

# Sorption and Transport of CO<sub>2</sub> in Poly(ethylene Terephthalate) Crystallized by Sorption of High-Pressure CO<sub>2</sub>

TAKUJI HIROSE, KEISHIN MIZOGUCHI, YOSHINORI KAMIYA, and KATSUHIKO TERADA, *Packaging Materials Division, Industrial Products Research Institute, 1-1-4 Higashi, Tsukuba, Ibaraki, 305, Japan*

## Synopsis

Sorption and permeation of CO<sub>2</sub> in poly(ethylene terephthalate) crystallized by sorption of high-pressure CO<sub>2</sub> were examined below 1 atm at temperatures from 15 to 65°C. A large solubility and a high permeability of CO<sub>2</sub> in this specimen were observed compared to poly(ethylene terephthalate) crystallized by thermal annealing to a similar degree. A large unrelaxed volume is expected to be left in the specimen after removal of high-pressure CO<sub>2</sub> compared to the data of other PET samples. The thermal history during the measurements up to 65°C, which causes relaxation of the specimen, was shown to decrease CO<sub>2</sub> solubility. On the other hand, permeation data after annealing show not only decreased permeability but also increased apparent diffusivity. The results mean a lower mobility of gases sorbed in the unrelaxed volume than that of ordinarily dissolved gases, which corresponds to the partial immobilization model.

## INTRODUCTION

The sorption and transport of penetrants in poly(ethylene terephthalate) (PET) have been extensively investigated for more than two decades.<sup>1-13</sup> Michaels et al. have reported the pioneering work on the solution and diffusion of several gases in glassy and rubbery PET at various pressure conditions.<sup>1</sup> They have analyzed the data at the glassy state by the dual-mode sorption model suggested by Barrer et al.<sup>14</sup> Vieth and Sladek have obtained the diffusivity of the dissolved CO<sub>2</sub> molecules from the sorption data on the assumption of the total immobilization model.<sup>3</sup> Koros and Paul have discussed the effect of the Langmuir capacity or the excess free volume in the glass on the permeability and the diffusional time lag.<sup>5,6</sup> They have also estimated two diffusion coefficients of CO<sub>2</sub> in the Henry and in the Langmuir population based on the partial immobilization model. Toi et al. have determined the dual-mode parameters from the pressure dependence of the apparent diffusion coefficients determined by the permeation measurements.<sup>9,10</sup> Light and Seymour have studied the effect of sub- $T_g$  relaxation or  $\beta$ -relaxation on the gas transport in PET.<sup>13</sup>

Such concern regarding PET is not only because it is industrially important as a packaging material<sup>15</sup> and is commercially available, but also because the characteristics of PET are interesting and convenient for theoretical discussions. Several kinds of samples with different crystallinities can be easily prepared from amorphous samples by different thermal treatments.<sup>1</sup> As the

glass transition temperature ( $T_g$ ) is not so high, it is possible to study the sorption and transport behaviors in a temperature range encompassing the  $T_g$ .<sup>1,4-6</sup> Recently two groups have shown another interesting feature of PET.<sup>16,17</sup> Crystallization of amorphous PET induced by sorption of CO<sub>2</sub> at high pressures. Mizoguchi et al. have mentioned that PET crystallized by sorption of high-pressure CO<sub>2</sub> has several microvoids resulting in a lower density amorphous region than that of samples crystallized by thermal annealing.<sup>17</sup> It is interesting to study the transport property of a PET film crystallized by sorbed CO<sub>2</sub> in connection with such a structure. In this report, the solubilities and permeabilities of CO<sub>2</sub> were determined below 1 atm and the effect of thermal history on the structure in glassy state and on the transport property was qualitatively discussed. Temperature dependences of the apparent diffusion and solubility coefficients were shown to be consistent with the discussion.

### EXPERIMENTAL

Amorphous PET film of 50  $\mu\text{m}$  thickness was kindly supplied by Mitsubishi Diafoil Co., Ltd. The sample film was prepared by crystallization of the amorphous one exposed to 50 atm of CO<sub>2</sub> at 35°C. As a reference, the PET film crystallized by thermal annealing at 100°C for 5.3 h was also prepared. Both crystallization procedures followed the literature.<sup>17</sup> In the following text, the amorphous PET and the crystallized samples by CO<sub>2</sub> exposure and by thermal annealing are abbreviated as a-PET, c-PET, and h-PET, respectively. The density measured by an Anton Paar DMA 02D was 1.362 g/cm<sup>3</sup> for c-PET and h-PET. But the amorphous content  $\alpha$  was 0.73 in volume for c-PET because the density of amorphous phase is expected to be 1.327 g/cm<sup>3</sup> for this sample, while  $\alpha$  of h-PET was 0.75 when the density of amorphous phase is assumed to be 1.331 g/cm<sup>3</sup>.<sup>17</sup> The density of a-PET was 1.336 g/cm<sup>3</sup> and  $\alpha$  was 0.96.

