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# Ageing of glass: role of the Vogel–Fulcher–Tamman law

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## Abstract

The ageing of various glass forming materials (polycarbonate, polystyrene, polyvinyl acetate and triphenylethene) has been studied by differential scanning calorimetry. The variation of the relaxation enthalpy  $\Delta H$  with the ageing time measured in a large domain of time is compared to the variation of volume  $\Delta V$  reported in the literature. Simple and complex thermal treatments (memory effect) can be distinguished.

In simple thermal treatments (annealing at a unique temperature) the following can be concluded.

(a) The glass at equilibrium is a liquid: the relaxation time  $\tau_f$  to reach equilibrium, the saturation of enthalpy, is the time predicted by the Vogel–Fulcher–Tamman (VFT) law and the heat capacity is equal to that of the liquid.

(b) The kinetic laws giving the enthalpy,  $\Delta H = k_H \log t$ , and the volume,  $\Delta V = k_V \log t$ , are observed between the initial  $\tau_i(H)$  and  $\tau_i^*(V)$  and final times  $\tau_f(H)$  and  $\tau_f^*(V)$ . For PS and PVAc we show that the times obtained by these two techniques are comparable,  $\tau_i = \tau_i^*$  and  $\tau_f = \tau_f^*$ . The initial relaxation times (or incubation times) follow the Arrhenius law and the final times (or equilibrium times) verify the VFT law. It is shown that for polymers the experimental slopes  $k_H$  and  $k_V$  can be deduced from this VFT (WLF) law,  $k_H = C_2 \Delta C_p / C_1$  and  $k_V = C_2 \Delta \alpha / C_1$ ,  $C_1$  and  $C_2$  being the coefficients of the WLF equation and  $\Delta C_p$  and  $\Delta \alpha$  being the jumps of the heat capacity and of the expansion coefficient at  $T_g$ .

In complex thermal treatments (annealing at two different temperatures) the enthalpy relaxation is compared to the volume relaxation (the memory effects) studied by Kovacs and Struik. In any case the kinetics presents two regimes, which defines an equivalent time  $t_{eq}$ ; this is the annealing time necessary to erase the previous thermal history of the glass; the origin of this time is discussed. Above  $t_{eq}$  the kinetics is not different from that of simple treatments; below  $t_{eq}$  no variation of  $\Delta H$  is observed.

## 1. Introduction

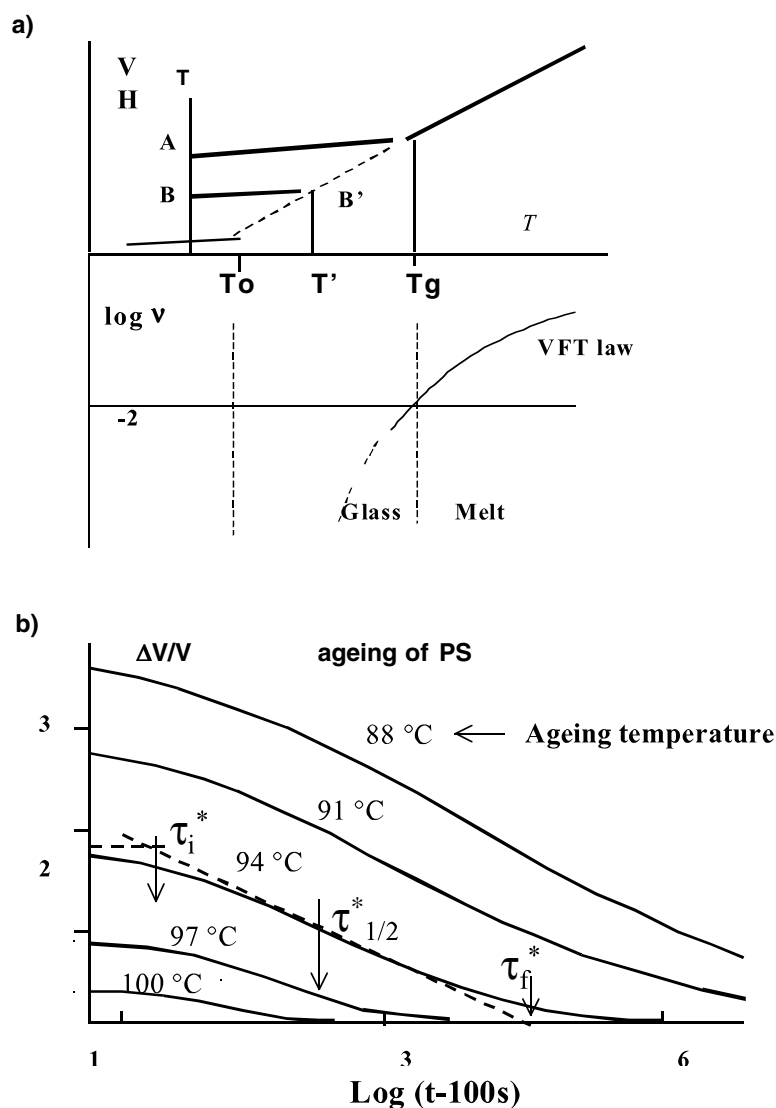
It is well known that glasses below  $T_g$  are far from equilibrium, all the properties (density, enthalpy, yield stress, compliance, ...) vary with ageing time and generally the equilibrium state is never reached. Near  $T_g$ ,  $T > T_g - 15^\circ\text{C}$ , equilibrium can be obtained in a time acceptable for reasonable experiments ( $t < \text{month}$ ); Tool [1], Kovacs *et al* [2, 3], Struik [4], Plazek *et al* [5] and many other authors have studied the kinetics of the densification of glassy materials (figure 1). Many authors have also measured the variation of the enthalpy with ageing time for mineral and organic glass by calorimetry; references can be found in the review papers of De Bolt *et al* [6] and of Hodge [7]. To our knowledge only a few authors have compared the enthalpy and volume relaxations of various glass forming materials (GFMs) with the ageing time; Sasabe and Moynihan [8], Adachi and Kotaka [9], Simon *et al* [10], Malek *et al* [11] and Cowie *et al* [12] concluded that the relaxation rates are comparable (when the data are normalized with respect to the capacity jump  $\Delta C_p$  and the dilatation coefficient jump  $\Delta\alpha$  at  $T_g$ ). For polyvinyl acetate (PVAc) the authors in fact found that enthalpy and volume relaxation times are somewhat different by a factor of two [8] or one decade [12]. It is to be remarked that all these studies are limited to a range of ageing time of three decades or less. Generally the phenomenological approach of Tool, Narayanaswamy and Moynihan (TNM) is used to calculate the relaxation rates and the time of equilibrium. The TNM model for explaining the non-exponential and non-linear behaviour of structural relaxation involves three parameters which have no straightforward physical meaning; this model also assumes that the shape of the distribution of relaxation times is independent of temperature (thermo-rheological simplicity); this assumption is obviously not verified [5, 13]. Although this model (and others reported in the review paper of Hodge) reproduces correctly the temperature dependence of a large number of experimental data (in particular the fictive relaxation rate), it does not give any clear interpretation of the relaxation times corresponding to the beginning and the end of the ageing process.

Concerning ageing of GFM many problems have not been resolved. What is the physical process which governs the kinetics and hence the equilibrium times of both parameters, density and enthalpy? Why in some circumstances of heat treatment are the evolutions of density and enthalpy similar during ageing, while in others they are completely different?

The aim of this paper is to give answers to these questions, without involving adjustable parameters as is generally the case in the various non-linear phenomenological models. The kinetics of the relaxation enthalpy of polycarbonate, polystyrene, polyvinyl acetate and triphenylethene (PC, PS, PVAc and TPE) during various thermal treatments have been studied in detail in a large domain of ageing times (four decades). We give here only some of our results which are more significant, and the enthalpy relaxation of PS and PVAc is compared with the volume relaxation obtained by Kovacs and Plazek *et al*; an example of densification of atactic PS obtained by these last authors at various temperatures below  $T_g$  is given in figure 1(b).

