Gas transport properties in polycarbonate films with various unrelaxed volumes

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The unrelaxed volume in polycarbonate (PC) was varied by thermal or pressure conditioning, and the sorption and permeation of CO_2 in PC films with various unrelaxed volumes were investigated. The dual-mode sorption and the partial immobilization models were used to analyse sorption and permeation behaviour. The amount of CO_2 sorption in PC films quenched from various temperatures above the glass transition temperature (T_g) was increased with increasing holding temperature above T_g, and was larger than that in PC film cooled slowly from a temperature above T_g. The increase in the amount of CO_2 sorption caused by the quenching was explained by the increase of the Langmuir sorption capacity term (C'_H). In contrast, other dual-mode sorption parameters were found to be unchanged by conditioning. The values of C'_H of various quenched PC films, which were obtained from CO_2 sorption isotherms, agreed with those evaluated from the specific volume–temperature curve. The amount of CO_2 sorption in PC film conditioned under 60 atm CO_2 was larger than that in quenched PC film. The two diffusion coefficients, D_D and D_H, of the partial immobilization model, for CO_2 of quenched PC film were also larger than those of slowly cooled PC film. The difference in D_H was found to be larger than that in D_D. The two diffusion coefficients of PC film conditioned under 60 atm CO_2 were also greater than those of quenched PC films.

(Keywords: polycarbonate; gas transport; quenching; pressure conditioning; unrelaxed volume; microvoid; dual-mode sorption model; partial immobilization model)

INTRODUCTION

Glassy polymer films are effective as permselective films owing to the existence of an unrelaxed volume and/or microvoids in spite of their low segmental mobility in the glassy state, and film properties of a glassy polymer are superior to those of a rubbery polymer in terms of mechanical strength and heat stability. It has been reported that gas transport in glassy polymer films depends on their thermal history[1–3]. In a previous paper, we reported that the sorption and permeation of gases in alternating copoly(vinylidene cyanide–vinyl acetate) (copoly(VDCN-VAc)) film were largely dependent on thermal history in the sub-T_g region. This was interpreted as a reflection of the change of the Langmuir sorption capacity term of the dual-mode sorption model and diffusivity caused by densification through sub-T_g annealing[1,2]. Also we reported on the transport properties of polyimide films quenched or slowly cooled from the liquid state above T_g. The permeability of the quenched polyimide film was enhanced as compared with that of slowly cooled polyimide, reflecting the fact that the solubility and diffusivity of the Langmuir mode increased[3]. It is known that the sorption isotherm of a glassy polymer is of the dual-mode type in the lower pressure region, while in the higher pressure region the isotherm is of the Henry type, reflecting the fact that a glassy polymer is plasticized at higher pressure by sorbed gases such as CO_2 (refs. 4–8). Therefore, owing to the glassification of plasticized polymer by sorbed CO_2, it is expected that the physical properties will vary.

In this work, the influence of quenching from various temperatures above T_g and that of pressure conditioning on gas sorption and permeation of polycarbonate (PC) films are studied using the dual-mode sorption[9,10] and the partial immobilization[11] models. Furthermore, the quenching and pressure conditioning of glassy polymer are examined to see whether these are effective methods to control the unrelaxed volume and/or microvoids that result in the variation of sorption and permeation properties.

EXPERIMENTAL

Materials

PC film was kindly supplied by the Idemitsukosan Central Research Lab. The glass transition temperature (T_g) of the PC film was determined to be ~150°C using a differential scanning calorimeter (SSC 560, Seiko Electronics Co. Ltd). The films were dried completely in a vacuum at room temperature until no weight decrease was observed. The quenching of the films was performed at atmospheric pressure as follows. As-received PC films were annealed at a temperature above T_g, viz. 180, 190 or 200°C, for 1 h, and then these films were either quenched from 180, 190 or 200°C to 0°C (ice-water), quenched from 200°C to −94°C (methanol gel) or slowly cooled at a rate of $1°C\ min^{-1}$ from 180°C to room temperature. Pressure conditioning was performed by exposure of slowly cooled PC film to CO_2 of 60 atm at 25°C for 12 h and then by lowering the temperature to liquid N_2 temperature and reducing the pressure to atmospheric pressure. Densities of quenched and pressure-conditioned PC films were determined at 25°C by the