Equipment and procedures for sorption and permeation measurements employed in this work have been described previously.<sup>16,19</sup> Both measurements were made monotonically increasing the temperature from 15 to 65°C in 10°C increments.

The CO<sub>2</sub> used was at least 99.99% pure and was used as received.

### RESULTS AND DISCUSSION

Figure 1 shows the Arrhenius plot of the permeability coefficients,  $P$ , for CO<sub>2</sub> in c-PET. Each recorded value is the mean of at least two experiments at different pressures between 30 and 60 cmHg. The plot shows a few interesting features. First, the permeability of CO<sub>2</sub> in c-PET was shown to be rather high. For example,  $P$  at 35°C is  $5.18 \times 10^{-11} \text{ cm}^3(\text{STP}) \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$  and the value is about two or three times larger than the value. The data read from the graphs in the literature are shown in Table I.<sup>1,4,9</sup> Second the temperature dependence is unusual because it is nonlinear to the reciprocal of temperature. Mizoguchi et al. proposed that c-PET has an abundance of microvoids due to the density measurements and the infrared spectroscopic data.<sup>17</sup> According to the dual-mode sorption and the partial immobilization models, therefore, the high permeability should be due to the microvoids or

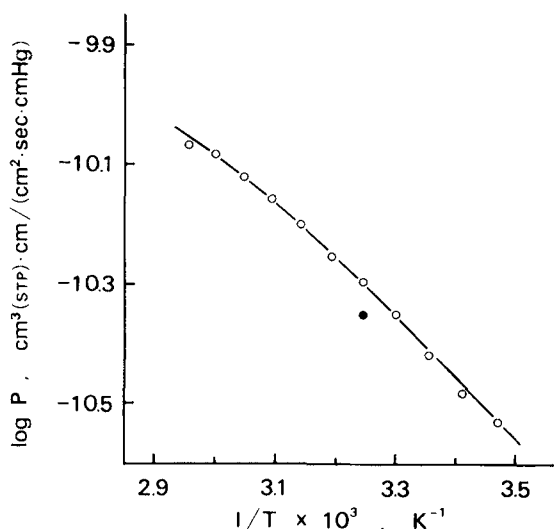


Fig. 1. Temperature dependence of the permeability coefficients of CO<sub>2</sub> in PET crystallized by sorption of CO<sub>2</sub> (c-PET). ●; after measurements at 65°C.

excess free volume in c-PET, in other words, due to the crystallization and the conditioning effect by sorption of high-pressure CO<sub>2</sub>. The unusual temperature dependence is also interpreted based on the existence of microvoids or unrelaxed volume. As mentioned in the Experimental section, the permeation measurements were performed by monotonically increasing temperature. The excess free volume is expected to reduce by relaxation as the temperature is increased, resulting in a smaller increase of  $P$  than is usual, which is in linear relationship with the reciprocal of temperature.

For comparison, the CO<sub>2</sub> solubility in c-PET was determined since the sorption isotherm exhibits the characteristics of a glassy polymer.<sup>1-8, 19-21, 23-27</sup> The gravimetric method was used for sorption measurement and the pressure was changed stepwise.<sup>19,20</sup> Before performing experiments at different temperatures, the specimen was conditioned at the temperature under reduced pressure for more than a day. As shown in Figure 2, the isotherms are concave to the pressure axis as is true for many glassy polymers. It took

TABLE I  
Comparison of the Permeability Coefficients of CO<sub>2</sub> in PET at 35°C

Sample	$P$ [cm <sup>3</sup> · cm/(cm <sup>2</sup> · s · cmHg)]	$\alpha^a$	Reference
Mylar	$4.35 \times 10^{-11}$	1.0	1
Mylar	$2.01 \times 10^{-11}$	0.57	1
Kinmar	$1.87 \times 10^{-11}$	0.40	4
Diafoil	$1.65 \times 10^{-11}$	0.48	9
Diafoil <sup>b</sup>	$5.17 \times 10^{-11}$	0.73	This study
Diafoil <sup>c</sup>	$4.45 \times 10^{-11}$	0.73	This study

<sup>a</sup>Amorphous fraction.

<sup>b</sup>Crystallized by sorption of CO<sub>2</sub> (c-PET).

<sup>c</sup>After annealing of c-PET at 65°C.

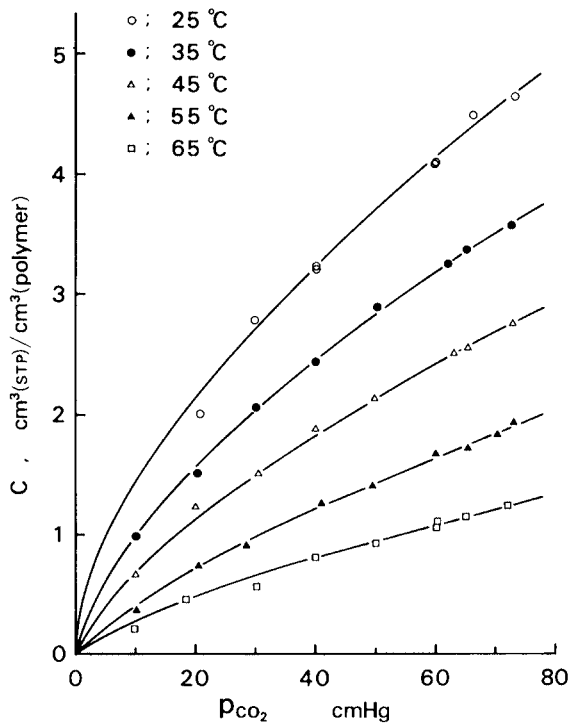


Fig. 2. Sorption isotherms of  $\text{CO}_2$  in PET crystallized by sorption of  $\text{CO}_2$  (c-PET).

