Annealing of polycarbonate below the glass transition temperature up to equilibrium: A quantitative interpretation of enthalpy relaxation

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The annealing time dependence of enthalpy relaxation of a sample of polycarbonate pre-annealed at various temperatures close to the glass transition temperature, T_g, is investigated over an extended range to check the consequences implied by a previous treatment. The basic assumption is that yielding and annealing may be described by the same elementary process. It is shown here, at least, that kinetics of both phenomena are identical. The previous model has been recently improved by one of us, making clearer the nature of the implied process. The response of the improved model is compared to the enthalpy relaxation data: a satisfactory fit is found, similar to that previously obtained with yield stress measurements below and above T_g.

(Keywords: polycarbonate; enthalpy relaxation; annealing process; yield process; entropy factor)

INTRODUCTION

In a previous paper[1], we attempted to establish a correlation between data obtained in tensile tests at yield and differential scanning calorimetry (d.s.c.) measurements on samples of polycarbonate (PC) pre-annealed below T_g. The interpretation relied on the assumption that yield deformation and structural change produced by annealing may be expressed using equations characterized by the same free energy. A WLF-type relation was used to give the configurational entropy change produced by annealing. This relation was written as a function of a structural temperature, θ, i.e. the temperature at which the structure of the sample in a metastable state related to a given thermal history would be in equilibrium. Recently, one of us proposed an improved model[2], which accounts for the effect of thermal treatments on the yield behaviour of PC above and below T_g. The basic assumption was that elementary processes implied in yield deformation and in annealing treatments were identical. The nature of this elementary process was more sharply defined: it was supposed to consist of a change in configuration of 20 segments of macromolecules activated simultaneously.

The present investigation was undertaken to confirm the limiting effect of thermal pre-treatments made near T_g on enthalpy relaxation, ΔH, as previously established[1] for the yield stress σ_y. A more extended range of annealing temperatures, T_a, and times, t_a, was now explored in d.s.c. experiments. A limiting value ΔH_m depending on T_a was effectively found, related to equilibrium. In this case T_a equals θ. The θ dependence of ΔH might therefore be established experimentally; results confirmed a relation previously assumed but not checked. This paper is aimed at ascertaining some consequences of the basic assumption recently advanced: (1) it is shown that the kinetics of yield and annealing processes as well as enthalpy relaxation are identical; (2) ΔH data are found to fit the response of the model. Moreover, we point out that enthalpy relaxation parallels yield stress measurements better than specific volume data, in contrast to what we suggested previously[1].

EXPERIMENTAL

Samples

Samples were machined from the same extruded sheet of Makrolon (Bayer).

Differential scanning calorimetry

Measurements were made with a Perkin–Elmer DSC-2, at a fixed heating rate of 20 K/min. Since the instrument was calibrated at 10 K/min, the observed temperature was 0.85 K too high. This effect of thermal lag was not corrected because it did not affect the enthalpy evaluation in the procedure used here. Thermal pre-treatments were made inside the calorimeter, in the range from T_g to $T_g - 35$ K, at various T_a and t_a. A single sample (13.4 mg) was used throughout and left untouched in the instrument cell in an attempt to reduce experimental scatter due to differences in heat transfer effects. Between runs and before annealing, the sample was cooled from 180°C at a nominal 320 K/min. Each scan related to a given annealing treatment was always followed by a second one taken as reference for estimating the magnitude of the endotherm. Both scans were superposed, the net area enclosed by the traces was taken as ΔH. An example is given in *Figure 1*. This procedure gave less scattered results than those obtained previously[1], following Petrie[3],

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where a mean reference peak was considered and a correction of the areas of the peaks related to annealed samples was required to take into account the increase in T_g on annealing. The specific heat change ΔC_p occurring at the glass transition was measured on each scan (*Figure 1*) and the mean value obtained is reported in *Table 1*.

Tensile tests

Specimens were annealed inside a dry oven after a quench from 180°C to 0°C. Tensile tests were made at room temperature on an Instron tensile machine at a strain rate $\dot{\varepsilon}$ equal to $4.17\times10^{-4}\,\mathrm{s}^{-1}$.