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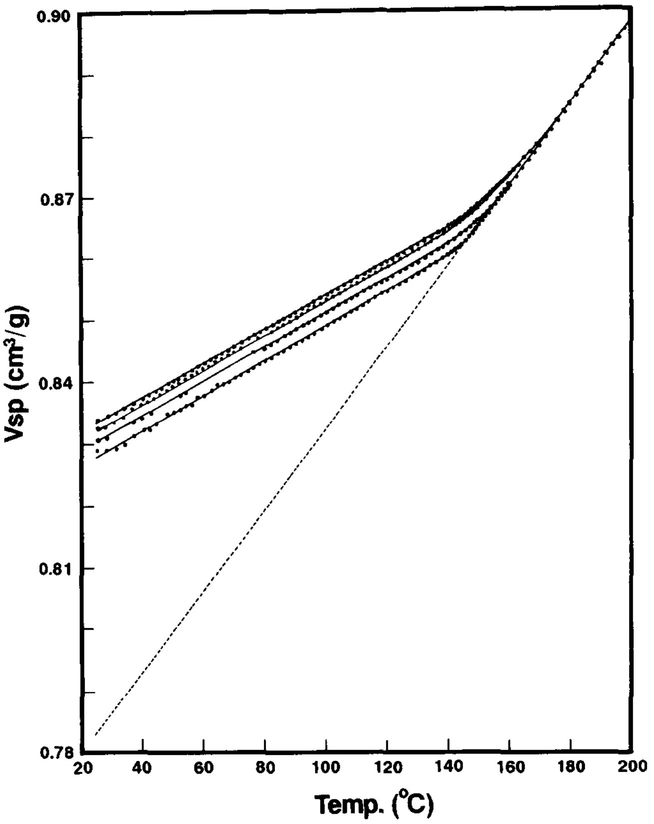

Figure 1 Specific volume–temperature curves of various PC films quenched from 200, 190 and 180°C to 0°C and cooled slowly from 180°C (curves are referred to from top to bottom)

flotation method using a mixed solvent of n-hexane and carbon tetrachloride.

The purity of CO_2 used in the sorption and permeation measurements exceeds 99.9%. The gas was used without further purification.

Methods

A dry slowly cooled PC film was confined by dry mercury in a dilatometer bulb fitted with a capillary tube of uniform inner diameter. The dilatometer was placed in an oil bath and heated at a rate of 1°C min^{-1} from 25 to 200°C. The meniscus height of the mercury in the capillary tube was measured using a cathetometer (0.005 cm precision). The specific volume–temperature curve was calculated from the variation of height of the mercury as described previously[12]. Dilatometry of the quenched sample was carried out as follows. After the dilatometer was held in the oil bath at 180, 190 or 200°C for 1 h, the dilatometer itself was quenched from that temperature to 0°C. The specific volume–temperature relation of each quenched PC film was determined from the data in a heating process.

The film installed in a permeation cell was degassed for 24 h at 10^{-4} mmHg in a permeation apparatus. The permeation measurement was made as follows. The downstream side of the film was evacuated to about 10^{-4} mmHg. Gas was introduced into the upstream side and the pressure of gas permeated through the film to the downstream side was monitored using an MKS-Baratron pressure transducer (227AA). The permeability coefficient was evaluated from the permeation rate at steady state.

The sorption measurement was carried out by using a gravimetric sorption apparatus with an electromicrobalance (Type-2000 Cahn Instruments Inc.). After sufficient drying of the films at about 10^{-4} mmHg, the amount of gas sorbed in the film under fixed pressure was determined after correcting for the buoyancy effect of the film at that pressure.

