Low-pressure CO_2 Sorption in Poly(vinyl Benzoate) Conditioned to High-pressure CO_2

TAKUJI HIROSE, KEISHIN MIZOGUCHI, YASUTOSHI NAITO, and YOSHINORI KAMIYA, *Packaging Materials Division, Industrial Products Research Institute, 1-1-4 Higashi, Yatabe-Machi, Tsukuba-Gun, Ibaraki, Japan, 305.*

Synopsis

Sorption of CO_2 in poly(vinyl benzoate) was gravimetrically measured at pressures up to 1 atm. Sorption isotherms were determined above and below the glass transition temperature T_g from 5 to 85°C. The isotherms were analyzed by the dual-mode sorption model assuming that the plasticizing effect of sorbed CO_2 is negligible at this pressure range. The solubilities and Henry's law dissolution parameters were compared with those obtained by the high-pressure sorption and permeation measurements. Henry's law dissolution parameters were in good agreement with one another. However, the solubilities first determined here were smaller than those determined by the high-pressure sorption experiment at the same temperature. It was clear that the Langmuir capacity of the present specimen was smaller in spite of similar high-pressure CO_2 exposure. Relaxation of the polymer was expected to be one of the reasons. This expectation was confirmed from the observation and analysis of sorption isotherms after two kinds of treatments. After annealing above T_g, the Langmuir capacity was shown to be decreased to 1/2 or even to 1/3 from the sorption isotherms below 45°C. This means that the conditioning to the high-pressure CO_2 surely has a large effect on the nature of glassy polymer. Just after high-pressure CO_2 exposure at 25°C, increased solubility was observed. Furthermore, the slow decrease of solubility, that is, the decrease of conditioning effect, was also followed from the continual measurements at 25°C. This result reflects not only the characteristic of sorption capacity after high-pressure CO_2 exposure, but also the relaxation of polymer in glassy state.

INTRODUCTION

Recently, several workers have demonstrated the large effect of CO_2 sorbed on polymers at high pressures.[1-8] Chiou et al.[1-3] and our group[4] have discussed plasticization of polymers, from the glassy to the rubbery states, from the change of character of sorption isotherms below their T_gs. The two groups discussed polymer plasticization by sorbed gas and depression of T_gs due to the rather high solubility of CO_2. In some cases, T_g falls below the observation temperature and the glassy polymers behave like rubbers. For some CO_2-glassy polymer systems, the plasticizing effect of sorbed CO_2 was proved by the crystallization of the polymer and polymer blend by both groups.[7,8]

In this way, sorption behaviors show the states of polymers and are important in order to understand the transport phenomenon of gases in polymers. The plasticizing effect of sorbed gas, such as CO_2 or other soluble gases, however, is a serious problem because sorption isotherms of such gases are not easy to analyze. In transport, the situation will be more complex because the state of polymer should change locally. For less soluble gases, on

CCC 0021-8995/88/071715-10$04.00

the other hand, plasticization by sorbed gases is not significant even at high pressures. This suggests that the plasticization will be negligible at low concentrations of CO_2, that is, at low pressures. Such information at low pressures is necessary to estimate the plasticizing effect of sorbed CO_2 and to make clear the complex phenomenon at high pressures.

We have recently reported that the solubilities of CO_2 in poly(vinyl cyclohexanecarboxylate) (PVCH) can be determined accurately by a gravimetric method at pressures below 1 atm.[9] Neglecting the plasticizing effect of sorbed CO_2, the sorption isotherms were analyzed by the dual-mode sorption model, Eq. (1). In this interpretation, the total concentration C is a sum of a Henry's law contribution C_D and a Langmuir contribution C_H:

$$C = C_D + C_H$$

$$= k_D p + \frac{C'_H bp}{1 + bp} \tag{1}$$

where k_D is the Henry's law dissolution parameter and C'_H and b are the hole saturation and the hole affinity constant in the Langmuir mode, respectively. This paper is concerned with the sorption behavior of CO_2 below 1 atm in poly(vinyl benzoate) (PVB), which was plasticized to a rubber by the sorption of CO_2 at high pressures below its T_g.[4] After confirmation of the little plasticizing effect by sorbed CO_2 at low pressures below 1 atm, the sorption isotherms were analyzed by Eq. (1). Furthermore, the relaxation of glassy polymer exposed to high-pressure CO_2 from the slow decrease of sorption capacity below T_g was investigated. These measurements and the quantitative analysis based on the dual-mode sorption model served as useful information on the state or structure of PVB. These results will be necessary to our discussion of the sorption behavior of CO_2 in the polymer at high pressures.

