

Annealing of polycarbonate below the glass transition: quantitative interpretation of the effect on yield stress and differential scanning calorimetry measurements

C. Bauwens-Crowet and J.-C. Bauwens

Physique des Matériaux de Synthèse, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

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This paper is concerned with the effect of thermal pre-treatments (below the glass transition) on the yield stress and on the enthalpy change of polycarbonate. A treatment is proposed which accounts quantitatively for experimental results. It relies both on free volume and activation concepts and makes use of classical equations and simple assumptions, chiefly that the same free energy is associated with the molecular motions giving rise to deformation at yield and densification during annealing.

Keywords Polycarbonate; annealing; physical ageing; yield stress; endothermic peak; free volume

INTRODUCTION

Thermal pre-treatments below the glass temperature T_g , raise the yield stress of glassy polymers. Although this fact has often been reported in papers related to polycarbonate (PC) since the early work of Golden *et al.*¹, one cannot find in the literature any expression giving the yield stress as a function of the thermodynamic variables associated with thermal history.

We intend, in this paper, to fill this gap, proposing a treatment linking together yield stress, enthalpy and structural temperature changes, configurational entropy and parameters of an Eyring-type equation which we have often used to describe the yield process²⁻⁵.

A fairly good agreement is found between theory and data obtained in tensile tests and differential scanning calorimetry (d.s.c.). Therefore, this paper confirms quantitatively some aspects of the effect of thermal history on the viscoelastic behaviour of PC previously assumed⁶; moreover, it is the first attempt, to our knowledge, using quantitative results to reconcile supporters of the free volume theory, on the one hand, and the activation theory, on the other hand.

One of us proposed to characterize the structure of glassy polymers, prior to mechanical testing by a time constant spectrum depending on thermal history⁷; although the present data indeed reveals the existence of such a spectrum, its influence is not checked quantitatively and here is a first approximation. We intend to come back to this subject later.

BASIC ASSUMPTIONS

Structure of a sample annealed below T_g

A thermal pre-treatment carried out on a sample of glassy PC at an annealing temperature T_A near, but below, T_g , is known to decrease the enthalpy and the free volume. Different thermal histories are considered to be equivalent

if they are related to the same value of the enthalpy change.

We stipulate that through the thermal pre-treatment, a structural change of the sample takes place. In the present investigation, a structural temperature θ , the temperature at which the structure would be in equilibrium, is associated with each sample (see Figure 1). Let θ_i denote the structural temperature of the unannealed sample, therefore $(\theta - \theta_i)$ will characterize the structural change produced by the annealing.

The enthalpy change ΔH is linked to this last parameter through the following relation:

$$\Delta H = (\theta - \theta_i) \Delta C_p \quad (1)$$

where ΔC_p denotes the specific heat change occurring at the glass transition.

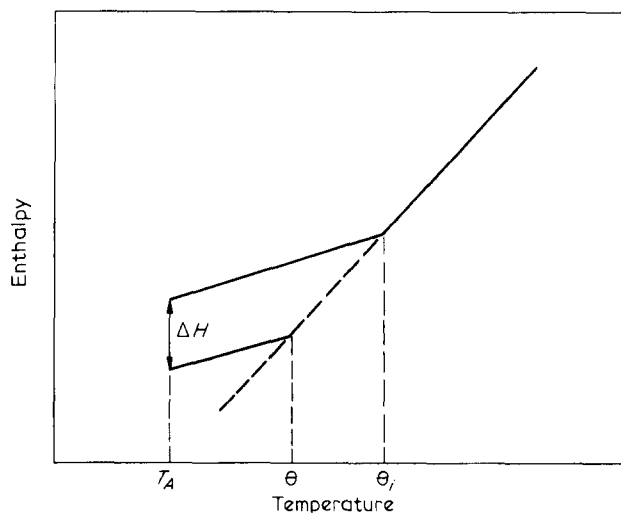


Figure 1 Schematic enthalpy versus temperature diagram

The decrease of free volume at constant temperature has been shown to follow the WLF equation⁸. It comes from a change of configurational entropy ΔS which we have chosen to express *via* this equation written for $(\theta - \theta_i)$ as:

$$\frac{\Delta S}{eR} = 10^{\frac{17.44(\theta - \theta_i)}{51.6 + (\theta - \theta_i)}} \quad (2)$$

where R is the universal gas constant. Let us point out that for PC, the WLF constants have been found to fit the universal values⁹, i.e. 17.44 and 51.6.

