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The origin and interpretation of the signals of MTDSC

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Abstract

In Modulated-Temperature Differential Scanning Calorimetry (MTDSC) a conventional heating programme is modulated cyclically. The heat-flow signal is split into an underlying and an approximately periodic part. We summarise the present state of the method with regard to chemical reactions and melting. We also give a more extensive treatment of the glass transition.

1. Introduction

Modulated-Temperature Differential Scanning Calorimetry is a technique in which the conventional heating programme is modulated by some form of perturbation. The resultant heat-flow signal is then analysed using an appropriate mathematical procedure to deconvolute the response to the perturbation from the response to the underlying heating programme. It was first proposed by Reading [3], [4], [6–9] and co-workers who used a heat-flux calorimeter subjected to a sinusoidal modulation. For the mathematical analysis they employed a combination of an averaging procedure to obtain the underlying response and a Fourier-transform analysis to measure the amplitude of the response to the temperature modulation and the phase lag. Many other types of modulation are possible as well as many alternative methods of mathematical analysis.

In this paper we summarise the current state of development of this technique and discuss, in some detail, the glass transition.

2. Review of the general theory of MTDSC

The simplest starting point for a general expression for describing the origin of the different types of contributions to the heat flow is as follows:

$$\frac{dQ}{dt} = C_{pt}\frac{dT}{dt} + f(t,T). \qquad (1)$$

Here dQ/dt = the heat flow into the sample, C_{pt} is the reversing heat capacity of the sample due to its molecular motions (vibrational, rotational and translational) and $f(t,T)$ is the heat flow arising as a consequence of a kinetically hindered event. There will be many forms of $f(t,T)$ and they will differ with different types of transition and different kinetic laws. Chemical reactions, crystallisation and melting were dealt with in detail in [15]. Here we summarise these results and provide a treatment of the glass transition.

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It is appropriate to define our nomenclature and describe what constitutes a reversing quantity. Eq. (1) assumes that at any time and temperature there is a process that provides a contribution to the heat flow that is proportional to the heating rate. This response is therefore rapid, given the time scale of the measurement. This is clearly a reversible process. However, the term reversing is preferred, to distinguish it from processes such as melting and crystallisation. These are reversible processes in the sense that with large temperature cycles they can be reversed. Reversing in this context means that at the time and temperature that the measurement is being made the process is reversible. Conversely, $f(t,T)$ represents the contribution to the heat flow that, at the time and temperature the measurement is made, is either irreversible or in some way kinetically hindered. It should be noted that C_{pt} is an inherently time-dependent quantity. A molecular motion that is frozen cannot contribute to the heat capacity. Whether it is considered frozen will sometimes depend on the time scale of the measurement. The clearest example of this is a glass transition in a polymer where the change in heat capacity as a function of temperature depends on the frequency at which the observation is made. This is true of DMA, DETA and MTDSC [12]. It follows that whether something is kinetically hindered sometimes also depends on the timescale of the measurement. This will be discussed in more detail below when the glass transition is considered.

In MTDSC the sample is subjected to a modulated heating programme viz:

$$T = T_0 + bt + B\sin\omega t, \tag{2}$$

where T_0 is the starting temperature, b is the heating rate, B is the amplitude of the modulation and ω is its angular frequency. When we combine Eq. (1) and Eq. (2) we obtain, for many processes,

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = BC_{pt} + \bar{f}(t,T) \ \text{(the underlying signal)} \tag{3}$$

$$+\omega BC_{pt}\cos\omega t + C\sin\omega t \ \text{(the cyclic signal)} \tag{4}$$

where $\bar{f}(t,T)$ is the average of $f(t,T)$ over the interval of at least one modulation and C is the amplitude of the kinetically hindered response to the temperature modulation. Both C_{pt} and C will vary with time and temperature but must be considered as effectively constant over the duration of a single modulation. For small enough oscillations, heat flows depend linearly upon the temperature modulation: heat flows as well as temperature are given by the linear superposition of the underlying and cyclic parts. Hence C_{pt} is independent of B while C is proportional to it. The term $f(t,T)$ can also give rise to a cosine contribution. However, for most kinetically hindered responses which can be modelled, at least approximately, by a law of Arrhenius type, the cosine response of $f(t,T)$ can be made insignificantly small by ensuring that there are many cycles over the course of the transition [15]. MTDSC normally requires that the frequency of the modulation and the underlying heating rate be adjusted to ensure that this criterion is met, not to do so would usually invalidate the use of this technique. Consequently, in most cases, except for melting (see below), it can be assumed that the cosine response derives from the reversing heat capacity. Inspection of Eqs. (3) and (4) clearly implies that the cyclic signal will have an amplitude and a phase shift that is determined by ωBC_{pt} and C. The relationships between these quantities are given by [5]:

$$C_c = A_{HF}/A_{HR}, \tag{5}$$

where C_c=the cyclic heat capacity (=|complex heat capacity|, see below), A_{HF}=the amplitude of the heat flow modulation and A_{HR}=the amplitude of the heating rate modulation. Then

$$C_{pt} = C_c\cos\delta \tag{6}$$

$$C = \omega BC_c\sin\delta, \tag{7}$$

where δ =the phase shift.

Consequently there are three basic signals derived from an MTDSC experiment; the average or underlying signal (which is equivalent to that of conventional DSC) the in-phase cyclic component, from which C_{pt} can be calculated, and the out-of-phase signal C.

Reading et al., when they first introduced MTDSC, made the observation that the phase-angle shift, except in the melt, is often small, thus it can neglected and C_c C_{pt} in many cases; Reading also proposed that it was useful to calculate another signal called the non-reversing signal [3], [4], [6–10]. Above, it is explained how C_{pt} can be calculated using the amplitude of the cyclic signal and the phase lag (the phase lag can be neglected if the shift during the transition is small). This can then be multiplied by b to calculate the reversing contribution to the underlying signal. By subtracting this from the underlying signal we obtain a value for the contribution derived from $\bar{f}(t,T)$, i.e. the non-reversing component, viz

$$\begin{aligned}&\text{non-reversing heat flow}\\&\quad= \text{the underlying heat flow} - BC_c\cos\delta\\&= f(t,T),\end{aligned}\tag{9}$$

where $\cos\delta\approx 1$ if the phase-angle shift during the transition is small, [4].

In this way the reversing contribution can be separated from the non-reversing contribution. This simple analysis has been applied many times to many transitions [3], [4], [6–10], [12], principally for polymer systems, and found to work well when the non-reversing process is the loss of volatile material, a cold crystallisation or a chemical reaction and C_{pt} is the frequency-independent heat capacity, [15]. The situation is somewhat more complex when considering glass transitions but the non-reversing signal can still be interpreted in a meaningful and useful way as discussed below. This analysis is not strictly valid when dealing with melting but useful information can nevertheless be gained from the non-reversing signal. This is also discussed in more detail below.