RESULTS AND DISCUSSION

Specific volume–temperature relationship

Figure 1 shows the specific volume–temperature curves of slowly cooled and quenched PC films. The values of the specific volume V_{sp} of quenched PC films in the glassy state were increased on increasing the holding temperature above T_g and were larger than that of slowly cooled PC film. The densities at 25°C obtained by the flotation method for slowly cooled PC film and film quenched from 180, 190 and 200°C were 1.206, 1.203, 1.202 and 1.199 g cm^{-3}, respectively. The densities at 25°C of quenched PC films obtained by dilatometry agreed with those obtained by the flotation method. The density of pressure-conditioned PC film as shown later was 1.182 g cm^{-3}. The V_{sp} values of PC films above 180°C are the same irrespective of their thermal history. This means that above 180°C the films are in the equilibrium liquid state. The results indicate that the unrelaxed volume and/or microvoids in the glassy state are increased on increasing the holding temperature. The glass transition region became broad on quenching. This behaviour may be influenced by micro-heterogeneous structures containing more microvoids formed on quenching.

Sorption properties

Figure 2 shows the CO_2 sorption isotherms of quenched and slowly cooled PC films at 25°C, where C is the total CO_2 concentration and p is the pressure of CO_2. Over the entire pressure range studied the concentration of sorbed CO_2 in quenched PC films was increased on increasing the holding temperature above T_g and was larger than that in slowly cooled PC film. However, a comparison of sorption isotherms of PC films quenched

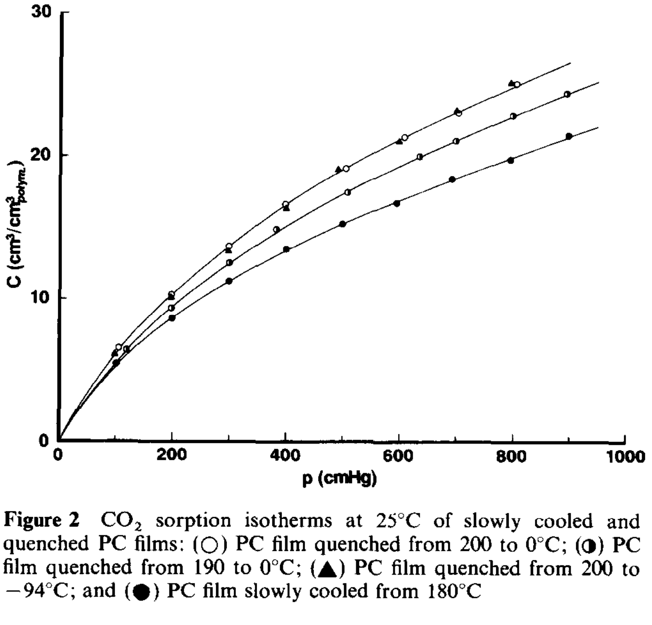

Figure 2 CO_2 sorption isotherms at 25°C of slowly cooled and quenched PC films: (○) PC film quenched from 200 to 0°C; (◑) PC film quenched from 190 to 0°C; (▲) PC film quenched from 200 to −94°C; and (●) PC film slowly cooled from 180°C

Table 1 Dual-mode sorption and mobility parameters of various PC films

Sample preparation	$k_D \times 10^2$ (cm^3/cm^3 cmHg)	C'_H (cm^3/cm^3)	$b \times 10^3$ ($cmHg^{-1}$)	$D_D \times 10^8$ ($cm^2 s^{-1}$)	$D_H \times 10^9$ ($cm^2 s^{-1}$)	F
180°C, slow cooling	1.00	16.2	3.45	9.07	4.45	0.049
190→0°C, quenching	1.00	22.5	2.42	9.11	5.76	0.063
200→0°C, quenching	1.04	24.7	2.53	9.13	6.17	0.068
200→ −94°C, quenching	1.06	24.9	2.39	–	–	–
60 atm CO_2, conditioning	1.01	30.1	2.56	12.4	7.28	0.059

from 200 to 0°C and to −94°C shows that C is independent of quenching temperature. This means that there is no difference in the effectiveness of quenching from the same holding temperature to different low temperatures considerably below T_g. On the other hand, there is a marked difference in quenching from various holding temperatures to the same low temperature, e.g. 0°C. These results suggest that the amount of unrelaxed volume and/or microvoids is controlled by the various quenching procedures. The effect of quenching on C will be discussed in terms of the dual-mode sorption parameters.