Although it is derived from the WLF equation, which is only true for $T > T_g$, the proposed equation (2) may be used in the range $(\theta - \theta_i) < 0$, because it is expressed as a function of θ instead of T .

Annealing process

As we assume that the annealing process consists in a configurational change producing a densification of the sample consistent with the decrease of free volume, let us characterize this process by ΔS and the activation energy Q_0 . Here the following expression will be adopted for J , the frequency of configurational change:

$$J = J_0 e^{\frac{\Delta S}{R} - \frac{Q_0}{RT_A}} \quad (3)$$

where J_0 denotes a rate constant containing the entropy factor related to θ_i .

At constant temperature T_A , θ decreases with increasing duration t and this variation parallels the volume change of the sample. We propose a basic differential equation for the annealing process, an expression analogous to that of Davies and Jones¹⁰ also used by Kovacs *et al.*¹¹ which can be rewritten for θ at constant temperature T_A :

$$d\theta = -(\theta - T_A)J dt \quad (4)$$

From equations (2) and (3), equation (4) becomes:

$$d\theta = -(\theta - T_A)J_0 10^{\frac{17.44(\theta - \theta_i)}{51.6 + (\theta - \theta_i)}} e^{-\frac{Q_0}{RT_A}} dt \quad (5)$$

Tensile yield stress of unannealed samples

Let σ_y denote the engineering yield stress of an unannealed sample related to θ_i . The yield behaviour of PC, in tensile tests conducted at temperature T and strain rate $\dot{\epsilon}$, may be fairly well described by an Eyring-type equation:

$$\frac{\sigma_y}{T} = A \left(\ln 2C\dot{\epsilon} + \frac{Q_0}{RT} \right) \quad (6)$$

with constant values of A , C and Q_0 over a very large range of experimental conditions²⁻⁵. These parameters have been developed by one of us¹² as a function of the segmental motion leading to yield deformation, assuming that the molecular origin of the yield process consists in a change of configuration produced by n segments of macromolecules characterized by a mean energy Q and simultaneously activated.

This number of segments was estimated to equal 25 monomer units for PVC and PMMA; it has not been

evaluated yet for PC due to the lack of thermodynamic data.

Here then we will assume that the elementary volume V , implicated in the yield process, is the volume occupied by n (not specified) segments and moreover that ϵ_0 , the deformation related to this volume, is equal to unity (ϵ_0 approaches unity in the case of PVC and PMMA¹²).

With these assumptions the expression of A becomes:

$$A = R/V \quad (7)$$

This parameter can easily be measured using a plot of σ_y/T against $\ln \dot{\epsilon}$. Such a plot accurately fits a set of parallel straight lines having a slope equal to A . The activation energy $Q_0 = nQ$ of the yield process can be calculated from the horizontal distances between the straight lines. This energy has been theoretically considered to equal the activation energy related to the formation of free volume¹² or, to the contrary, to densification during annealing. The same value of Q_0 will therefore be considered in equations (3), (5) and (6).

Yield of stress of a sample annealed below T_g prior to testing

Let $\sigma_y(\theta)$ denote the yield stress of a sample annealed at T_A during t and tested at T , the strain rate being $\dot{\epsilon}$.

It will be assumed here that the volume V involved in the elementary yield process, and therefore the parameter A , are the same as those related to unannealed samples.

Let M be the weight of polymer contained in this volume, then:

$$M = 1.2 R/A \quad (8)$$

where 1.2 denotes the specific weight of PC.

