CO_2 sorption properties and enthalpy relaxation in alternating copoly(vinylidene cyanide–vinyl acetate)s

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To elucidate the mechanism of gas sorption by amorphous glassy alternating copoly(vinylidene cyanide–vinyl acetate), the effect of annealing just below the glass transition temperature (T_g) on CO_2 sorption properties of the polymer was investigated. A comparison of the reduction in the Langmuir sorption-capacity constant, C'_H, with enthalpy relaxation during annealing was made. The values of C'_H were obtained by application of the dual-mode sorption theory to the experimental sorption data. The equilibrium amount of CO_2 sorption at 25°C in copoly(vinylidene cyanide–vinyl acetate) annealed at sub-T_g decreased with increasing annealing period. The amount of sorption in the annealed films, however, did not change after physical ageing at room temperature. Good correlation has been obtained between the change in C'_H and the decrease in the enthalpy deduced from thermal analysis of the polymers. The magnitude of C'_H and the enthalpy of copoly(vinylidene cyanide–vinyl acetate) have been interpreted in terms of the densification of the glassy polymer during sub-T_g annealing.

INTRODUCTION

Understanding the sorption and permeation mechanisms of small molecules in glassy polymers has been an active area in membrane science and technology. It is well known that the solubility of gases and vapours in glassy polymers can be analysed by the dual-mode sorption model[1], composed of an ordinary Henry's law term, C_D, and a Langmuir term, C_H, associated with an unrelaxed volume such as holes or microvoids in polymer glasses:

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

where C (cm³/cm³ polymer) is the total concentration of small molecules in the glassy polymer; C_D and C_H are the concentrations of small molecules for Henry's law and Langmuir modes, respectively; k_D (cm³/cm³ cmHg) is the Henry's law constant, b (cmHg^{-1}) the hole affinity constant, C'_H (cm³/cm³ polymer) the Langmuir capacity constant and p (cmHg) the pressure of the small molecules in the gas phase. A few approaches have been made to correlate C'_H with variables that characterize the non-equilibrium glassy state of the polymer. Chan and Paul[2] investigated the annealing effect of polycarbonate just below T_g on its CO_2 sorption behaviour at 35°C, and showed that the reduction in C'_H could be compared well with the volume and enthalpy relaxations that occurred during sub-T_g annealing. The present authors[3] have also shown that volume relaxation at 25°C in polystyrene quenched from the melt contributed primarily to the decrease in C'_H. The relation between the volume, enthalpy and sorption relaxations for various glassy polymers

would be useful to clarify the sorption mechanism in polymer glasses.

It has been reported[4] that the amorphous alternating copolymer of vinylidene cyanide and vinyl acetate (copoly(VDCN–VAc)) showed a large enthalpy relaxation and a densification during isothermal annealing just below T_g. It is therefore expected that the annealing of glassy copoly(VDCN–VAc) can produce structural changes that considerably influence its sorption properties. To elucidate the gas sorption mechanism in glassy polymers, we report here changes in the sorption isotherms of CO_2 at 25°C by copoly(VDCN–VAc) annealed just below T_g for various periods, and correlate the changes with the enthalpy relaxation behaviour of annealed copoly(VDCN–VAc) samples.