DATA ANALYSIS

Enthalpy relaxation

Dependence of ΔH *on* θ. Enthalpy relaxation data obtained after annealing at several temperatures T_a below T_g are given in *Figures 2* and *3*. At constant T_a of the order of T_g-15 K, the reported data exhibit a plateau as a function of ln t_a, indicating that thermal treatments have a limiting effect on ΔH as well as on the tensile strength[1] (*Figure 3*). In these cases, it may be assumed that the annealing times approach the value required to reach the equilibrium state of the glassy sample and therefore that $T_a=\theta$. To establish the θ-dependence of ΔH, the mean value of the data in the plateau region was taken as ΔH_m and plotted as a function of $T_a=\theta$ in *Figure 4*. A straight line was drawn throughout the data, the slope of which was found to equal 0.056 cal g^{-1} K^{-1}, i.e. the mean value of ΔC_p as it can be measured on the d.s.c. scans (given in *Table 1*). The structural temperature of the unannealed sample θ_i might also be obtained by extrapolation on the same graph; the value of 416.6 K was found (recalled in *Table 1*). Therefore, these data were found to fit the relation

$$\Delta H=\Delta C_p(\theta-\theta_i) \tag{1}$$

previously assumed[1] and experimentally checked here.

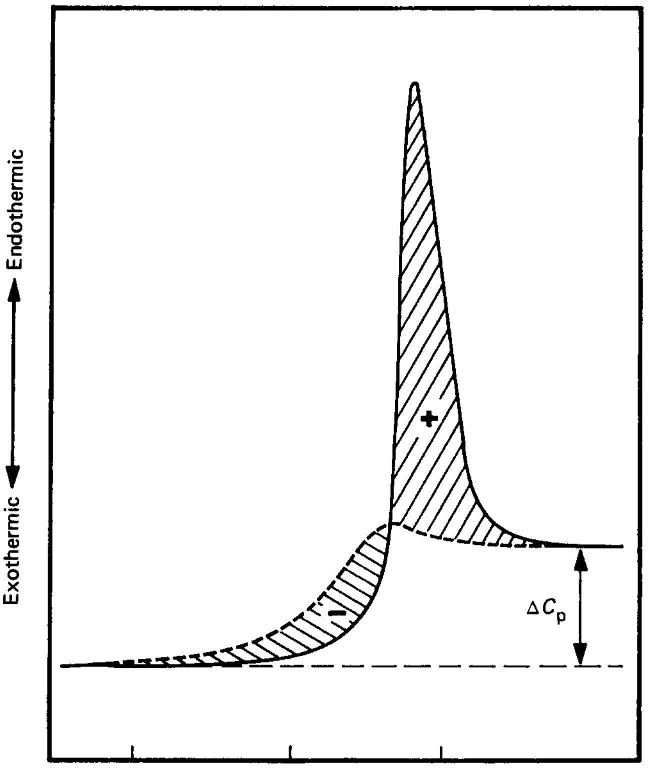

Figure 1 Example of d.s.c. scans and determination of ΔH and ΔC_p. The full trace is recorded after a thermal treatment of 30 h at 120°C; the broken trace corresponds to the unannealed state of the sample. The related value of ΔH is calculated from the net shaded area

Table 1 Values of parameters obtained from the data

ΔC_p (cal g^{-1} K^{-1})	θ_i (K)	A (kg mm^{-2} K^{-1})	Q_0 (kcal mol^{-1})
0.056*	416.6*	4.35×10^{-4}†	76†