The free energy change ΔF for the yield process will in this case depend on the enthalpy and the configurational entropy changes such as:

$$\Delta F = \Delta H - T\Delta S \quad (9)$$

From equations (1), (2), (8) and (9), equation (6) may be rewritten for $\sigma_y(\theta)$; considering that the energy terms are expressed in kcal mol⁻¹ (mole of elementary processes) gives:

$$\frac{\sigma_y(\theta)}{T} = A \left[\left(\ln 2C\dot{\epsilon} - 2.3 \left(\frac{17.44(\theta - \theta_i)}{51.6 + (\theta - \theta_i)} \right) + \frac{1}{RT} (Q_0 + (\theta - \theta_i)M\Delta C_p) \right) \right] \quad (10)$$

Or, equivalently:

$$\frac{\sigma_y(\theta)}{T} = A (\ln 2C(\theta)\dot{\epsilon} + \frac{1}{RT} (Q_0 + (\theta - \theta_i)M\Delta C_p)) \quad (11)$$

with

$$C(\theta) = \frac{C}{10^{\frac{17.44(\theta - \theta_i)}{51.6 + (\theta - \theta_i)}}} \quad (12)$$

If σ_y and $\sigma_y(\theta)$ are measured at the same temperature and strain rate, let $\Delta\sigma_y(\theta)$ be the increase of the yield stress

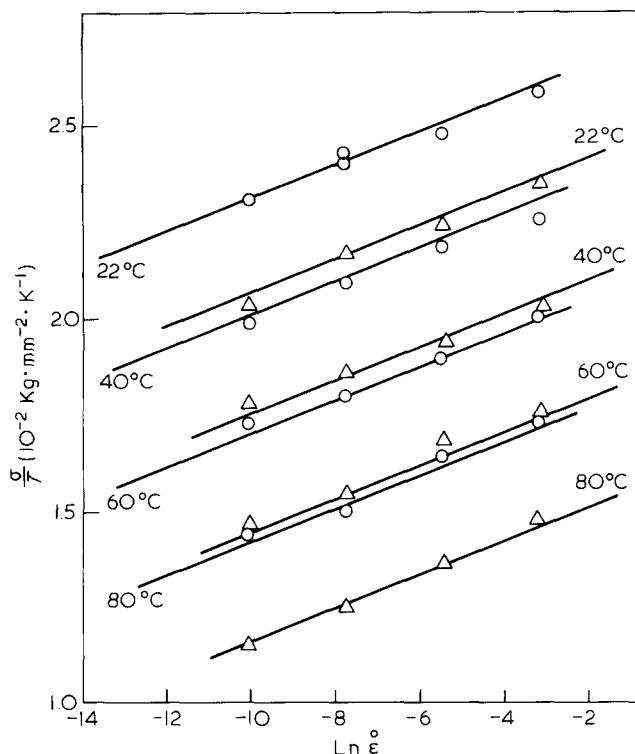


Figure 2 Ratio of the engineering yield stress to temperature against the logarithm of the strain-rate ($\dot{\epsilon}$ in s^{-1}) for tensile tests performed on unannealed samples (Δ) and on samples annealed at 120°C during 46 h (\circ). The set of parallel straight lines is calculated from equation (6) and Table 1

due to the thermal pre-treatment, which can be expressed from equations (6) and (10), by:

$$\Delta\sigma_y(\theta) = AT(\theta - \theta_i) \left(\frac{M\Delta C_p}{RT} - \frac{40}{51.6 + (\theta - \theta_i)} \right) \quad (13)$$

EXPERIMENTAL

Samples

Makrolon (Bayer) was used throughout with a viscosity average molecular weight of 26 000.

Tensile and d.s.c. test-pieces are machined from the same extruded sheet 0.2 cm thick. For d.s.c. test-pieces, the thickness is reduced to 0.08 cm.

Samples were not quenched before annealing, so the initial unannealed state is the 'as-received' one as a truly instantaneous quenching is not possible. This choice has led to less scattered results compared with those obtained on quenched samples, confirming the conclusions of some authors that the quenched state is highly sensitive to the quenching rate^{13,14}, a parameter difficult to control, especially for large specimens as used in tensile tests.