EXPERIMENTAL

Materials

Copoly(VDCN–VAc) with $[\eta] = 4.9$ was kindly supplied by Mitsubishi Petrochemical Co. Ltd. The sample was dried under reduced pressure for 24 h before film preparation. The copoly(VDCN–VAc) films were prepared by casting from a 1% dimethylformamide solution at 60°C. The solid films obtained were dried under vacuum for 24 h. After drying, the films were immersed in a 1:1 mixture of methanol and acetone for 24 h and dried again under vacuum for 48 h at room temperature. The films obtained in this manner were called 'as-cast' films. The thickness of the as-cast films was $\sim 30 \, \mu m$. Annealing was performed as follows. The as-cast films obtained were heated under reduced pressure (<1 mmHg) to 160°C at a heating rate of 3.0 K min^{-1}. The temperature of the films was kept just below T_g
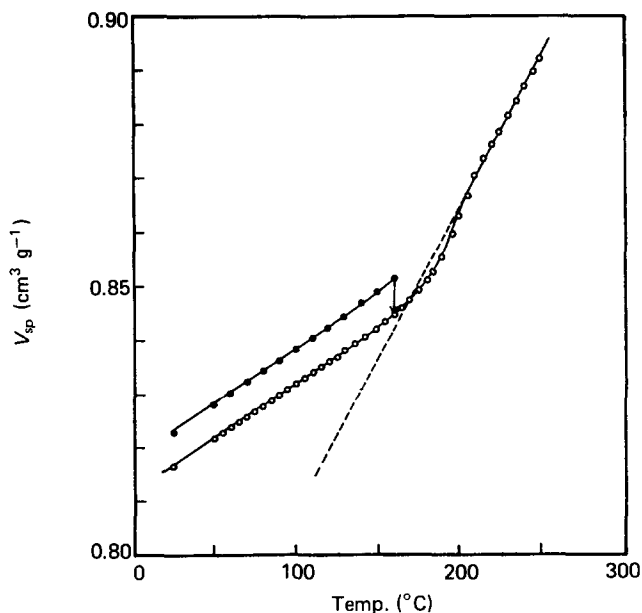

Figure 1 Specific volume vs. temperature curves for as-cast (●) and 30 h annealed (○) copoly(VDCN-VAc)

(160°C) for various periods, and they were then cooled to room temperature at a rate of 0.6 K min^{-1}. The films thus prepared were called 'annealed' films.

X-ray and thermal analyses demonstrated that as-cast and annealed films were completely amorphous. Because of moisture-sensitive properties, all the films obtained were handled in a vacuum system.

The CO_2 gas used for sorption measurements was of at least 99.9% purity and was used without further purification.

Methods

Dilatometry measurements were carried out as follows. A dried as-cast film of copoly(VDCN-VAc) was confined by dry mercury in a dilatometer with a capillary of uniform inner diameter. The dilatometer was placed in an oil bath and heated at a heating rate of 3 K min^{-1} from room temperature to 160°C. Then the dilatometer was kept at 160°C for 30 h to observe volume relaxation and/or densification of the copoly(VDCN-VAc) after various annealing periods, and the temperature was lowered slowly to room temperature. The dilatometer was heated again to 250°C in order to get a specific volume vs. temperature curve for the annealed copoly-(VDCN-VAc) film. The height of the mercury column in the capillary of the dilatometer was measured using a precise cathetometer (0.005 cm precision).

The thermal properties were measured using a differential scanning calorimeter (d.s.c.) (type SSC 560, Seiko Electronics Co. Ltd). D.s.c. thermograms were obtained by heating at a scanning rate of 15 K min^{-1} from -80 to 310°C. The T_g was determined from the midpoint between the heat capacities corresponding to the glassy and liquid states; and the net enthalpy difference ΔH_n was determined from the area of the endotherm in the T_g region as described in detail later.

CO_2 sorption measurements were carried out at 25°C using a gravimetric sorption apparatus with an Electromicrobalance (type 2000, Cahn Instruments Inc.). A buoyancy correction at each pressure was made for all

measurements, estimated from the volume of the samples used and the CO_2 density calculated from the van der Walls equation of state. The buoyancy correction comprised 17–35% of the corrected amounts of CO_2 sorption.

RESULTS AND DISCUSSION

Volume relaxation

Specific volumes of the as-cast and 30 h annealed copoly(VDCN-VAc) films are shown as a function of temperature in *Figure 1*. The specific volume of copoly-(VDCN-VAc) annealed at 160°C decreased with increasing annealing period, as shown in *Figure 2*. It is seen that densification and/or volume relaxation of the copoly-(VDCN-VAc) film occurs due to annealing just below T_g (160°C). The specific volume vs. temperature curve of the 30 h annealed film exhibits a characteristic undershoot in the glass transition region (*Figure 1*). The undershoot corresponds to enthalpy relaxation, namely the endothermic peak shown later, although that of the as-cast film is not usually observed.