* In the present investigation
† In ref. 1

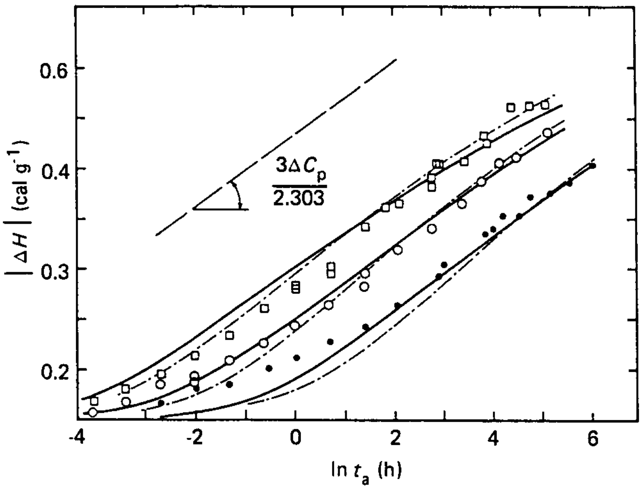

Figure 2 Enthalpy relaxation data as a function of the logarithm of the annealing time for various annealing temperatures: 110°C (●); 120°C (○); 130°C (□) and comparison of the responses of the model calculated from (17) (———) and calculated from (18) (–·–·–). The broken straight line represents the slope resulting from equation (2)

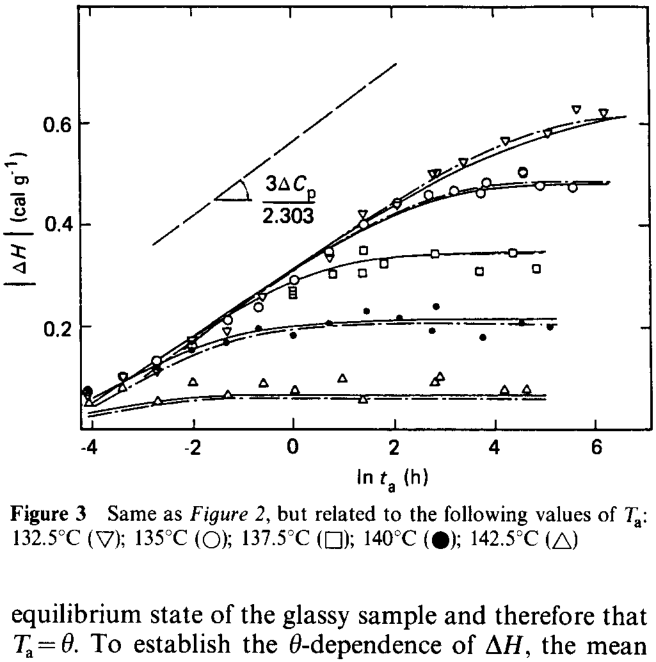

Figure 3 Same as *Figure 2*, but related to the following values of T_a: 132.5°C (▽); 135°C (○); 137.5°C (□); 140°C (●); 142.5°C (△)

Kinetics of ΔH. Data of *Figures 2* and *3* suggest that the evolution of ΔH towards ΔH_m as a function of ln t_a may be assumed to be linear to a first approximation. We have previously proposed[1] the expression of this evolution through the WLF relation, with universal constants, written as a function of $\theta-\theta_i$ instead of T_a-T_g. For θ close to θ_i, this relation predicts that at constant T_a each

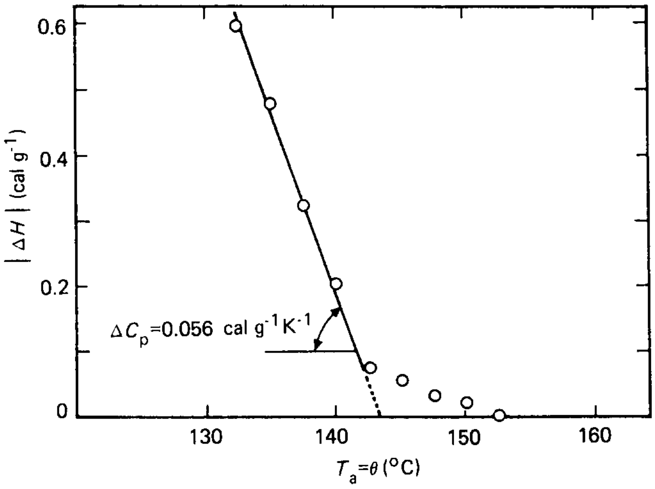

Figure 4 Plot of the value of enthalpy relaxation at equilibrium as a function of $T_a = \theta$, and determination of the structural temperature related to the unannealed state of the sample