Thermal pre-treatments are performed inside a dry oven on both kinds of test-pieces.

Tensile tests

Specimens and equipment used in tensile tests in order to determine the engineering yield stress are described elsewhere².

Differential scanning calorimetry

D.s.c. measurements were carried out with a Perkin-

Elmer calorimeter, model DSC-2, calibrated with the melting transition of Indium.

The scanning rate used throughout this investigation was $20^\circ\text{C}/\text{min}$.

Specific heats were determined by comparison with a sapphire disc. Assuming that annealing has no influence on ΔC_p , an average value of $0.056 \text{ cal g}^{-1} \text{ K}^{-1}$ was taken.

In this study, T_g was determined as the temperature at which the specific heat was midpoint between those of glass and fluid; a significant increase was observed in T_g with annealing time.

RESULTS

Tensile yield stress data obtained at different temperatures and strain rates

The yield stress was measured at different temperatures from 22° to 80°C and at four strain rates from 4.17×10^{-5} to $4.17 \times 10^{-2} \text{ s}^{-1}$, for unannealed samples and for samples annealed at 120°C for 46 h. The plot of σ_y/T as a function of $\text{Ln } \dot{\epsilon}$ is given in Figure 2.

For unannealed samples an acceptable fit is obtained using equation (6) with the values of the constants listed in Table 1; the value obtained for M by means of equation (8) is also given in Table 1.

A good fit is obtained also for the annealed samples using equation (6) with the same value for A and Q_0 as for the unannealed samples; only the value found for C differs and it is given in Table 1. This experimental result has been observed previously⁶ and it implies that the same volume V is involved in the elementary yield process related to both kinds of samples (this agrees with our assumption) and also the same value of the activation energy, which at first sight seems to disagree with equation (11). However, referring to Table 1, one can see that:

$$(\theta - \theta_i)M\Delta C_p \ll Q_0 \quad (14)$$

so that only Q_0 is measured within the experimental errors.

Tensile yield stress data measured at the same temperature and strain rate on samples differing by their thermal pre-treatments

Tensile tests were performed at 22°C at a strain rate equal to $4.17 \times 10^{-4} \text{ s}^{-1}$. $\Delta\sigma_y(\theta)$ is plotted as a function of the logarithm of the annealing time in Figure 3 for the samples pre-treated at 110° , 120° and 130°C , and in Figure 4 for those pre-treated at 135° , 140° and 145°C .

The yield stress related to samples annealed at 140°C reaches a limiting value with increasing t , while at 145°C the annealing effect seems to be independent of the duration of the annealing. Moreover, no effect on the yield stress was observed for samples pre-treated at 155°C .

Table 1 Value of the constants used in equation (6) to generate the set of parallel straight lines of Figure 2

Samples	A ($\text{kg mm}^{-2} \text{ K}^{-1}$)	Q_0 (kcal mol^{-1})	C (s)
Unannealed	$4.35 \cdot 10^{-4} *$	76	$6.23 \cdot 10^{-32}$
Annealed at 120°C for 46 h	$4.35 \cdot 10^{-4} *$	76	$1.97 \cdot 10^{-29}$

* This value leads to $M = 2.34 \cdot 10^3 \text{ g mol}^{-1}$ by means of equation (8)

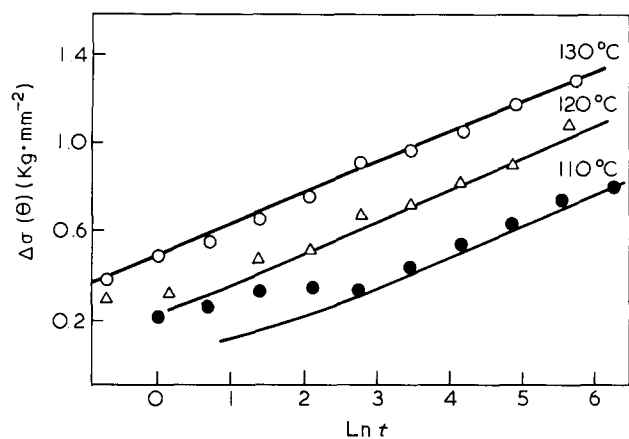


Figure 3 Increase in yield stress produced by annealing at 110°C (●), 120°C (Δ) and 130°C (○) as a function of the logarithm of annealing time (t in hours). Full curves are calculated from equations (13) and (16) and Table 2