Enthalpy relaxation

Figure 3 shows d.s.c. thermograms for as-cast and annealed copoly(VDCN-VAc) films. No endothermic peak was observed for the as-cast film. On the other hand, d.s.c. thermograms for the annealed films showed enthalpy relaxation near T_g, as observed in other classes of glassy polymer films that were subjected to annealing. It is clear that the endothermic peak increases with increasing annealing period at 160°C. The area of the endotherm corresponds to the net enthalpy difference in the T_g region, ΔH_n, as shown in *Figure 4*, which represents schematically the enthalpy–temperature relation of glassy polymers. The values of ΔH_n and T_g, which were estimated in the manner illustrated in the insert of *Figure 5a*, are shown as a function of annealing period in *Figures 5a* and *5b*, respectively, and are tabulated in *Table 1*.

As illustrated in *Figure 4*, the unrelaxed enthalpy $\Delta H(T_A, t)$, at annealing temperature T_A and annealing period t, is expressed by:

$$\Delta H(T_A, t) = H(T_A, t) - H(T_A, \infty)$$

$$= \Delta C_p(T_{gt} - T_A) - \Delta H_n(T_A, t) \qquad (2)$$

where $\Delta C_p = C_{pl} - C_{pg}$ is the heat-capacity difference between liquid and glassy states. The value of ΔC_p obtained by d.s.c. measurement was $0.58 \text{ J g}^{-1} \text{ K}^{-1}$ for the copoly(VDCN-VAc) sample. Thus the value of $\Delta H(T_A, t)$ can be evaluated from values of ΔH_n and ΔC_p, and T_g determined by d.s.c. measurements of the copoly-
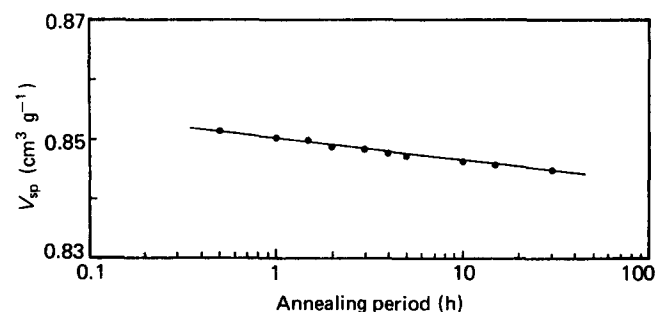

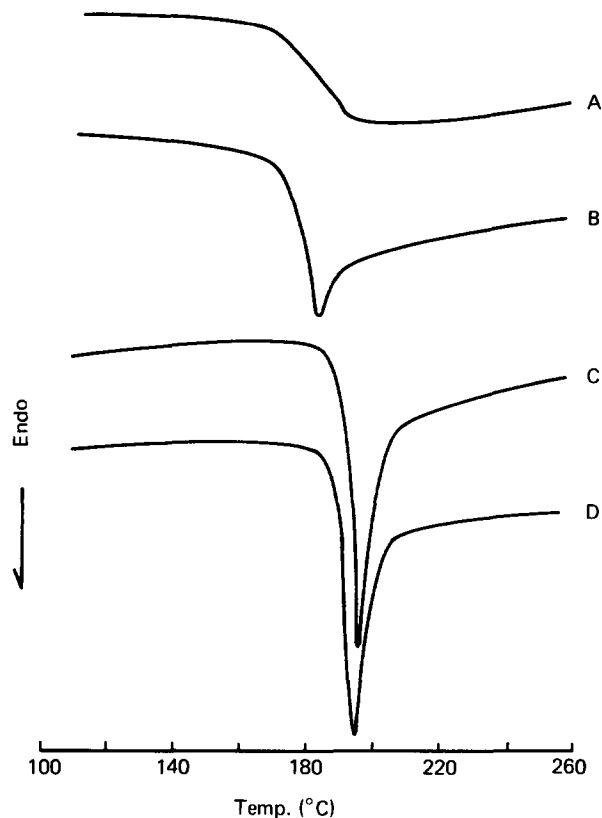Figure 2 Dependence of specific volume on annealing period for copoly(VDCN-VAc) annealed at 160°C

Figure 3 D.s.c. thermograms for copoly(VDCN–VAc) annealed for various periods at 160°C: A, as cast; B, 10 min annealing; C, 5 h annealing; and D, 15 h annealing

Figure 4 Schematic representation of the temperature dependence of enthalpy of liquid and glassy polymers

(VDCN–VAc) annealed for various periods. The dependence of $\Delta H(T_A, t)$ on t is shown in *Figure 6*. The plot did not give a straight line. This may suggest that the enthalpy relaxation time depends on the annealing period.