increase in t_a by a factor of ten causes a decrease of θ by 3 K. As a consequence, taking (1) into account, the following relation must be fulfilled

$$\left(\frac{\mathrm{d}\Delta H}{\mathrm{d}\ln t_a} = \frac{3\Delta C_p}{2.303}\right)_{T_a = ct} \tag{2}$$

A straight line having a slope calculated from equation (2) with the value of ΔC_p given in *Table 1* is drawn in *Figures 2* and *3* (broken straight line) and is found to be in agreement with the evolution of the data at constant T_a, except at small values of ΔH. It may therefore be considered that, at constant T_a, kinetics of ΔH are expressed by relation (2) to a first approximation.

Tensile yield stress

Kinetics of the yield process. We have previously shown that, in tensile tests made at constant temperature, T, kinetics of σ_y/T are given by the relation

$$\left(\frac{\mathrm{d}\sigma_y/T}{\mathrm{d}\ln \dot{\varepsilon}} = A\right)_{T = ct} \tag{3}$$

where A (recalled in *Table 1*) is a constant parameter that is not affected by thermal history[1].

Kinetics of the effect of annealing on σ_y. We give in *Figure 5* the plot of σ_y/AT *versus* $\ln t_a$ for samples annealed at 130°C and tested at the same strain rate at room temperature. Data agree with a straight line, the slope of which is found to equal unity. It follows from equation (3) that

$$\frac{\mathrm{d}(\sigma_y/AT)}{\mathrm{d}\ln t_a} = \frac{\mathrm{d}(\sigma_y/AT)}{\mathrm{d}\ln \dot{\varepsilon}} = 1 \tag{4}$$

Therefore any change in t_a or $\dot{\varepsilon}$ by the same factor has an equivalent effect on σ_y; kinetics of the yield and the annealing processes are identical.

Dependence of σ_{ym} on θ. The yield stress related to samples annealed in the range from T_g to $T_g - 15$°C reaches a limiting value[1], σ_{ym}, with increasing t_a. The level of σ_{ym} is measured here at constant $\dot{\varepsilon}$ and room temperature, T, for samples annealed for about 50 h at various T_a given in *Table 2* together with the data. In this case, it may be assumed that $T_a = \theta$. For convenience, let us consider $\log a_\theta$ defined by

$$\log a_\theta = \frac{\sigma_{ym}}{2.303\,AT} \tag{5}$$

From *Table 2*, it can be evaluated that an increase of θ by 3 K causes a decrease of a_θ by a factor of ten, i.e.

$$\frac{\mathrm{d}\theta}{\mathrm{d}\log a_\theta} = 3\ \mathrm{K} \tag{6}$$

By comparing relations (5), (6) and (2), it may be concluded that kinetics of both the effect of annealing on the yield stress and enthalpy relaxation are the same (3 K in θ for one decade in t_a or a_0). Moreover, through equation (4), the same kinetics govern the yield process too.

MODEL

For convenience, let us outline Bauwens's improved treatment[2]. The molecular motions giving rise to the elementary process are those of a main chain segment (c.s.) of a macromolecule between two entanglements. Such a c.s. contains n small segments (s.s.) defined as the smallest chain portion containing two non-rigid and non-collinear bonds, as in Robertson's theory[4]. For PC, n was found to equal 20, from the results of Donald and Kramer[5]. Configurational changes can occur when the 20 s.s. of a c.s. are activated simultaneously, such as in the annealing process[2]. Let Q denote the mean increase in energy of a mole of activated s.s. and ΔS the entropy related to each s.s. The fraction of activated c.s. below and above T_g is given by[2]