about one week to determine one sorption isotherm and no evidence of relaxation of the polymer was observed from repeated measurements during this period, that is, the sorption-desorption hysteretic behavior was not detectable.<sup>19-21,26,27</sup> These isotherms were analyzed by the dual-mode sorption model assuming no plasticization by sorbed  $\text{CO}_2$ .<sup>19,20</sup> According to the dual-mode sorption model, the total concentration  $C$  is the sum of one population  $C_D$  described by Henry's law and the other  $C_H$  described by a Langmuir isotherm, Eq. (1);

$$\begin{aligned}
 C &= C_D + C_H \\
 &= k_D p + \frac{C'_H b p}{1 + b p}
 \end{aligned}
 \quad (1)$$

where  $k_D$  is the Henry's law parameter and  $C'_H$  and  $b$  are the hole saturation and affinity constants for the Langmuir sorption, respectively. The dual-mode parameters were determined by a nonlinear regression technique but the range of displacement of  $k_D$  was loosely limited with reference to the literature values of  $k_D$  on a-PET in the rubbery state.<sup>21,22</sup> The parameters listed in Table II show usual temperature dependencies observed for many gas-glassy polymer systems.<sup>6,18,19,26,28-31</sup> The parameters at 25°C were compared to the literature values of the  $\text{CO}_2$ -PET systems<sup>1-3,5,6</sup> in Table III. The parameters, except the  $b$  values, seem similar when the amorphous fraction is considered.

TABLE II  
 Dual-Mode Parameters for CO<sub>2</sub> in c-PET<sup>a</sup>

T(°C)	$k_D$	$C'_H$	$b$	$K$
	$\frac{\text{cm}^3(\text{STP})}{\text{cm}^3(\text{polymer}) \cdot \text{atm}}$	$\frac{\text{cm}^3(\text{STP})}{\text{cm}^3(\text{polymer})}$		
25	0.733	7.05	1.30	12.5
35	0.633	5.22	1.36	11.2
45	0.522	3.94	1.30	9.28
55	0.485	3.45	0.739	5.26
65	0.429	2.15	0.668	3.35
35 <sup>b</sup>	0.633	3.19	1.50	7.56

<sup>a</sup>PET crystallized by sorption of CO<sub>2</sub>.

<sup>b</sup>After annealing of c-PET at 65°C.

The large  $b$  values are a little strange as it means the present sample has a much stronger affinity with CO<sub>2</sub> than others. The small pressure range of measurements may be the main reason for this, but it is not yet clear. The point is, the product  $C'_H b$  is quite large, that is, the present  $K$  value ( $= C'_H b / k_D$ ) is significantly large. This is the result of the largest conditioning effect of the reports on sorption,<sup>21-26</sup> since the present c-PET was prepared at 50 atm of CO<sub>2</sub>.

To determine the effect of thermal history during the measurements, the sorption isotherm was measured again at 35°C. As expected, there were significant differences of solubilities as shown in Figure 3, but change in sample density was not detected. When the decreased solubility is assumed to be due to the unrelaxed volume reduced by thermal annealing, the dual-mode parameters in the last row of Table II reflect the change. In this analysis, the  $k_D$  value was fixed to the data obtained previously because of the assumption. Permeability was also measured after the measurements at 65°C and the data at 35°C is shown in Figure 1 as a filled circle. The  $P$  value was decreased about 30% which corresponded closely to that of solubility. Though it is still difficult to discuss quantitatively, the so-called Langmuir species sorbed in the excess free volume seem to be related to diffusion permeation.

 TABLE III  
 Comparison of the Dual-mode Parameters of CO<sub>2</sub> in PET at 35°C

Sample	$k_D$	$C'_H$	$b$	$K$	$\alpha^a$	Reference
	$\frac{\text{cm}^3(\text{STP})}{\text{cm}^3(\text{polymer}) \cdot \text{atm}}$	$\frac{\text{cm}^3(\text{STP})}{\text{cm}^3(\text{polymer})}$				
Mylar	0.38	5.30	0.44	6.15	1.0	1
Mylar	0.23	4.20	0.45	8.20	0.57	1
Mylar	0.69	5.7	0.52	8.90	0.51	2
Kinmar	0.362	7.91	0.351	7.66	0.40	5
Diafoil <sup>b</sup>	0.733	7.05	1.30	12.5	0.73	This study

<sup>a</sup>Amorphous fraction.

