derived assuming individual diffusion coefficient for Henry's law and Langmuir mode, D_D and D_H, respectively. Figure 3 provides plots of permeability coefficients for O$_2$ and N$_2$ through the various annealed copoly(VDCN–VAc)s as a function of $(1 + bp)^{-1}$. The agreement between the theoretical line derived by eq. (3), and the experimental data is excellent as seen for other glassy polymers obeying the partial immobilized model.[9] It was clarified that the permeability coefficient of the copoly(VDCN–VAc) membranes annealed as well as cast membranes was well interpreted by the partial immobilized model. The intercepts of these lines at high- and low-pressure sides ($p = \infty$ and 0) correspond to the values of $k_D D_D$ and $k_D D_D + C_H' b D_H$ in eq. (3), respectively, and the decreases of these values with increasing annealing period may demonstrate the effect of the densification by the sub-T_g annealing. Once one knows dual-mode sorption parameters the two diffusion coefficients, D_D and D_H, can be calculated from the slope and intercept at the high pressure range and are listed in Table II along with their ratio F ($= D_H/D_D$). The reduction in the Langmuir mode diffusion coefficient D_H owing to the sub-T_g annealing is larger than that in the Henry's law mode diffusion coefficient D_D. This result was correlated with the fact that the sub-T_g annealing mainly affected the values of the Langmuir sorption capacity term C_H' of the dual-sorption parameters. Namely, the reduction of D_H by the annealing could be ascribed mainly to the decrease in the unrelaxed volume or microvoids in the copoly(VDCN–VAc) with increasing annealing period. The reduction of D_D may, on the other hand, be due to the decrease in free volume of segmental mobility owing to the densification.
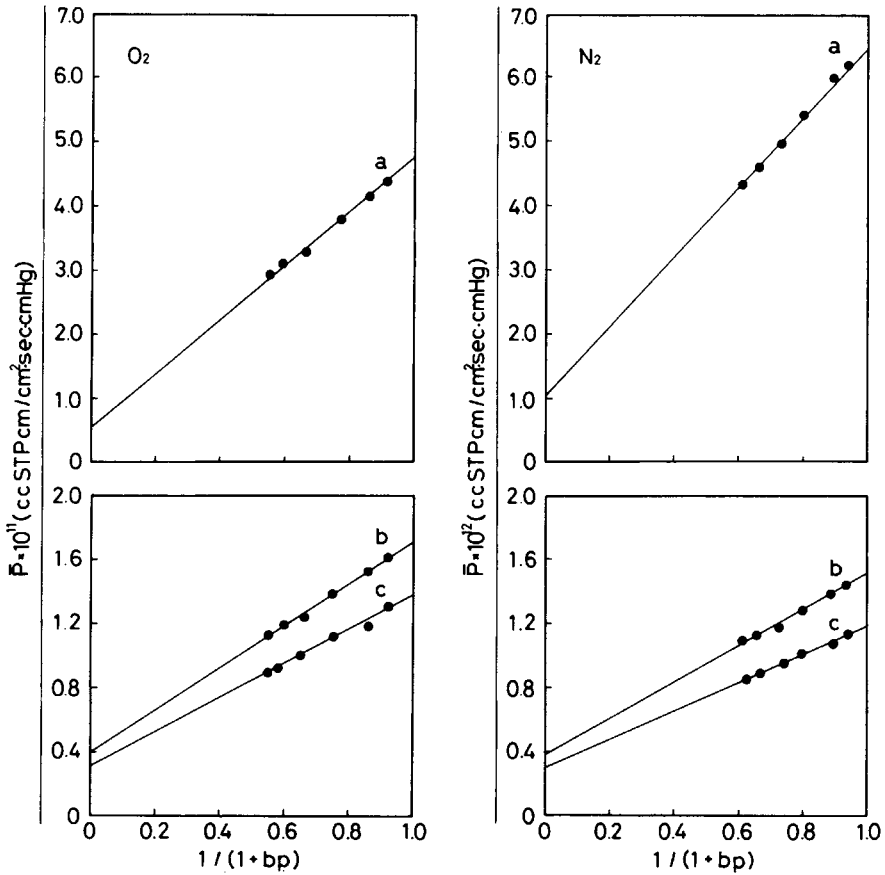
Fig. 3. Plots of permeability coefficients for O_2 and N_2 through the copoly(VDCN–VAc) membranes annealed for various periods against the value of $(1 + bp)^{-1}$; (a): as cast; (b) 5 h annealing; (c) 15 h annealing.

TABLE II
Diffusion Coefficients of Various Annealed Copoly(VDCN–VAc)s for O_2 and N_2 Gases

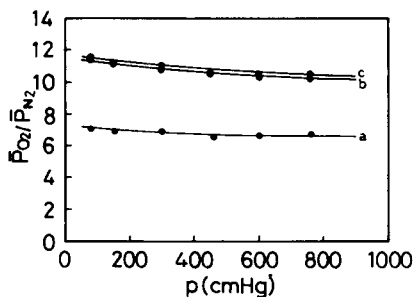| Time	Gas	$D_D \times 10^9$ (cm²/s)	$D_D O_2/D_D N_2$	$D_H \times 10^9$ (cm²/s)	$D_H O_2/D_H N_2$	F
As cast	O_2	21.3		18.5		0.70
	N_2	5.3	4.0	3.9	4.7	0.74
5 h	O_2	15.5		5.6		0.36
	N_2	1.9	8.2	0.8	7.0	0.44
15 h	O_2	12.4		4.7		0.38
	N_2	1.5	8.3	0.7	6.7	0.45

Fig. 4. The pressure dependence of the ratio of permeability coefficient at 25°C for the copoly(VDCN–VAc) membranes annealed for various periods at 160°C; (a) as cast; (b) 5 h annealing; (c) 15 h annealing.