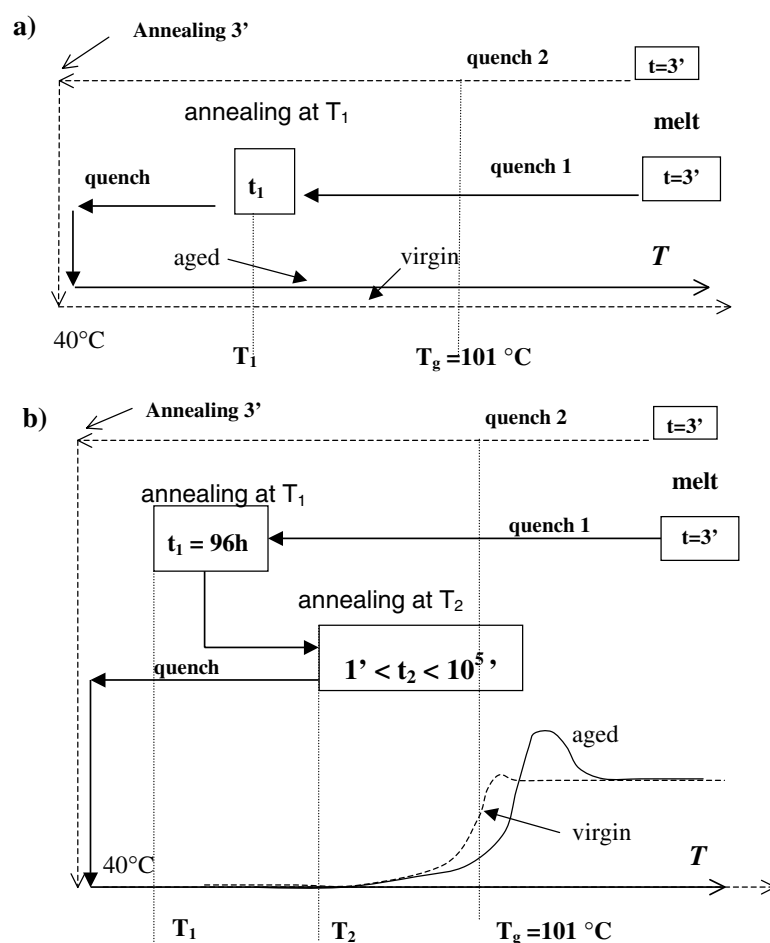
## 2. Experimental details

Here, two types of thermal treatment are distinguished in the following: simple and complex thermal treatments (figure 2); in the first treatment the material has been aged at one temperature, in the second the material is aged at two different temperatures (and different times). To obtain good accuracy for the measurements of the relaxation enthalpy, each series of thermal treatments and measurements is done on the same sample (typically 10 mg, 4 mm<sup>2</sup>,  $e = 0.1\text{--}0.3$  mm) without changing the position (thermal contact) of the sample in the DSC pan. For the simple treatment each measurement of relaxation enthalpy,  $\Delta H(T_1, t_1)$ ,



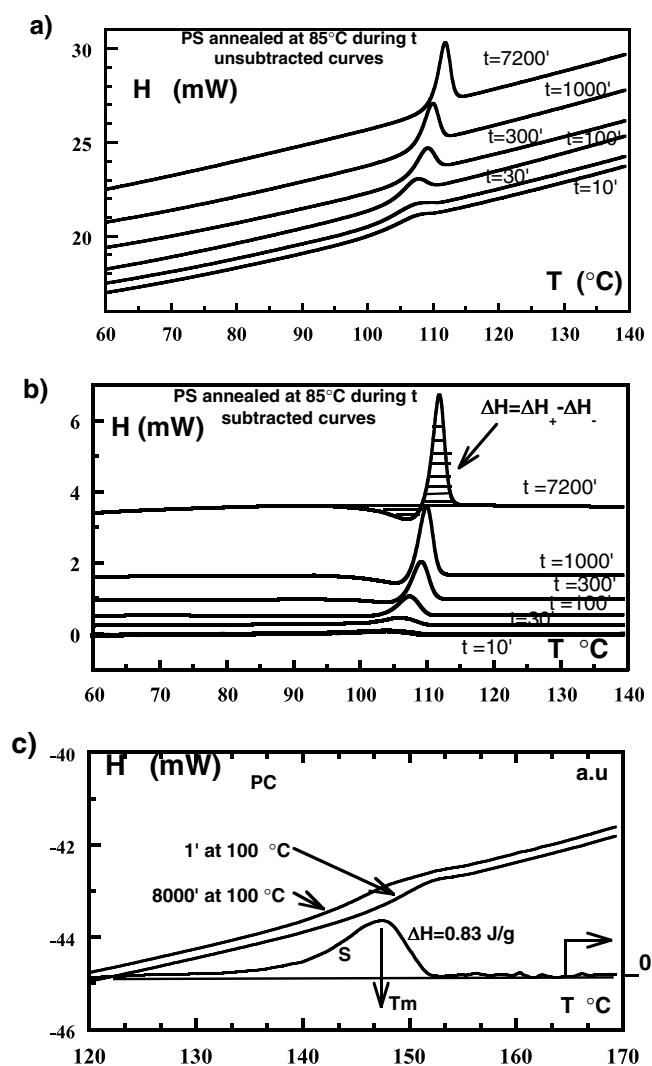
**Figure 1.** (a) Variation of the enthalpy  $H$ , specific volume  $V$  and relaxation time  $\tau_\alpha$  of the  $\alpha$  process with temperature above and below  $T_g$ . According to the VFT law the relaxation time  $\tau_\alpha = 1/2\pi\nu$  diverges at the Kauzmann temperature  $T_0$ . At  $T < T_g$ ,  $V$  and  $H$  decrease with the ageing time. At point B the glass has the equivalent temperature  $T'$ ; at that temperature the characteristics of the liquid extrapolated to point B' and that of the solid at point B are the same. (b) Relative variations of the specific volume  $V$  of a glass during ageing. Example of PS quenched at different temperatures below  $T_g$  according to Plazek *et al* (figure 12.6 of [5](b)). Definition of the initial and final relaxation times  $\tau_i^*$ ,  $\tau_f^*$  and  $\tau_{1/2}^*$ .

involves ten steps as indicated in figure 2(a). The sample which has not been subjected to any annealing below  $T_g$  is called the virgin sample; this reference sample is obtained by a quench at  $50^\circ\text{C min}^{-1}$  in the DSC pan. During steps 6 and 10 the DSC curves of the aged and virgin samples are obtained at  $10^\circ\text{C min}^{-1}$ ; an example is given in figure 3(a). This last curve gives the conventional value of the  $T_g$ , corresponding to the inflexion point of the DSC curve obtained



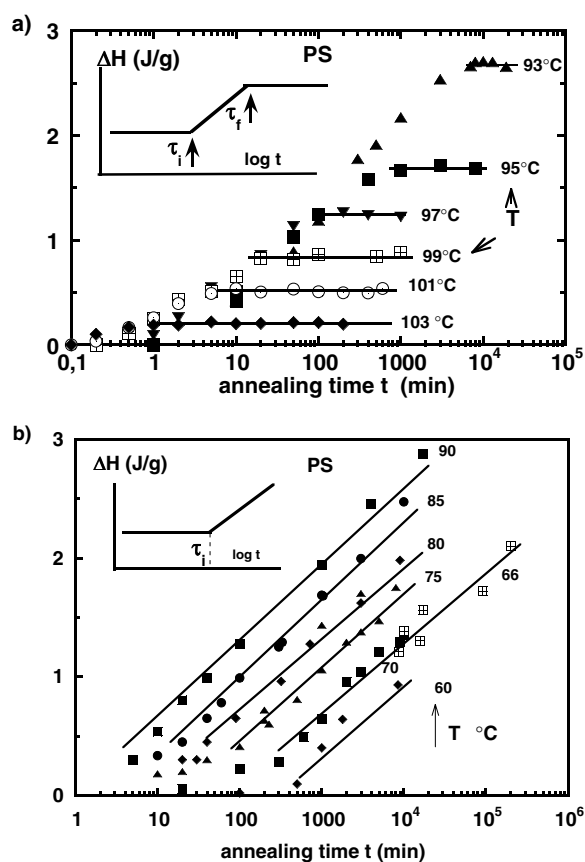
**Figure 2.** Simple (a) and complex (b) thermal treatment in the calorimeter for analysing the kinetics of the glass enthalpy during ageing at one temperature (a) and at two different temperatures (b). These two methods include respectively ten and 12 steps. The reference sample, called the virgin sample, has been obtained by a quench in the DSC pan at  $50\text{ }^{\circ}\text{C min}^{-1}$  (quenches 1 and 2). In complex thermal treatments (b) the temperature jumps are obtained at the heating or cooling rate of  $50\text{ }^{\circ}\text{C min}^{-1}$ . The DSC thermograms of aged samples, steps 6(a) and 8(b), and of virgin samples, steps 10(a) and 12(b), are recorded at  $10\text{ }^{\circ}\text{C min}^{-1}$  from  $T_g - 80\text{ }^{\circ}\text{C}$  to  $T_g + 40\text{ }^{\circ}\text{C}$ .

at  $10\text{ }^{\circ}\text{C}$ . The thermogram of the aged sample presents an enthalpy peak above or below the glass transition depending on the nature of the material and of the thermal treatment. Using the software of the DSC instrument (Pyris, Perkin Elmer) the virgin curve is subtracted from this curve. This leads to the so-called subtracted curve, which presents only a peak without  $\Delta C_p$  jump (typical curves are shown in figures 3(b), (c)). Before and after the enthalpy peak the subtracted curves merge with the  $x$  axis, then by integration one measures the relaxation enthalpy  $\Delta H(t_1 \text{ at } T_1)$  with an accuracy better than  $0.2\text{ J g}^{-1}$ . As shown in figure 3(b) the total enthalpy  $\Delta H$  is the sum of two different contributions, a positive  $\Delta H+$  and negative  $\Delta H-$  enthalpy; one calls the temperature corresponding to the maximum of the peak  $T_m$ . In the following only the total enthalpy  $\Delta H$  and the temperature  $T_m$  are studied; here one is not interested in the form of the peak. Complex annealing is represented in figure 2(b); it involves



**Figure 3.** (a), (b) Typical DSC curves of PS annealed at 85°C during various ageing times  $t$ , heat flow as a function of the temperature, DSC scan at 10°C min<sup>-1</sup>. The unsubtracted (a) and subtracted (b) curves are shifted vertically for more clarity. Far from the enthalpy peak all the subtracted curves merge with the  $x$  axis,  $\Delta H = 0$ . (c) Typical DSC curves of PC annealed at low temperature ( $T = 100^\circ\text{C} = T_g - 50^\circ\text{C}$ ) for 1 and 8000 min. The subtracted curve shows a simple enthalpy relaxation peak of width 20 to 30°C. The accuracy, on the value of  $\Delta H$ , obtained by integration, is better than 0.2 J g<sup>-1</sup>.