Each isotherm shown in *Figure 2* can be described fairly well with the dual-mode sorption model, which is represented by the following equation[9,10]:

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

where C_D is the concentration due to Henry's law contribution, C_H is the concentration of penetrant held in 'microvoids' or the Langmuir sorption sites, k_D is the Henry's law constant, b is the affinity constant of penetrant to the Langmuir site and C'_H is the hole saturation constant in the Langmuir sorption mode.

The dual-mode sorption parameters were evaluated using the non-linear least-squares method. Maximum errors in the determination of the parameters were 5, 24 and 20% for C'_H, k_D and b, respectively. The parameters obtained are listed in *Table 1*. The C'_H of quenched PC films is increased on increasing the holding temperatures above T_g, even if the error of C'_H was considered. This means that the unrelaxed volume is increased by the quenching. On the other hand, the b of quenched PC films did not vary systematically, although the parameter b of quenched PC films was slightly smaller than that of slowly cooled PC film. Therefore we assumed that b is almost independent of quenching conditions. The independence of b on quenching has been reported for polyimide[3] and poly(phenylene oxide)[13]. Also, sub-T_g annealing did not affect the values of b for copoly(VDCN-VAc)[1,2] and polycarbonate[14]. In addition, k_D was almost independent of thermal history such as quenching. These results suggested that the difference of C'_H contributes mainly to the variation in the amount of CO_2 sorption.

The C'_H parameter has been represented as a measure of the unrelaxed volume of glassy polymers by the following equation:

$$C'_H = 22\,400 \left(\frac{V_g - V_l}{V_g} \right) \frac{1}{V_{CO_2}} \quad (2)$$

where V_g and V_l are the specific volumes of polymer in the glassy state and the supercooled liquid state, respectively, and V_{CO_2} is the molar volume of liquid-like CO_2. The value of V_{CO_2} has been estimated[15] to be about 55 cm^3 mol^{-1}. Equation (2) has been used with success for a number of glassy polymers[16–19]. As the values of $(V_g - V_l)/V_g$ can be determined from *Figure 1*, C'_H can be evaluated using equation (2). *Figure 3* shows the agreement of C'_H obtained from both sorption and specific-volume measurements. The relationship between the two C'_H values indicated good linearity. This indicates the validity of equation (2).

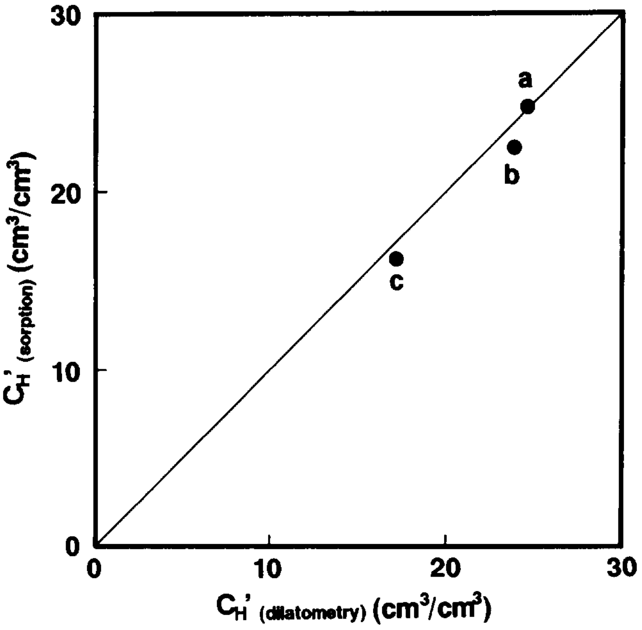

Figure 3 Relationship between C'_H obtained according to equation (1) from sorption data and that calculated according to equation (2) by using *Figure 1*: a, PC film quenched from 200 to 0°C; b, PC film quenched from 190 to 0°C; and c, PC film slowly cooled from 180°C

It was clarified that the sorption properties depended on the quenching conditions. Another physical method for the glassification of polymer was also tried, i.e. glassification of plasticized polymer by sorbed CO_2. It is anticipated that the sorption properties of PC film depend on the amount of unrelaxed volume that results from the cooling of PC film that has been exposed to high CO_2 pressure and to liquid N_2, since glassy polymers are plasticized by sorbed gas such as CO_2 at high pressures[20–24]. Here we call this 'pressure conditioning'. *Figure 4* shows the CO_2 sorption isotherms of PC films conditioned under 60 atm CO_2, including the results of PC films quenched from 200 to 0°C and cooled slowly, which are shown by broken curves. The value of C in pressure-conditioned PC film is larger than that in