$$\alpha_2 = [1 + \exp(-\Delta S/R + Q/RT_a)]^{-20} \tag{7}$$

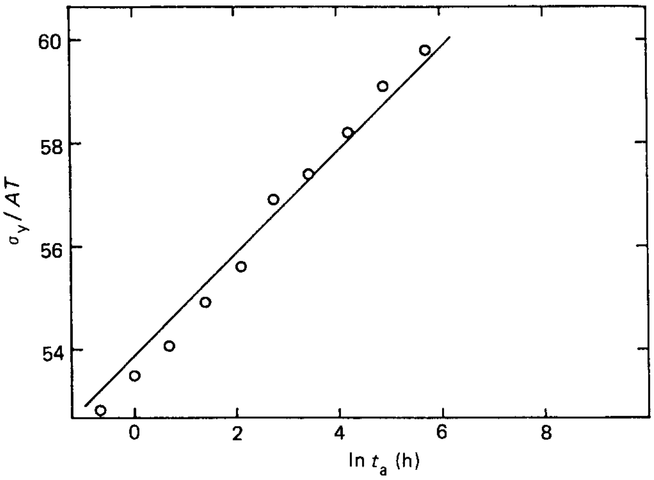

Figure 5 Kinetics of the effect of annealing on the yield stress. Data are related to samples annealed at $T_a = 130$°C. The slope of the straight line drawn through the data equals unity

Table 2 Measured values of σ_{ym} as a function of $T_a = \theta$

$T_a = \theta$ (°C)	σ_{ym} (kg mm^{-2})	$\log a_\theta$
135	7.57	25.61
140	7.01	23.72
145	6.57	22.23

where R is the gas constant. Such a change of configuration of a c.s. occurs at a frequency given by

$$J=\nu\alpha_2 \tag{8}$$

where ν may be taken to be equal to the Debye frequency, as a first approximation,

$$\nu=10^{13.875}T_a \tag{9}$$

with ν in h^{-1} and T_a in K.

The differential equation of Davies and Jones[6], rewritten for θ at constant T_a, is chosen, as previously[1], to express the annealing process:

$$d\theta=(T_a-\theta)J\,dt_a \tag{10}$$

Taking into account equations (7), (8) and (9), equation (10) becomes

$$\frac{[1+\exp(-\Delta S/R+Q/RT_a)]^{20}}{(T_a-\theta)T_a 10^{13.875}}=dt_a \tag{11}$$

To evaluate ΔS and Q, let us come back to the previous expression[1] proposed for J, namely

$$J=J_0 10^f \exp(-Q_0/RT_a) \tag{12}$$

where f is the expression $17.44(\theta-\theta_i)/(51.6+\theta-\theta_i)$ and J_0 (adjusted to the data) was a rate constant containing the entropy factor related to θ_i; with Q_0 (recalled in *Table 1*) the activation energy of the elementary annealing or yield process.

Below T_g, the exponential term contained in equation (7) is high compared to unity; in this case, it results from equations (7), (8) and (12) that

$$Q_0=20Q \tag{13}$$

and

$$J_0=10^{13.875}T_a\exp\left(-\frac{20\Delta S(\theta_i)}{R}\right) \tag{14}$$

where $\Delta S(\theta_i)$ denotes the entropy of a s.s. at the structural temperature in the unannealed state of the sample.

Then, from the value of θ_i given in *Table 1*, $\Delta S/R$ may be written

$$\Delta S/R=\frac{\Delta S(\theta_i)}{R}-2.008+\frac{103.6}{\theta-365}=b+\frac{103.6}{\theta-365} \tag{15}$$

where b has to be adjusted to the data.