Next, a trial was performed to describe quantitatively the enthalpy relaxation behaviour. The enthalpy relaxation at the annealing temperature T_A is represented as:

$$\frac{dH(T_A, t)}{dt} = -\frac{H(T_A, t) - H(T_A, \infty)}{\tau} \qquad (3)$$

where τ is the relaxation time; τ is dependent on the annealing period, in other words, on the free volume, similar to the case of volume relaxation[5]. The relaxation time τ is generally given by the following equation using fractional free volume[6]:

$$\ln \tau = A + (B/f_V) \qquad (4)$$

where A and B are constants similar to constants in the Doolittle viscosity equation[7], and f_V is the fractional free
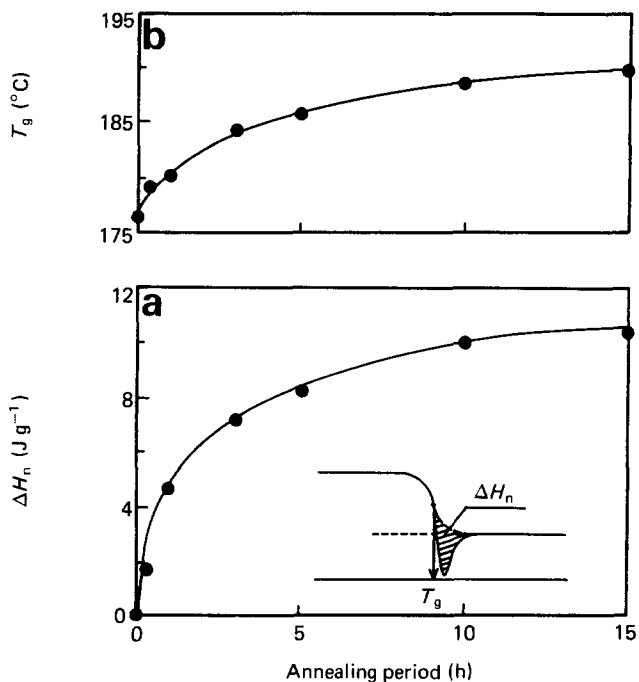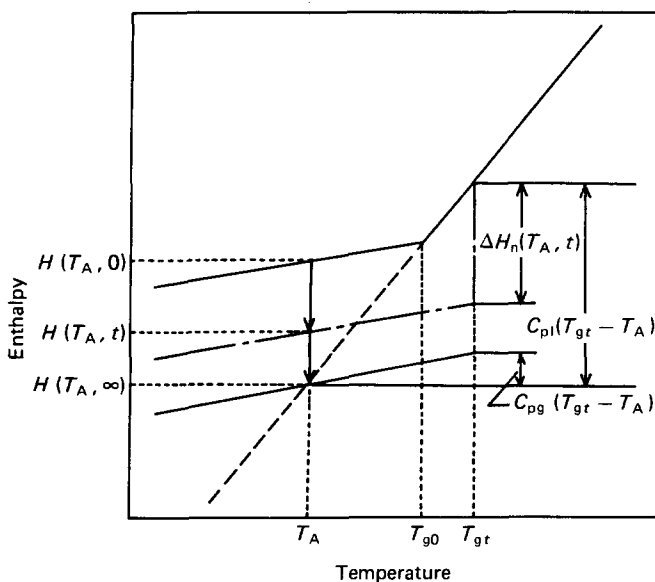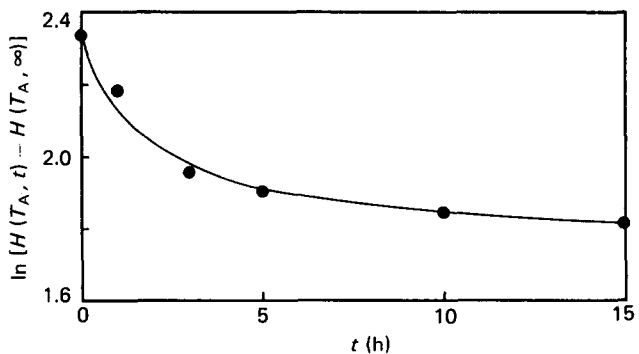

