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Modulated differential scanning calorimetry

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Abstract

Modulated differential scanning calorimetry (MDSC) is a recently developed extension of DSC that adds a new dimension to the conventional approach. The usually linear temperature programme is modulated by a small perturbation, in this case a sine wave, and a mathematical treatment is applied to the resultant data to deconvolute the sample response to the perturbation from its response to the underlying heating programme. In this way the reversible (within the time scale of the perturbation) and irreversible nature of a thermal event can be probed. The advantages include disentangling overlapping phenomena, improving resolution and enhancing sensitivity. A further benefit is that metastable melting can be detected in cases where it is not normally observed. This new technique offers considerable scope for further development.

INTRODUCTION

Differential scanning calorimetry (DSC) is an invaluable technique in polymer science for studying glass transitions, reaction kinetics, melting behaviour, thermal history, degree of crystallinity and other aspects of polymer morphology. Modulated differential scanning calorimetry (MDSC) is a recently developed extension of DSC in which the usually linear or isothermal heating or cooling programme is modulated by some form of perturbation [1–4]. A mathematical treatment is then used to deconvolute the calorimetric response to the perturbation from the calorimetric response to the underlying temperature profile. The original idea was conceived and demonstrated by M. Reading. A practical automated instrument was then developed by M. Reading, B. Hahn and B. Crowe (Hahn and Crowe are from TA Instruments) [5]. Here we use a sinusoidal modulation and the deconvolution was carried out using a discrete Fourier transform method.

Either heat flux or power compensation instruments can be used for MDSC which can be achieved with no fundamental change to the conventional apparatus. The principle of its operation does not depend on

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any particular design of calorimeter provided it is able to accurately measure heats of reactions, latent heats, etc., even when used in a non-modulated mode.

THEORY

The response of an ideal DSC under conditions where no significant temperature gradients exist in the sample, is a combination of a signal that is dependent on the rate of change of temperature and one that is dependent on the value of the temperature. The former depends on heat capacity. In contrast, the rate of a thermally activated or kinetic process is determined by the temperature. A process of this type is often, thought not always, irreversible. Mathematically this can be expressed as

$$\mathrm{d}Q/\mathrm{d}t = C_{p,t}\,\mathrm{d}T/\mathrm{d}t + f(t, T) \tag{1}$$

Where Q is the amount of heat absorbed by the sample, $C_{p,t}$ is the thermodynamic heat capacity (defined here as that due to the energy stored in the vibrational, rotational and translational motions of the sample), T is the absolute temperature, t is time, and $f(t, T)$ is some function of time and temperature that governs the kinetic response of any physical or chemical transformation.

We have chosen the term thermodynamic heat capacity, here and in ref. 4, in order to convey that we are referring to some change in the energy of the sample that is not kinetically hindered and can, therefore, occur practically instantaneously. Clearly we are not wishing to suggest that there is something 'un-thermodynamic' about energy changes that arise from kinetically hindered processes.

Equation (1) is based on a somewhat idealised picture, but it serves as a first approximation model that does, as we shall see, enable us to interpret many of our results. The simplest case to consider is that of a linear macromolecule that is functinalised to allow it to undergo a cure reaction. If the sample is being heated from some low temperature at which no chemical reaction is occurring then the energy it absorbs as the temperature is increased is dictated by the heat capacity which is in turn determined mainly by the vibrational modes available to the sample. Wunderlich [6] has demonstrated such heat capacities can be calculated from approximate vibrational spectra. If we assume that, (a) the sample is sufficiently thin to avoid any significant temperature gradients occurring within it as it is heated and cooled, and (b) the rate at which heat is supplied to the sample is measured by a perfect device that responds instantaneously, then the rate of change of sample temperature multiplied by $C_{p,t}$ will perfectly match the rate of heat flow. The process of heat loss on cooling or heat gain on heating will be completely reversible and contain no hysteresis. This will be true regardless of the nature of the temperature programme.

When the temperature is increased the system will start curing. The energy flow due to the bond breaking and forming process of the cure reaction is fundamentally different from that due to the sample's thermodynamic heat capacity. The rate of this chemical reaction is governed by the fraction of molecules that have sufficient energy to overcome the activation barrier for the reaction which is, in turn, determined by the temperature at any instant. Furthermore, this process is completely irreversible. As the temperature of the sample increases and the rate of the chemical reaction increases correspondingly, both it and the thermodynamic heat capacity will contribute to the heat flow signal but they will respond in different ways to changes in the heating programme. Because of this, it is possible to separate out the two different contributions.

As mentioned above, in MDSC the temperature programme consists of an underlying trend that is modulated by a small perturbation. The underlying trend is usually the conventional linear temperature rise with time. Here we have used the simplest modulation to achieve in practice which is the superimposition of a sine wave. The temperature programme can be expressed as

$$\text{Temperature} = T_0 + bt + B\sin(\omega t) \qquad (2)$$

Where T_0 is the starting temperature, ω is the frequency, b is the heating rate and B is the amplitude of temperature modulation.

