CO_2-induced crystallization of poly(ethylene terephthalate)

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Crystallization of amorphous poly(ethylene terephthalate) (PET) induced by sorbed CO_2 has been investigated at several temperatures and pressures up to 50 atm and compared with thermal crystallization. From the results of X-ray diffraction, infra-red spectroscopy and density measurements, it was shown that, by sorption of CO_2, crystallization takes place even at temperatures well below the T_g measured in air, and the crystallization rate at temperatures above T_g was greatly increased. This means the sorbed CO_2 acts as an intensive plasticizer for PET. From the effects of the sorbed CO_2 on the crystalliation rate, the plasticizing ability of CO_2 was estimated in terms of temperature, which is equivalent to enhancement of the mobility of the polymer segments. The density of the sample crystallized by sorbed CO_2 was smaller than that of a thermally crystallized sample having the same crystallinity determined by infra-red measurements. It is assumed that the sample crystallized by sorbed CO_2 contains more microvoids than that crystallized by thermal annealing.

(Keywords: crystallization; sorption; carbon dioxide; poly(ethylene terephthalate); plasticizing effect)

INTRODUCTION

It is well known that poly(ethylene terephthalate) (PET) quenched at temperatures below the glass transition point (T_g) takes an amorphous structure. Crystallization of the amorphous PET can be induced by solvent as well as by heat and strain. The interaction between polymer and the solvent reduces the effective T_g and, if the reduction of T_g is large enough to put the system in the crystallization temperature region, the polymer chains rearrange themselves into a lower free energy state[1-5].

On the other hand, Wang *et al.*[6] have observed the reduction of T_g from measurements of the mechanical relaxation of polystyrene exposed to a CO_2 environment. They concluded that, at high pressures, CO_2 gas is an effective plasticizer for polystyrene. In our previous work, it was shown from high-pressure CO_2 sorption measurements that, at a certain pressure of CO_2, the T_g of poly(vinyl benzoate) was reduced by the sorption of CO_2, i.e. the T_g was reduced from 65°C to 45 and 35°C by CO_2 sorbed at 25 and 37 atm, respectively[7]. Thus T_g is affected by sorbed CO_2 just like the effect of solvents. It is assumed, therefore, that amorphous PET can be crystallized by CO_2 sorption, if it is plasticized sufficiently to reduce the T_g well below the temperature at which the sorption is made. Recently, Chiou *et al.*[8-10] have reported the plasticization and crystallization of some polymers by sorption of CO_2. In their reports, PET was recognized to be crystallized by CO_2 sorption as in the case of blends of poly(vinylidene fluoride) and poly(methyl methacrylate)[10]. By a differential scanning calorimetric technique they observed the reduction of T_g of PET from 74°C to 52 and 35°C by CO_2 sorbed at 20 and 35 atm, respectively. They also reported that crystallization of PET at 35°C was induced by the sorption of CO_2 at 20 atm, which is surprising because under these conditions the polymer should be in a glassy state.

In this study, the crystallization of amorphous PET induced by sorbed CO_2 is studied isothermally up to 50 atm and at 35–85°C. The crystallization process is kinetically investigated by X-ray diffraction, infra-red spectroscopy and density measurements. The effects of sorbed CO_2 on the crystallization rate are discussed and estimated in terms of temperature. The fine structure of PET crystallized by CO_2 is also discussed from the comparison with density of PET crystallized by thermal annealing.

EXPERIMENTAL

Material

Amorphous quench-rolled PET films of 40 and 62 μm thickness were obtained courtesy of Diafoil Co. Ltd. The PET was stated to be without fillers and additives. Wide-angle X-ray diffraction (WAXD) measurements revealed the amorphous and unoriented structure of the film (*Figure 1a*). The degree of crystallinity (X_c) was estimated as 4.4 ± 0.9 wt% from density measurements[11,12]. The glass transition temperature (T_g) was about 75°C as measured by differential scanning calorimetry (d.s.c.) at the rate of 20°C min^{-1}.