EXPERIMENTAL

Materials

The preparation of PVB film and its properties were reported in previous papers.[10,11]

CO_2 gas was at least greater than 99.99% pure and no further purification was performed.

Apparatus and Procedure

Sorption measurements were made using facilities and procedures described previously.[9] In this study, the sample films were exposed to CO_2 of 50 atm at 35°C before measurements. After they were set in the sorption apparatus, the system was evacuated to a constant weight at 35°C for two days. The time taken to obtain each isotherm is a few days to a week depending on the experimental temperature.
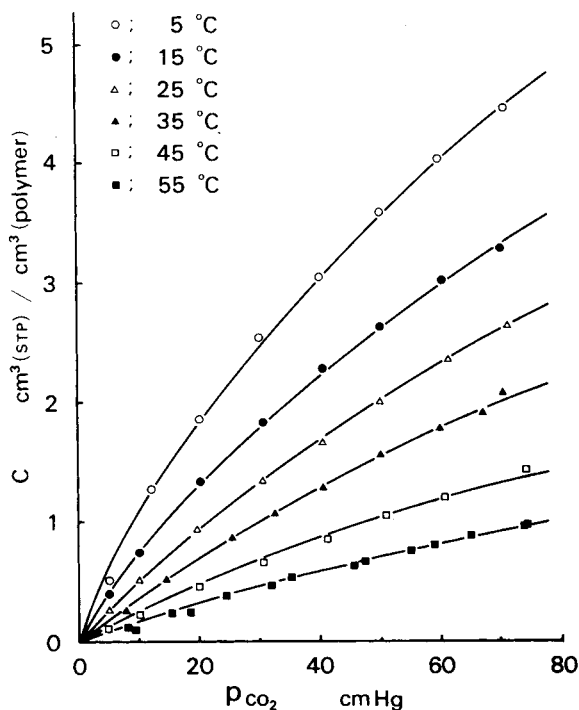
Fig. 1. Sorption isotherms of CO$_2$ in PVB between 5 and 55°C. ○; 5°C, ●; 15°C, △; 25°C, ▲; 35°C, □; 45°C, ■; 55°C.

RESULTS AND DISCUSSION

Sorption isotherms for CO$_2$ in PVB below 55°C are shown in Figure 1. The isotherm at 35°C was measured first and the experimental temperature was lowered to 5°C with the decrement of 10°C and then raised to 55°C. They are concave to the pressure axis and are characteristic of dual-mode sorption in glassy polymers.[3-6,12] Above 65°C, however, the isotherms are linear and are described by Henry's law as shown in Figure 2. They show that the polymer is in the rubbery state above 65°C. This temperature corresponds well to T_g determined by the dilatometry results and the permeation measurements.[10] In addition, the present result is in the good agreement with those of the high-pressure sorption of N$_2$ and Ar on this polymer.[4] The change of characteristic of sorption isotherms at T_g for poly(ethylene terephthalate)-CO$_2$ system has been observed by Koros and Paul[12] and for PVCH-CO$_2$ by our group.[9] It will be mentioned later that the sequence of experiments should have affected the isotherms below T_g.