The timescale dependence of C_{pt} can be explicitly expressed, [10], as

$$\frac{DQ}{dt} = bC_{pb} + \bar{f}(t,T) + B\omega C_{p\omega}\cos\omega t + C\sin\omega t\tag{10}$$

where C_{pb} is the reversing heat capacity at the frequency or distribution of frequencies implied by the heating rate b and $C_{p\omega}$ is the reversing heat capacity at the frequency ω. (The precise frequency ω contrasts with the range associated with b and different reversing heat capacities result. Eq. (10) then generalises Eq. (3) and Eq. (4).) It should be noted that $B\omega\ C_{\omega p}$ is the reversing signal at frequency ω by definition when it contains no or an insignificant contribution from any non-reversing event such as a chemical reaction. This follows because it is proportional to and synchronous with the dT/dt modulation. C_{pb} would normally be the same as $C_{p\omega}$ except in the region of the glass transition where some frequency cooling/heating rate equivalence might be used to obtain its value (see Section 6). The out-of-phase term $C\sin\omega t$ arises from the kinetic contribution, exhibited by f in Eq. (3).

In the above example only reversing quantities are expressed as heat capacities. This approach can also be applied to the out-of-phase signal by treating it as if it were a heat capacity. Thus out-of-phase "AC component" is given in [4], by

$$\text{out-of-phase or kinetic heat flow} = b\frac{C}{\omega B}\tag{11}$$

where $C/\omega B$ is an apparent heat capacity. It has been proposed that the cyclic signal be expressed as a complex quantity [10], [14], by analogy with DMA and DETA, viz:

$$C^* = C' - IC''\tag{12}$$

and thence

$$C_C^2 = |C^*|^2 = C'2 + C''^2\tag{13}$$

where C^* is a complex heat capacity, C' is its real part and C'' is its imaginary part. The analogy with DMA and DETA should, however, be treated with caution. In these techniques mechanical work or electrical energy is lost from the sample as heat and this is expressed through the imaginary component which is then referred to as the loss component. In MTDSC, during an endothermic process, such as a glass transition, energy is not lost from the sample yet there will be a measurable C'' component. For this reason it should not be referred to as a loss signal. We prefer the term kinetic heat capacity. The relationships between the different approaches are then

$$\begin{aligned}C_{p\omega} &= \text{the reversing or in-phase cyclic}\\&\quad\ \text{heat capacity} = C'\end{aligned}\tag{14}$$

$$\begin{aligned}\frac{C}{\omega B} &= \text{the kinetic or out-of-phase cyclic}\\&\quad\ \text{heat capacity} = C''.\end{aligned}\tag{15}$$

Therefore Eq. (10) can be expressed as(see[10]),

$$\frac{dQ}{dt} = BC_{pb} + \bar{f}(t,T) + \omega B(C'\cos\omega t + C''\sin\omega t).\tag{16}$$

This can be taken a step further viz:

$$\frac{dQ}{dt} = b(C_{pb} + C_E) + \omega B(C'\cos\omega t + C''\sin\omega t),\tag{17}$$

where $C_E = f(t,T)/b$ and can be referred to as the non-reversing or excess heat capacity. While expressing these different contributions to the measured heat flow in terms of heat capacities is sometimes convenient, in general terms only quantities C_{pb} and $C_{\mathrm{p}\omega}$ are true heat capacities in the normal use of this word. The others should be referred to as apparent heat capacities.

3. Chemical reactions and similar processes

For irreversible processes like chemical reactions it can be shown, [15], that

$$C = Br', \tag{18}$$

where r' =the derivative of the rate of production of heat from the chemical reaction with respect to temperature. For most polymer samples the contribution to the heat flow from the reversing heat capacity is usually a significant part of the total (of the order of a tenth or more). When this is the case and when it is ensured that there are many modulations over the course of the reaction it has been observed that C is often small and can be neglected when compared to ωBC_{pt} [3–12], thus:

$$C_c \simeq C_{\mathrm{p}\omega}. \tag{19}$$

Therefore $C_{\mathrm{p}\omega}$ can be calculated to a good approximation without the use of the phase angle [3], [4], [6–10], [12]. (It should always be possible to select a combination of frequency and underlying heating rate where this is true.) In fact $C_{\mathrm{p}\omega}$ is generally independent of frequency and thus $C_{\mathrm{p}\omega}$=C_{pt}. A very similar result applies to crystallisation, [15], and the loss of volatiles such as moisture and retained solvent.

4. Experiments

All experiments were carried out using a TA Instruments 2920 MDSC with a helium purge. The calibration methodology was the same as we have used previously [9] with the additional step of shifting the data to fit the ATHAS database values for Polystyrene immediately above and below the glass transition region using a linear baseline correction. The phase lag was exploited after the baseline correction procedure we have already described, [4], [15].

5. Phenomenology of the glass transition

We shall start by presenting MTDSC results for the glass transition of polystyrene. In Fig. 1, Fig. 2, Fig. 3 and Fig. 4 we show the results for the total, reversing, kinetic and non-reversing heat capacities respectively for a sample that has been annealed for different periods of time. The total heat capacity shows the increasing peak at the T_{g} that is typical of annealed samples. It is noticeable that the reversing and kinetic signals are much less affected thus it follows that the non-revering signal increases on annealing.

The reversing signal has a frequency dependence as shown in Fig. 5 for a series of cooling experiments at 1°C min^{-1}. In this series of experiments we can take the baselines provided by the ATHAS values for the amorphous and crystalline phases and express the glass transition in terms of the percentage devitrification as shown in Fig. 6. We can then assume an Arrhenius-type-relationship between frequency and temperature and so obtain values for the activation energy at different extents of devitrification starting at 10% and increasing in steps of 10%. We can see from the results plotted in Fig. 7 that the activation energy is, within experimental uncertainty, the same across the transition. In Fig. 7 we also show the result for the underlying signal at 1°C min^{-1}. It can be seen that it has a different shape to that of the cyclic results thus, if we are seeking a heating-rate-frequency equivalence, the underlying signal will have to be expressed as a distribution of frequencies at different extents of devitrification. In Fig. 8 we show a comparison of the reversing heat capacity at different frequencies on heating and cooling. There are some differences but they are very small.