If we assume that the temperature modulation is small and that over the interval of the modulation the response of the rate of the kinetic process to temperature can be approximated as linear, we can rewrite eqn. (1) as

$$\mathrm{d}Q/\mathrm{d}t = C_{p,t}(b + B\omega\cos(\omega t)) + f'(t,T) + C\sin(\omega t) \qquad (3)$$

where $f'(t,T)$ is the average underlying kinetic function once the effect of the sine wave modulation has been subtracted, C is the amplitude of the kinetic response to the sine wave modulation and $(b + B\omega\cos(\omega t))$ is the measured quantity $\mathrm{d}T/\mathrm{d}t$. It may be thought that the assumption of a linear response for the kinetic process is inadvisable given the normally exponential relationship between reaction rate and $-1/T$. However, over a small temperature interval of a few tenths of a degree, this is a excellent approximation for most commonly encountered chemical reactions.

It can be seen from eqn. (3) that the heat flow signal will contain a cyclic component that will depend on the value of B, ω and C. Below we illustrate a method of separating this cyclic response of the sample from its response to the underlying heating rate and quantifying these two signals separately.

Another technique that is used to study responses to periodic temperature perturbations is AC calorimetry [7–9]. It consists of heating a sample in a cyclic manner using a controlled amount of electrical or electromagnetic energy and measuring the corresponding increase in temperature. Although the background temperature of the sample and measuring system is often ramped, to date these instruments have been designed and used to study the effects of the cyclic perturbation only, without taking any account of the underlying signal. Most often the heat source is placed on one side of the sample and the temperature sensor is on the opposite side. This approach can confer some advantages when investigating the cyclic response of liquid samples. However, this, and other features of their design, make them unsuitable for making quantitative measurements of heats of reaction, latent heats of melting, etc., even when a differential configuration is used (this is especially true when the sample changes it physical form during a transition, e.g. from a powder to a liquid). MDSC provides all the usual calorimetric information obtainable with conventional DSC and it is able to cope with changes in physical form. This makes it a more appropriate technique for studying polymer systems and irreversible phenomena generally.

The arguments presented so far do not account for sharp first order transitions. Under the ideal conditions posited above the melting of a pure metal would occur instantaneously and appear as a sharp spike that would not be affected by the temperature modulation (though recrystallisation might occur if the transition were reversible and the heating programme included periods when the heating rate was negative). However, real calorimeters cannot respond instantaneously and polymers rarely give sharp melting peaks. We have shown that the underlying signal from MDSC can give equivalent data to a conventional DSC for polymer melts [4], thus latent heats, etc., can be measured in the normal way. A qualitative interpretation of the cyclic signal obtained during polymer melting is given below. However, a full quantitative interpretation is not straightforward and must include some consideration of the non-ideal behaviour of the calorimeter cell. Work on this topic is being carried out in our laboratory and will be the subject of a future publication.

Clearly, real samples and real calorimeters do not conform to the idealised specifications given above. Similarly the distinction between heat flows arising from heat capacity and those arising from kinetic events is not as clear cut in many systems as it is in the example given. However, we have found this simple model provides a reasonable first approximation for many thermal transitions and leads to a method of analysis that yields considerable practical benefits [4].

EXPERIMENTAL

All of the following results were obtained on a TA Instruments DSC 2910 modified to allow the MDSC mode of operation. In all these experiments an underlying heating rate of 0.05°C s^{-1} was used with a modulation with a period of 50 s at an amplitude of 0.2°C controlled at the reference (this is currently a non-standard implementation). Wunderlich

[10] has observed that control of the reference is advantageous when studying melting behaviour as the sample temperature itself cannot be properly controlled.

The samples were all ICI poly(ethylene terepthalate) (PET) and were treated by heating the sample rapidly to 270°C in the DSC. The temperature was held for 10 min before the sample was removed and rapidly placed on a metal surface at room temperature. All of the heat capacity measurements, including the cyclic heat capacity (see below) were performed by first running an empty pan (mass about 15 mg), then a 60.638 mg sapphire standard, then the PET sample. The sapphire and PET runs were corrected for the empty pan offset and then the sample c_p was calculated by reference to the known c_p values for sapphire (these were fitted to a third order polynomial to provide a continuous reference over the whole temperature range). Sample pans were all flattened using a specially made steel former and lids were used but not crimped so that the same crucible could be used for the calibrations and PET runs.

RESULTS

Figure 1 shows the raw data for a MDSC response for a sample of quenched PET using an underlying heating rate of 0.5°C s^{-1}. The two basic measurements are the heat flow, shown in Fig. 1(a), and the phase lag, shown in Fig. 1(b). It should be noted that in the experiments presented here, the heating rate is never negative. This avoids possible asymmetries in the heat-flow response that might arise from supercooling. The deconvolution algorithm consists of an averaging process that effectively subtracts the effects of the modulation. When applied to the temperature programme and the heat-flow response the average signals can be plotted against each other as shown in Fig. 2. This process effectively reconstitutes the results that would have been obtained had a non-modulated experiment been performed. We refer to these outputs as the underlying heat flow and temperature. As mentioned above, we have found these curves to be virtually indistinguishable from traditional DSC results obtained at the same underlying heating rate provided the rate at which a transition occurs is not too rapid compared to the frequency of the perturbation [4]. A rough guide is that there should be at least six modulations over the course of any single thermal event.