Methods and apparatus

High-pressure CO_2 treatment of amorphous PET films was carried out in a stainless-steel autoclave. The autoclave (300 cm^3) with a pressure gauge and valves was

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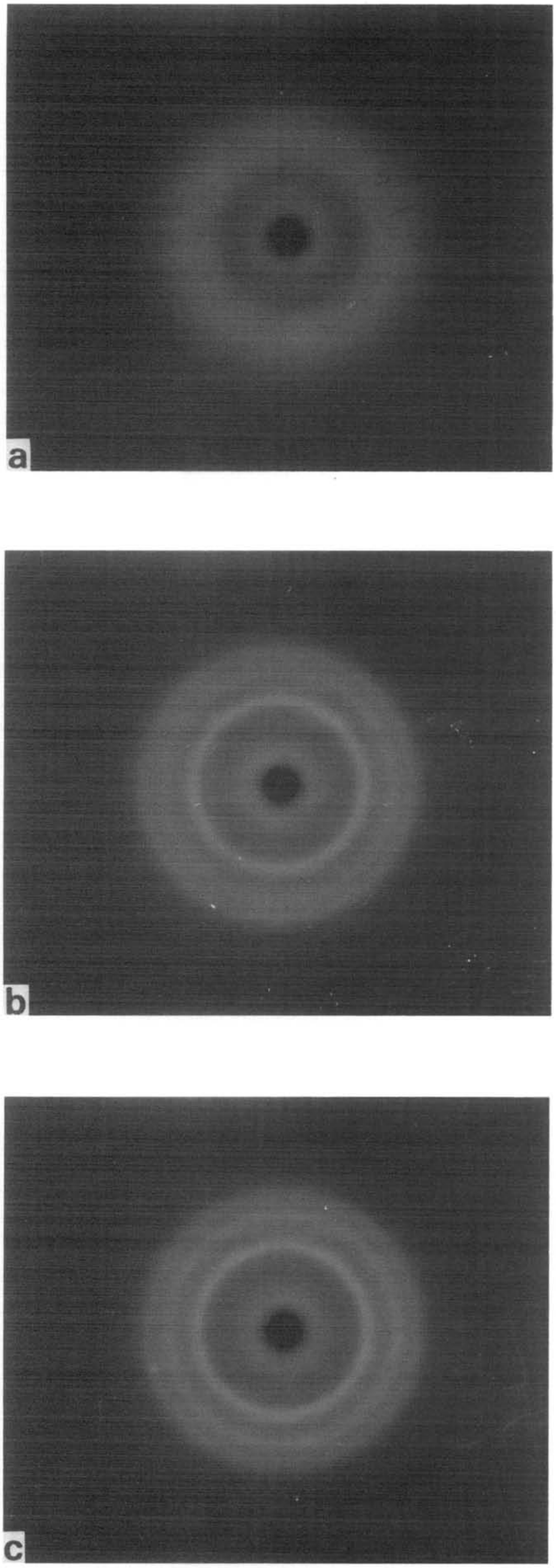

Figure 1 WAXD photographs of poly(ethylene terephthalate): (a) original film; (b) film exposed to 50 atm CO_2 at 35°C for 136 h; (c) film annealed at 100°C for 7 h

placed in a thermostatically controlled water bath regulated to within ± 0.1°C. The treatment was made at temperatures between 35 and 85°C. The CO_2 treatment procedure was as follows. To remove the air from the autoclave which contains the film sample (3.5 × 2.0 cm), CO_2 was blown through the autoclave. Then CO_2 was introduced up to the desired gas pressure. The film sample was exposed to this CO_2 environment for an adequate time, from several minutes to several days, to provide a complete map of crystallization under different CO_2 pressures and thermal conditions. The time for introducing or for releasing the CO_2 was several seconds, respectively.

In order to make comparisons with the film exposed to CO_2, another amorphous PET sample was crystallized by isothermal annealing in an air bath at temperatures between 85 and 150°C.

The density of the sample was determined by the floating method using an inert liquid medium (KI aqueous solution) and a density meter (Anton Paar, model DMA 02D) at 25.0 ± 0.1°C.

The WAXD measurements were carried out on an X-ray diffraction unit (Rigaku Denki Co. Ltd) with a Ni-filtered Cu Kα beam.

Infra-red (i.r.) spectra were measured by an i.r. spectrometer (Japan Spectroscopic Co. Ltd, model A-3).

RESULTS AND DISCUSSION

The 'as-received' transparent film became opalescent on exposure to high-pressure CO_2. The WAXD photograph of this exposed film is shown in *Figure 1* with those of the 'as-received' and annealed films. An amorphous halo is seen in *Figure 1a*, while some crystalline diffractions are observed for the sample treated by 50 atm CO_2 at 35°C for 136 h (*Figure 1b*). This result shows that the sample was crystallized by exposure to high-pressure CO_2, i.e. crystallization was induced even at a temperature well below the T_g measured in air. This means that the T_g of this polymer was reduced to at least 35°C in this environment. In addition, the diffraction pattern of the sample treated by CO_2 is much the same as the pattern of the same PET crystallized by annealing (*Figure 1c*).