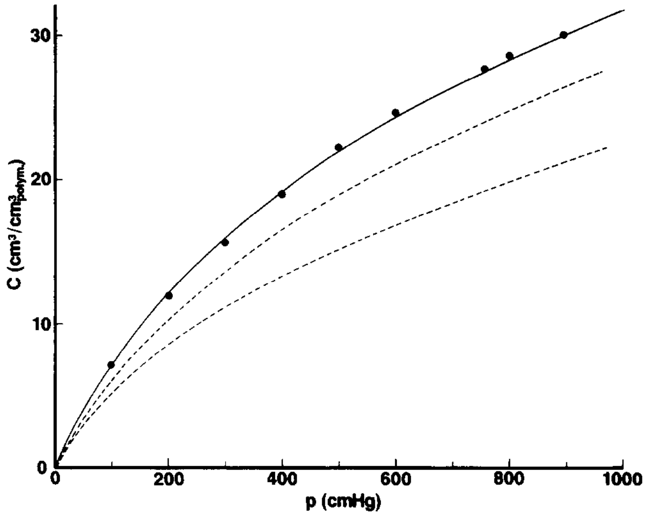

Figure 4 CO_2 sorption isotherms at 25°C of PC film conditioned under 60 atm CO_2. Broken curves show the isotherms of PC films quenched from 200 to 0°C (upper) and cooled slowly (lower) as shown in *Figure 2*

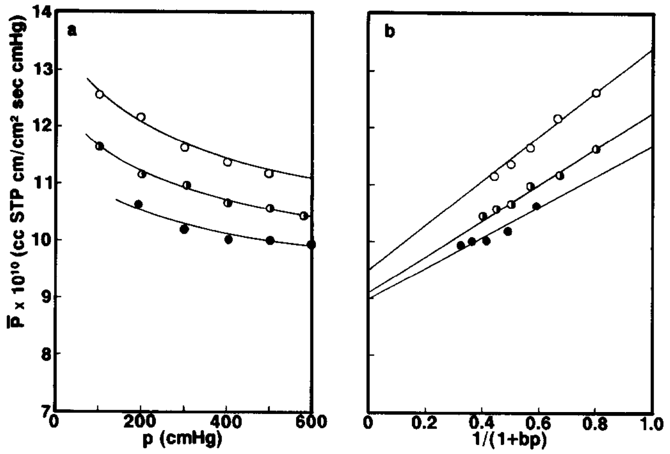

Figure 5 (a) Pressure dependence of CO_2 permeability coefficients at 25°C and (b) permeability coefficients plotted in accordance with the partial immobilization model (equation (3)) for CO_2 of various PC films: (○) PC film quenched from 200 to 0°C; (◑) PC film quenched from 190 to 0°C; and (●) PC film slowly cooled from 180°C

unconditioned slowly cooled and quenched PC films. This means that pressure conditioning by CO_2 gives rise to an increase of microvoid content in the process of glassification. The sorption behaviour was also analysed by the dual-mode sorption model, and the parameters obtained are also shown in *Table 1*. The C'_H value was increased more markedly by pressure conditioning than by quenching , while k_D and b were almost independent of the pressure conditioning. The real implication of the observed independence of the dual-mode parameters k_D and b on the thermal and pressure conditionings is not known to us.