A discrete Fourier transform (DFT) algorithm is then used to evaluate the magnitude of the cyclic component. The amplitude of the cyclic component of the temperature signal can be compared with that from the dQ/dt signal, thus enabling a value for heat capacity to be determined which we refer to as the cyclic C_p. It is important to realise that this cyclic measurement comprises a contribution from the thermodynamic heat capacity as defined above plus a contribution from any kinetic event, such

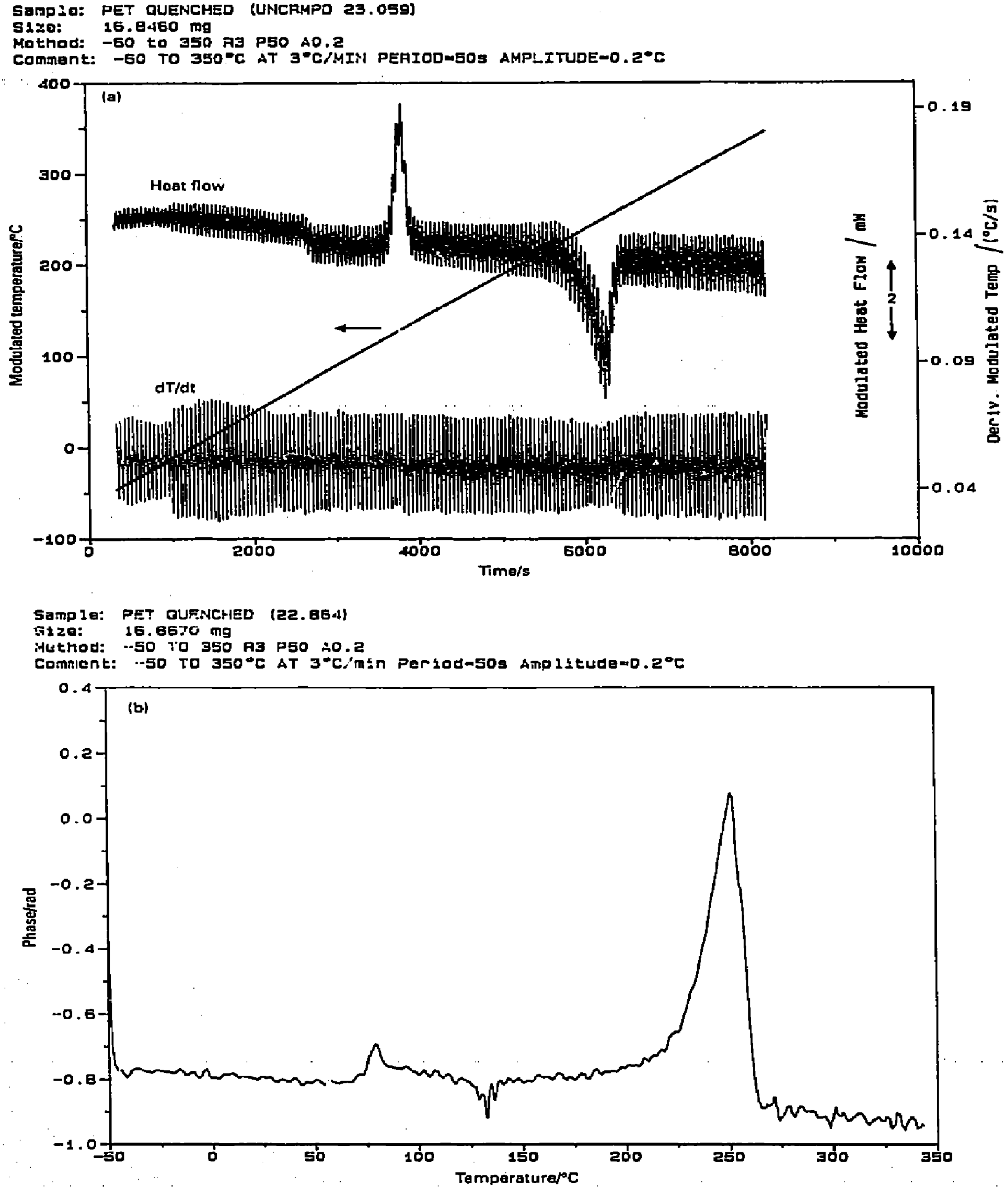

Fig. 1. Raw MDSC data for quenched PET. (a) Temperature, d*T*/d*t* and heat flow data (no baseline correction applied); endo. is downward and exo is upward. (b) The phase lag.