12 thermal steps. The integration of the subtracted curve (steps 8–12) gives the change  $\Delta H$  ( $t_1$  at  $T_1$ ,  $t_2$  at  $T_2$ ) of enthalpy of the glass during the ageing. The integration for all aged materials is done over a large range of temperature, between  $T_g - 50^\circ\text{C}$  and  $T_g + 15^\circ\text{C}$ ; figure 3(c) shows that the relaxation peak for long ageing time spreads over a large temperature range, 20–30°C (during the DSC scan). The characteristics of the materials, PC, PS (from Goodfellow) and TPE, PVAC (from Aldrich) are given in table 1:



**Figure 4.** Enthalpy relaxation of PS as a function of the ageing times at different temperatures near  $T_g$  (a) and far below  $T_g$  (b). All the annealings have been done in the calorimeter, except the annealings for a long time at 66 °C (square with cross) which were done in a Haak oven (estimated regulation  $\pm 2$  °C). The heavy lines represent linear regression fits. In the inset the definitions of the initial  $\tau_i$  and final  $\tau_f$  times (incubation and equilibrium times) are given.

**Table 1.** Glass transition  $T_g$  of the glass forming materials studied by relaxation enthalpy measurements and values of the jump capacities measured at  $T_g$  and by the calorimetry method given in the text.

	PC	PS	PVAC	TPE
$T_g$ (°C)	145	101	40	-25
$\Delta C_p$ at $T_g$	0.23	0.28		0.34
$\Delta C_p^* = -d\Delta H_{sat}/dT$	0.16	0.18	0.35	0.29

### 3. Results

#### 3.1. Simple thermal treatment

The relaxation enthalpy as a function of the annealing time (ageing time  $t$ ) is reported in figures 4–7, for various annealing temperatures below  $T_g$ , for the different glass forming materials. Obviously the trends observed and the measured values of  $\Delta H$  are very similar to

those obtained by other authors. In this study one has many more data, the ageing time domain is larger, between 1 and  $10^4$  min, and the ageing temperature domain is also larger, between  $T_g$  and  $T_g - 50^\circ\text{C}$ .

From all these results one draws the following conclusions.

- (a) The kinetics of ageing follows the simple law

$$\Delta H = k_H \log t / \tau_i; \quad \tau_i < t < \tau_f \quad (1)$$

where  $\tau_i$  is the incubation time,  $\tau_f$  is the saturation time and the slope  $k_H$  is constant, independent of the annealing temperature.

- (b) For  $T_g < T < T_g - 10^\circ\text{C}$ , the  $\Delta H_{\text{sat}}$  value at saturation is obtained rather suddenly for an ageing time  $\tau_f$  called here the final relaxation time.
- (c) The fit with a stretched exponential, as generally accepted, is not really good.
- (d) The ageing process occurs at any temperature; this is in contradiction to the conclusion of Struik [4] who claimed that, for most polymers, ageing stops when the ageing temperature decreases below the  $T_\beta$  temperature (measured at 10 Hz). If no effect is observed in an ageing experiment, one must only conclude that the ageing time is smaller than the incubation time.

**3.1.1. Saturation enthalpy.** The saturation enthalpy  $\Delta H_{\text{sat}}$  varies linearly with the ageing temperature. Examples of PVA and TPC are given in figures 5(b) and 6(b). From the slope one deduces the heat capacity jump  $\Delta C_p^*(\text{sat}) = -d\Delta H_{\text{sat}}/dT$ . In table 1 this capacity jump is given and compared to the capacity jump  $\Delta C_p$  measured at  $T_g$ . Both values are comparable. Therefore, one concludes that the enthalpy of the glass at equilibrium at  $T < T_g$  decreases linearly with temperature like the enthalpy of the liquid above  $T_g$ . The slopes  $\Delta C_p^*(\text{sat})$  and  $\Delta C_p$  are somewhat different (mean deviation 20%); this is due in our opinion to the accuracy of both types of measurement; this difference, if real, should be studied in more detail.

**3.1.2. Incubation and equilibrium time:  $\tau_i$  and  $\tau_f$ .** Figures 4(a) and 5(b) show how these (relaxation) times are defined, by extrapolation of the linear law  $\Delta H = k_H \log t / \tau_i$  with the axis  $\Delta H = 0$  and  $\Delta H_{\text{sat}}$ . These initial and final times are reported in figures 8 and 9 for PS and PVAc.

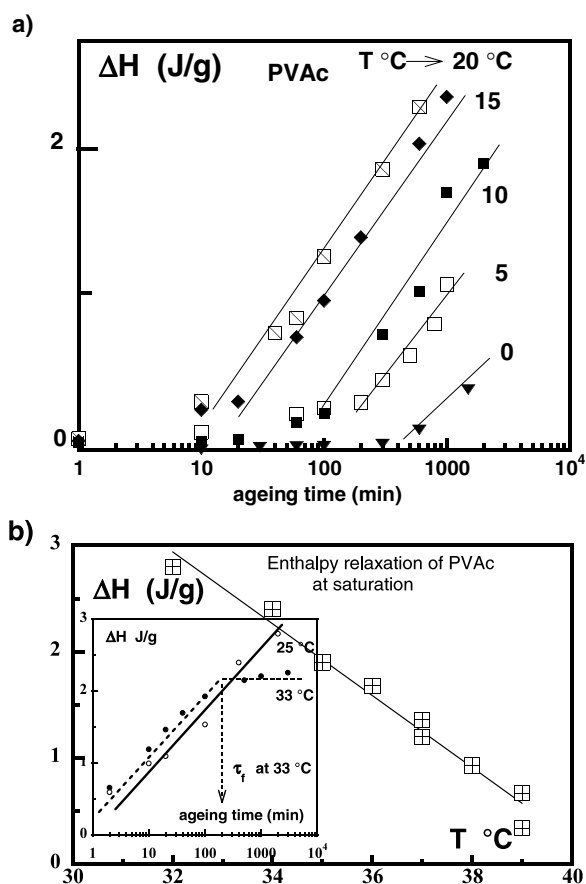
For these two polymers one knows the relaxation maps giving the relaxation times  $\tau_\alpha$  and  $\tau_\beta$  of the cooperative  $\alpha$  and localized  $\beta$  processes as a function of the inverse of temperature; these relaxation times have been measured generally by mechanic and dielectric spectroscopy (see the books of Hedwig [14] and McCrum *et al* [15]); the  $\alpha$  process follows the VFT law  $\log \tau_\alpha \sim -1/(T - T_0)$  and the  $\beta$  process the Arrhenius law. For PS one has the data of Pschorn *et al* [16] obtained by NMR. The kinetics of densification of PVAc and PS during similar simple heat treatments have been given respectively by Kovacs [2] and by Plazek *et al* [5].

As shown in figure 1(b) the variation of specific volume during annealing below  $T_g$  follows a similar logarithmic law, which allows definition of the three relaxation times:  $\tau_i^*$  and  $\tau_f^*$ , the beginning and the end of the process;  $\tau_{1/2}^*$  is the time corresponding to the mean value  $(V_{(t=0)} - V_{(t=\alpha)})/2$  of the specific volumes at the beginning and at the end of ageing.

From figures 4 and 5 one draws the following conclusions.