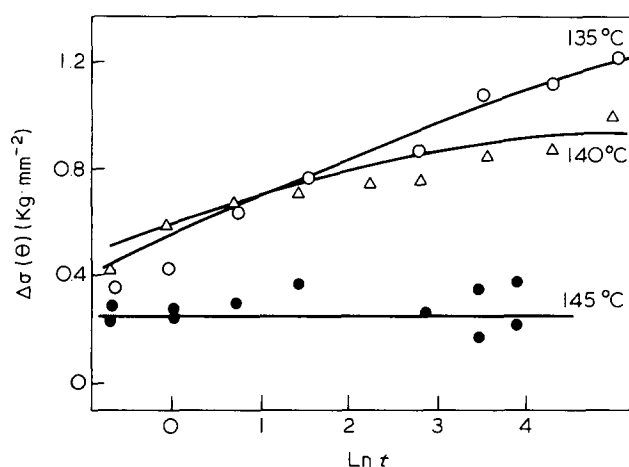


Figure 4 Same plot as in Figure 3, but related to the following annealing temperatures: 135°C (○), 140°C (Δ), 145°C (●)

THEORETICAL RESULTS

In order to compare the response of equations (1) and (13) with the data, we must try to express θ as a function of t

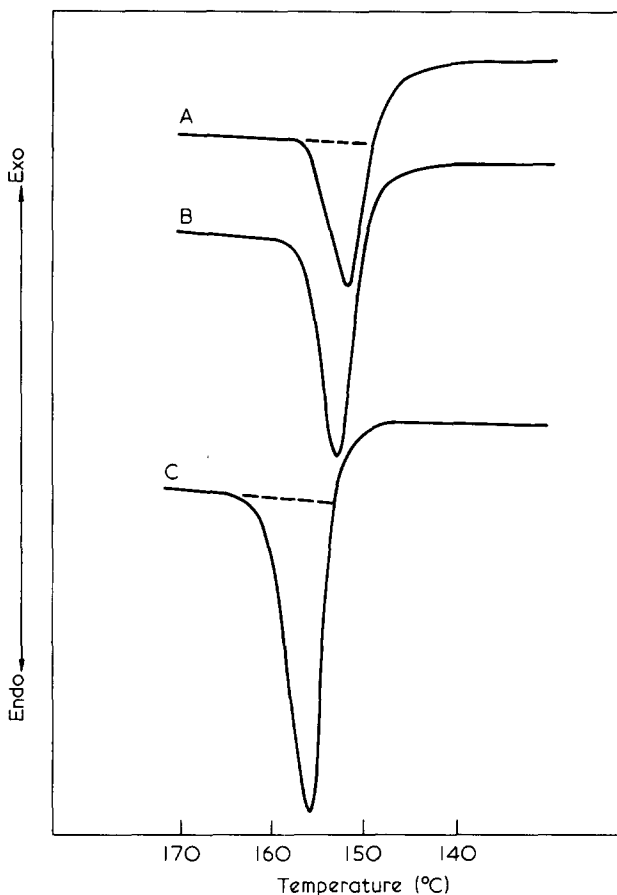


Figure 5 D.s.c. scans at a heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ after various thermal histories: (A) annealed 128 h at 110°C; (B) annealed 8 h at 130°C; (C) annealed 128 h at 130°C

D.s.c. data

For each sample, the magnitude $\Delta H'$ of the endothermic peak is measured by the area enclosed between the d.s.c. trace and the extrapolation of the baseline established at temperatures above the transition range. Typical d.s.c. traces are illustrated in Figure 5. Data are given in Figure 6; the parallel straight lines represent best fitting plots. The value of $\Delta H'$ related to unannealed samples was found to equal 0.06 cal g^{-1} .