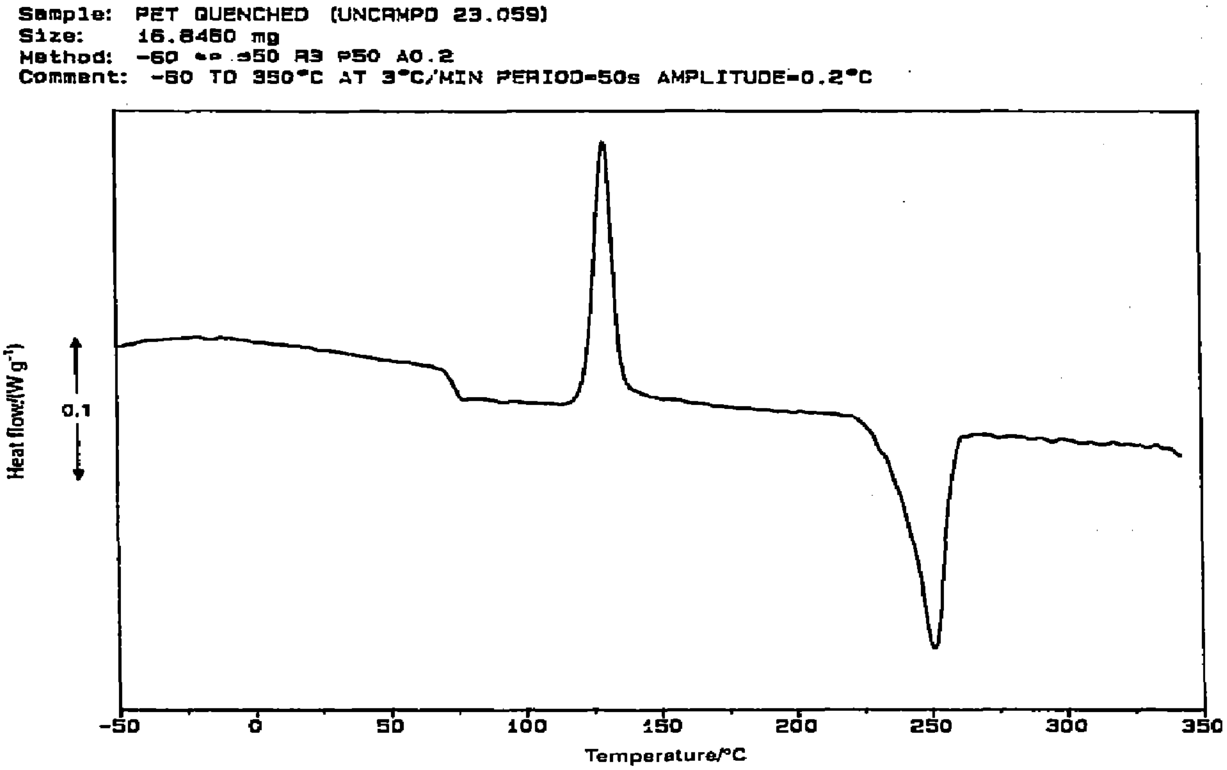

Fig. 2. Underlying heat flow (no baseline correction applied) vs. underlying temperature. Endo is downward and exo is upward.

as a cure reaction, arising from $C\sin(\omega t)$. A kinetic contribution can only occur when there is an enthalpic process (such as an exotherm from a crystallisation or cure reaction or an endotherm arising from a melting or a relaxation event) whereas the heat capacity contribution is always present. In principle the phase lag measurement could be used to separate the cyclic C_p into the in- and out-of-phase components of the response to the perturbation. However, before doing this, ways must be found of properly calibrating and testing this signal. We are currently working on this topic and this will be the subject of a future article. Here we use only the amplitude of the cyclic component of the heat flow to calculate an overall value for the cyclic heat capacity.

As stated above, the cosine wave ($C_{p,t}$) contribution is always present and is, in the case of the PET sample shown in Fig. 1(a), by far the major part of the cyclic component in the heat flow signal for all of the transitions except the melting. This can be seen by reference to Fig. 1(b) where the peaks in the phase lag seen at the T_g and the crystallisation are small; consequently the kinetic contribution must also be small. We have generally found this to be the case for all the polymer samples we have looked at when the amplitude of the modulation is a few tenths of a degree.