- (a) The final (equilibrium) times  $\tau_f$  and  $\tau_f^*$  deduced from the enthalpy and density kinetics are very similar and follow the relaxation time  $\tau_\alpha$  of the  $\alpha$  process extrapolated below  $T_g$ . For PS the two relaxation times verify the WLF (VFT) law; the shift when compared

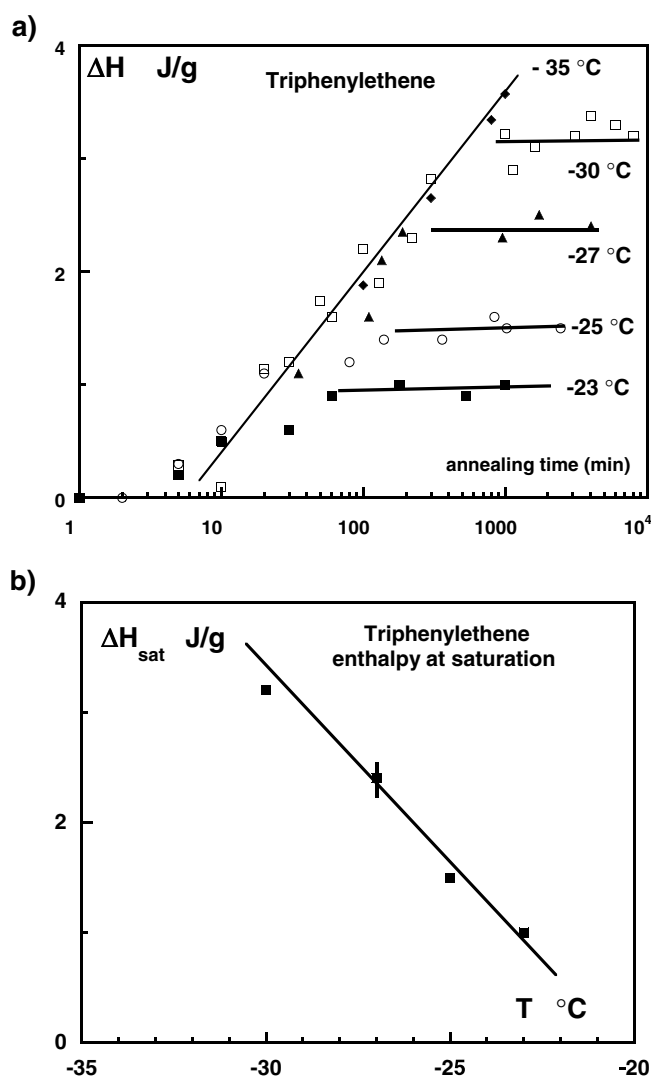




**Figure 5.** (a) Enthalpy relaxation of PVAc annealed at different temperatures  $T < T_g - 20 \text{ } ^\circ\text{C}$  as a function of the ageing time. (b) Enthalpy at saturation  $\Delta H_{\text{sat}}$  as a function of the annealing temperature. In the inset the variation of  $\Delta H$  with the ageing time at 25 and 33 °C saturation is obtained at 33 °C for  $t > 200$  min.

with the experimental curve of Pschorn *et al* is only one decade. For PVAc the shift is somewhat higher (1.5 decades). This weak difference could be due to the use of different techniques, as reported in the book of McCrum *et al*. A small difference in  $T_g$  of the materials could also explain this small observed shift (as noted by Malek, 1.8% of water in PVAc produces a decreases of  $T_g$  of  $10 \text{ } ^\circ\text{C}$ ).

- (b) The incubation times  $\tau_i$  and  $\tau_i^*$  also vary similarly. The domain of variation of  $\tau_i$  is much larger than that of  $\tau_i^*$ . Densification during ageing has only been studied in a small domain of ageing temperature between  $T_g$  and  $T_g - 12 \text{ } ^\circ\text{C}$  for PVAc and PS. The domain of ageing studied here by enthalpy relaxation is  $40 \text{ } ^\circ\text{C}$  for PS and PVAc and  $50 \text{ } ^\circ\text{C}$  for PC.
- (c) The incubation time  $\tau_i$  follows the Arrhenius law; the activation energy is approximately equal to the activation energy of the  $\beta$  process ( $8\text{--}12 \text{ kcal mol}^{-1}$ ).
- (d) All the relaxation curves  $\log \tau = f(1/T)$  deduced from the density and enthalpy kinetics merge to the same point corresponding to the glass temperature (figures 8(b) and 9(b)). Obviously at that temperature the process of ageing becomes too fast to be measured, and too fast compared to the Fourier time ( $t = e^2/a$ :  $e$  thickness of the sample,  $a$  thermal diffusivity) to reach the thermal equilibrium of the sample in the calorimeter.



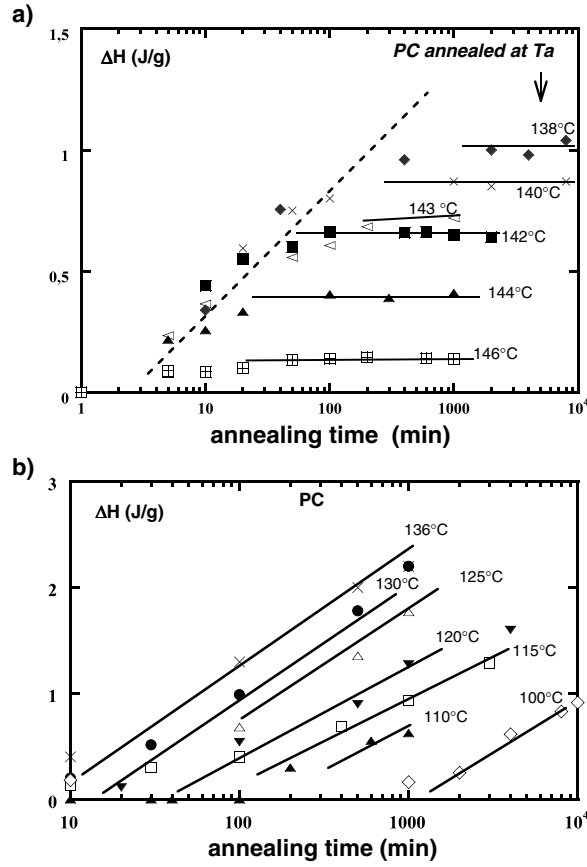
**Figure 6.** (a) Enthalpy relaxation curves of triphenylethene (TPE) annealed at different temperatures as a function of the ageing time. (b) Relaxation enthalpy  $\Delta H_{\text{sat}}$  at saturation of TPE as a function of the ageing temperature. The heavy line obtained by linear regression crosses the X axis for  $T \sim T_g$ , the glass temperature being measured at  $10^\circ\text{C min}^{-1}$ .

From the generalized relaxation maps given in figures 4 and 5, one concludes that the  $\alpha$  process governs the kinetics of ageing for density and enthalpy, in the case of simple thermal treatment.

In figure 1(a) one recalls the definition of the equivalent temperature  $T'$ . This temperature, often called the fictive temperature, was introduced by Tool [1], Rusch [17] and then by many other authors. At temperature  $T < T_g$ , during the ageing time  $t$ , the variation of enthalpy is

$$\Delta H = \Delta C_p (T_g - T'); \quad (2)$$

it is well known that the capacity jump  $\Delta C_p$  is independent of ageing. One writes that the



**Figure 7.** Relaxation enthalpy of PC annealed at different temperatures near  $T_g$  (a) and far below  $T_g$  (b) in the domains  $150^\circ\text{C} > T > 138^\circ\text{C}$  and  $136^\circ\text{C} > T > 100^\circ\text{C}$  as a function of the ageing time.

ageing time  $t$  is the equilibrium time of the liquid at  $T'$ , then the WLF equation [18] is written

$$\log t/t_g = -C_1(T' - T_g)/(T' - T_g + C_2); \quad (3a)$$

the equivalent temperature is then

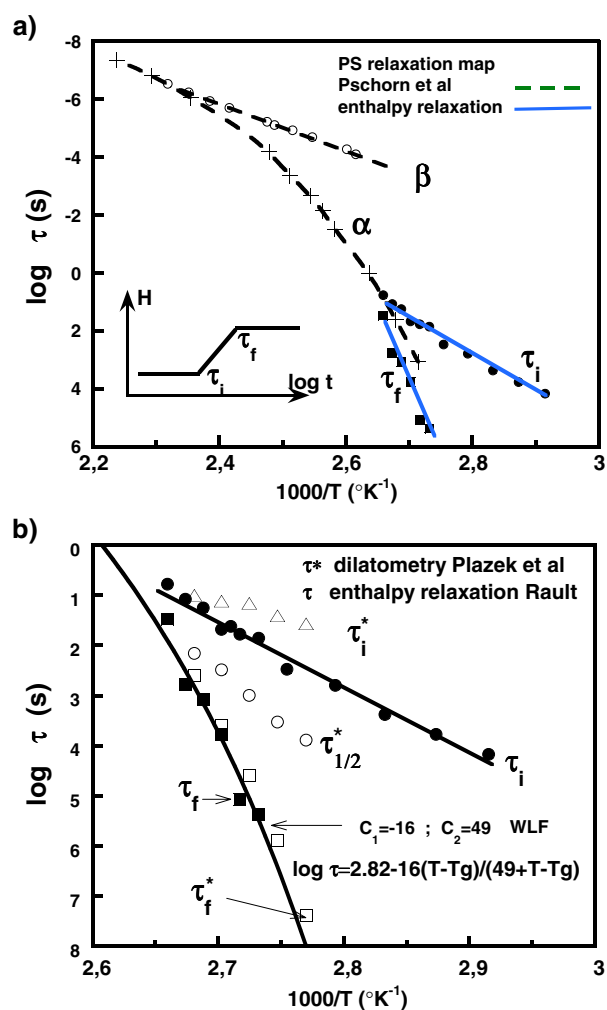
$$T' - T_g = C_2 \log t/t_g / (C_1 + \log t/t_g) \quad (3b)$$

$T_g$  being measured at  $10^\circ\text{C min}^{-1}$ ; the WLF constants have the classical values  $C_1 = 16$ ,  $C_2 = 50$  K. In our works (and also in all the published works) the ageing time is less than  $10^4 t_g$ , then  $\log t/t_g \ll C_1$ . Therefore taking into account relation (2) one obtains

$$\begin{aligned} \Delta H &= k_H \log t/t_g \\ k_H &= C_2 \Delta C_p / C_1 \end{aligned} \quad (4)$$

$\Delta C_p$  is about  $0.3 \text{ J g}^{-1} \text{ K}^{-1}$  for the materials studied here, for PS  $k_H = 0.75$ .