Figure 5 Dependence on annealing period of (a) enthalpy difference ΔH_n and (b) T_g for copoly(VDCN–VAc) annealed at 160°C

Table 1 Variation of T_g and ΔH_n by sub-T_g annealing

Annealing period (h)	T_g (°C)	ΔH_n (J g^{-1})
As cast	176.0	0
1	181.9	3.8
3	184.8	7.3
5	186.0	8.3
10	188.4	10.1
15	189.2	10.3

Figure 6 Dependence of unrelaxed enthalpy on annealing period for copoly(VDCN–VAc) annealed at 160°C

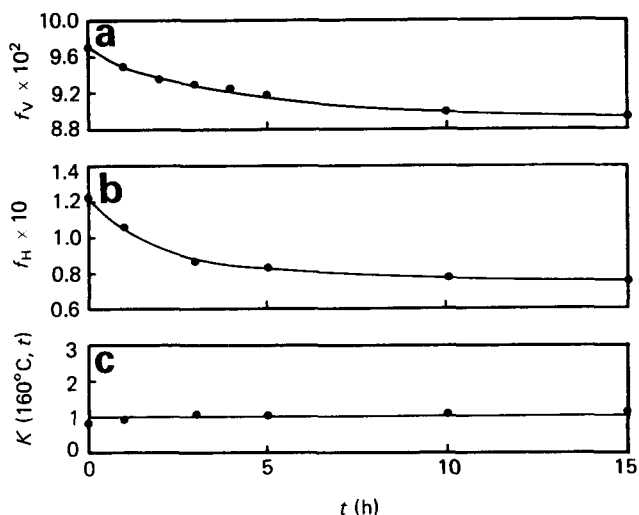**Figure 7** Annealing-period dependence of (a) f_V, (b) f_H and (c) $K(160°C, t)$ for copoly(VDCN–VAc) annealed at 160°C

volume at temperature T_A, that is:

$$f_V = \frac{V(T_A, t) - V_o(T_A)}{V(T_A, t)} \qquad (5)$$

Here $V(T_A, t)$ is the specific volume at T_A and annealing period t. $V_o(T_A)$ is the occupied volume at T_A. We evaluated the value of $V_o(T_A)$ using the fluid theory developed by Sanchez et al.[8], and the dependence of f_V on annealing period is shown in *Figure 7*. Once one can obtain the fractional free volume, one can predict the relaxation time.

Alternatively, the relaxation time may be estimated from enthalpy data. In view of *Figure 4*, the fractional unrelaxed enthalpy is represented by the following equation:

$$f_H = \frac{H(T_A, t) - H(T_A, \infty)}{H(T_A, t)} \qquad (6)$$

In order to apply equation (6) to equation (3) through equation (4), the following relation between the fractional free volume and fractional unrelaxed enthalpy is introduced, that is:

$$f_V = K(T_A, t) f_H \qquad (7)$$

where $K(T_A, t)$ is an empirical parameter to correlate f_H with f_V. Solution of equation (3) using equations (4)–(7) gives the enthalpy relaxation as follows:

$$Ei\left(\frac{H(T_A, \infty)/K(T_A, t)}{H(T_A, t_2) - H(T_A, \infty)}\right) - Ei\left(\frac{H(T_A, \infty)/K(T_A, t)}{H(T_A, t_1) - H(T_A, \infty)}\right)$$