<sup>b</sup>Crystallized by sorption of CO<sub>2</sub>.

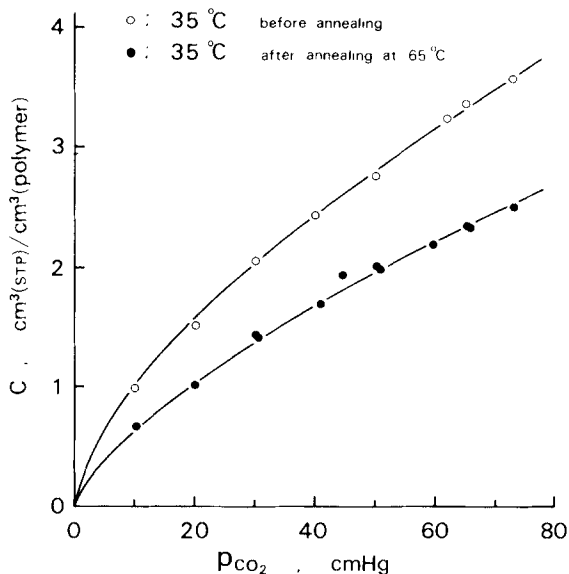


Fig. 3. Comparison of solubilities of  $CO_2$  in PET crystallized by sorption of  $CO_2$  (c-PET) before (○) and after (●) thermal annealing at  $65^\circ C$ .

In the previous paragraphs, the change of solubility and permeability of  $CO_2$  by thermal annealing was shown and attributed to the unrelaxed volume in c-PET. The validity of the discussion is further justified here by the measurement of sorption and permeation in other PET films. Figure 4 shows that the sorption isotherms for  $CO_2$  in h-PET are obviously smaller than those in c-PET. Except at  $65^\circ C$ , isotherms were also analyzed by the dual-mode model and the parameters are listed in Table IV. It was impossible to obtain the proper parameters for the isotherm at  $65^\circ C$  probably because the solubility, especially the Langmuir contribution, was so small. The Langmuir capacity,  $C_H b$ , is shown to be less than half of that in Table II, though the  $b$  values again seem larger than usual. The solubility in c-PET after annealing at  $65^\circ C$  is still higher than the data of h-PET at  $35^\circ C$ . On the other hand, only a slight change of solubility was detected for h-PET after measurements at  $65^\circ C$ . The result is reasonable because the sample obtained by crystallization at  $100^\circ C$  is expected to be stable at the experimental temperatures.

The permeability data at  $35^\circ C$  are shown as a function of feed pressure in Figure 5. The  $P$  value in a-PET is in good agreement with that in amorphous poly(ethylene terephthalate) as reported by Michaels et al.<sup>1</sup> These results are not normalized by the amorphous fractions. However, it is evident that h-PET has the lowest permeability and even c-PET annealed at  $65^\circ C$  has a higher  $P$  value than a-PET. These permeability data are consistent with the other results and discussion mentioned above.

The character of c-PET has been revealed from the comparison of sorption and permeation data to those of other PET samples with different conditioning histories. c-PET has a high permeability as well as a high solubility due to the Langmuir species sorbed in several microvoids. Regarding gas transport, it is interesting to obtain the diffusivity information of  $CO_2$  in c-PET. On the

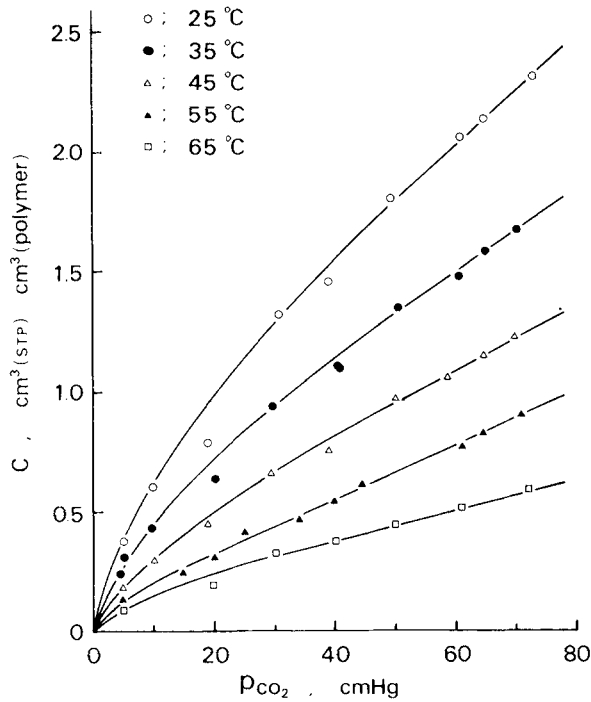


Fig. 4. Sorption isotherms of CO<sub>2</sub> in PET crystallized by thermal annealing (h-PET).