This is the experimental relation (1). Between  $T_g$  and  $T_g - 15^\circ\text{C}$ , the incubation time can be considered as constant,  $\tau_i = \tau_g = 100$  s. From all polymers the value of  $k_H$  is nearly the same (between  $0.3$  and  $1 \text{ J g}^{-1}$ ); this is due to the fact that for these materials the capacity jump at  $T_g$  and the WLF constants do not vary continuously with the nature of the polymer ( $\Delta C_p = 0.3 \text{ J g}^{-1}$ , K,  $C_1 = 17$ ,  $C_2 = 50^\circ\text{C}$ ).



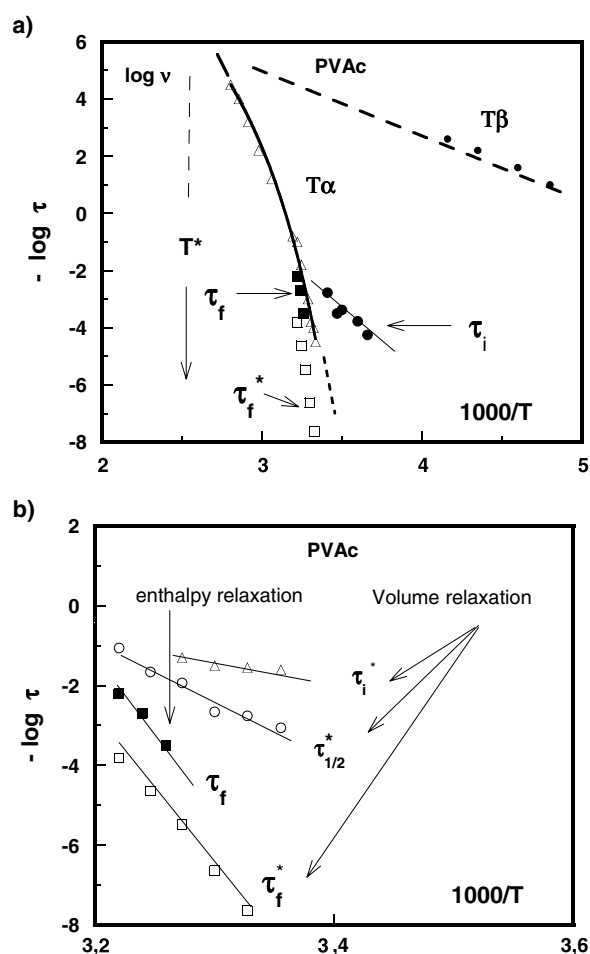
**Figure 8.** Generalized relaxation map of PS melt and glass; relaxation times as a function of the inverse of the temperature. The  $\alpha$  and  $\beta$  curves (a) are the data of Pschorn *et al* [16], obtained by different NMR methods above  $T_g$ . Below  $T_g$  (b) filled squares and circles represent the initial  $\tau_i$  and final  $\tau_f$  times (incubation and equilibrium times) deduced from enthalpy relaxation measurements. Open symbols represent the corresponding initial and final times  $\tau_i^*$  and  $\tau_f^*$  deduced from dilatometry (data according to figure 1(b) deduced from figure 12.6 of [5] b). Heavy lines are the best fit with the WLF equation ( $\tau_f$ ) and with the Arrhenius law ( $\tau_i$ ). See figure 1(b) for the definition of the relaxation times.

(This figure is in colour only in the electronic version)

Writing the same equations for the density one finds

$$\begin{aligned} \Delta V/V &= k_d \log t/t_g \\ k_d &= C_2 \Delta\alpha / C_1. \end{aligned} \quad (5)$$

Typically for polymers, the difference between the expansion coefficient of the liquid and solid states near  $T_g$  is  $\Delta\alpha = 3 \times 10^{-4} \text{ K}^{-1}$ . The slope  $k_d = 10^{-3}$  given by relation (5) is the observed value for PS and PVAc [2–5].



**Figure 9.** Generalized relaxation map of PVAc melt and glass. Symbols are as in figure 8. The  $T_\alpha$  and  $T_\beta$  curves represent the Ishida *et al* [21] results concerning the cooperative  $\alpha$  (triangle) and localized  $\beta$  (plain circle) motions observed by dielectric spectroscopy, see the book of McCrum *et al* [15]. The curves, heavy lines, in (a) represent the best fit with the WLF and Arrhenius laws. In (b) the initial and final times determined by enthalpy relaxation and by dilatometry [2] are compared, see figure 1(b) for the definition of the relaxation times.

In conclusion, for simple thermal treatments during ageing the similar evolutions of the density and of the enthalpy reported here and by other authors [9, 11, 12] are quantitatively explained by the VFT (or WLF) law. This conclusion is not totally exact for certain complex thermal treatments.

#### Remarks.

- (a) In simple thermal treatments it is to be remarked that the value of  $k_H$  found in this work is not dependent on the final temperature and not very different from the values reported by other authors. One must recall that for PS in the same domain of temperature  $T_g < T < T_g - 60^\circ\text{C}$  studied here, Adachi and Kotaka have found that  $k_d$  is also independent of  $T$  (see figure 3 of [9]).

- (b) The plateau value  $\Delta H_{\text{sat}}$  reported here is obtained rather abruptly when compared to other measurements of  $\Delta H$  and  $\Delta V$  by the various authors quoted above; this is puzzling and we must wonder whether this is due to the method or the accuracy of measurement. The epoxy glass called DGBA + PPO studied by the McKenna group [19] is an exception; in this case, as shown by Struik, the ageing produces a shift  $\log a$  of the creep curves along the time axis (and a corresponding shift of the specific volume versus  $t$ ). This shift factor increases first linearly with the logarithm of the ageing time as expected ( $\mu \sim d \log a / d \log t \sim 1$ ) and becomes constant at a time called  $t^*$  by these authors (one recalls that according to Struik  $\log a$  and density vary similarly). The transition between the two regimes is very sharp as is the transition  $\Delta H(t)$  observed here at  $\tau_f$ . This time  $t^*$  to reach the equilibrium (see figure 9(a) of [19](b) and figure 3 of [19](c)) at three different temperatures corresponds exactly to the value predicted by the WLF law (with the classical values:  $C_1 = 17$ ,  $C_2 = 50$  K, the  $\alpha$  relaxation time shift of three decades when  $T$  increases from  $T_g$  to  $T_g + 10^\circ\text{C}$ ).
- (c) Generally the authors report the value of the stabilization period  $\log t_m / t_0$  deduced from the enthalpy and volume relaxation,  $t_m$  and  $t_0$  being the extrapolated times  $\tau_i$  and  $\tau_f$  defined here, and then they deduce the various parameters of the TNM model (see for example [11](d)). In our approach the stabilization period is a simple function of the activation energy  $E_\beta$  of the individual motions, the initial temperature  $T_0$ , the final temperature  $T$  and the WLF coefficients; there are no adjustable parameters. In our approach  $\tau_f$  is independent of the initial temperature; this seems to be observed by Kovacs and by Malek *et al* (see for example figure 4 of [11](d) concerning the stabilization period of  $\text{As}_2\text{S}_3$ ). In the following, we will show that small differences in  $\tau_f$  values are however observed for positive and negative temperature jumps.

In conclusion, the equilibrium times of aged glasses observed by density, enthalpy and creep measurements are not different; they obey the VFT law. For this reason one could call  $\tau_f$  the final relaxation time, the  $\alpha$  relaxation time of the glass at equilibrium or the  $\alpha$  relaxation time of the equivalent liquid.