6. Theory of the glass transition

We use a model of the form employed by Hutchinson and Montserrat [16] (see also [1]). This takes the enthalpy difference δ of the sample from its equilibrium value (TC_{pl}) to satisfy a law

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = -\Delta C_{\mathrm{p}}\frac{\mathrm{d}T}{\mathrm{d}t} - \frac{\delta}{\tau} \tag{20}$$

where $\Delta C_{\mathrm{p}} = C_{\mathrm{pl}} - C_{\mathrm{pg}}$ is the difference in heat capacities of the two states. For simplicity we assume

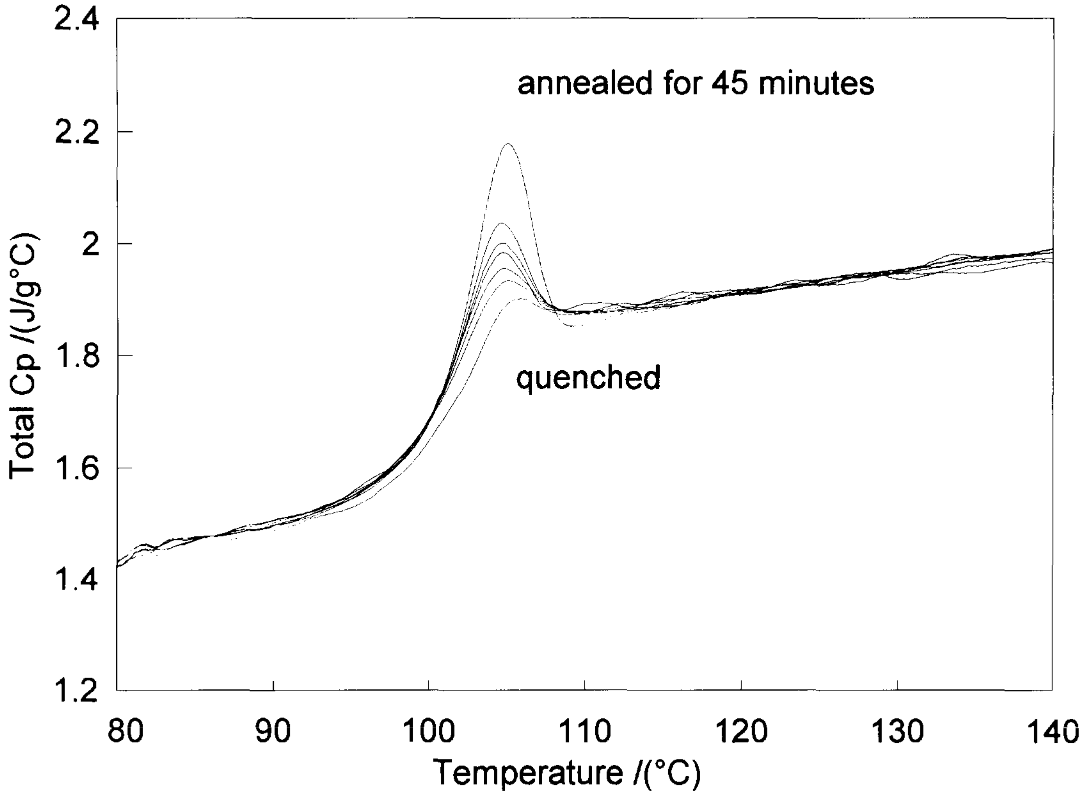

Fig. 1. Total heat capacity for a polystyrene sample quenched then annealed at 93°C for 0, 5, 10, 15, 20, 30 and 45 mins.

here that the relaxation time τ has Arrhenius dependence upon temperature, $\tau=\tau_g e^{E/RT}$, and that the activation energy is large ($E/RT_g \gg 1$). Our calculations can be extended to more complicated nonlinear rate laws. Using the alternative variable $\eta = \delta + T\,\Delta C_p =$ enthalpy − the glassy value (TC_{pg}), making approximations based on high activation energy, and taking T as in Eq. (2),

$$\begin{aligned}\frac{d\eta}{dt} &= \frac{e^{KT}}{\tau_0}(T\Delta C_p - \eta)\\ &= \frac{1}{\tau_0}\exp[Kbt + KB\sin\omega t]\\ &\quad\times(bt\Delta C_p + B\Delta C_p\sin\omega t - \eta).\end{aligned} \tag{21}$$

Here $\tau_0 = \tau_g e^{KT_g} e^{E/RT_g} = \tau_g e^{2KT_g}, K = E/RT_g^2$, and $\tau_g Eb/RT_{g^2} = \exp(-E/RT_g)$. ($T_g$ is the (underlying) glass-transition temperature for the rate b.)

As usual the amplitude B is taken to be small enough for us to linearize and the frequency is sufficiently high for there to be many oscillations during transitions. It is then convenient to write $\eta = \bar{\eta} + BRe\{\hat{\eta}e^{i\omega t}\}$ where: $\bar{\eta}$ is the underlying part of η and satisfies

$$\frac{d\bar{\eta}}{dt} = \frac{e^{Kbt}}{\tau_0} + (bt\Delta C_p - \bar{\eta}); \tag{22}$$

$\hat{\eta}$ is the "complex amplitude" (it gives the amplitude and phase of the cyclic part of η) and, since it is assumed to vary over the time scale of the transition, i.e. slowly compared with sin ωt, is given, approximately, by

$$\begin{aligned}i\omega\hat{\eta}e^{i\omega t} &= \frac{e^{Kbt}}{\tau_0}[K(bt\Delta C_p - \bar{\eta}) + \Delta C_p]e^{i\omega t}\\ &\quad - \frac{e^{Kbt}}{\tau_0}\hat{\eta}e^{i\omega t}.\end{aligned} \tag{23}$$