other hand, there have been many reports of two diffusivities in glassy polymers based on the partial immobilization model.<sup>6, 7, 9, 10, 24, 31</sup> According to the model, it is possible to determine the diffusivities from the pressure dependence of permeability by Eq. (2);

$$P = k_D D_D \left( 1 + \frac{FK}{1 + bp} \right) \tag{2}$$

where  $D_D$  is the diffusion coefficient of the gas in Henry's law population,  $F$  is the ratio of the diffusion coefficient of the gas in the Langmuir population,  $D_H$ , to  $D_D$ , ( $F = D_H/D_D$ ), and  $p$  is the upstream pressure when the down-

TABLE IV  
Dual-Mode Parameters of CO<sub>2</sub> in h-PET<sup>a</sup>

T (°C)	$k_D$ cm <sup>2</sup> (STP) cm <sup>2</sup> (polymer) · atm	$C_H'$ cm <sup>3</sup> (STP) cm <sup>3</sup> (polymer)	$b$ atm <sup>-1</sup>	$K$ (= $C_H' b / k_D$ )
25	0.770	2.59	1.52	5.11
35	0.665	1.64	1.79	4.41
45	0.579	1.12	1.59	3.08
55	0.509	0.72	1.33	1.88

<sup>a</sup> PET crystallized thermally.

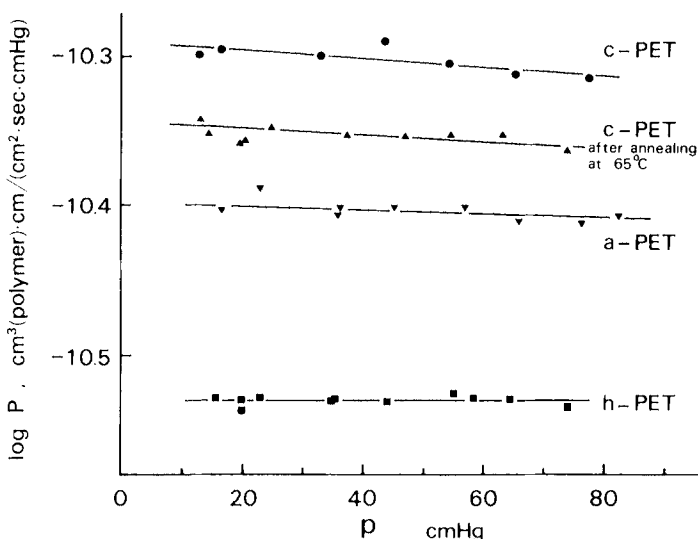


Fig. 5. Comparison of the permeability coefficients of  $\text{CO}_2$  in some PET films at  $35^\circ\text{C}$ : c-PET; PET crystallized by sorption of  $\text{CO}_2$ , h-PET; PET crystallized by thermal annealing, a-PET; amorphous PET.

stream pressure is assumed to be nearly zero. However, interpretation of the difference or the change of the  $b$  parameter of the same sample before and after various conditionings is not easy. Even considering the results, presented in Table II, the exact meaning of the differences in  $b$  is difficult to clarify. In other words, we hesitate to analyze the diffusivity quantitatively by use of Eq. (2). Another method to estimate the diffusivity is to calculate the average diffusion coefficient  $\bar{D}$  by Eq. (3) from the ratio of the permeability and the solubility determined as a secant slope of a sorption isotherm, respectively.

$$\bar{D} = P/S = P/(C/p) \quad (3)$$

As the dual-mode sorption and the partial immobilization models insist,  $\bar{D}$  does not mean the true diffusivity of  $\text{CO}_2$  in a glassy polymer as the pressure dependences of gas solubility and diffusivity are ignored in this treatment. But  $\bar{D}$  is available as a mean value for the qualitative comparison and the  $\bar{D}$  values obtained from the permeation and sorption data for c-PET and h-PET were compared at  $35^\circ\text{C}$  in Figure 6. Apparently c-PET has a smaller diffusivity than h-PET. Several workers have reported that the diffusivity of the Langmuir species in PET is about 10% that of the Henry species.<sup>3,6,8</sup> When assuming such a low diffusivity of the Langmuir species contribution, the present result is explained as due to that species. Diffusion through the microvoids causes small apparent diffusion coefficients. After annealing, therefore, the apparent diffusivity is increased because of the decrease of diffusion through the unrelaxed volume, that is, the decrease of fraction of the Langmuir species in the permeant molecules.