$$= \int_{t_1}^{t_2} \frac{dt}{\exp[1/K(T_A, t)]} \qquad (8)$$

$$Ei(az) = \int_z^\infty \frac{\exp(az)}{z} dz \qquad (z > 0) \qquad (9)$$

The constant B is set to unity, as is usually done, and $A \ll (B/f_H)$ since f_H is expected to be very small below T_g. One can obtain agreement between the experimental and calculated enthalpy relaxation curves by insertion of an appropriate value of $H(T_A, \infty)$ into equation (8). Such a curve-fitting method is able to give values of $H(T_A, \infty)$ and $K(T_A, t)$. *Figures 7b* and *7c* show the dependences on

the annealing period of f_H and $K(160°C, t)$, respectively. Although there are some small differences among the values of $K(160°C, t)$ after various annealing periods, it is possible to assume that $K(160°C, t)$ is independent of annealing period. The average value of $K(160°C, t)$, i.e. 1.0, was employed in this study. The curve fitting of the calculated curve with the experimental data on copoly-(VDCN–VAc) annealed for various periods at 160°C yielded $H(160°C, \infty) = 75.3$ J g^{-1}.

Furthermore, using the value of $H(160°C, \infty)$ obtained in this manner and putting $t_1 = 0$ in the second term on the left-hand side of equation (8), the value of $H(160°C, t_2)$ after various annealing periods can be calculated from equation (8). The values of $H(160°C, t) - H(160°C, \infty)$ and $H(160°C, 0) - H(160°C, \infty)$ can also be determined. Thus a theoretical curve for the enthalpy relaxation of copoly(VDCN–VAc) annealed at 160°C can be obtained, and this is shown as a full curve in *Figure 8*. It is seen that the theoretical curve fits very well with the experimental data. The enthalpy relaxation can basically be expressed by equation (3), similarly to the volume relaxation.

Sorption

Sorption isotherms at 25°C for CO_2 in copoly-(VDCN–VAc) annealed at 160°C for various periods are shown in *Figure 9*. The full curves were calculated with equation (1) using the dual-sorption parameters described later. As expected, the equilibrium amount of CO_2 sorption decreased with increasing annealing period. This suggests that the difference in the amount of sorption is due to a change in the microvoids. It was also found that the amount of CO_2 sorption obtained in annealed films did not change upon physical ageing at 25°C. This implies that the non-equilibrium structures in copoly(VDCN–VAc) that have been attained by sub-T_g annealing cannot be changed appreciably at temperatures far below T_g. *Figure 10* shows the change in the equilibrium amount of CO_2 sorption in the annealed films compared to that in the as-cast film at fixed CO_2 pressures. The decrease in sorption caused by annealing has a comparable trend to enthalpy relaxation (*Figure 8*). It is also clear that the rate of decrease in the amount of sorption in copoly-(VDCN–VAc) at lower pressure is larger than that at
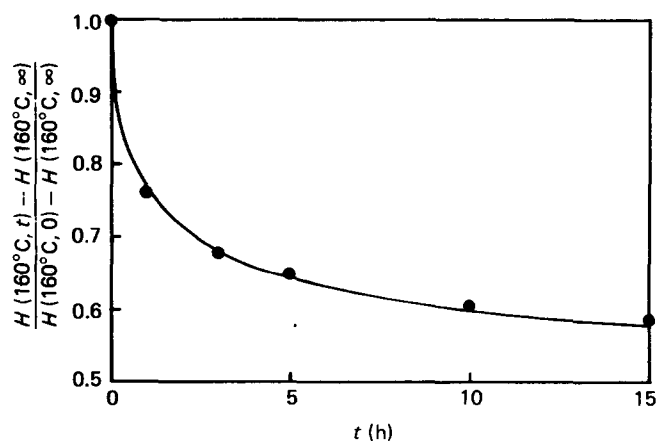