It is well known that the intensities of some bands of the i.r. spectra of PET films change by thermal- and solvent-induced crystallization[13–19]. In this study also the i.r. spectra of PET crystallized by CO_2 and annealing were measured to check the changes of conformation of the polymer segments and to follow the crystallization process. *Figure 2* shows the typical spectral changes after exposure to 50 atm CO_2 at 35°C for 136 h. As shown in the figure, the intensity increased near 973 and 848 cm^{-1} and decreased at 898 cm^{-1}. The spectral changes are just the same as observed on annealing. They are assigned to *gauche–trans* transitions of the ethylene glycol segments by crystallization[20]. Another spectral change was observed near 382 cm^{-1}, the assignment of which is not yet clear. The crystalline band at 973 cm^{-1} and the amorphous band at 898 cm^{-1} have been frequently used to follow the crystallization[13–18]. Here, however, the bands at 973 and 382 cm^{-1} were utilized to study the crystallization process because the intensity change of these bands is greater than that of the other bands.

The correlations between the intensity and the time ($\log t$) of exposure to CO_2 and of annealing at various

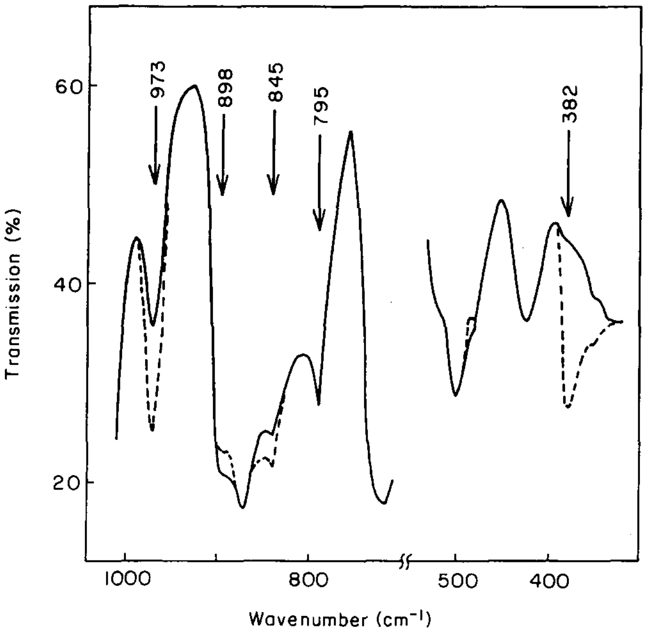

Figure 2 Infra-red spectra of PET: (———) original amorphous film; (– – –) film exposed to 50 atm CO_2 at 35°C for 136 h

temperatures are shown in *Figure 3*. The intensity of each band is expressed by a relative absorbance (A_r) derived by the following equations, since the absorbance (A) of the band at 795 cm^{-1} has been ascertained to be almost constant during crystallization[13]:

$$A_r(973) = A(973)/A(795) \qquad (1)$$

$$A_r(382) = A(382)/A(795) \qquad (2)$$

where the numbers in parentheses show the wavenumber in cm^{-1}. As shown in *Figures 3a* and *3b*, $A_r(973)$ and $A_r(382)$ increase sigmoidally with increase of log t. In the thermal crystallization at 85°C ($\sim$10°C above T_g), the first detectable sign of crystallization was observed after about one month. This corresponds to a crystallization half-life, $t_{1/2}$, of 36 days. On the other hand, in the case of exposure to 50 atm CO_2 at 85°C, PET began to crystallize within several minutes and $t_{1/2}$ was about 10 min, which was close to that of thermal crystallization at 120°C. Namely, the crystallization rate was greatly increased by the sorption of CO_2. Further, *Figure 3* shows that the crystallization was induced even at 35°C in CO_2 at 50 atm and $t_{1/2}$ was about 25 h. When the experimental temperature was increased up to 65°C, $t_{1/2}$ was reduced to about 6 h.