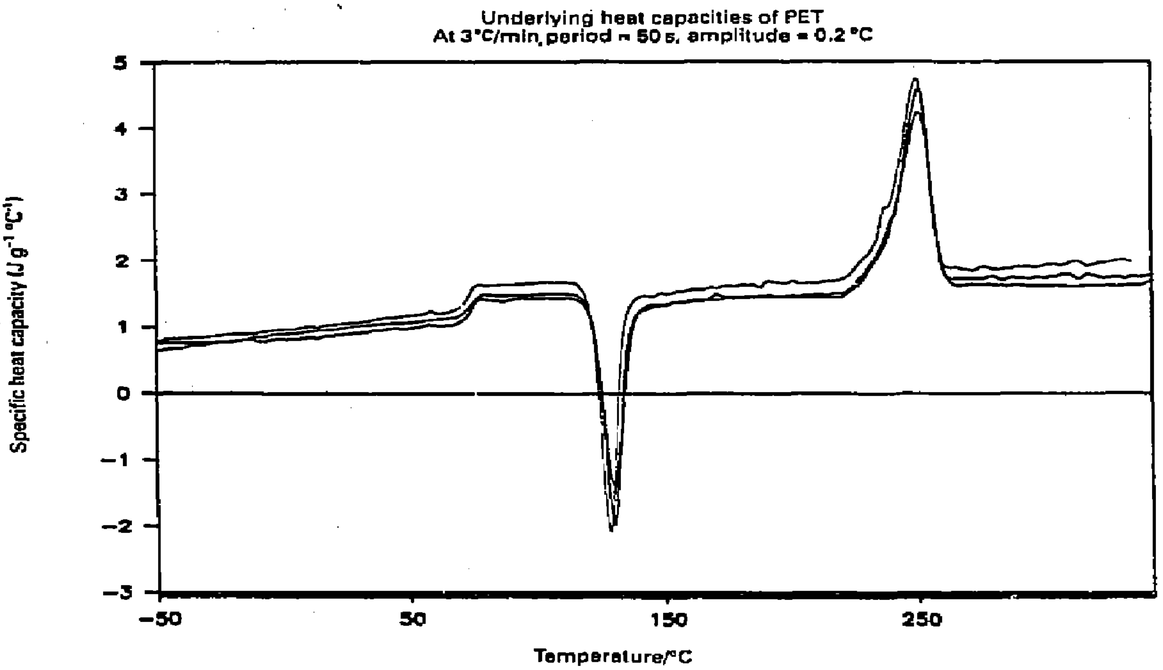

Fig. 3. Underlying c_p for PET from three independent MDSC experiments.

One way of presenting MDSC data is in terms of apparent specific heat capacity which we denote here as c_p. The underlying heat flow can be converted to this form simply by dividing by the underlying heating rate. Figure 3 gives the results expressed in this fashion for three independent experiments on PET. Figure 4 gives the corresponding cyclic heat capacity measurements. There are minor differences in the sizes of the peaks between the runs due to the difficulty of exactly duplicating the quenching conditions.

It is appropriate to make a few observations regarding the accuracy of the cyclic heat capacity values. Some very encouraging initial results [2, 4] led us to the conclusion that heat capacities could be measured from the cyclic component without even the need for empty pan corrections. It was observed that most of the empty pan curvature typically found even in modern instruments was expressed in the underlying signal but not in the cyclic signal and, in our first instrument, the deviation from zero for the cyclic measurement when using carefully matched pans was very small. As the number of MDSC cells has grown, further experience has shown that it is advisable to carry out a full calibration involving an empty pan and sapphire run if very accurate results are required. Furthermore, the thermal conductivity of the sample plays a far more important role in the cyclic measurement than in the underlying one and great care must be taken to ensure good thermal contact between the pan and the conducting plate. A lid must be used to ensure that the sample is completely

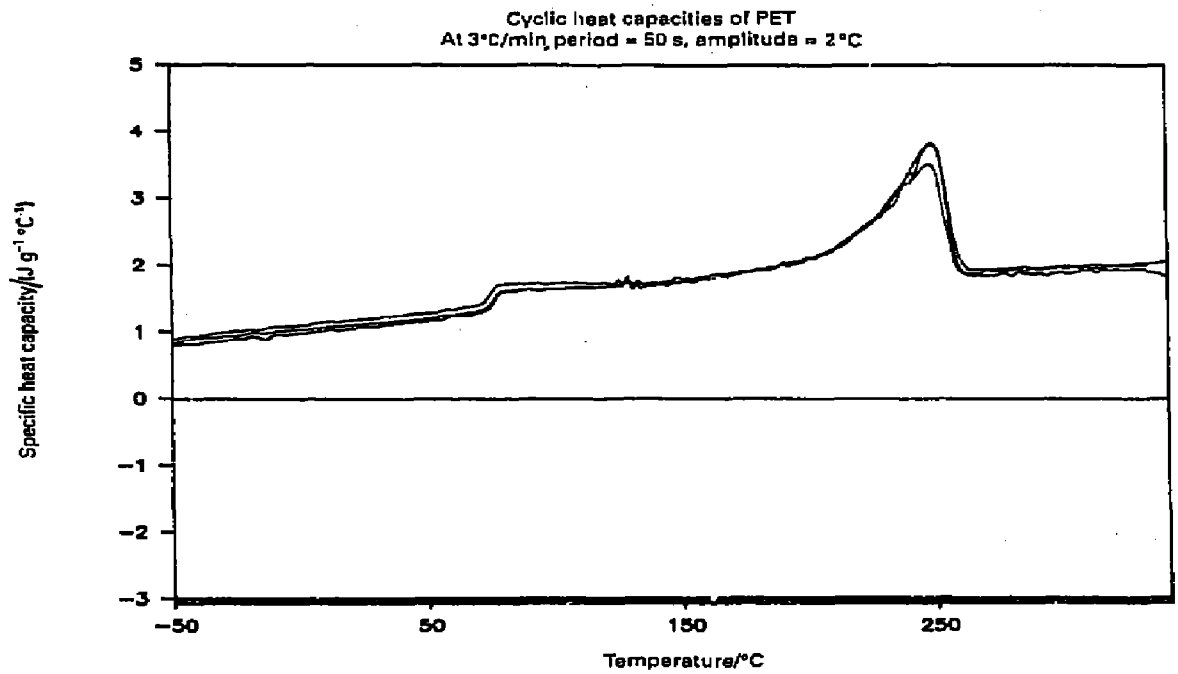

Fig. 4. Cyclic c_p for PET from three independent MDSC experiments.

surrounded by a good thermal conductor and samples must not be too thick. Further, work is required to optimise all the parameters including the underlying heating rate, the amplitude and period of the perturbation, the sample mass and configuration and the crucible type. We have found the parameters we have used here (see above) give acceptable results but better results will probably be achieved with further experience.