In the last two paragraphs, we would like to point out that changes in the polymer state can be followed qualitatively by the simplest treatment of the



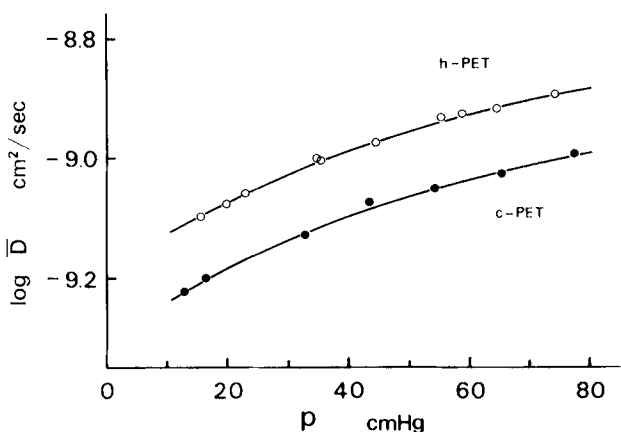


Fig. 6. Comparison of the average diffusion coefficients ( $\bar{D}$ ) of CO<sub>2</sub> in PET crystallized by sorption of CO<sub>2</sub> (c-PET) (○) and in PET crystallized by thermal annealing (h-PET) (●) at 35°C.

permeation data. By the permeation measurement, the diffusional time lag,  $\theta$ , as well as  $P$  can be obtained. For rubbers, the diffusion coefficient,  $D$ , is related to the  $\theta$  value by Eq. (4);

$$D = l^2/6\theta \quad (4)$$

where  $l$  is the film thickness. For glassy polymers, the  $D$  value obtained by this equation is only apparent,  $Da$ , because the pressure dependence of the solubility coefficient is evident from the dual-mode behavior of sorbed gases. However it is more convenient to obtain the diffusivity information from the permeation measurement, especially for gases which are sparingly soluble, as in many previous studies.<sup>32-37</sup> As CO<sub>2</sub> shows the typical character of dual-mode sorption, comparison between  $Da$  and  $l$  shows the limit of this treatment. The  $\bar{D}$  values, shown by the filled marks and the solid lines, and the  $Da$  values, shown by the open marks, are compared in Figure 7. It is shown that  $Da$  is in accord with  $\bar{D}$  in the pressure range above approx. 30 cmHg, it is not clear why the disagreement below 30 cmHg is slightly larger than expected. It seems possible, therefore, to use the  $Da$  values for the estimation of diffusivity. The diffusivities of CO<sub>2</sub> in PET films were compared in the form of  $Da$  at 35°C in Figure 8 as a function of pressure in the range above 30 cmHg. As in the case of comparison by the  $\bar{D}$  values, the diffusivity in c-PET was shown to be smaller than in h-PET. Furthermore, the  $Da$  values in h-PET are smaller than in a-PET, but the difference corresponds closely to the crystallinity of h-PET. This result is reasonable, since the excess free volume in h-PET is expected to be quite small. As a result, the following relationship is plausible as Michaels et al. mentioned;<sup>1</sup>

$$D = D^* \times \alpha \quad (5)$$

where  $D^*$  and  $D$  are the diffusion coefficients in amorphous and crystallized samples, respectively. As Langmuir species involvement in penetrants grows, the situation becomes more complex.

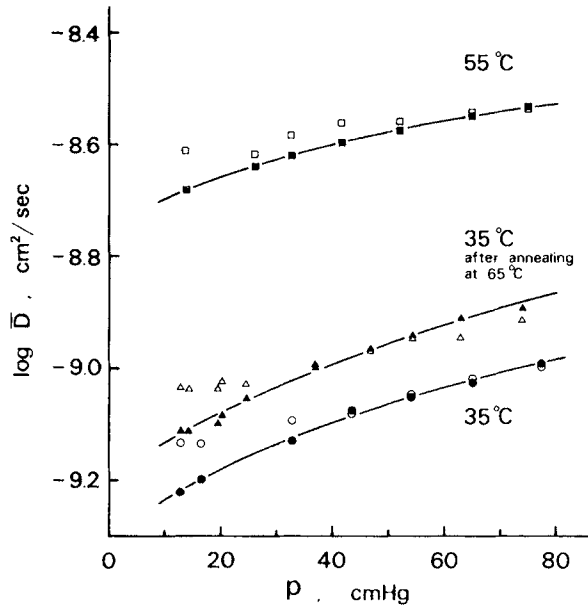


Fig. 7. Comparison of the average ( $\bar{D}$ ) and the apparent ( $D_a$ ) diffusion coefficients of  $\text{CO}_2$  in PET crystallized by sorption of  $\text{CO}_2$  (c-PET). ●, ▲, ■; the average diffusion coefficient obtained from the permeation and sorption data. ○, △, □; the apparent diffusion coefficient calculated from the diffusional time lag.

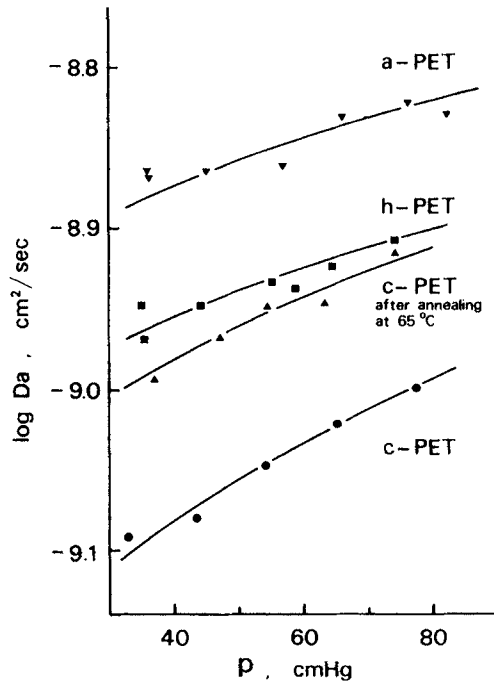


Fig. 8. Comparison of the apparent diffusion coefficients of  $\text{CO}_2$  in some PET films at  $35^\circ\text{C}$ . c-PET; PET crystallized by sorption of  $\text{CO}_2$ , h-PET; PET crystallized by thermal annealing, a-PET; amorphous PET.