The relationships between $t_{1/2}$ and the experimental temperature are plotted for various conditions in *Figure 4*. The figure shows the plasticization effect of the sorbed CO_2 on $t_{1/2}$ obtained from the time dependence of the i.r. spectra at each temperature. For example, the $t_{1/2}$ of crystallization induced by 50 atm CO_2 at 85°C was equal to that of thermal crystallization at 118°C. That is, sorbed CO_2 worked to increase the motions of polymer segments and to compensate for the temperature difference of 33°C, the difference of 118 and 85°C. At 35°C, the plasticizing effect of the sorbed CO_2 corresponds to the temperature increase of 59°C because, as above, the $t_{1/2}$ of this system was equal to that of thermal crystallization at 94°C. The degree of plasticization and the kinetics of crystallization

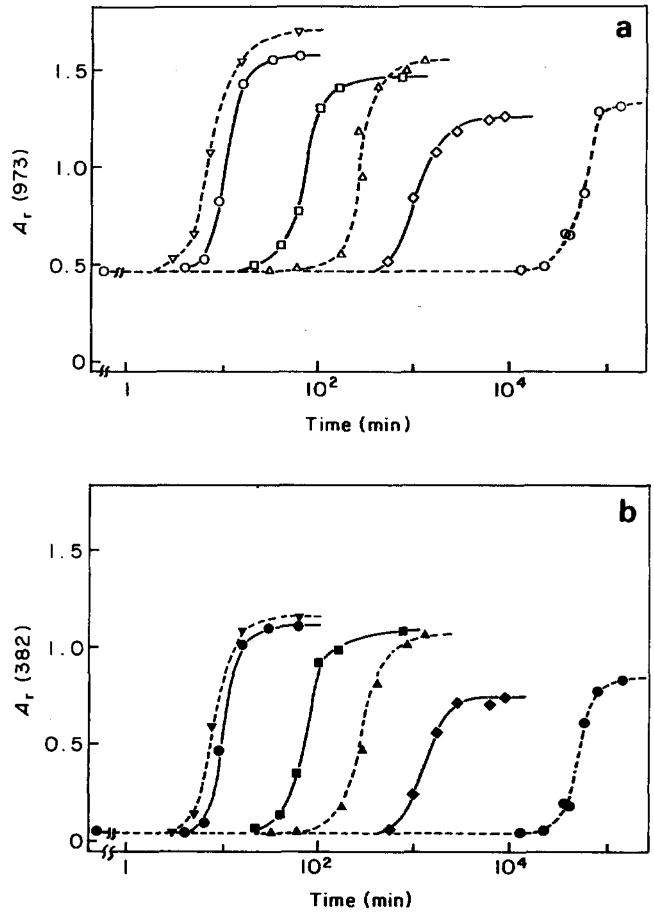

Figure 3 Crystallization curves obtained by i.r. for PET. (a) Relative absorbance $A_r(973)$ vs. log t: (– – –) thermal crystallization at 85 (○), 100 (△) and 120°C (▽); (———) crystallization by exposure to 50 atm CO_2 at 35 (◇), 65 (□) and 85°C (○). (b) $A_r(382)$ vs. log t: (– – –) thermal crystallization at 85 (●), 100 (▲) and 120°C (▼); (———) crystallization by exposure to 50 atm CO_2 at 35 (◆), 65 (■) and 85°C (●)

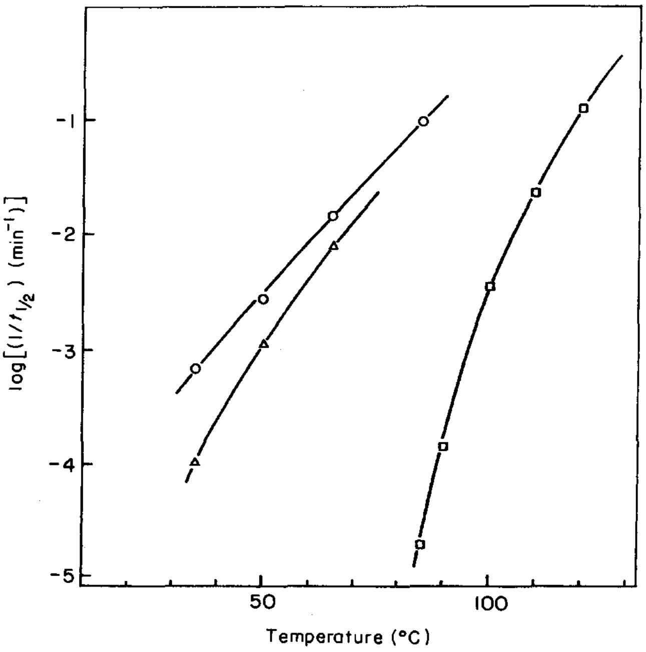

Figure 4 Relations between crystallization half-life ($t_{1/2}$) and experimental temperature at atmospheric air (□), 45 atm of CO_2 (△) and 50 atm of CO_2 (○)