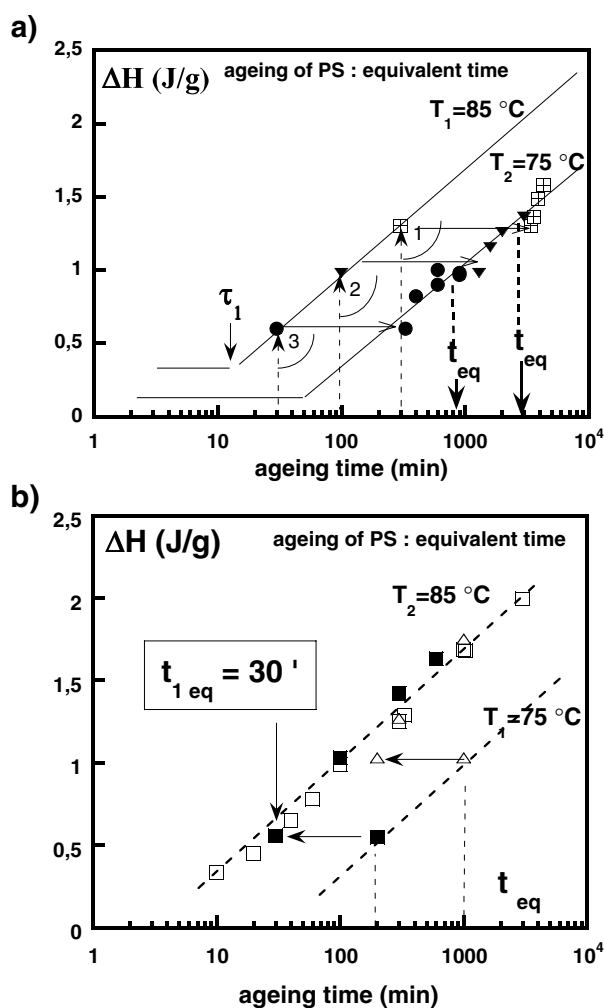
### 3.2. Complex thermal treatment

Here one analyses the change of enthalpy of materials which have been subjected to two different annealings below  $T_g$ , the first annealing at  $T_1$  for time  $t_1$  and the second at  $T_2$  for the ageing time  $t_2$ . The various steps in the calorimeter are shown in figure 2(b).

In figure 10, one reports the similar behaviour of PS when  $T_1 > T_2$ , case (a), and when  $T_1 < T_2$ , case (b). Case (a) is the simplest case; during the first ageing at  $T_1 = 85^\circ\text{C}$ , sample 1, for example, acquires a change of enthalpy  $\Delta H(t_1 T_1) = 1.25 \text{ J g}^{-1}$  for the time  $t_1 = 300$  min when annealed at  $T_2 = 75^\circ\text{C}$ ; no change of enthalpy occurs when  $t_2$  increases from 0 to  $t_{eq}$ . After this time  $t_{eq} = 2000$  min the change of enthalpy of this sample 1 follows the general law of simple ageing. This behaviour is quite general; see samples 2 and 3 of both cases (a) and (b) of figure 10. The equivalent time  $t_{eq}$  at  $T_2$  is given by the relation  $\Delta H(t_{eq}, T_2) = \Delta H(t_1, T_1)$ , that is to say

$$\log t_{eq} / \tau_i = \Delta H_{\text{start}} / k_H; \quad (6)$$

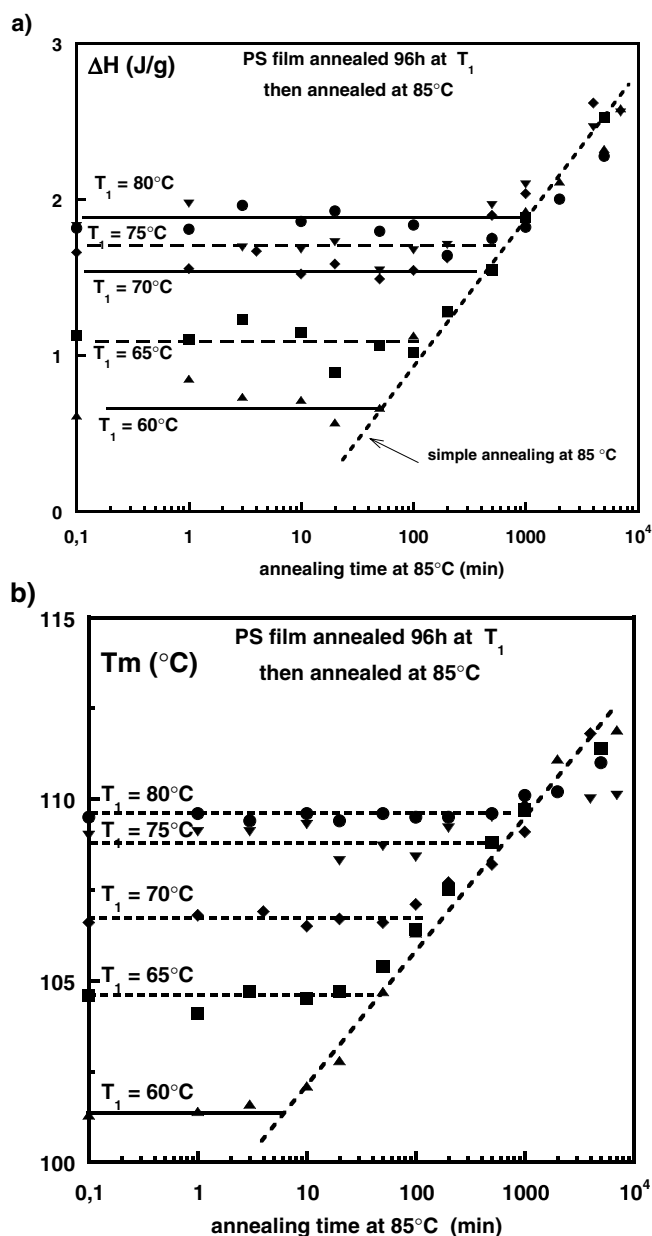
the incubation time  $\tau_i$  as a function of temperature  $T_2$  is shown in figures 4–8. It is important to remark that the equivalent time  $t_{eq}$  is independent of  $t_1$  and  $T_1$  if  $\Delta H(t_1, T_1) = \Delta H_{\text{start}}$  is constant,  $k_H$  for all the materials being independent of  $T$ . In the figure dashed straight lines represent the effect of ageing during a simple annealing at temperature  $T_1$  and  $T_2$ . In other words, a material has been aged previously during a certain time at a certain temperature and



**Figure 10.** Relaxation enthalpy of PS subjected to a complex thermal treatment below  $T_g$  as a function of the annealing time at  $T_2$ . Samples have been annealed at  $T_1$  and then at  $T_2$ . In (a)  $T_1 > T_2$ ; in (b)  $T_1 < T_2$ . The heavy dashed lines represent the simple thermal treatments (see isotherms in figure 4). The first annealing at  $T_1$  does not change the kinetics of ageing at  $T_2$ ; it only changes the new incubation time  $t_{eq} > \tau_i$ . At that temperature and at the equivalent time  $t_2 = t_{eq}$ ,  $\Delta H$  begins to increase.

then has acquired an certain relaxation enthalpy  $\Delta H_{start}$ ; if this material is aged at temperature  $T_2$  the new incubation time  $t_{eq}$  given by relations (1) and (6) is only dependent on the starting enthalpy and on the final temperature  $T_2$  via the incubation time  $\tau_i(T)$  measured during a simple annealing.

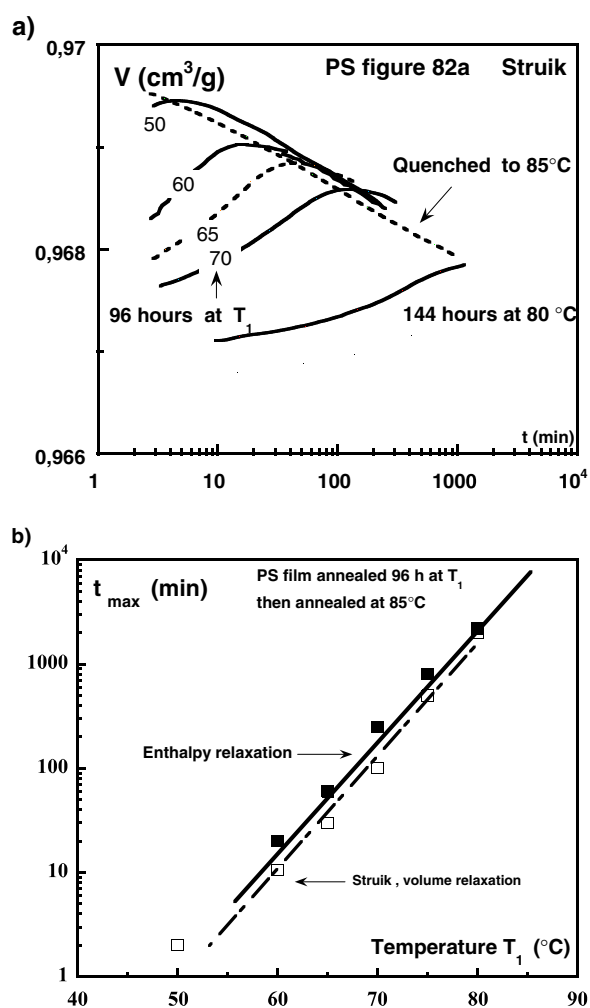
Between  $t_2 = 0$  and  $t_{eq}$  one verifies that the DSC curves do not show any differences in heat flow or position of the enthalpy peak (value of  $T_m$ ); this new incubation time  $t_{eq}$  is the annealing time necessary to erase the memory of the sample, previously annealed at  $T_1$ , or previously annealed at different temperature, or having been subjected to other types of thermal treatment. In dilatometry measurements on PS and PVAc and for the same type of thermal treatment, Kovacs, Adachi *et al* have shown that the behaviour is somewhat different.