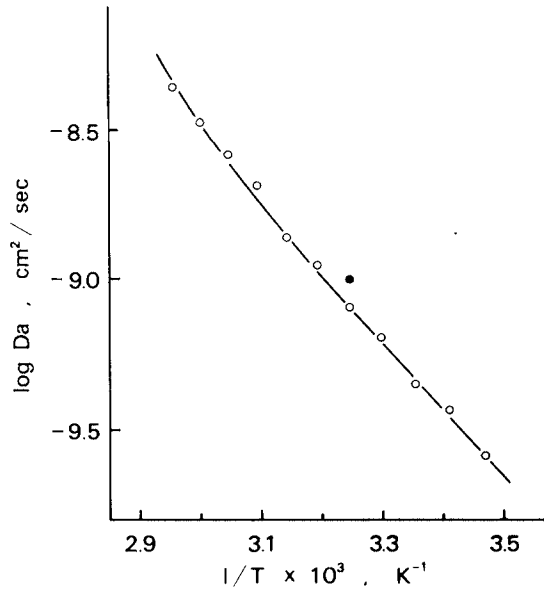


Fig. 9. Temperature dependence of the apparent diffusion coefficients of CO<sub>2</sub> in PET crystallized by sorption of CO<sub>2</sub> (c-PET). ●; after measurements at 65°C.

The temperature dependence of *Da* and the apparent solubility coefficients, *Sa*, obtained by Eq. (6) are shown in Figures 9 and 10, respectively, in order to see the scope of this treatment.

$$S_a = P/D_a \tag{6}$$

Every plot of *Da* is the average of two or three experiments at pressures

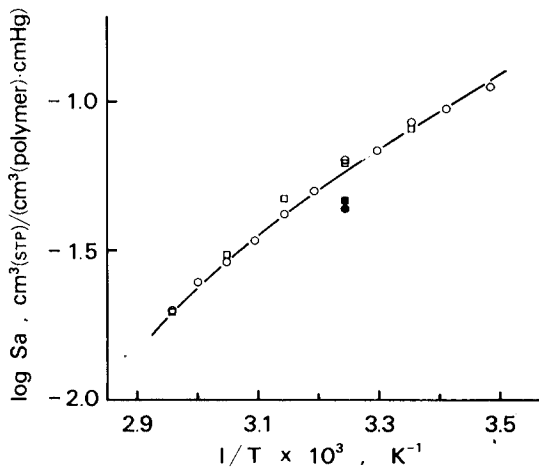


Fig. 10. Temperature dependence of the apparent solubility coefficients in PET crystallized by sorption of CO<sub>2</sub> (c-PET). ○, ●; the apparent solubility coefficients obtained from the permeability and the apparent diffusion coefficients, □, ■; the solubility coefficients calculated from the dual-mode parameters in Table I, ●, ■; after measurements at 65°C.

between 30 and 60 cmHg. Contrary to the usual temperature dependence, the Arrhenius plot of  $Da$  is not linear but slightly convex to the abscissa. It is believed that the figure also illustrates the decrease of the unrelaxed volume qualitatively. Relaxation of the excess free volume, which is the cause of low diffusivity in c-PET, leads to greater increases of diffusivity than the well-known temperature dependence. The temperature dependence of  $Sa$  also seems to be plausible since it shows a greater decreased solubility than expected from the usual temperature dependence. Of course, this analysis is too simple for a glassy polymer but the data are in accord with the sorption data plotted (square marks) which were calculated from the dual-mode parameters in Table I at 40 cmHg of  $\text{CO}_2$ . At high pressures, the problem is so complex that this method is totally invalid not only because of the dual-mode behavior but because of the plasticization of a polymer. However, the present data means that permeation data at low pressures of  $\text{CO}_2$  and their simple analysis are useful even for the discussion of diffusivity and solubility. The situation will improve for less soluble gases because of the smaller Langmuir species contribution. The permeation data of such gases as  $\text{O}_2$  and  $\text{N}_2$  will be reported in the future.

### SUMMARY

The effect of relaxation on gas sorption and transport of  $\text{CO}_2$  has been shown with poly(ethylene terephthalate) crystallized by sorption of high-pressure  $\text{CO}_2$  (c-PET). Comparing amorphous and crystallized PET by thermal annealing, high solubility and permeability were observed for c-PET. But the effect of thermal relaxation on solubility and permeability was quite large. The sorption behavior was in accord with the dual-mode sorption model when a large unrelaxed volume was assumed. The average diffusion coefficient,  $\bar{D}$ , in c-PET was shown to be lower than those in other samples. The result and the effect of polymer relaxation on the diffusivity were interpreted based on the concept of the partial immobilization model.