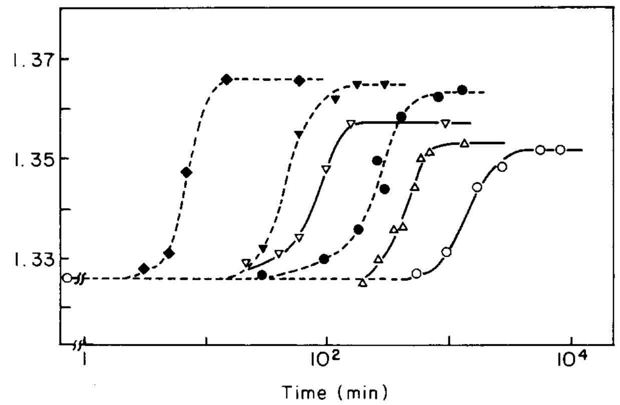

Figure 5 Crystallization curves obtained by density measurements: (---) thermal crystallization at 100 (●), 110 (▼) and 120°C (◆); (———) crystallization by exposure to 50 atm CO_2 at 35 (○), 50 (△) and 65°C (▽)

are expected to depend on the concentration of CO_2 in polymers[7,9]. Analysis of the plasticization effect of the sorbed CO_2 in terms of concentration will be reported in the near future.

Recently, Chiou *et al.* have found from d.s.c. measurements that PET crystallizes by the sorption of CO_2 at relatively high pressure[10]. In their paper, they reported that T_g of the sample exposed to 35 atm CO_2 at 35°C is lower than 35°C and this sample crystallized within 4 days. However, we could not observe any indications of crystallization after 4 days under exposure to 45 atm CO_2 at 35°C, which is 10 atm higher than their condition, and $t_{1/2}$ was about 7 days as shown in *Figure 4*. Comparing with the result at 50 atm, the decrease of 5 atm delayed the crystallization and the $t_{1/2}$ value became ~6.7 times as large as that at 50 atm. Therefore it is deduced that $t_{1/2}$ will be more than 300 days at 35 atm and 35°C. Further, it seems to be impossible to detect crystallization at 20 atm in the experimental timescale. As mentioned in the introduction, however, they reported that crystallization occurred in 12 days at this condition[10]. Contrary to our isothermal procedure, they observed the glass transition and the crystallinity by heating the systems above their T_g. The difference between the two methods seems to affect the results a great deal, but it is difficult to discuss it in detail here.

From the results of WAXD and i.r. measurements, the structure of crystals made by CO_2-induced crystallization is the same as that in samples crystallized by annealing. In the case of solvent-crystallized PET, however, it is well known that voids formed during crystallization can affect the specimen's apparent density[2,17,21,22]. In order to discuss the fine structure of crystallized PET by sorption of CO_2, the density of a sample treated at each condition was measured and then compared with the results of the i.r. measurements. *Figure 5* shows the time dependence of the density at different temperatures for both thermal- and CO_2-induced crystallization. The crystallization curves are almost the same as those obtained by the i.r. measurement. The maximum density increased slightly with increase of conditioning temperature. For amorphous as well as crystallized PET prepared by annealing, the degree of crystallinity is directly related to density. For example, when annealed at 120°C the density was 1.376 g cm^{-3}, which is nearly equal to the literature values[13,23,24], and the degree of crystallinity was calculated as 38.6 wt% from it.

Cobbs and Burton correlated the i.r. absorption with density[13]. In addition, it is plausible to assume that i.r. absorbance is not appreciably influenced by void formation. Therefore, if void formation occurs during crystallization, the above-mentioned relationship for the PET sample crystallized by CO_2 sorption is expected to be different from that of PET crystallized thermally. As shown in *Figures 6* and *7*, linear relationships for the two bands, $A_r(973)$ and $A_r(382)$, were obtained for both samples. In *Figure 7*, the straight lines in *Figure 6* are replotted as broken lines which show a little but obvious difference (~0.003 g cm^{-3} on average) from the data obtained for the CO_2 crystallized samples. This difference means that the density of the CO_2 crystallized sample is smaller than that of the thermally crystallized sample, because the same relative absorbance means the same degree of crystallinity. As expected, the decrease should be caused by voids formed during crystallization. That is, the amorphous density (d_a) of the CO_2 crystallized sample is smaller than that of the thermally crystallized one. The