In contrast to the high-pressure sorption of CO$_2$,[1-8] there is no sign of plasticization of the polymer by sorbed gas. As we expected, Figure 1 shows no sorption/desorption hysteretic behavior and no change of character of curvature in the isotherms of the glassy state. Consequently, the sorption data in this pressure range were analyzed by the simple dual-mode sorption model, Eq. (1), without regard to the discussion by some workers.[3,5,13] The dual-mode
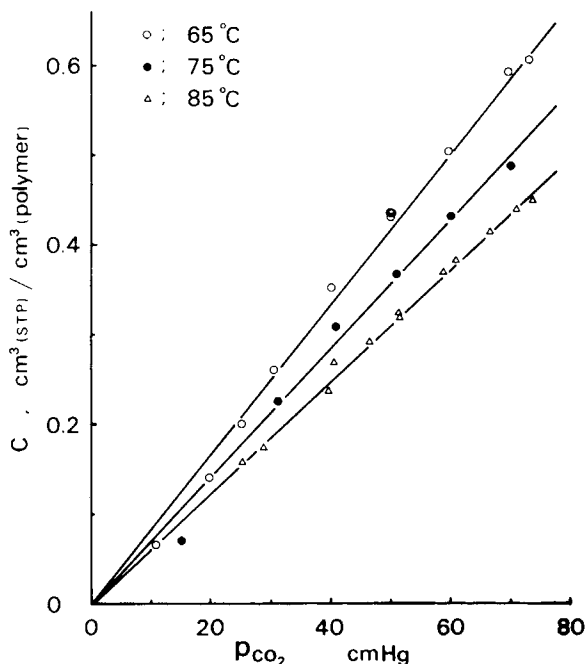
Fig. 2. Sorption isotherms of CO_2 in PVB between 65 and 85°C. ○; 65°C, ●; 75°c, △; 85°C.

parameters summarized in Table I were determined by a nonlinear regression technique except the Henry's dissolution parameters, which were extrapolated from the data above T_g as reported earlier.[4,9] k_D and the low-pressure apparent Henry's law parameters below T_g, $k_D + C'_H b$, are plotted as a function of temperature in Figure 3. The open circles are the Henry's law dissolution parameters estimated from the linear parts of sorption isotherms determined by high-pressure sorption of CO_2. Because they can be extrapolated to the coordinate origin, the polymer must be in the rubbery state at

TABLE I
Dual Sorption and Henry's Law Parameters for CO_2 and PVB

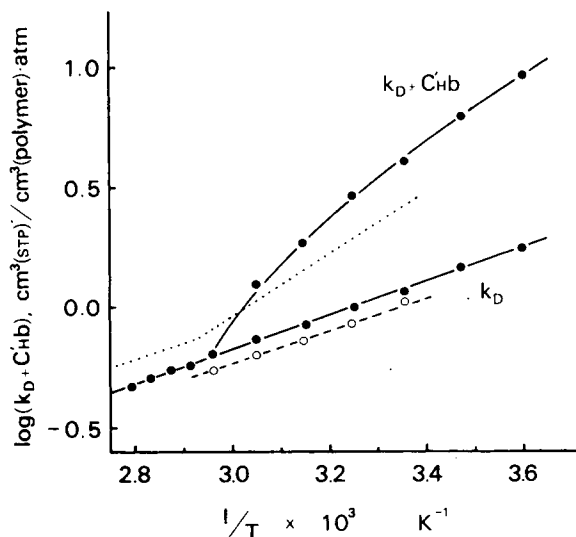| T (°C)	k_D $\dfrac{cm^3(STP)}{cm^3(polymer) \cdot atm}$	C'_H $\dfrac{cm^3(STP)}{cm^3(polymer)}$	b (atm^{-1})
5	1.78	4.69	1.60
15	1.45	3.59	1.35
25	1.18	3.52	0.821
35	1.00	3.05	0.623
45	0.851	1.78	0.547
55	0.730	0.666	0.760
65	0.641	—	—
70	0.577	—	—
75	0.545	—	—
80	0.511	—	—
85	0.472	—	—

Fig. 3. Van't Hoff plot of true and low-pressure apparent Henry's law parameters (●). Open circles are the data estimated by the high-pressure sorption of CO_2 (Ref. 4). Dotted lines is the data determined by the permeation measurement (Ref. 10).