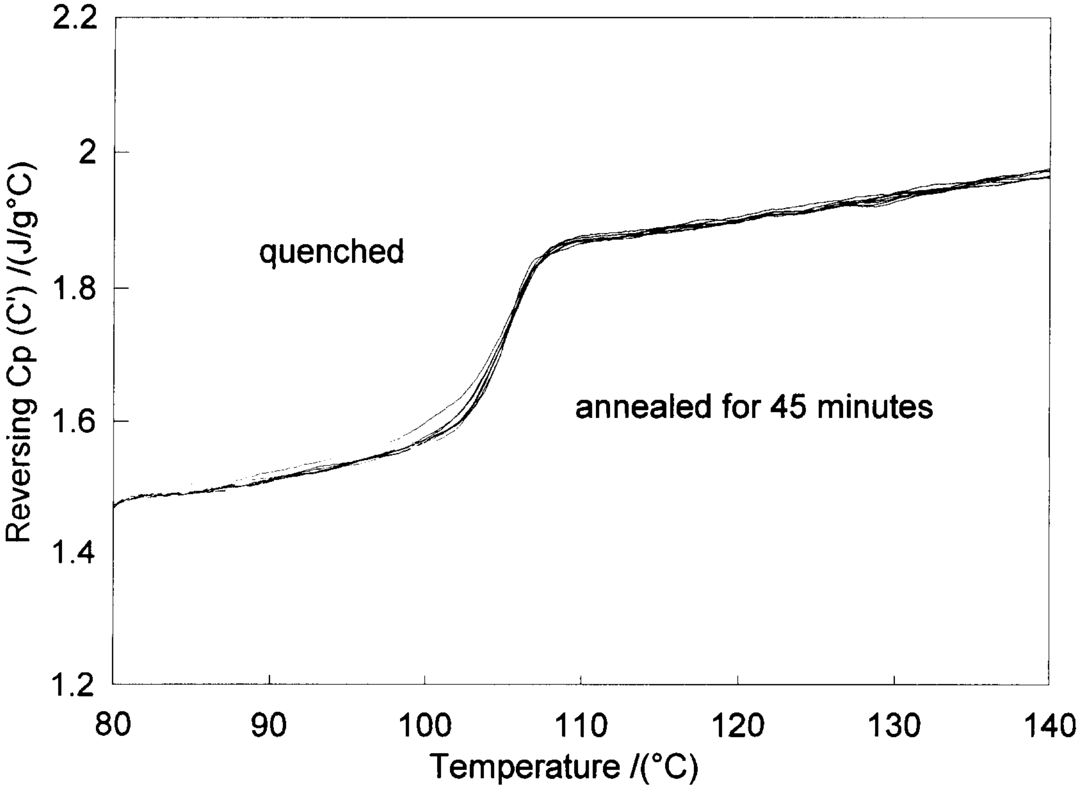

Fig. 2. Reversing heat capacity (=C′) for a polystyrene sample quenched then annealed at 93°C for 0, 5, 10, 30 and 45 mins.

Then

$$\bar{\eta} = A\exp\left[-\frac{e^{Kbt}}{Kb\tau_0}\right] + bt\Delta C_\mathrm{p} - b\Delta C_\mathrm{p} \times \exp\left[-\frac{e^{Kbt}}{Kb\tau_0}\right]\int_0^t \exp\left[\frac{e^{Kb\tilde{t}}}{Kb\tau_0}\right]\mathrm{d}\tilde{t} \tag{24}$$

and

$$\hat{\eta} = i[K(\bar{\eta} - bt\Delta C_\mathrm{p}) - \Delta C_\mathrm{p}]/\left[1 + i\omega\tau_0 e^{-Kbt}\right]. \tag{25}$$

The constant A is a measure of initial enthalpy and is related to previous annealing (it decreases with longer annealing). In the first of these expressions we should note that $\tau_0 Kb = e^{KT_\mathrm{g}}$ and $KT_\mathrm{g} \gg 1$ so $e^{Kbt}/Kb\tau_0$ is very small before the (underlying) glass transition and very large after it. This indicates that $\bar{\eta} \simeq A$ before the transition and $\bar{\eta} \simeq bt\Delta C_p/ - (\Delta C_p/K)e^{-Kbt}$ afterwards.

In the second expression we see that the denominator is initially dominated by $\omega\tau_0 e^{-Kbt}$ and later by 1. The change occurs where $\omega\tau_0 e^{-Kbt}$ is of order 1. But we have been assuming that the frequency is large, in relation to the relevant time scale, here $1/Kb$, i.e. $\gg Kb$ and the "cyclic transition" takes place much later than the underlying one. By this time $K(\bar{\eta} - bt\Delta C_\mathrm{p}) \simeq \Delta C_\mathrm{p} e^{-Kbt} \ll \Delta C_\mathrm{p}$ so $\hat{\eta}$ changes to $-i\Delta C_\mathrm{p}$ from something very much smaller.

Of course we are really interested in the signal, e.g. Eq. (10). Since $\frac{\mathrm{d}Q}{\mathrm{d}t} = C_\mathrm{pg}\frac{\mathrm{d}T}{\mathrm{d}t} + \frac{\mathrm{d}\eta}{\mathrm{d}t}$, we find that the underlying signal is

$$bC_\mathrm{pb} + \bar{f} = bC_\mathrm{pg} + \frac{d\bar{\eta}}{dt} \tag{26}$$

while the cyclic signal is

$$\begin{aligned} &B\omega C_{\mathrm{p}\omega}\cos\omega t + C\sin\omega t \\ &\quad = \omega B[(C_\mathrm{pg} - Im\{\hat{\eta}\})\cos\omega t - Re\{\hat{\eta}\}\sin\omega t]. \end{aligned}$$

Before the underlying transition, $bC_\mathrm{pb} + \bar{f} = bC_\mathrm{pg}$, and after it, $bC_\mathrm{pb} + \bar{f} = bC_\mathrm{pl}$. In the transition it is

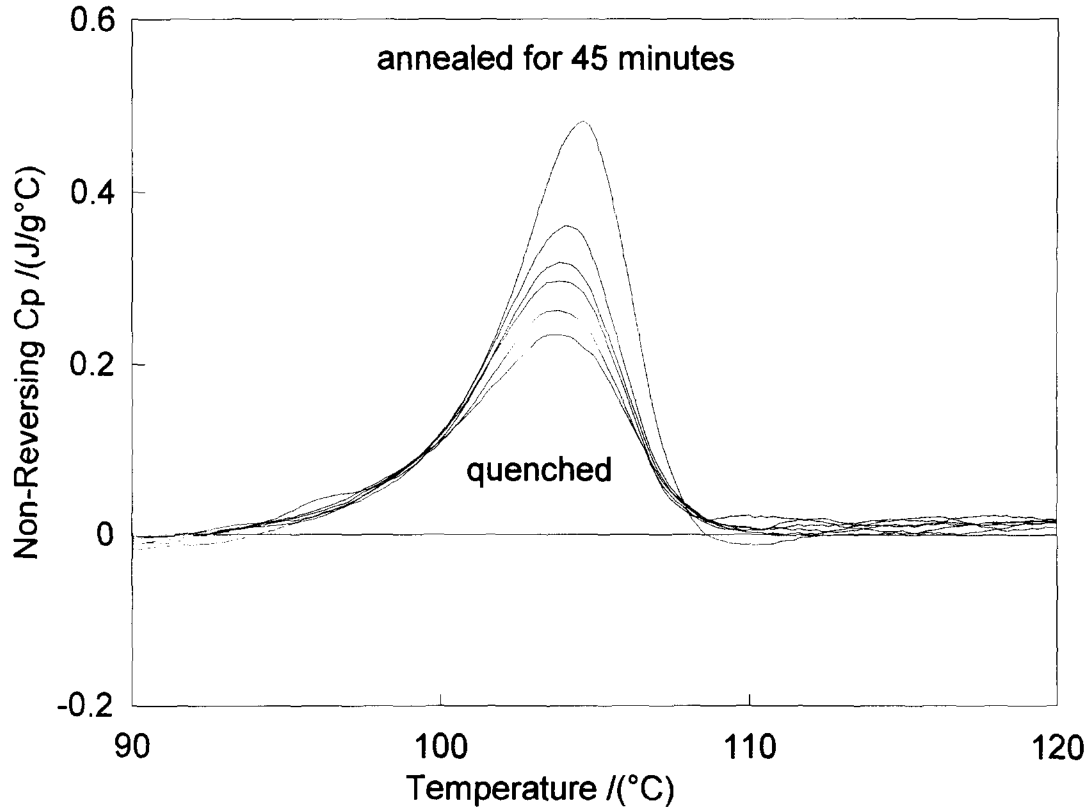

Fig. 3. Kinetic heat capacity ($=C''$) for a polystyrene sample quenched then annealed at 93°C for 0, 5, 15, 20, 30 and 45 mins.