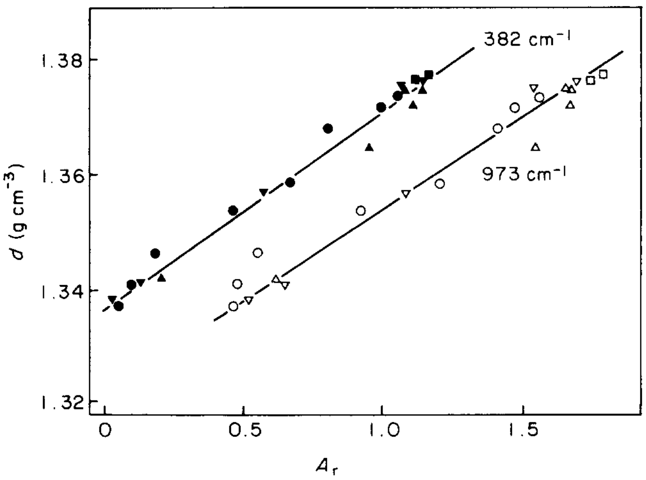

Figure 6 Relation between density (d) and i.r. absorbance (A_r) of PET crystallized thermally at 100 (○, ●), 110 (△, ▲), 120 (▽, ▼) and 150°C (□, ■), respectively

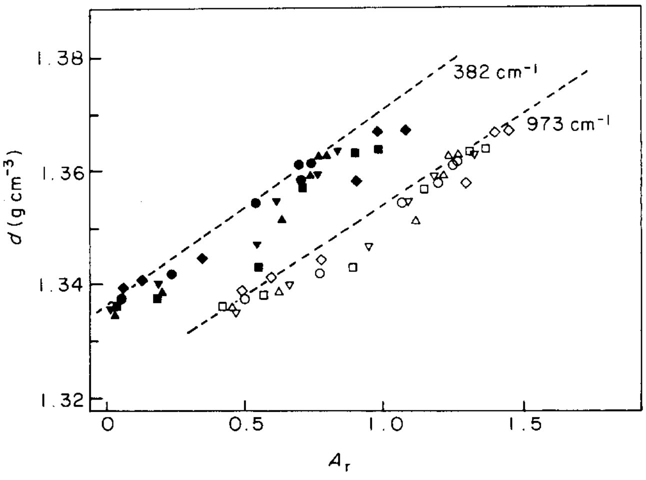

Figure 7 Relation between density and i.r. relative absorbance of crystallized PET induced by exposure to 50 atm CO_2 at 35 (○, ●), 45 (△, ▲), 50 (▽, ▼), 55 (□, ■) and 65°C (◇, ◆). Open and full symbols represent $A_r(973)$ and $A_r(382)$, respectively. The broken lines are the results for thermally crystallized PET shown in *Figure 6*

d_a of the former was estimated to be $1.327\ g\ cm^{-3}$ using the crystalline density ($d_c = 1.455\ g\ cm^{-3}$)[11] of both samples and the amorphous density ($d_a = 1.331\ g\ cm^{-3}$)[12] of the latter. This result seems to suggest the effect of sorbed CO_2, which will be discussed in the next paragraph. From the maximum density, d_c, and the newly estimated d_a, the degree of crystallinity of crystallized PET by sorption of 50 atm CO_2 at 35°C was estimated as 29.2 wt%.

The present study reveals the effect of sorbed CO_2 in CO_2-induced crystallization of amorphous PET as follows. At first, CO_2 sorbed at high pressures reduces the T_g of the polymer and the polymer changes to the rubbery state. Crystallization was induced by the plasticization effect of the sorbed gas just as in the solvent or vapour effect. For a mixture of crystalline and rubbery polymers, e.g. low-density polyethylene, dilation due to sorbed CO_2 has been observed[25]. Therefore, the rubbery PET, which has some crystallinity, should also be dilated. Upon CO_2 removal, the polymer changes from the rubbery to the glassy state but the volume structural relaxation in this change was hindered by the presence of crystallites. In addition, as Wonders *et al.*[26] mentioned, the glassy polymer relaxes so slowly that a portion of the increased volume is not recovered. As a result, many microvoids remain in the amorphous region after crystallization.

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