high-pressure range of CO_2, that is, the slope should be k_D.[4] On the other hand, the dotted line is the data extrapolated from k_D determined by permeation measurements above T_g.[10] The three sets of k_D agree well with one another and this agreement further supports the discussion on plasticization of PVB from the glassy to the rubbery state by sorbed CO_2. The heat of solution for the dissolved species, ΔH_D, is -3.2 kcal/mol and is very close to the values (-3.0 kcal/mol) obtained previously.[4,10]

It is well known that the sorption capacity of glassy polymer varies with the conditioning to high-pressure of CO_2.[4,5,13-17] As mentioned in the Experimental section, the polymer was exposed to CO_2 of 50 atm at 35°C with the intention that the sample condition would be identical to that of the previous paper.[4] The expectation was that the present isotherms would be a part of those determined by the high-pressure sorption measurements. Two sets of the data, however, do not agree so well in the glassy state. From the isotherm at 25°C in Figure 1, for example, the solubility at 1 atm is expected about 3 cm³(STP)/cm³(polymer) while 4.28 cm³(STP)/cm³(polymer) was measured previously.[4] The present solubilities at 35 and 45°C are also a little smaller. There appear to be two reasons for the difference of solubilities. The first is that the polymer was exposed to CO_2 at 35°C only once, not at 25°C or at any other temperature. At high-pressure sorption, the measurement is equal to conditioning to the highest pressure at each temperature. Therefore, at 25°C, the measurements at 50 atm of CO_2 in the previous study must be a greater conditioning than that of the present study. The second reason is that relaxation of polymer during the measurement could decrease the conditioning effect. After conditioning by high-pressure CO_2, the polymer specimens, which has a large Langmuir sorption capacity, such as polycarbonate (PC) and

polysulfone (PSUL), show little difference in their sorption isotherms for months, when they are not annealed.[5,16,17] On the other hand, it has been shown that the CO_2 conditioning effect was diminished quickly for PVCH because of its relatively low T_g.[9,11] The T_g of PVB is about 10°C higher than PVCH and C'_H values in Table I are larger than those of PVCH (Table II in Ref. 9), which has the same main structure as PVB. It is expected, therefore, that PVB will show the intermediate behavior between PC or PSUL and PVCH. That is, the sorption capacity will be decreased gradually from that created initially by high-pressure CO_2. In other words, it will be possible to follow the time dependence of the sorption capacity by continual measurement of sorption isotherms. At the same time, the conditioning effect change will be an evidence of relaxation of glassy polymer. This is the point with which we are primarily concerned in this study and the expectation was examined by the experiments in the following three paragraphs.

Thermal annealing is known to reduce the sorption capacities of polymers with various processing and treatment histories.[16,17] At first, this was confirmed for the present system after measurements above T_g. After the determination of sorption isotherm at 85°C, the apparatus was cooled slowly and the solubility was measured again at temperatures from 15°C to 45°C. The isotherms are concave to the pressure axis again as shown in Figure 4. But it is clear that solubility of CO_2 decreased largely from the comparison of each isotherm to that of corresponding temperature in Figure 1. Naturally the relaxation of polymer chains above T_g eliminated the conditioning effect of
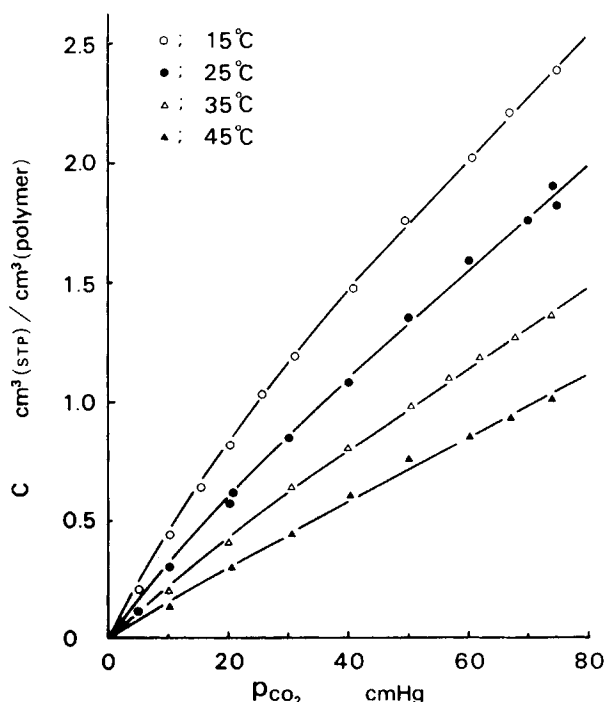

Fig. 4. Sorption insotherms of CO_2 in PVB between 15 and 45°C after annealing at 85°C. ○; 15°C, ●; 25°C, △; 35°C, ▲; 45°C.