The enthalpy difference ΔH between initial and annealed samples is evaluated using Petrie's procedure¹⁵, correcting $\Delta H'$ for enthalpy contributions associated with the increase in T_g on annealing. In order to minimize the scatter resulting from this correction, $\Delta H'$ is plotted as a function of T_g and a mean curve is drawn throughout the data (see Figure 7). The reference value of T_g related to untreated samples was taken to be equal to 418 K from this last graph. The value of ΔH is calculated using the following expression:

$$\Delta H = \Delta H' - 0.056(T_g - 418) - 0.06 \quad (15)$$

where, for a given $\Delta H'$, T_g is determined using the mean curve from Figure 7. Results are plotted as a function of the logarithm of the annealing time in Figure 8.

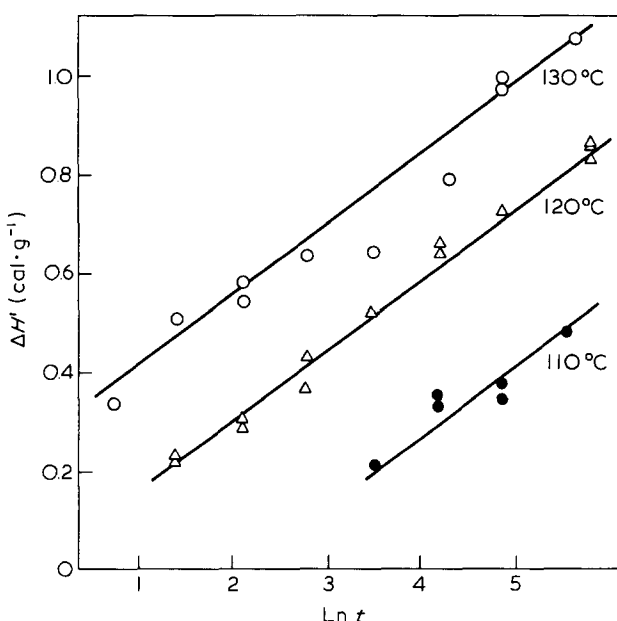


Figure 6 Magnitude of the endothermic peak related to samples annealed at 110°C (●), 120°C (Δ) and 130°C (○) as a function of the logarithm of annealing time (t in hours). Parallel straight lines represent merely a best fit to the data

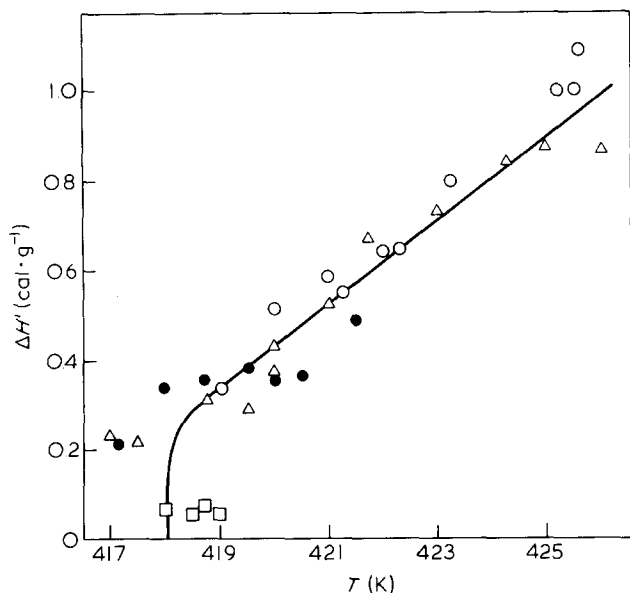


Figure 7 Magnitude of the endothermic peak as a function of the glass transition temperature for samples annealed for various times at 110°C (●), 120°C (△), 130°C (○) and unannealed (□). An average curve is drawn throughout the data