**Figure 11.** Relaxation enthalpy (a) and temperature  $T_m$  (b) of PS as function of the annealing time at  $85^\circ\text{C}$ . The sample has been subjected to a previous annealing at various temperature  $T_1$  for 96 h. The oblique dashed line represents the  $\Delta H$  and  $T_m$  values obtained in case of a unique annealing at  $85^\circ\text{C}$  (see isotherms  $\Delta H(t)$  in figure 4). For any temperature  $T_1$  one defines the equivalent time  $t_{eq}$  (see figure 10), above this incubation time  $\Delta H$  and  $T_m$  increases linearly with  $\log t$ . This equivalent time  $t_{eq}$  increases with  $T_1$ .

In figure 11 another example of the memory effect of PS corresponding to case (b) of figure 10 is reported. The thermal treatment corresponds to the case of the memory effect reported by Struik in figure 82a of his book [4]. The samples have been annealed first at





**Figure 12.** (a) Volume relaxation of PS subjected to the same complex thermal treatment (figure 2(b)) as samples of figure 11 analysed by DSC (data from figure 82a of [4]). The dashed line represents the data in the case of a unique annealing at 85°C. The volume passes through a maximum at ageing time  $t_{\text{max}}$ , dependent on the temperature of the previous annealing. (b) Variation of the relaxation time  $t_{\text{eq}}$  and  $t_{\text{max}}$  deduced from the enthalpy (heavy line) and volume (dashed line) measurements of PS subjected to the complex thermal treatment of figure 2(b) (results of figures 11 and 12(a)). The time  $t_{\text{eq}} = t_{\text{max}}$  is the time necessary to erase the previous thermal history of the material (memory effect).

different temperatures  $T_1$  for 96 h and then annealed for a time  $t_2$  at  $T_2 = 85^\circ\text{C}$ . The variation of specific volume  $V$  at temperature  $T_2$  reported by this author are schematized in figure 12(a).  $V$  first increases and then has a maximum for a time  $t_2 = t_{\text{max}}$  and finally decreases and follows the dashed curve representing the variation of  $V$  in the case of simple annealing at  $T_2$ .

The time  $t_{\text{max}}$  is the time of annealing at  $T_2$  necessary to erase the memory of the sample (concerning the volume) previously annealed at  $T_1$ .

In figure 11(a) one sees a different behaviour concerning the enthalpy. During ageing at times  $0 < t_2 < t_{\text{eq}}$  no variation of enthalpy is observed, and no change of position of the

enthalpy peak temperature  $T_m$  (figure 11(b)). The important point to note is that the equivalent time increases with the temperature  $T_1$ . This time  $t_{eq}$  deduced from our enthalpy measurements and the time  $t_{max}$  deduced from the density measurements of Struik are reported in figure 12(b) as a function of  $T_1$ .

One concludes that these two times are equal. For ageing time longer than this time the kinetics of densification and of enthalpy are the same and equal to the kinetics of samples subjected to a simple annealing; in other words, for density and enthalpy the time  $t_{eq} = t_{max}$  is the ageing time necessary to erase the memory of the materials due to the first annealing. For shorter times  $t_2 < t_{eq}$  the two kinetics are very different; the volume increases whereas the enthalpy stays constant. Finally, one must explain why the logarithm of the equivalent time  $t_{eq}$  varies linearly with the initial temperature  $T_1$  during this complex thermal treatment. All the starting samples have been annealed for 96 h at  $T_1$ ; in figure 4(b) the linear regression curves for each annealing temperature give the value of  $\Delta H$  for this long annealing. Plotting these values as a function of  $T$  for  $t = 96$  h (and other annealing times) one finds that the relaxation enthalpy acquired by the sample obeys the relation

$$\Delta H_{start} = 0.06(T - T^*(t)) \text{ J g}^{-1} \quad (T^* = 50^\circ\text{C for } t = 96 \text{ h}); \quad (7)$$

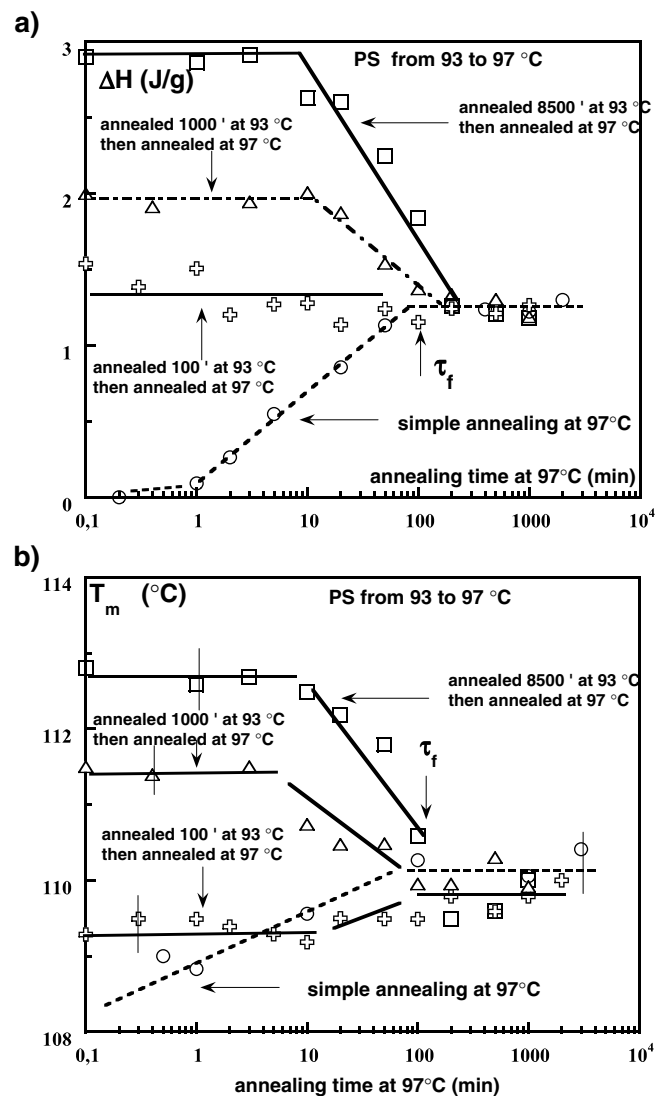
the correlation factor of the fit is  $R = 0.98$  (in this fit the point at  $66^\circ\text{C}$  in figure 4(b) are not taken into account, the annealing having not been done in the calorimeter). Similar equations are obtained for any annealing time; relation (6) indicates that the annealing time  $t = 96$  h would be the incubation time at  $T^* = 50^\circ\text{C}$ . Therefore relations (5) and (6) give for PS  $\log t_{eq}/\tau_i = 0.08(T - 50^\circ\text{C})$ . The predicted slope,  $m = d \log t_{eq}/dT = 0.08$ , is very near the experimental value,  $m = 0.11$  observed in figure 12(b). Here one verifies again that the equivalent time is dependent on the starting relaxation enthalpy  $\Delta H_{start}$  and not on the thermal path used to obtain this starting enthalpy.

#### Remarks

Adachi and Kotaka [9] have done similar double temperature jumps on PS ( $T_1 = 90^\circ\text{C}$ ,  $T_2 = 96^\circ\text{C}$ ); the samples were not subjected to different  $T_1$  temperatures but to different times  $t_1$  at  $90^\circ\text{C}$ . These authors found that the time to reach the maximum volume at  $T_2$  is slightly longer than that for reaching the maximum of enthalpy, by about a factor of two. This is what is observed in figure 12(a). Taking into account the accuracy of the measurements we think that this factor of two between the  $t_{max}$  values determined by these two different techniques is not significant. The fact that  $\log t_{max}$  (figure 10 of [9]) is a linear function of the annealing time  $t_1$  at constant  $T_1$  is another proof that  $t_{max}$  depends only on the value  $\Delta H_{start}$  of the starting material (acquired at  $T_1$ ). Another point must be noted: in the experiments of these authors there is no incubation time at  $T_2$ . This effect is puzzling and should be studied in detail.