appropriate to make the change of time variable $t=\ln(Kb\tau_0)/Kb+s/Kb$, so that, from, Eq. (24), $\bar{\eta}$ can be written in terms of the dimensionless time s:

$$\bar{\eta} = A\exp(-e^{s})+\Delta C_{p}\ln(Kb\tau_0)/K+s(\Delta C_p/K) - (\Delta C_p/K)\exp(-e^{s})\int_{-\ln(Kb\tau_0)}^{s}\exp(e^{\tilde{s}})d\tilde{s}.$$

Then

$$\frac{d\bar{\eta}}{dt} = b\Delta C_p\left\{e^{s}\exp(-e^{s})\int_{0}^{s}\exp(e^{\tilde{s}})d\tilde{s} + \left[\int_{-\ln(Kb\tau_0)}^{0}\exp(e^{\tilde{s}})d\tilde{s}-\left(\frac{AK}{\Delta C_p}\right)\right]e^{s}\exp(-e^{s})\right\}.$$

It follows that the graph of $bC_{pg}+d\bar{\eta}/dt$ against t is simply that of

$$\bar{f}_s \equiv \left\{e^{s}\exp(-e^{s})\int_{0}^{s}\exp(e^{\tilde{s}})d\tilde{s}+\tilde{A}e^{s}\exp(-e^{s})\right\} \tag{28}$$

against s, subject to the changes of axes and scales: $bC_{pg}+d\bar{\eta}/dt=b(C_{pg}+\Delta C_p\bar{f}_s)$ and $t=(\ln(KB\tau_0)+s)/Kb$. The actual shape, as opposed to the scale ($1/Kb$ horizontally and $b\Delta C_p$ vertically) and position ($\ln(Kb\tau_0)/Kb$ horizontally and bC_{pg} vertically), only depends upon the dimensionless parameter $A=\int_{-\ln(Kb\tau_0)}^{0}\exp(e^{\tilde{s}})d\tilde{s}-\left(\frac{AK}{\Delta C_p}\right)$, which is seen to be crucially affected by the annealing through A.

With regard to the cyclic signal, the significant change occurs when $\omega\tau_0 e^{-Kbt}$ is of order one. i.e. in the "cyclic transition" $t=\ln(\omega\tau_0)/Kb+s/Kb$: the time varies logarithmically with frequency. The scale, $1/Kb$, is independent of frequency and the same as that for the underlying transition. Using this new dimensionless times, Eq. (25) reduces to

$$\hat{\eta} \simeq -i\Delta C_p/(1+ie^{-s})$$

and the cyclic signal is

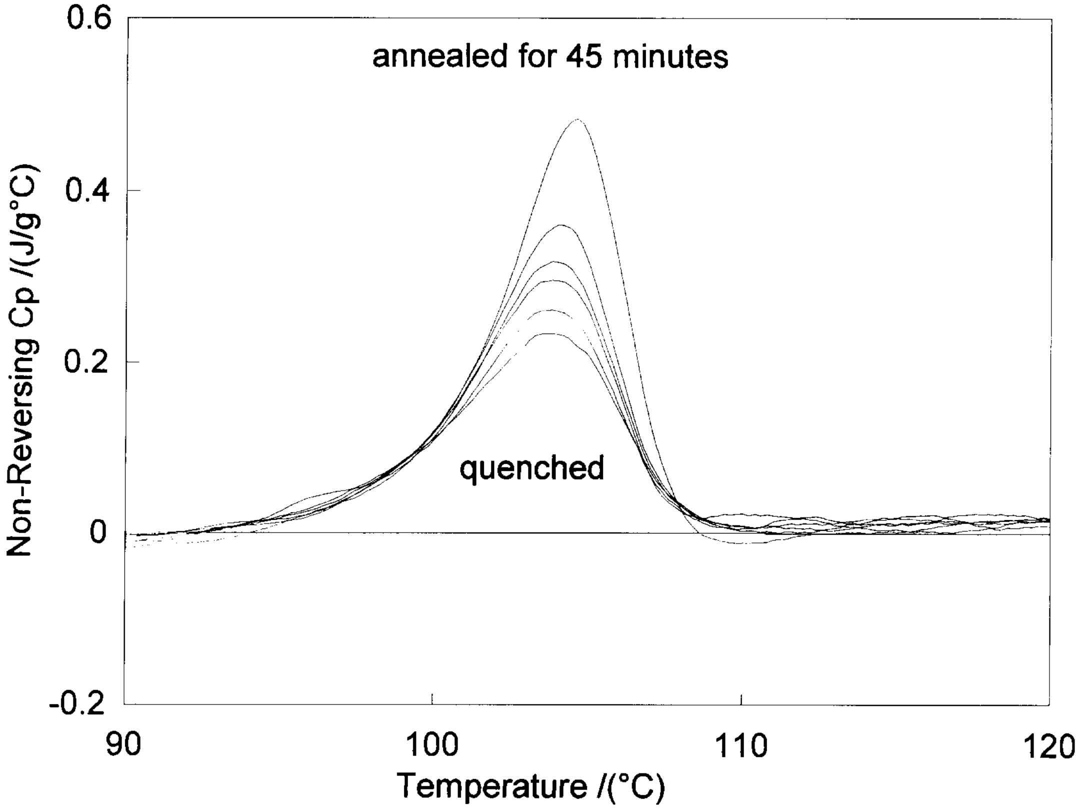

Fig. 4. Non-reversing heat capacity for a polystyrene sample quenched then annealed at 93°C for 0, 5, 10, 15, 20, 30 and 45 mins.

$$Re\{iB\omega(\hat{\eta} - C_{\mathrm{pg}})e^{i\omega t}\} \simeq B\omega Re\{e^{i\omega t}[C_{\mathrm{pg}} + \Delta C_{\mathrm{p}}(1 - ie^{-s})/(1 + e^{-2s})]\}.$$

It follows that the cyclic signal changes from $B\omega C_{\mathrm{pg}}$ cos ωt to $B\omega C_{\mathrm{pl}}$ cos ωt and the in-phase signal has a shape determined by $1/(1 + e^{-2s})$ in terms of the dimensionless time. The out-of-phase signal, $\omega B\,Re\{\hat{\eta}\}\sin\omega t \simeq B\omega\Delta C_{\mathrm{p}}[e^{-s}/(1 + e^{-2s})]\sin\omega t$, is insignificant away from the cyclic transition. There is of course a simple relation between the in-phase and out-of-phase signals (i.e. the real and imaginary heat capacities C' and C'': see [2] for a study of glycerol and propylene glycol). The shape and position of the cyclic transition do not depend upon the annealing. (Note that the cyclic signal is linear in B but depends nonlinearly upon frequency through the variation in position of this transition.)