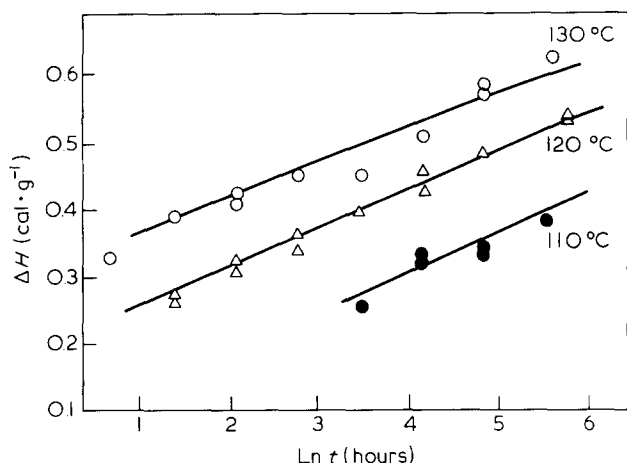


Figure 8 Enthalpy change produced by annealing at 110°C (●), 120°C (△) and 130°C (○) as a function of the logarithm of annealing time (t in hours). Full curves are calculated from equations (1) and (16) and Table 2

and T_A . From equation (5), we have:

$$\int_{\theta}^{\theta_i} \frac{1}{(\theta - T_A)} e^{-\frac{4Q(\theta - \theta_i)}{51.6 + (\theta - \theta_i)}} d\theta = -J_0 e^{\frac{Q_0}{RT_A} t} \quad (16)$$

By numerical integration of equation (16), the required relation can be obtained.

Firstly, the theoretical results are calculated from

equation (13) and plotted as full curves on the graphs of Figures 3 and 4. The value of the constants used to generate these curves are given in Table 2. Only J_0 was adjusted to obtain the best fit with the data. The value of $\theta_i = 147^\circ\text{C}$ was estimated from the limiting value of the yield stress at long times on the curve at 140°C and from the constant level of the yield stress related to samples annealed at 145°C. In these cases, it may be considered that the equilibrium state is reached, therefore $\theta = T_A$ and θ_i may be easily evaluated.

All values in equations (1) and (16) are now uniquely determined, without any further adjustments. The theoretical curves related to equation (1) are drawn as full curves in Figure 8. Let us point out that equation (16) has a solution very similar to that calculated by Kovacs *et al.*^{11,16}, provided one considers that $(\theta - T_A)$ is proportional to the recoverable part of the fractional free volume.

DISCUSSION

The accuracy of the fit is very promising in both types of measurements especially for yield stress data in the range where $\Delta\sigma_y(\theta)$ exhibits high values. The disagreement between the theory and the experimental data related to samples annealed at low temperatures for short times, arises because of the crude approximation of a model ignoring a distribution of retardation times, which has been shown by Kovacs *et al.*¹⁶ to reach about four decades. Clearly the treatment must be improved along these lines.

Accurate d.s.c. data on PC have been reported by Marshall and Petrie¹⁷. As a function of T_A and t , these authors have studied the variation of the excess of enthalpy, i.e. the difference at T_A between the enthalpy of the polymer annealed during t and the enthalpy under equilibrium conditions. Their data are plotted at constant temperature T_A as a function of the logarithm of annealing time and are approached by parallel straight lines having a slope quite consistent with that of straight lines which could be drawn throughout our data in Figure 8 (provided one considers the absolute value of this slope). However, Marshall and Petrie have determined an apparent activation energy of 317 kcal mol⁻¹ which cannot be compared with our evaluation as it results from a quite different theoretical treatment. The present investigation shows that the increase of the yield stress must be associated to ΔH , the enthalpy difference from the initial state.