#### Asymmetry of the contraction and dilatation during ageing

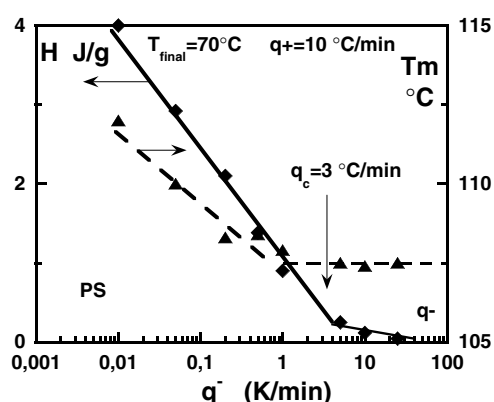
The two-temperature-jump experiments described above permit us to compare the effects of contraction and dilatation of a GFM in equilibrium or out of equilibrium. According to Kovacs [2] the volume recovery of polymers (PS) and simple liquids (glucose) at  $T_2 < T_g$  after a temperature jump  $\Delta T$  is different if the initial temperature  $T_1$  is higher (contraction) or smaller (dilatation) than the final temperature  $T_2$ . The dilatation isotherm is auto-catalytic and the contraction one auto-retarded; in these experiments the starting GFMs were in equilibrium at  $T_1$ ; the recovery process is said to be asymmetric. In figures 13(a) and (b) one analyses the variation of enthalpy and temperature  $T_m$  with  $\log t$  at  $T_2$  during these two-jump experiments. The symmetrical jumps  $\Delta T = -3^\circ\text{C}$  (from  $T_g = 100$  to  $97^\circ\text{C}$ ) and  $\Delta T = 3^\circ\text{C}$  (from  $93$  to



**Figure 13.** Enthalpy relaxation  $\Delta H$  (a) and temperature  $T_m$  (b) deduced from the DSC peak as a function of the ageing time at temperature  $T_2$ . Complex heat treatment: the samples have been first annealed at 93 °C for different times  $t_1$  (100, 1000 and 8500 min) and then annealed at 97 °C. Dashed lines represent the variation of  $\Delta H$  and  $T_m$  during a simple annealing at 97 °C (without a previous annealing at  $T_1$ ). Lines are guides for the eyes.

97 °C) corresponds to the case analysed by Kovacs, the two starting materials at  $T_1$  being at the equilibrium. The jump  $\Delta T = -3$  °C corresponds to the simple thermal treatment and is represented by the dashed line (empty circles) in the figure. The jump  $\Delta T = 3$  °C corresponds to the heavy line (squares) in the figure; the starting material has been annealed for 8500 min at 93 °C (see figure 4(a) for the time of equilibrium). From these results one concludes that the equilibrium time for a positive jump is about twice that for a negative jump.

In the figure, results for two other positive jumps are reported. In this case the starting material annealed at  $T_1 = 93$  °C has an enthalpy  $\Delta H_{start} = \Delta H(t_1, T_1 = 93$  °C) equal



**Figure 14.** Enthalpy relaxation and temperature  $T_m$  of PS as a function of the cooling rate  $q_-$ . The samples are cooled from 120 to 70 °C ( $T_g = 100$  °C). DSC measurements have been made at 10 °C. Above the critical cooling rate  $q_c = 0.8\text{--}3$  °C, there is no difference between the virgin (quenched) and the aged (slow cooled) samples.

to (double cross) or higher (triangle) than that of the material at equilibrium at  $T_2 = 97$  °C ( $\Delta H_{\text{sat}} = 1.3 \text{ J g}^{-1}$ ). For the first sample obviously  $\Delta H$  and  $T_m$  are constant and one cannot define any equilibrium time and for the second the equilibrium time is found to be of the same order as previously,  $100 \text{ min} < \tau_f < 200 \text{ min}$ . It is important to remark that in this case,  $\Delta H_{\text{start}}(T_1) > \Delta H_{\text{sat}}(T_2)$ , a new incubation time is defined (about 10 min); the origin of this characteristic time is puzzling; this effect is obviously different from what is observed in figures 10 and 11 for the inverse situation  $\Delta H_{\text{start}}(T_1) < \Delta H_{\text{sat}}(T_2)$ .

From the results of Kovacs one remarks that the final relaxation time  $\tau_f^*$  at  $T_2$  is constant, for each type of temperature jump when  $T_1$  is changed, but is somewhat different for contraction and dilatation. This is a small effect, typically  $\tau_f^*$  (contraction) =  $2\tau_f^*$  (dilatation) for PS at  $T_2 = 87.5$  °C. One concludes that enthalpy and dilatometry give the same results: the same relaxation times  $\tau_f \sim \tau_f^*$  which is the VFT time extrapolated at  $T_2$ , and the same kind of asymmetry of the kinetics. The fact that the final time  $\tau_f$  at  $T_2$  is constant (or nearly constant) independent of  $T_1$  (figure 11, same time  $t_1$ ) and of  $t_1$  (figure 13, same temperature  $T_1$ ) obviously suggests that the equilibrium time is an intrinsic parameter of the material: the  $\alpha$  relaxation time.

### 3.3. Effect of the cooling rate

The effect of cooling rate on the density and the relaxation enthalpy is well documented, but to our knowledge there is no work on the comparison of these two parameters when the glass is subjected to the same thermal treatment with varying cooling rates  $q_-$ . Here one wants to stress that the relaxation enthalpy in these particular heat treatments can be deduced from the simple isotherm treatments. For example, the enthalpy relaxation of PS as a function of  $q_-$  is reported in figure 14; the samples have been cooled from  $T_g + 15$  to 70 °C and then the DSC curves are obtained at  $q_+ = 10$  °C;  $\Delta H$  varies linearly with the cooling rate below a critical cooling rate  $q_c = 3$  °C  $\text{min}^{-1}$  and the slope  $d\Delta H/d \log q$  is about  $1 \text{ J g}^{-1}$  per decade of cooling rate. Similar results have been reported by Hutchinson and Ruddy [20].

From figure 4 one remarks that the incubation time of PS at 70 °C is  $\tau_i = 100$  min; therefore, if this material is cooled at a rate greater than  $q_c = (T_g - 70 \text{ °C})/\tau_i$  its enthalpy will not change,  $\Delta H = H(T_g) - H(70 \text{ °C}) = 0$ . This value,  $q_c = 3$  °C, corresponds exactly

to the experimental value observed in figure 14. Below this critical rate the annealing at any temperature between  $T_g$  and  $70^\circ\text{C}$  produced a change of enthalpy according to relation (1); therefore, as the slope  $k_H$  is independent of the temperature one obtains  $\Delta H \sim k_H \log t \sim -k_H \log q_-$ . In figure 4(b) the variation of the temperature  $T_m$  with  $q_-$  is reported; again, one notes similar behaviour, linear variations with  $\log q_-$ , and the existence of a critical rate  $q_c$ . This analogy between the behaviour of  $\Delta H$  and  $T_m$  was noted above in figures 11 and 13.

In this paper the reference material (virgin sample) is the GFM quenched at  $q_{ref} = 50^\circ\text{C min}^{-1}$ ; the critical cooling rate  $q_c$  is one order of magnitude smaller. Therefore, one thinks that  $q_c$  (and  $\Delta H$ ) is independent of  $q_{ref}$  but not of the heating rate  $q_+$ , that is to say of the ageing time during heating. This dependence should be studied in detail.

#### 4. Conclusion

The results reported here are quite general; they are observed in polymers (PC, PS, PVAc) and non polymers (TPE). The most important points demonstrated here are the following.

- (a) The kinetics of ageing, enthalpy and density, are the same in simple thermal treatments (isotherm at one temperature).

From these isotherms one is able to predict the effect of the cooling rate on  $\Delta H$ . The initial and final times  $\tau_i$  and  $\tau_f$  which define the beginning and the end of the ageing ( $H$ ,  $V$ ) are found to be equal. This has been verified on PS and PVAc. The final time  $\tau_f$  is the VFT relaxation time; this has been verified on PS and PVAc and also on PC (not reported here). From the VFT law one deduces the values of the slope of the curves  $H(\log t)$  and  $V(\log t)$  (relations (4) and (5)). The initial time (or incubation)  $\tau_i$  is of the order of  $t_g = 100$  s near  $T_g$ ; in a large range of temperature  $T_g > T > T_g - 50^\circ\text{C}$  this time follows the Arrhenius law.

- (b) In complex thermal treatments (annealing at two temperatures), the kinetics of ageing concerning  $H$  and  $V$  are somewhat different.

Memory effects are observed in both experiments; comparison with the work of Struik shows that the memory effects seen by calorimetry and dilatometry are erased after the same time  $t_{eq}$  which depends (relation (6)) only on the enthalpy gained by the material during the first annealing.

For longer ageing times  $t > t_{eq}$  the kinetics observed by these two techniques are the same.

For smaller ageing times  $t < t_{eq}$  the kinetics are very different;  $\Delta H$  does not vary, whereas the specific volume changes.

In conclusion, it is well known that that a liquid above  $T_g$  can have the behaviour of a solid; it should not be surprising that a solid below  $T_g$  has some properties of a liquid—the same relaxation time and the same value of the enthalpy and of the density (at equilibrium); the role of the VFT law in the properties of the glass is then not astonishing. The existence of the initial incubation time and its dependence on the previous thermal treatment is very puzzling. During the first stage of ageing  $t < t_{eq}$  the material is subjected to a structural rearrangement, a change of volume at constant enthalpy. What are exactly the local motions which permit these rearrangements? What is the process which explains the dependence of this time on the temperature and on the initial enthalpy of the material? Obviously these effects must be analysed at a local level by other methods.

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