TABLE II
Dual Sorption Parameters for CO$_2$ and PVB after Annealing at 85°C

T (°C)	k_D $\dfrac{\text{cm}^3(\text{STP})}{\text{cm}^3(\text{polymer}) \cdot \text{atm}}$	C'_H $\dfrac{\text{cm}^3(\text{STP})}{\text{cm}^3(\text{polymer})}$	b (atm^{-1})
15	1.45	1.71	1.338
25	1.55	1.73	0.739
35	1.00	0.890	0.828
45	0.851	0.477	0.760

high-pressure CO$_2$, that is, the unrelaxed volume forcibly made by CO$_2$ exposure was removed. The isotherms were also fitted by Eq. (1) based on the assumption that k_D does not change by annealing, and the parameters are listed in Table II. Here this assumption means only that the decrease of solubility should be attributed to C_H. Chan and Paul discussed that analysis by letting b and k_D constant represent the true effects of annealing,[14] however, it seems to be possible that the hole affinity of gases changes when the holes or microvoids themselves change. While k_D is related to the equilibrium liquid-like state in glass, the microvoids, to which C'_H and b are related, are the result of the unrelaxed state of the polymer and can change by relaxation. Table II indicates that the Langmuir contribution reduced the conditioning effect to half or to one third of that before annealing. Though the parameters show not only the decrease of $C'_H b$ but also the changes of C'_H and b, it is difficult now to discuss the meaning of changes in b in detail. C'_H in Tables I and II are plotted against temperature in Figure 5. The difference between open and closed circles shows how the amount of sorption capacity decreased on annealing. At least, the C'_H corresponding to this difference can be increased by high-pressure CO$_2$ exposure at 50 atm.

Next the time dependence of sorption capacity was followed by measuring the change of solubility at 25°C. The sample specimen of PVB was exposed to CO$_2$ of 50 atm at 25°C and was set in the sorption apparatus, evacuated overnight, and the solubility was measured for several days. The slow change of sorption isotherms is revealed in Figure 6. The top isotherm, which was measured in two days, shows that the solubility at 1 atm is about 4.4 cm^3(STP)/cm^3(polymer) and this value is about 45% larger than the data of Figure 1 and almost compares with that reported previously.[4] This increase is mainly caused by the difference of temperature, at which the sample was conditioned. As the temperature is lowered, the amount of sorbed gas increased and the conditioning effect becomes larger. The isotherms in Figure 1 were determined after to CO$_2$ exposure and treatment to outgas at 35°C, not 25°C. There is no wonder that the isotherms are largely different. The situation will be the same for other temperatures below 25°C.

The second isotherm in Figure 6, which was determined the day after the measurements of the top one, shows a small decrease of solubility. Ten days later, the third isotherm was measured over a period of two days. It is usually said that the volume expansion caused by CO$_2$ exposure gives rise to an increased sorption capacity. On the contrary, the decrease of sorption capacity
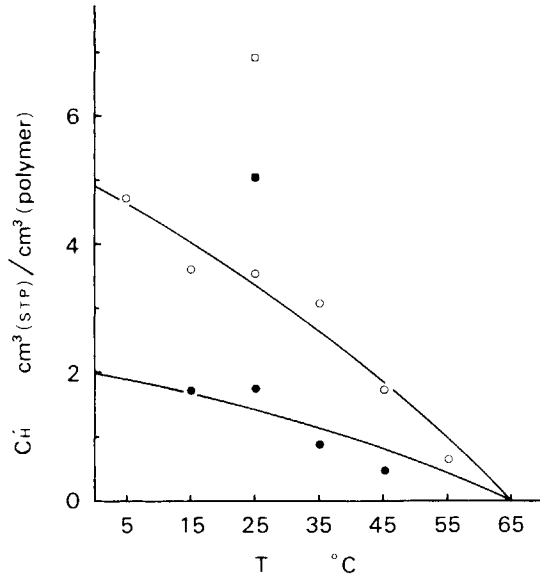
HIROSE ET AL.