The structure of a sample is characterized here by θ ; this choice allows us to easily evaluate other physical changes, such as the volume change Δv , for instance, which may be expressed as:

$$\Delta v = v_i(\theta - \theta_i)\Delta\alpha \quad (17)$$

where v_i and $\Delta\alpha$ are the specific volume related to θ_i and

Table 2 Experimental data required to test equations (1) and (13) taking into account equation (16)

J_0 (s ⁻¹)	ΔC_p (cal g ⁻¹)	M (g mol ⁻¹)	θ_i (°C)	A (kg mm ⁻² K ⁻¹)	Q_0 (kcal mol ⁻¹)
$4 \cdot 10^{37}$	0.056	$2.34 \cdot 10^3$	147	$4.35 \cdot 10^{-4}$	76
Adjusted to the data of Figure 3	From d.s.c. measurements	From Table 1	From limiting value of $\Delta\sigma_y(\theta)$	From Table 1	From Table 1

the increase of thermal expansivity at the glass transition, respectively.

The major interest of the treatment is that it predicts, from equation (16), a limiting effect of annealing on glassy PC. It does not require that a horizontal $\ln t$ shift will produce a yield or enthalpy change master curve.

It must be pointed out that the factor J_0 related to the densification is found to have a far higher value than the frequency factor of the yield process which can be roughly assimilated to the reciprocal of factor C (see *Tables 1* and *2*). This fact means that the number of segmental rearrangements giving rise to densification is high compared with that implied in the yield process; a plausible implication because this last process is governed by the Levy-von Mises relation¹⁸ which is a drastic restriction.

CONCLUSIONS

The proposed treatment is able to check quantitatively the increase of the yield stress and the enthalpy change of PC produced by annealing below T_g . It is supported by classical equations (WLF, Eyring) and simple assumptions, namely:

(i) the chief parameter to be adopted is the structural temperature change;

(ii) the elementary volume implied in the yield process is not affected by annealing;

(iii) the free energy associated with the yield process is that related to the formation of free volume or to densification during annealing.

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REFERENCES

- 1 Golden, J. H., Hammant, B. L. and Hazell, E. A. *J. Appl. Polym. Sci.* 1967, **11**, 1571
- 2 Bauwens-Crowet, C., Bauwens, J.-C. and Homès, G. *J. Polym. Sci. A-2* 1969, **7**, 735
- 3 Bauwens, J.-C., Bauwens-Crowet, C. and Homès, G. *J. Polym. Sci. A-2* 1969, **7**, 1745
- 4 Bauwens, J.-C. *J. Mater. Sci.* 1972, **7**, 577
- 5 Bauwens-Crowet, C., Ots, J.-M. and Bauwens, J.-C. *J. Mater. Sci.* 1974, **9**, 1197
- 6 Bauwens-Crowet, C. and Bauwens, J.-C. *J. Mater. Sci.* 1979, **14**, 1817
- 7 Bauwens, J.-C. *J. Mater. Sci.* 1978, **13**, 1443
- 8 Kovacs, A. J. *J. Polym. Sci.* 1958, **30**, 131
- 9 Mercier, J.-P. and Groeninckx, G. *Rheol. Acta* 1969, **8**, 510
- 10 Davies, R. O. and Jones, G. O. *Proc. Roy. Soc.* 1953, **A217**, 26
- 11 Kovacs, A. J., Hutchinson, J. M. and Aklonis, J. J. 'The structure of non-crystalline materials', Ed. P. H. Gaskell, Taylor and Francis, (1977), 153
- 12 Bauwens, J.-C. *Polymer* 1980, **21**, 699
- 13 Robertson, R. E. *J. Appl. Phys.* 1978, **49**, 5048
- 14 Lagasse, R. R. *J. Polym. Sci. Polym. Lett. Edn.* 1980, **18**, 357
- 15 Petrie, S. E. B. *J. Polym. Sci. A-2* 1972, **10**, 1255
- 16 Kovacs, A. J., Aklonis, J. J., Hutchinson, J. M. and Ramos, A. R. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 1097
- 17 Marshall, A. S. and Petrie, S. E. B. *ACS Symposium Series*, Ed. R. K. Eby, 1979, **95**, 245
- 18 Bauwens, J.-C. *Rheol. Acta* 1974, **13**, 92