It should be noted that the $C_{\mathrm{p}\omega}$ term $(= C_{\mathrm{pg}} - Im\{\hat{\eta}\})$ is reversible (again see [2]) and derived from molecular motions and thus corresponds to our definition of a reversing heat capacity. The C term $(= \omega BRe\{\hat{\eta}\})$ arises because the kinetic response of the sample is sufficiently fast for it to be detectable but is still too slow to keep pace with dT/dt, as it does above the transition. Therefore the C term is a function of the degree to which the sample response is kinetically hindered. We can observe that reducing A by increasing the annealing has the effect of enlarging the peak, corresponding to the e^{s} exp$(-e^{s})$ term, this is what is seen experimentally, as shown in Fig. 1 and Fig. 4. It can also be observed that this analysis predicts that the reversing and kinetic heat capacities remain unchanged by annealing and this, to a first approximation, is also what we see experimentally, as seen in Fig. 2 and Fig. 3. It follows from this that the non-reversing heat capacity is linearly related to the heat removed from the sample during annealing plus a contribution from the

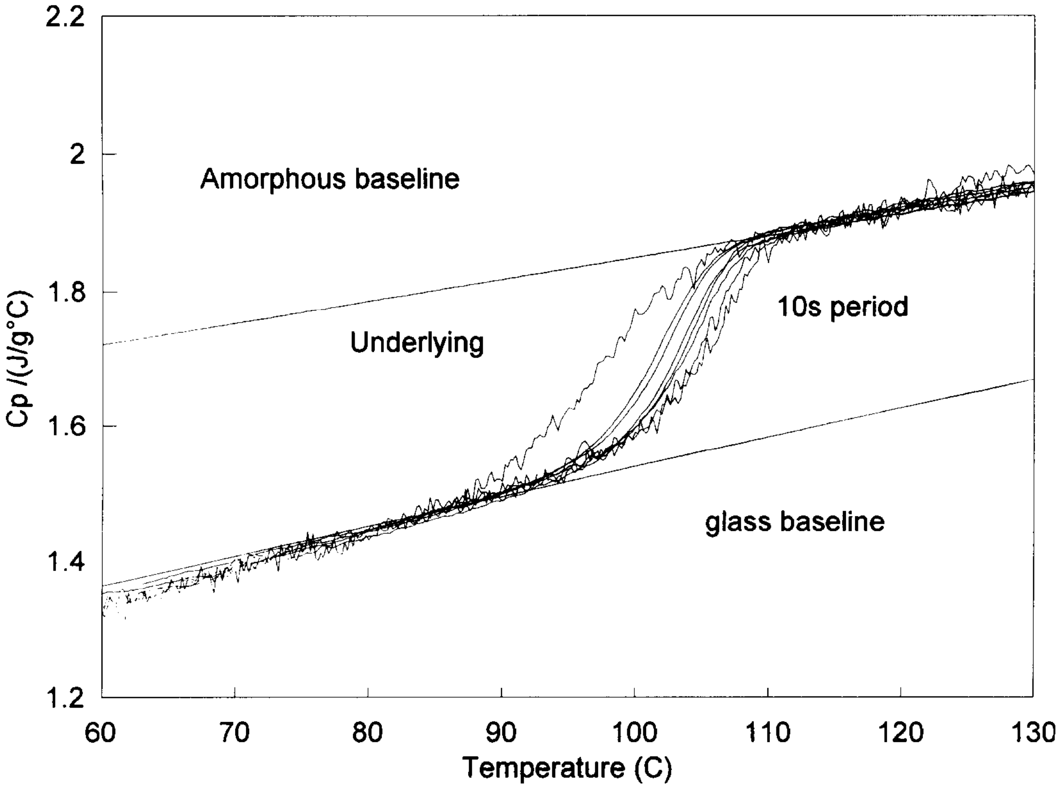

Fig. 5. Cyclic heat capacities ($=C''$ to an excellent approximation in all cases) for a polystyrene sample cooled at 1°C min using a 10, 15, 20, 30, 50, 70 and 100 s periods plus the underlying (=total) C_p averaged over the different experiments. The straight lines are from Wunderlich's ATHAS database for the glass and amorphous heat capacities of polystyrene.

different shape terms for the underlying and cyclic signals.

It has been suggested, [14], that our analysis cannot deal with time-dependent events such as glass transitions, clearly this is incorrect. It is also maintained in [14] that the non-reversing signal is "illogical" and contains no more information than that contained in the cyclic (complex) heat capacity. Our analysis shows this is also false. The non-reversing signal contains information on the enthalpy loss on annealing which is either not available from C' and C'' or is only present as a second-order effect. The difference in shape between the underlying and cyclic signals gives a non-reversing peak even on cooling which does not arise from enthalpy loss. The size of this non-reversing peak will change with changing modulation frequency and underlying heating rate. It gives a measure of the activation energy just as experiments at different frequencies can. This peak can, therefore, be interpreted in terms of there being a different effective frequency for the cyclic and underlying signals thus $C_{\mathrm{pb}} = h(C_{\mathrm{p}\omega}, b)$ and this effect can be treated as being in addition to that arising from annealing. Different types of equivalence can be proposed and we will comment further on this in a future article.