Permeation properties

Figure 5a shows the pressure dependence of the CO_2 permeability coefficient ($\bar{P}_{CO_2}$) at 25°C through slowly cooled and quenched PC films. The decrease of $\bar{P}_{CO_2}$ with increasing pressure, which is characteristic of gas permeation through a glassy polymer film, is observed in *Figure 5a*. The $\bar{P}_{CO_2}$ value of various quenched PC films was larger than that of slowly cooled PC film. This can be attributed qualitatively to the fact that diffusivity was enhanced by the increase of frozen free volume as shown in *Figure 1*. To elucidate the variation of diffusivity in detail, diffusion coefficients D_D and D_H of the partial immobilization model were determined from the pressure dependence of permeability using the following equation[11]:

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

Figure 5b shows plots of $\bar{P}_{CO_2}$ through the slowly cooled and quenched PC films as a function of $(1+bp)^{-1}$. The plots demonstrate a fairly good linearity. The slope and intercept of the straight line on the high-pressure side ($p=\infty$), corresponding to the values of $D_H C'_H b$ and $k_D D_D$ in equation (3), respectively, were determined using a linear least-squares method. The D_D and D_H obtained are tabulated in *Table 1* with their ratio, F $(=D_H/D_D)$. The change in D_H caused by quenching is more marked than that in D_D. The enhancement of D_H by quenching may be associated with the increase of the unrelaxed volume in the PC film. On the other hand, the little enhancement of D_D by quenching is observed.

Variation of permeability is also expected by pressure conditioning in addition to the increase of solubility. *Figure 6a* shows the pressure dependence of $\bar{P}_{CO_2}$ of PC films conditioned under 60 atm CO_2 together with that of PC films quenched from 200 to 0°C and cooled slowly, which are shown by broken curves. The $\bar{P}_{CO_2}$ of pressure-conditioned PC film was enhanced as compared with that of quenched and slowly cooled PC films. Similarly D_D and D_H were determined from the data shown in *Figure 6b*. The two diffusion coefficients were also increased by the pressure conditioning. The increase of D_H by the pressure conditioning was larger than that of D_D, but D_D was increased more markedly by pressure conditioning than by quenching. It is probable that CO_2 molecules dissolved by Henry's law mode are influenced by coarse structures caused by the marked increase of microvoid content with pressure conditioning, resulting in ease of diffusion.

CONCLUSIONS

In conclusion, the amount of CO_2 sorption in PC films quenched from holding temperatures above T_g to various

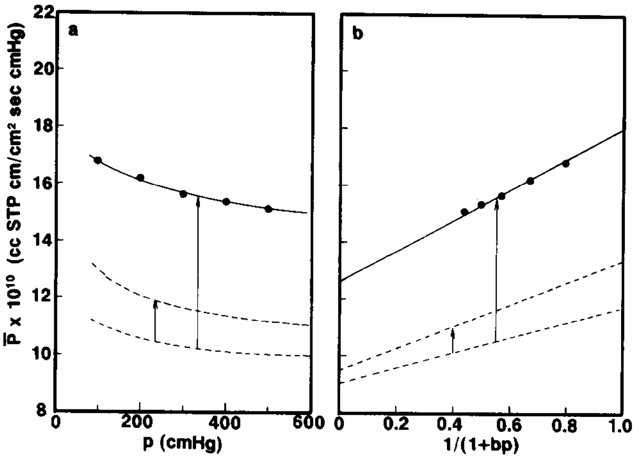

Figure 6 (a) Pressure dependence of CO_2 permeability coefficients at 25°C and (b) permeability coefficients plotted in accordance with the partial immobilization model (equation (3)) for CO_2 of PC film conditioned under 60 atm CO_2. Broken curves show values of PC films quenched from 200 to 0°C (upper) and cooled slowly (lower) as shown in *Figure 5*

quenching temperatures did not vary with the quenching temperature but was increased with the increase of the holding temperature in the region above T_g. The amount of sorption in pressure-conditioned PC film was increased more than that in quenched PC films. This increase in the amount of CO_2 sorption can be associated with the increase of the Langmuir capacity constant, but not with the Langmuir affinity and the Henry's law constants. The change in the amount of CO_2 sorption was explained in terms of the change in microvoid content, or unrelaxed volume, or frozen free volume by either quenching or pressure conditioning. The two diffusion coefficients, D_D and D_H, of the dual-mode mobility model, for CO_2 were also increased by quenching or pressure conditioning, compared with those of slowly cooled films. The change in D_H was found to be larger than that in D_D. Furthermore it was found that thermal or pressure conditioning could control microvoid content, or unrelaxed volume, or frozen free volume of glassy polymers. A quantitative discussion of these will follow.

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