Fig. 5. Hole saturation constant of PVB conditioned to 50 atm of CO_2 at 35°C versus temperature before (○) and after (●) annealing at 85°C. Squares show the hole saturation constants of PVB conditioned to 50 atm of CO_2 at 25°C. Just after the conditioning (□) and 7 days later (■) at 25°C.
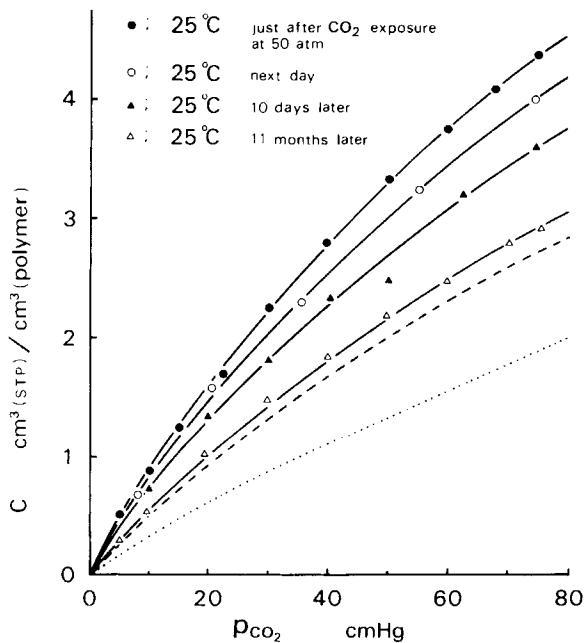

Fig. 6. Time-dependence of sorption isotherms at 25°C after CO_2 exposure at 50 atm. Dashed line is the sorption isotherm at 25°C in Fig. 1. Dotted line is the sorption isotherm at 25°C after annealing at 85°C (Fig. 4). ●; Just after CO_2 exposure at 50 atm, ○; Next day, ▲; 10 days later, △; 11 months later.

TABLE III
Dual Sorption Parameters for CO$_2$ and PVB at 25°C
after Exposure to 50 atm of CO$_2$

	k_D cm^3(STP)	C'_H cm^3(STP)	b
	cm^3(polymer · atm	cm^3(polymer)	(atm^{-1})
Just after			
Exposure	1.18	6.88	0.889
Next day	1.18	5.74	0.990
7 days			
later	1.18	5.00	0.942
11 months			
later	1.18	3.54	1.008
Isotherm			
in Fig. 1[a]	1.18	3.52	0.827
After annealing			
at 85°C	1.18	1.73	0.739

[a]After measurements at 35°C.

in Figure 6 means the expansion was recovered just like the relaxation by thermal annealing mentioned in the previous section, the rate of change is much different, though. After determination of each isotherm, the polymer sample was evacuated at 25°C so the recovery of volume is the result of relaxation of polymer in the absence of sorbed gas of 25°C. In addition, as mentioned before, most of the decrease should be attributed to the change of unrelaxed volume formed by CO$_2$ exposure. This is one reason that solubilities at 35°C shown in Figure 1 are smaller than we expected. The polymer is expected to have relaxed even during the process to outgas at 35°C. After these measurements, the polymer sample was taken out of the sorption apparatus and was kept at room temperature for 11 months. The fourth isotherm in Figure 6 shows the solubility of CO$_2$ in this sample and is close to one at 25°C in Figure 1. It is evident that relaxation of the glassy polymer proceeded at room temperature, but the sorption capacity did not decrease so much as when annealed above T_g. This isotherms were analyzed in the same way, and the dual-mode parameters are summarized in Table III. Open and closed squares in Figure 5 show the C'_H values of the top and third isotherms, respectively. The sorption capacity increased by CO$_2$ conditioning is revealed to decrease rather easily at 25°C or at room temperature. But the relaxation in glassy state almost stops at some point and does not proceed so much as with annealing above T_g. Chan and Paul observed the effect of sub-T_g annealing on PC and similar changes of dual-mode parameters, that is, the effect of annealing, have been reported with thermal analysis.[14] But their results are rather complex because of the conditioning to 20 atm of CO$_2$ before the measurements. The present result clearly shows the affect of sub-T_g annealing at temperatures about 40 or 30°C below T_g.