In Fig. 5 we have taken the average of the three experiments for both the underlying and cyclic C_p and coplotted them with the values for the amorphous and glassy C_p for PET taken from the ATHAS database [10] which provides carefully verified reference C_p data. It can be seen that there is reasonably good agreement between the literature values and the cyclic C_p below the glass transition and above the melting transition. The agreement with the underlying values is not as good but this is not surprising given the slowness for the heating rate. Much higher values are generally preferred for accurate measurements of C_p using conventional DSC (to which the underlying MDSC signal is equivalent). However, using a higher underlying heating rate would have degraded the quality of the cyclic data; thus a compromise has been reached. The underlying and cyclic C_p should be the same below the glass transition and above the melting transiton as no kinetic events are occurring. Following the procedures we have previously used [4], a linear baseline correction, shown in Fig. 5, has been applied to the underlying data to bring them into alignment with the cyclic values. These results are shown in Fig. 6 which also shows the difference between the two signals.

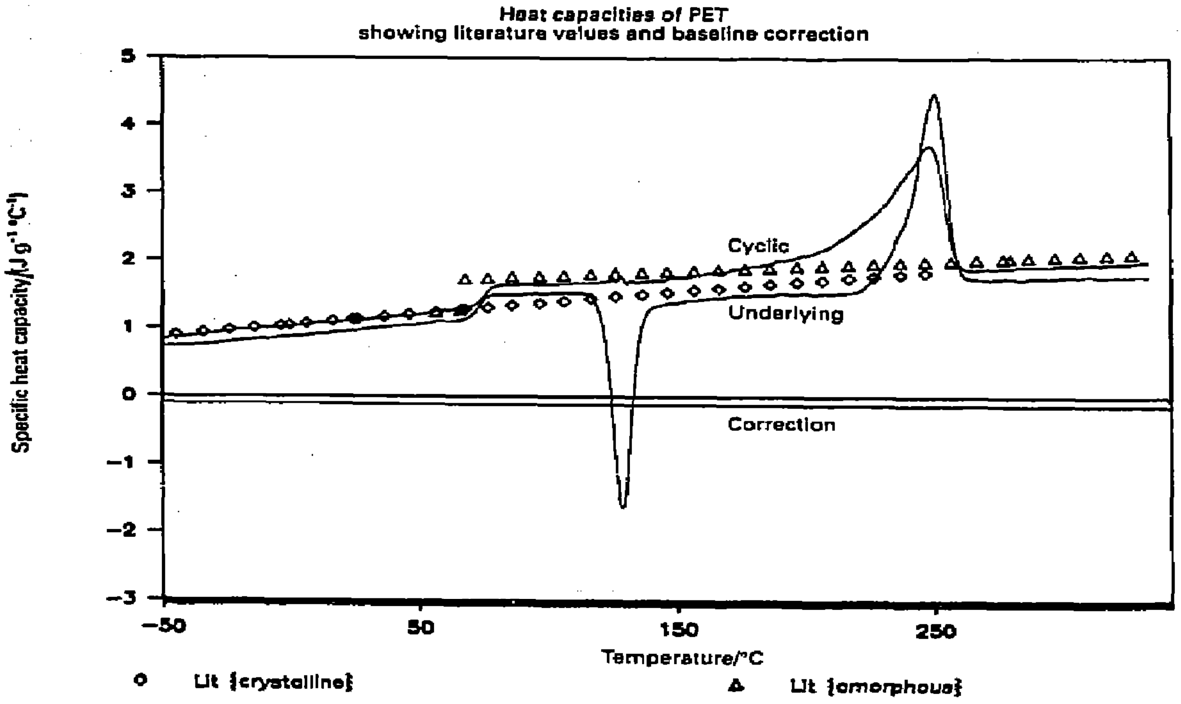

Fig. 5. Averaged results from Figs. 3 and 4 plus the literature values for the c_p of PET from the ATHAS database. Also shown is the baseline used to correct the underlying plot.