### References

1. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 1 (1963); 13 (1963).
2. W. R. Vieth, H. Alcalay, and A. J. Frabetti, *J. Appl. Polym. Sci.*, **8**, 2125 (1964).
3. W. R. Vieth and K. J. Sladek, *J. Colloid Sci.*, **20**, 1014 (1965).
4. W. J. Koros, D. R. Paul, M. Fujii, H. B. Hopfenberg, and V. Stannett, *J. Appl. Polym. Sci.*, **21**, 2899 (1977).
5. W. J. Koros and D. R. Paul, *J. Polym. Sci.: Polym. Phys. Ed.*, **16**, 1947 (1978).
6. W. J. Koros and D. R. Paul, *J. Polym. Sci.: Polym. Phys. Ed.*, **16**, 2171 (1978).
7. W. J. Koros and D. R. Paul, *Polym. Eng. Sci.*, **20**, 14 (1980).
8. K. Toi, *J. Polym. Sci.*, **11**, 1829 (1973).
9. K. Toi, *Polym. Eng. Sci.*, **20**, 30 (1980).
10. K. Toi, K. Oba, Y. Maeda, T. Ito, T. Shirakawa, I. Ikemoto, and T. Tokuda, *J. Polym. Sci.: Polym. Phys. Ed.*, **24**, 121 (1986).
11. N. Kuroda, *Sen-i Gakkaishi*, **35**, T-413 (1979).
12. N. Kuroda, *Sen-i Gakkaishi*, **36**, T-527 (1980).
13. R. R. Light and R. W. Seymour, *Polym. Eng. Sci.*, **22**, 857 (1982).
14. R. M. Barrer, J. A. Barrie, and J. Slater, *J. Polym. Sci.*, **27**, 177 (1958).
15. R. Masi and D. R. Paul, *J. Membr. Sci.*, **12**, 137 (1982).
16. J. S. Chiou, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **30**, 2633 (1985).
17. K. Mizoguchi, T. Hirose, Y. Naito, and Y. Kamiya, *Polymer*, **28**, 1298 (1987).

18. T. Hirose, K. Mizoguchi, and Y. Kamiya, *J. Appl. Polym. Sci.*, **30**, 401 (1985).
19. T. Hirose, K. Mizoguchi, and Y. Kamiya, *J. Appl. Polym. Sci.*, **34**, 1657 (1987).
20. T. Hirose, K. Mizoguchi, Y. Naito, and Y. Kamiya, *J. Appl. Polym. Sci.*, **35**, 1715 (1988).
21. Y. Kamiya, T. Hirose, Y. Naito, and K. Mizoguchi, *J. Polym. Sci.: Part B: Polym. Phys.*, **26**, 159 (1988).
22. K. Terada, K. Mizoguchi, Y. Naito, T. Hirose, and Y. Kamiya, *Polym. Preprints, Japan*, **36**, 1240 (1987).
23. A. G. Wonders and D. R. Paul, *J. Membr. Sci.*, **5**, 63 (1979).
24. A. H. Chan and D. R. Paul, *J. Appl. Polym. Sci.*, **24**, 1539 (1979).
25. A. J. Erb and D. R. Paul, *J. Membr. Sci.*, **8**, 11 (1981).
26. Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, *J. Polym. Sci.: Part B: Polym. Phys.*, **24**, 535, (1986).
27. Y. Kamiya, T. Hirose, K. Mizoguchi, and Y. Naito, *J. Polym. Sci.: Part B: Polym. Phys.*, **24**, 1525 (1986).
28. A. H. Chan, W. J. Koros, and D. R. Paul, *J. Membr. Sci.*, **3**, 117 (1978).
29. S. A. Stern and A. D. DeMeringo, *J. Polym. Sci.: Polym. Phys.*, **16**, 735 (1978).
30. S. A. Stern and S. S. Kulkarni, *J. Membr. Sci.*, **10**, 235 (1982).
31. G. S. Huvard, V. T. Stannett, W. J. Koros, and H. B. Hopfenberg, *J. Membr. Sci.*, **6**, 185 (1980).
32. P. Mears, *J. Am. Chem. Soc.*, **76**, 3415 (1954).
33. P. Mears, *Trans. Faraday Soc.*, **53**, 31 (1957).
34. C. A. Kumins and J. Roteman, *J. Polym. Sci.*, **55**, 683 (1961).
35. F. J. Norton, *J. Appl. Polym. Sci.*, **7**, 1649 (1963).
36. V. Stannett and J. L. Williams, *J. Polym. Sci.: Part C*, **10**, 45 (1965).
37. W. H. Burgess, H. B. Hopfenberg, and V. T. Stannett, *J. Macromol. Sic.-Phys.*, **B5**, 23 (1971).

Received November 20, 1987

Accepted March 10, 1988