The annealing also affects notably the ratio of the permeability coefficient for O$_2$ to that of N$_2$, $\overline{P}$O$_2$/$\overline{P}$N$_2$, as shown in Figure 4. It was also found that $\overline{P}$O$_2$/$\overline{P}$N$_2$ slightly decreased with increasing upstream pressure. The value of the permselectivity of O$_2$ to N$_2$ was enhanced remarkably with the increasing annealing period and was 11.8 at upstream pressure of 80 cmHg for the membrane annealed for 30 h. The sorption parameters k_D, b, and C'_H ratio of O$_2$ to N$_2$ gases were almost independent on the annealing period (Table I), indicating that the changes in the sorption properties of the copoly(VDCN–VAc) have no contribution to the enhancement of the permselectivity. As shown in Table II, on the other hand, the two diffusion coefficients, D_D and D_H, for N$_2$ were decreased much more remarkably than those for O$_2$ with the increasing annealing period. The excellent permselectivity of the annealed copoly(VDCN–VAc) in Figure 4 can, therefore, be explained in terms of the increase in the difference of the diffusion coefficient between O$_2$ and N$_2$ on the annealing.

Figure 5 is plots of O$_2$ permeability coefficient vs. permselectivity for O$_2$ to N$_2$ for the copoly(VDCN–VAc) membranes prepared by the sub-T_g annealing including many other polymer membranes.[2] It is obvious that the annealed copoly(VDCN–VAc) membranes possess high value of the permselectivity in comparison with other polymers. These results suggest that the sub-T_g annealing can greatly enhance the permselectivity for O$_2$, although it gives rise to the slight decrease in the magnitude of O$_2$ permeability coefficient.

In conclusion, the copoly(VDCN–VAc) relaxed considerably by sub-T_g annealing, accompanied with the densification. The Langmuir sorption capacity term C'_H as well as the sorption for O$_2$ and N$_2$ decreased with the annealing, although the other dual-mode sorption parameters were nearly constant. In addition, the diffusion coefficients for Langmuir mode and Henry's law mode, D_H and D_D, decreased by the annealing, especially the former exhibited the remarkable reduction. Furthermore, the two diffusion coefficients for N$_2$ were decreased much more remarkably than those for O$_2$ with the increasing annealing period. The value of the permselectivity of O$_2$ to N$_2$ was enhanced by the increase in the difference of the diffusion coefficient between O$_2$ and N$_2$ on the annealing. The permselectivity of O$_2$ to N$_2$ increased up to about 12 by the sub-T_g annealing for 30 h. Such sub-T_g annealing was found to be available to enhance the permselectivity.
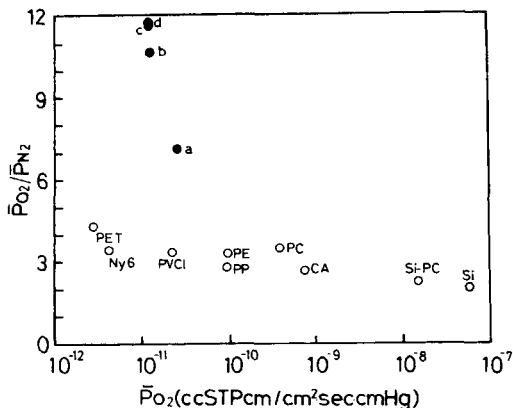
Fig. 5. Plots of O_2 permeability coefficient vs. permselectivity for O_2 of the copoly(VDCN–VAc) membranes annealed for various periods: (a) as cast; (b) 1 h annealing; (c) 15 h annealing; (d) 30 h annealing; and that of other polymer membranes[2]: PET = poly(ethylene terephthalate), Ny6 = nylon 6; PVCl = poly(vinyl chloride); PC[10] = polycarbonate; CA = cellulose acetate; Si–PC = dimethyl siloxane-carbonate block copolymer; and Si = poly(dimethyl siloxane).

References

1. W. J. Ward, III, W. R. Browall, and R. M. Salemme, *J. Membr. Sci.*, 1, 99 (1976).

2. S. Asakawa, Y. Saito, M. Kawahito, Y. Ito, S. Tsuchiya, and K. Sugata, *Natl. Tech. Rep.*, 29, 93 (1983).

3. H. Hachisuka, Y. Tsujita, A. Takizawa, and T. Kinoshita, *Polym. Prepr. Jpn.*, 34, 1181 (1985).

4. H. Hachisuka, Y. Tsujita, A. Takizawa, and T. Kinoshita, *Polymer*, 29, (1988).

5. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, 34, 1 (1963).

6. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, 34, 13 (1963).

7. K. Toi, G. Morel, and D. R. Paul, *J. Appl. Polym. Sci.*, 27, 2997 (1982).

8. W. J. Koros, D. R. Paul, and A. A. Rocha, *J. Polym. Sci., Polym. Phys. Ed.*, 18, 1103 (1980).

9. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, 16, 2171 (1978).

10. H. Hachisuka, Y. Tsujita, A. Takizawa, and T. Kinoshita, unpublished result.