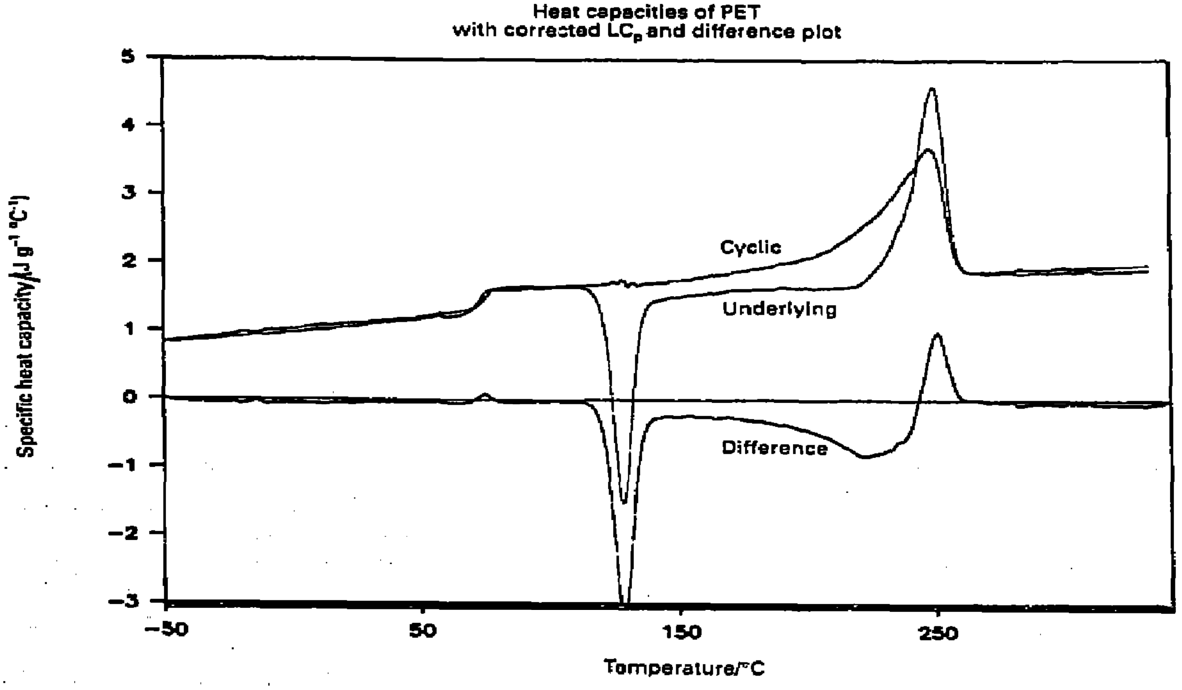

Fig. 6. Average cyclic c_p and baseline corrected average underlying c_p for PET plus the difference between these two curves.

Inspection of Fig. 6 gives rise to some interesting observations. Instantaneously (on the time scale of the modulation) reversible phenomena such as glass transitions appear in the cyclic measurement and in the underlying measurement but not in the difference plot. When the T_g occurs the difference plot appears to show a small relaxation endotherm. Simple irreversible (on the time/temperature scale of the modulation) kinetic events such as the crystallisation appear in the underlying measurement and in the difference signal but not in the cyclic data. This is intuitively satisfactory when one considers eqn. (3). The modulation of the temperature is comparatively small (of the order of tenths of a degree) whereas the modulation in heating rate is comparatively large, ranging from 0.5 to 5.5°C min^{-1}. Thus, for many kinetically controlled phenomena, C can be approximated to zero and the cyclic measurement 'sees' only the thermodynamic heat capacity. The melting event presents a complex mixture of thermodynamic and kinetic effects and appears in all three plots. These observations are in agreement with those made above with respect to the phase lag.

Another way of presenting the data is in terms of heat flow. This is achieved simply by multiplying the cyclic C_p by the underlying heating rate. The underlying signal is then termed the total heat flow, the cyclic signal is called the reversing heat flow and the difference is the non-reversing heat flow. These last two signals are illustrated in Fig. 7. MDSC has now been commercialised and this is the basic form of the data given by the current MDSC system manufactured by TA Instruments.

One feature that is apparent on inspection of Fig. 6 is that for the cyclic measurements the onset of the melting peak starts immediately after the cold recrystallisation. In PET it is known that a process of melting and subsequent recrystallisation occurs continuously from the point where a distribution of metastable crystallites is formed during the cold crystallisation event until complete melting occurs [6]. This is not clearly detected by conventional DSC but is revealed by the cyclic measurement of MDSC. This can be understood when the effect of heating rate on irreversible melting of this kind is considered. It is well known that changing the heating rate affects the balance between the melt and recrystallisation processes and consequently the amount of crystalline and amorphous material at any point in time [6]. It is, therefore, not surprising that the cyclic measurement, which spans many heating rates, gives a different answer from the underlying measurement which is equivalent to single heating rate. This type of behaviour is a powerful signature for metastable behaviour and equivalent results can only be obtained from conventional DSC by multiple experiments at different heating rates.

The practical benefits of MDSC compared to conventional DSC have been already been illustrated [4]. They include, (1) making interpretation clearer by defining an event as reversing (e.g. a glass transition) or