From equation (1) and using the values of ΔC_p and θ_i reported in *Table 1*, θ is calculated for a given ΔH. By putting this value of θ in the following relation, found from combining equations (11), (13) and (15)

$$\int_{\theta_i}^{\theta}\frac{\left[1+\exp\left(-b-\frac{103.6}{\theta-365}+\frac{Q_0}{20RT_a}\right)\right]^{20}}{(T_a-T)T_a\times 10^{13.875}}d\theta=t_a \tag{16}$$

and by numerical integration, the response of the model yields the value of t_a related to given ΔH and T_a. The value of b adjusted to fit the data was 5.13, while that of Q_0 may be found in *Table 1*. Theoretical curves obtained from equation (16) are drawn on *Figures 2* and *3* (full curves). Another simpler approach is proposed here to express the entropy term; let us try a linear relation such as

$$\exp(-\Delta S/R)=u+v(\theta-\theta_i) \tag{17}$$

where u and v have to be adjusted to the data. By combining equations (11) and (17), the following relation can be obtained

$$\int_{\theta_i}^{\theta}\frac{\left[1+(u+v(\theta-\theta_i))\exp\left(\frac{Q_0}{20RT_a}\right)\right]^{20}}{(T_a-\theta)T_a\times 10^{13.875}}d\theta=t_a \tag{18}$$

By using the same procedure as for equation (16), curves are calculated from equation (17) and put in turn in *Figures 2* and *3* (broken curves). The adjusted values of u and v are 21.07 and 0.627 K^{-1}; the other parameters are identical to those of (16).

DISCUSSION

Both responses of the model, from using equation (15) or (17) to express the entropy term, give an acceptable fit to the data and succeed in taking into account the tendency of the data to merge at short t_a in *Figure 2*. As a consequence, the use of a power law with an exponent equal to 20 seems to be suitable. The fit obtained does not allow one to distinguish which of equations (15) or (17) is a better expression of ΔS. In fact relation (15) contains three adjustable parameters; an explicit one, namely b, and two implicit ones, those of the WLF relation; while equation (17) only requires two. We have used the WLF equation below T_g for convenience and because it works, but the same holds for equation (18), which has the merit of being simpler. Both relations take into account the important experimental fact in describing annealing effects, i.e. the correspondence of a change of 3 K in the value of θ for one decade in time near θ_i or T_g; but in fact neither the physical meaning of equation (17) nor that of (15) is defined.

Let us emphasize the poor fit of the model to the data related to short t_a at $T_a=110°C$ (*Figure 2*). It must be pointed out that such thermal treatments lead to endothermal peaks with an unusual shape: the temperature related to the maximum of the peak is lower for the annealing state, i.e. just the reverse situation, as given in *Figure 1*. This may be attributed to a sub-T_g peak, like that observed by Hodge and Berens[7] on PVC, partially superimposed on the T_g overshoot. The present treatment could be of use to separate both types of peaks. Moreover, a better fit could perhaps be obtained by using a distribution of relaxation times. We intend to come back to this subject later.

Since our previous paper[1], in which we suggested that the decrease of free volume during annealing, as well as enthalpy relaxation, paralleled the increase of yield stress, densitometric measurements have been made by Washer[8] on samples of PC annealed in the same conditions as ours. No quantitative correlation was found in this investigation between the decrease of free volume during annealing and enthalpy relaxation. Analogous results were also obtained by Bubeck and Bales[9], who pointed out that the free volume argument was inadequate for explaining physical changes induced by annealing in polycarbonates. Consequently we have to reject our previous assumption that the free energy associated with the yield or the annealing process is that related to the formation of free volume or to densification during annealing. Therefore, to date we have been unable to identify the nature of the structure related to this free energy.

Finally, let us note that relations (16) and (18) and the one used previously[1] to calculate t_a from T_a and ΔH, become practically identical below T_g; but above T_g, where the exponential term is no longer high compared to unity, only equations (16) and (18) derived from α_2 reflect the evolution of the polymer through a WLF-type relation, well known to have been checked experimentally in this range. This is the major reason why the use of α_2 provides an improvement.

CONCLUSIONS

From the present investigation, it can be concluded that: the θ dependence of ΔH is experimentally established through the measured value at equilibrium; kinetics of yield and annealing processes as well as enthalpy relaxation are identical; the response of a model derived from a power law with exponent 20 gives an acceptable fit to the enthalpy relaxation data. The value assigned for the exponent equals the number of s.s. assumed to be involved in the elementary yield or annealing process.

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