Figure 8 Dependence on annealing period of the relative change in enthalpy $[H(160°C, t) - H(160°C, \infty)]/[H(160°C, 0) - H(160°C, \infty)]$ of copoly(VDCN–VAc) annealed at 160°C: the full curve is calculated using equation (8) and the full circles are experimental data
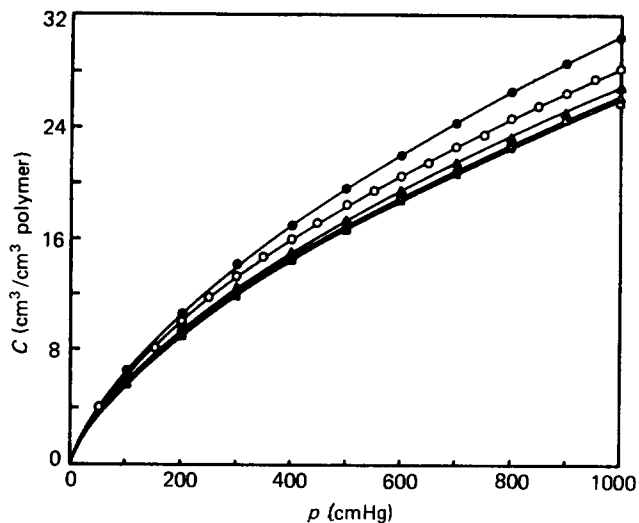
Figure 9 Sorption isotherms at 25°C for CO_2 in copoly(VDCN–VAc) annealed at 160°C for various annealing periods: (●) as cast; (○) 1 h annealing; (▲) 5 h annealing; (△) 10 h annealing; and (□) 15 h annealing
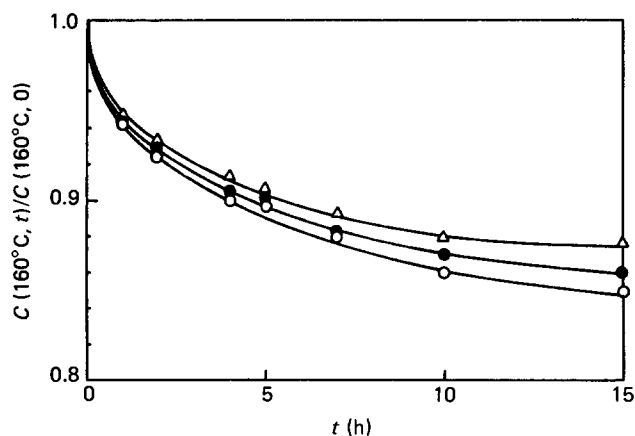

Figure 10 Dependence on annealing period of the amount of CO_2 sorption at different pressures in copoly(VDCN–VAc) annealed at 160°C: (○) 200 cmHg; (●) 500 cmHg; and (△) 1000 cmHg

higher pressure. This indicates that annealing mainly affects the Langmuir-mode term in equation (1), since the contribution of the Langmuir term to the total amount of sorption becomes predominant in the lower-pressure region. The dual-sorption parameters, k_D, C'_H and b, are estimated by the application of equation (1) to each experimental sorption data set using a non-linear least-squares optimization method. The results are shown as a function of annealing period in *Figure 11*. It is seen that k_D and b are almost independent of annealing period, and that C'_H decreases remarkably with increasing annealing period. The latter behaviour is similar to that of the enthalpy relaxation. For polycarbonate, Chan and Paul[2] showed that the change in C'_H during sub-T_g annealing, which could be quantitatively related to the unrelaxed volume in the polymer, agrees well with that of enthalpy. This indicates that the two relaxation processes during sub-T_g annealing may be correlated with each other through the unrelaxed volume relaxation in polymer glasses. In addition, the changes in the unrelaxed enthalpy[9] of the glassy polymers are, in general, interpreted in terms of the densification in packing as the glassy polymers

approach the equilibrium state. Therefore, the reduction in the amount of sorption upon the annealing of glassy polymers may be correlated closely with enthalpy relaxation. A quantitative comparison of the effect of sub-T_g annealing on C'_H in copoly(VDCN–VAc) with enthalpy relaxation was attempted below.