For the present it should be noted that when an irreversible process such as a chemical reaction occurs and the frequency is high, $C_{\mathrm{p}\omega}$ (= C_{c} to a good approximation) gives the sample's frequency-independent specific heat capacity while the non-reversing signal provides information about the irreversible reaction. At the glass transition the situation is more complex because $C_{\mathrm{p}\omega}$ (= C_{c} to a good approximation) is frequency dependent. However, the non-reversing signal provides information about annealing which is an irreversible phenomenon on the time scale of and at the temperature of the measurement. There is, therefore, an equivalence between the meaning of the non-

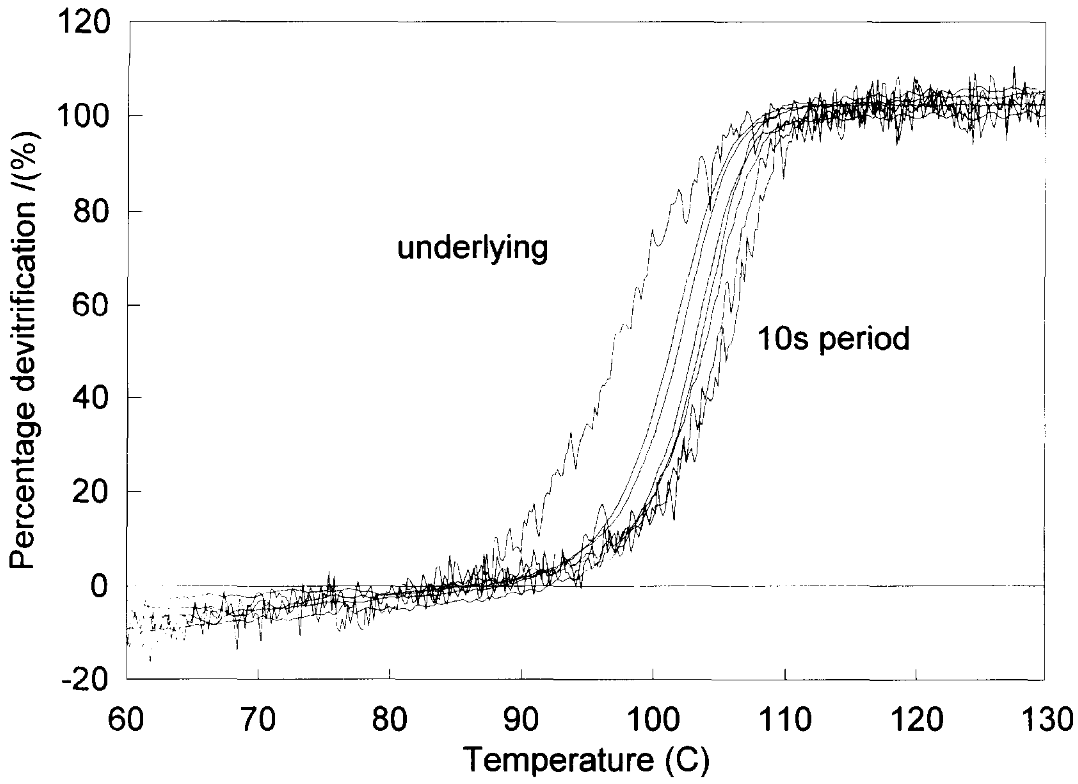

Fig. 6. The same information as shown in Fig. 5 expressed as percentage devitrification.

reversing signal in these two different types of measurement for highly annealed samples.

We finally note in this section that the approach of linearizing and separating into underlying and cyclic parts, allows us to treat rate laws which are more general than Eq. (21). Supposing instead that

$$\frac{\mathrm{d}\eta}{\mathrm{dt}} = g(\eta, T)$$

the same steps lead to, in place of Eq. (26) and Eq. (27),

$$bC_{\mathrm{pb}} + \bar{f} = bC_{\mathrm{pg}} + \bar{g}$$

and

$$B\omega C_{\mathrm{p}\omega}\cos\omega t + C\sin\omega t = \omega B[C_{\mathrm{pg}}\cos\omega t + \bar{g}_T(\omega\sin\omega t - \bar{g}_\eta\cos\omega t)/(\omega^2 + \bar{g}_\eta^2)]$$

for the underlying and cyclic signals. Here $\bar{g}_{\mathrm{T}}$ and $\bar{g}_\eta$ denote the averaged values of the derivatives of the rate g with respect to T and η.

7. Melting

When considering melting it is necessary to make an addition to the simple starting Eq. (1).

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = [C_{\mathrm{pt}} + g(t,T)]\frac{\mathrm{d}T}{\mathrm{d}t} + f(t,T). \qquad (29)$$

This introduces the possibility of a contribution to the heat flow that is proportional to dT/dt but is fundamentally different from that derived from C_{pt}. In an earlier study, [4], using the phase lag to investigate the in-and-out-of-phase response to the modulation in the melt region of PET, Reading et. al. observed that: "*if the crystallite melting temperatures have a distribution and they are able to melt rapidly without extensive superheating, something that would normally be true given their instability, then at least part of the signal will be in phase with dT/dt, as this determines the speed with which a fresh population of crystallites find*

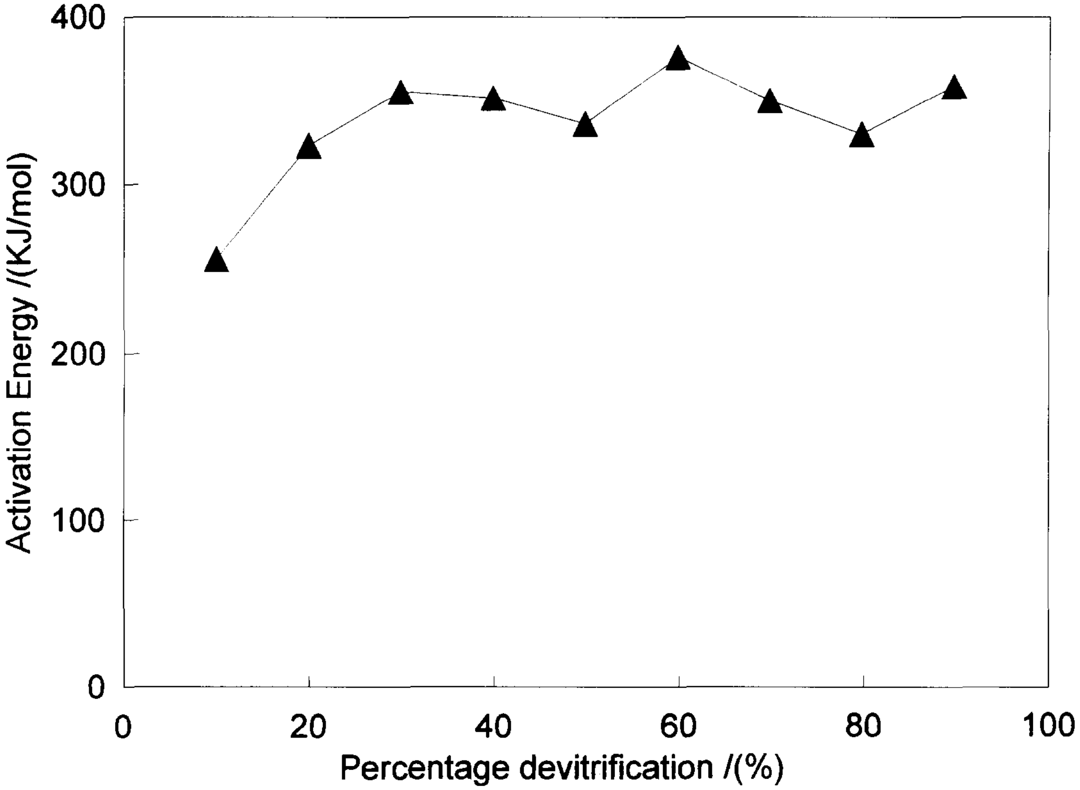

Fig. 7. Activation energies taken at different degrees of devitrification.