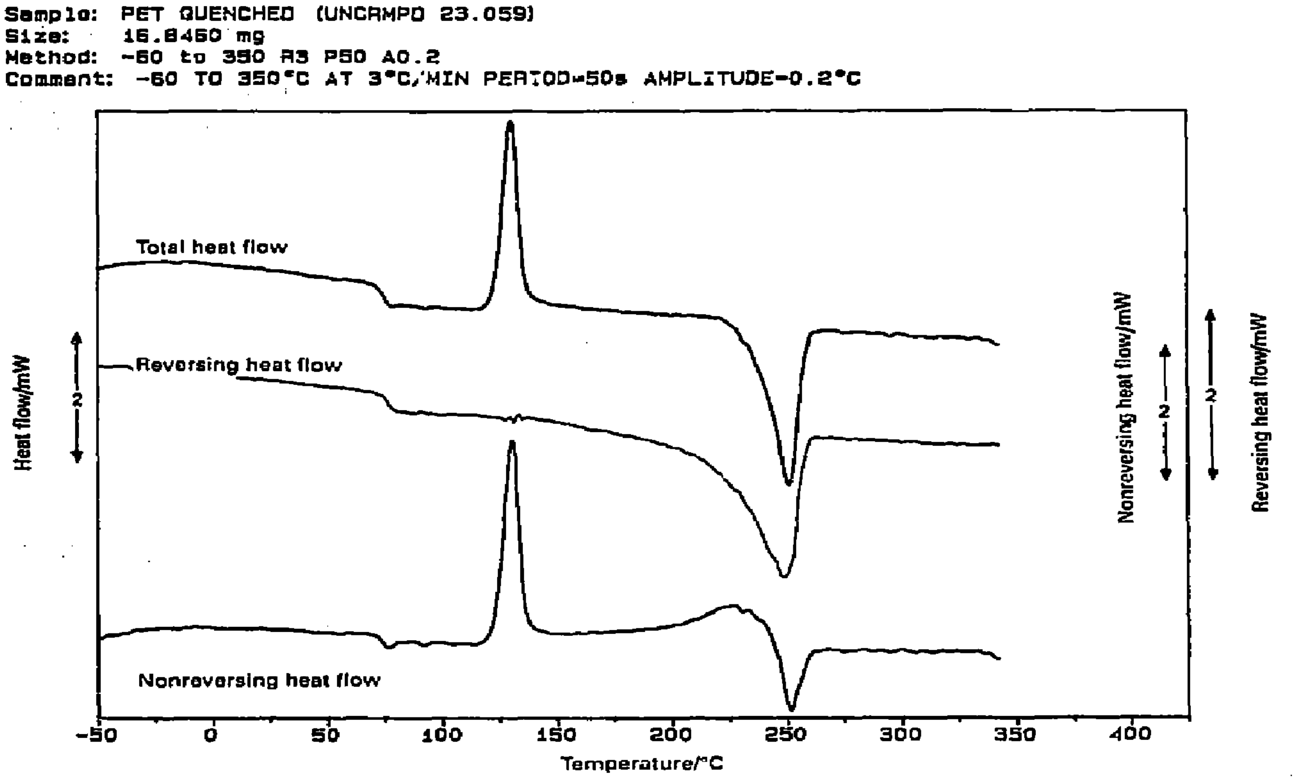

Fig. 7. Results from an MDSC experiment on quenched PET expressed in terms of heat flow (no baseline correction applied). Endo is downward and exo is upward.

non-reversing (e.g. loss of volatile material), (2) revealing hidden transitions by disentangling overlapping processes, (3) improving resolution for second order transitions by making changes in heat capacity easy to detect at low underlying heating rates, (4) improving the detection limit for changes in heat capacity, (5) detecting metastable behaviour, (6) making possible quasi-isothermal heat capacity measurements thus enabling, for example, vitrification under isothermal conditions to be studied.

Though further work must be done, there are some encouraging indications that MDSC will ultimately make possible more accurate measurements of heat capacity [11] and thermal conductivity [12]. There is even the interesting prospect of continuously measuring both of these quantities simultaneously as a function of temperature.

The current deconvolution methodology is very simple and leaves enormous scope for improvement. The key to progress is a proper understanding of how real calorimeters and samples behave when subjected to a cyclic perturbation. We are currently engaged in modelling and testing the behaviour of the heat-flux cell used by us as a first step to improving our deconvolution methodology. Beyond this there is the question of interpreting the results of frequency scanning experiments. At very low frequencies the cyclic response will contain information on the kinetics of any irreversible (or 'slowly reversible') process occurring. As the frequency is increased the signal will become dominated by the thermodynamic heat capacity. As it is increased still further the sample's response will be determined by its thermal conductivity. By using MDSC concepts we have in prospect a considerable increase in the amount of information that can be obtained from scanning calorimetry and it may well become the preferred calorimetric technique for most polymer applications.

REFERENCES

1 M. Reading, D. Elliot and V.L. Hill, Proc. 9th ICTA Meeting, Hatfield, UK, August 1992; J. Therm. Anal., 40 (1993) 949–955.

2 P.S. Gill, S.R. Saurbrunn and M. Reading, Proc. 9th ICTA Meeting, Hatfield, UK, August 1992; J. Therm. Anal., 40 (1993) 931–939.

3 J.C. Seferis, I.M. Salin, P.S. Gill and M. Reading, Proc. Acad. Greece, 67 (1992) 311–346.

4 M. Reading, Trends Polym. Sci., 8(1) (1993) 248–253.

5 M. Reading, B. Hahn and B. Crowe, United States Patent 5,224,775, 1992.

6 B. Wunderlich, Thermal Analysis, Academic Press, Boston, 1990.

7 I. Hatta and A.J. Ikushima, J. Appl. Phys., 20(11) (1981) 1995–2011.

8 G.S. Dixon, S.G. Black, C.T. Butler and A.K. Jain, Anal. Biochem., 121 (1982) 55–61.

9 O.L. Mayorga, W.W. Osdol, J.L. Lacomba and E. Freire, Proc. Natl. Acad. Sci. USA, Biophysics, 85 (1988) 9514–9518.

10 B. Wunderlich, personal communication, 1992.

11 Y. Jin, A. Boller, and B. Wunderlich, Abstr. 22nd NATAS Conf., Denver, CO, 19–22 September 1993, pp. 56–64.

12 S.M. Marcus and R. Blaine, Abstr. 22nd NATAS Conf., Denver, CO, 19–22 September 1993, pp. 102–108.