SUMMARY

Previously the plasticization of PVB by sorbed CO$_2$ was recognized from the observations of not only the hysteresis in sorption isotherms but also the

change of sorption isotherms from concave to linear at high pressures.[4] In this study, however, it has been demonstrated that CO_2 sorption isotherms of PVB do not show any signs of plasticization below 1 atm. The isotherms were analyzed by the simple dual-mode sorption model without the consideration of plasticizing effect of sorbed gas.

After annealing above T_g, the decrease of sorption capacity was revealed. Most of that is expected to come from the decrease of unrelaxed volume formed by high-pressure CO_2 exposure. Moreover the time dependence of sorption capacity was measured at 25°C and the method of change was also followed from the analysis of isotherms by the dual-mode sorption model. The slow decrease of unrelaxed volume is the first and clear evidence of relaxation of glassy polymer exposed to high-pressure CO_2. From the results, therefore, it is clear the polymer should have much larger solubilities than shown in Figure 1 when the measurement is performed soon after CO_2 conditioning at the experimental temperature. In other words, for PVB, the measurements and evacuation to outgas at 35°C could be the so-called sub-T_g annealing because the observation temperature is not so far below T_g. But the data at 25°C just after CO_2 exposure was in good agreement with the previous one determined by high-pressure sorption measurements and they will be important and of help in discussing the sorption isotherms of CO_2 at high pressures, where plasticization of the polymer is so much that it is impossible to analyze them by the simple dual-mode sorption model.

References

1. J. S. Chiou, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **30**, 2633 (1985).
2. J. S. Chiou, Y. Meada, and D. R. Paul, *J. Appl. Polym. Sci.*, **30**, 4019 (1985).
3. J. S. Chiou and D. R. Paul, *J. Appl. Polym. Sci.*, **32**, 2897 (1986).
4. Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, *J. Polym. Sci.: Part B: Polym. Phys. Ed.*, **24**, 535 (1986).
5. Y. Kamiya, T. Hirose, K. Mizoguchi, and Y. Naito, *J. Polym. Sci.: Part B: Polym Phys. Ed.*, **24**, 1525 (1986).
6. G. K. Fleming and W. J. Koros, *Macromolecules*, **19**, 2285 (1986).
7. J. S. Chiou, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **30**, 3911 (1986).
8. K. Mizoguchi, T. Hirose, Y. Naito, and Y. Kamiya, *Polymer*, **28**, 1298 (1987).
9. T. Hirose, K. Mizoguchi, and Y. Kamiya, *J. Appl. Polym. Sci.*, **34**, 1657 (1987).
10. T. Hirose, K. Mizoguchi, and Y. Kamiya, *J. Appl. Polym. Sci.*, **30**, 401 (1985).
11. T. Hirose, K. Mizoguchi, and Y. Kamiya, submitted to *J. Appl. Polym. Sci.* (in print).
12. W. J. Koros and D. R. Paul, *J. Polym. Sci. Polym. Phys. Ed.*, **16**, 1947 (1978).
13. G. R. Mauze and S. A. Stern, *J. Membr. Sci.*, **12**, 51 (1982).
14. A. H. Chan and D. R. Paul. *Polym. Eng. Sci.*, **20**, 87 (1980).
15. A. H. Chan and D. R. Paul, *J. Appl. Polym. Sci.*, **24**, 1539 (1979).
16. A. J. Erb and D. R. Paul, *J. Membr. Sci.*, **8**, 11 (1981).
17. A. G. Wonders and D. R. Paul, *J. Membr. Sci.*, **5**, 63 (1979).