themselves at the melting temperature". This means that, when considering Eq. (17), there is a contribution to C' that is not from $C_{p\omega}$ and is not a reversing quantity as it derives from the latent heat of melting. Supercooling would usually prevent this additional quantity from reversing if the modulation cycle involves a cooling component (this has been demonstrated by Reading et. al. [10] using a method of analysis called parsing where the heating, cooling and reheating parts of the cycle are analysed separately). The picture becomes further complicated by the fact that melted material can participate in structural reorganisations within the sample thus an exothermic kinetic process is involved. In this way $g(t,T)$ "feeds into" $f(t,T)$. It is therefore convenient to define a composite kinetic function that includes all terms other that the reversing C_{pt} itself, viz:

$$f_2(t,T) = g(t,T)\frac{dT}{dt} + f(t,T). \tag{30}$$

Under modulated conditions

$$f_2(t,T) = \bar{f}_2(t,T) + D\sin\omega t + \omega BE\cos\omega t. \tag{31}$$

Eq. (10) would now become

$$\frac{dQ}{dt} = bC_{pb} + \bar{f}_2(t,T) \text{ (the underlying signal)} \tag{32}$$

$$+\omega B(C_{p\omega} + E)\cos\omega t + D\sin\omega t \text{ (the cyclic signal)}. \tag{33}$$

We can still use Eq. (17) except now $C' = C_{p\omega} + E$ and $C'' = D/\omega B$ thus the interpretation is different.

Although there has been some theoretical work to address the problem of melting behaviour under MTDSC conditions, [15], much remains to be done. There is also evidence that temperature gradients strongly affect the results obtained in the melt region thus this aspect of sample behaviour needs to be

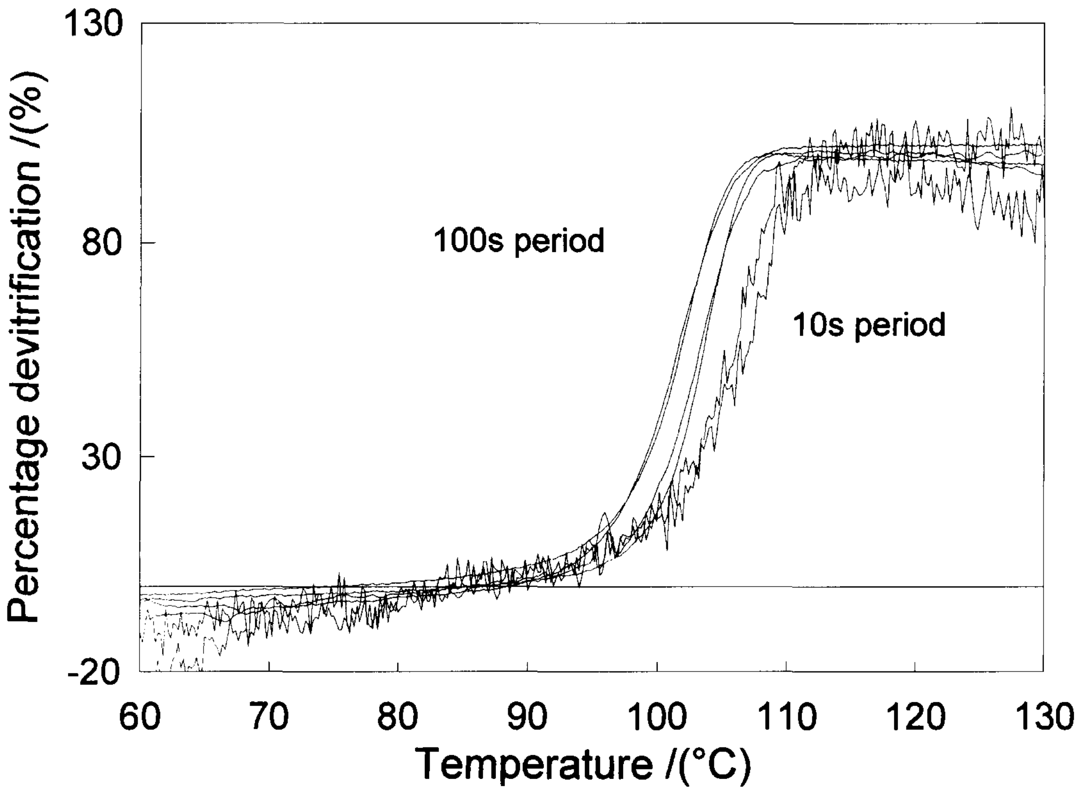

Fig. 8. Comparison of cyclic heat capacities ($=C''$ to an excellent approximation in all cases) for heating and cooling a polystyrene sample at 1°C min. at 10, 50 and 100 s periods.

addressed before a quantitative analysis of MTDSC results in the melt region can be undertaken.

Because the in-phase cyclic heat capacity ($= C'$) now no longer depends solely on $C_{p\omega}$ the calculation of the non-reversing signal given by Eq. (8) and Eq. (9) is no longer valid. However, the structural rearrangements that can occur during melting involve an exothermic process thus it has been observed that during the lower heating rate part of the cycle, exotherms occur that are balanced against endotherms during the higher heating rate segment of the modulation. This occurs as the dynamic equilibrium between the melt and crystalline phases oscillates back and forth. The result of this is that the C' appears very large thus the reversing signal does also, consequently the non-reversing signal appears exothermic. While this does not mean that there is a large net exotherm it does indicate the presence of an exothermic process during the cycle. Because conventional DSC often shows very little when this kind of reorganisation is taking place this characteristic behaviour of the non-reversing signal is a useful indication that it is occurring.

8. Conclusions

With the analysis of the glass transition presented here we have now provided a theoretical treatment of most of the aspects of MTDSC required for polymer studies. These include a theoretical analysis of heat flux calorimeters that supports the calibration methodology we have presented including the correction of instrumental effects when using the phase lag, [4], [15], see also [11] and [13], chemical reactions, crystallisation, melting and now the glass transition. Further work is required to deal with melting when combined with structural rearrangement and we will be publishing on this topic in the near future.

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