The reduction in C'_H was assumed to be represented by equation (8), on replacing H by C'_H. The procedure yielded $C'_H(160°C, \infty) = 9.8$ (cm³/cm³ polymer), which is the equilibrium value of C'_H in copoly(VDCN–VAc) annealed at 160°C. Using the value of $C'_H(160°C, \infty)$, the relative change of C'_H in copoly(VDCN–VAc) annealed at 160°C, which is defined by:

$$\frac{C'_H(160°C, t) - C'_H(160°C, \infty)}{C'_H(160°C, 0) - C'_H(160°C, \infty)}$$

is shown as a function of annealing period in *Figure 12*. The full curve in *Figure 12* corresponds to the calculated relative change in H defined below for annealed copoly-(VDCN–VAc):

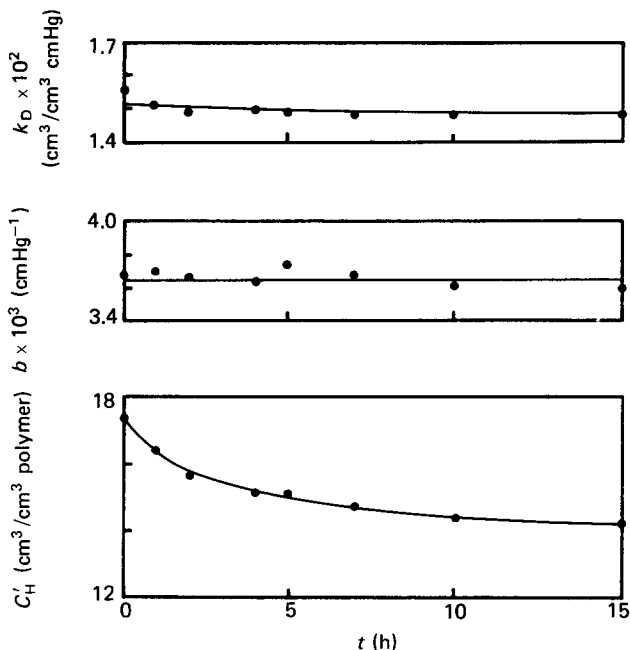$$\frac{H(160°C, t) - H(160°C, \infty)}{H(160°C, 0) - H(160°C, \infty)}$$

Figure 11 Dependence on annealing period of the dual-sorption parameters, k_D, b and C'_H, of copoly(VDCN–VAc) annealed at 160°C
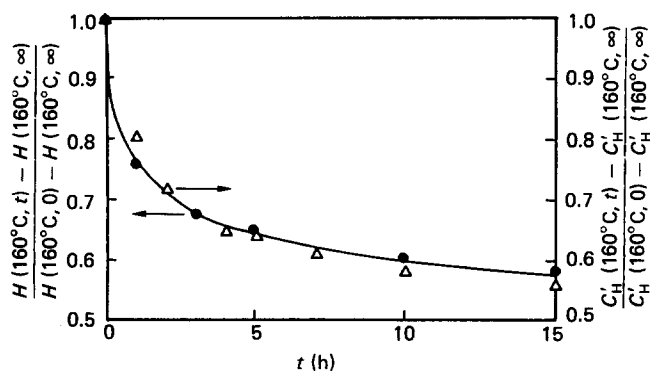

Figure 12 Dependence on annealing period of the relative change in the Langmuir sorption-capacity term C'_H (△) and enthalpy H (●) of copoly(VDCN–VAc) annealed at 160°C

The direct correlation between the two relative changes in the sorption (C'_H) and the enthalpy relaxation (H) was obtained in *Figure 12*. The same dependence on t of changes in the Langmuir capacity term and the reduction in unrelaxed enthalpy shown in *Figure 12* may lead to the conclusion that the magnitude of C'_H in copoly-(VDCN–VAc) has altered as a consequence of the densification of the glassy polymer during approach of copoly(VDCN–VAc) films to the equilibrium state.

In conclusion, it is emphasized that the magnitude of the Langmuir sorption-capacity term in glassy polymers, which might be coupled to the gas separation properties of glassy polymers, can be directly controlled by sub-T_g annealing. Furthermore, it is clarified that the relaxation behaviour of C'_H of glassy polymers can be predicted by enthalpy relaxation, as is shown in *Figure 12*, which is determined by a simple thermal analysis.

ACKNOWLEDGEMENTS

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