High Heating Rate DSC

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ABSTRACT

The use of fast DSC heating rates has been reported in several laboratories. TA Instruments' Q Series[TM] DSC with Advanced Tzero™ Technology offers advantages for such experiments. Indium is analyzed to assess calorimetric performance, and polylactide is used to demonstrate the utility of fast rates to suppress crystallization. Tzero™ Technology eliminates most thermal lag related errors, and permits fast heating rates to be used as a practical technique.

INTRODUCTION

From the early days of thermal analysis, the accepted "standard" heating rate has been 10 ºC/min. Faster high heating rates increase the sensitivity and productivity, but do so at the expense of temperature resolution and accuracy. Also, high heating rates suppress kinetically hindered processes, such as crystallization, so that the thermodynamic properties of unstable materials may be investigated. Recently Mathot and co-workers have reported on a number of high heating rate polymer applications (1). In another example, gathering data to construct phase diagrams for polymorphic forms of a pharmaceutical compound is benefited by the use of fast heating rates to determine the transition temperatures of metastable forms.

One challenge with the use of high heating rates is that while the furnace may achieve a rapid rate, there is a finite time delay before the sample achieves the same rate. Even after that program rate is achieved, the temperature of the sample, the sample container, and parts of the DSC lag behind the furnace control temperature. The amount of thermal lag (*T-lag*) the sample experiences is described by Newton's Law of Cooling:

$$T\text{-}lag = R_0 \, dq/dt = R_0 \, (Cp \, m + Cp \, (pan) \, m(pan)) \; dT/dt \qquad (1)$$

Where: R_0 is the thermal resistance between the sample and sensor
dq/dt is the heat flow to the sample
Cp is the specific heat capacity
m is the mass, and
dT/dt is the heating rate experienced by the sample and pan

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The thermal lag is proportional to heating rate, sample and pan mass, sample and pan specific heat capacity and the thermal resistance between the sensor and the sample.

All other conditions being equal, the use of 100 °C/min heating rate produces a thermal lag 10 times greater than at 10 °C/min.

Of course, for a given set of conditions, calibration using a melting point standard may allow the sample temperature to be known even at a fast rate. However, there is uncertainty in the temperature measurement due to uncertainty in contact resistance (R_0) and in the heating rate experienced by the sample. Also, calibration at a particular heating rate does not always ensure temperature calibration at other heating rates even when a scanning rate dependency calibration has been established using an ideal material such as with indium.

Another problem is that different heating rates experienced by the sample and reference positions during transitions broaden and distort the DSC peak. These problems are greatly amplified by fast heating rates.

EXPERIMENTAL

The Q1000 DSC with its Advanced Tzero™ Technology provides a solution to these problems. Figure 1 is a schematic diagram of the Tzero DSC cell showing the positions of the sample and reference platforms and the Tzero sensor (*2*). It utilizes a new measurement principle employing an additional element on the DSC sensor that provides compensation for intrinsic instrument distortion of the DSC signal (*3*). The heat flow to the sample specimen is determined using the multiple term relationship given by Equation 2:

$$\dot{q} = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{dt} - C_r\frac{d\Delta T}{dt} \tag{2}$$

where
q = differential heat flow
ΔT = temperature difference between sample and reference
ΔT_o = temperature difference between sample and sensor base
R_s = sample sensor thermal resistance
R_r = reference sensor thermal resistance
C_s = sample sensor thermal capacitance
C_r = reference sensor thermal capacitance
dT_s/dt = sample temperature rate of change, and
$d\Delta T/dt$ = differential change in temperature.

The first term is the differential temperature signal used in traditional DSC instruments, the second and third terms are compensation for asymmetry in the resistance and thermal capacitance elements of the DSC cell, and the fourth term treats the differences in heating rate between the sample and reference sensors.

Equation 2 is a more general form of the heat flow equation used by other DSCs. It is derived from a model of the DSC cell that takes into account asymmetry in the cell construction, including asymmetry in the heat distribution in the cell caused by thermal effects from the presence of the sample on one side of the cell. A more complete instrumental calibration is performed to solve for the R and C cell parameters. The additional T_0 thermocouple is key to being able to perform this calibration and to compensate for asymmetry (*3*). Using this more complete derivation causes peak shapes to be less distorted from thermal lag, and temperature output is properly corrected for all

temperature gradients. No place is this more important than when using fast heating rates that produce large temperature gradients.

To illustrate these benefits, three samples are run for this evaluation; a 0.42 mg sample of indium metal calibration standard, a 0.31 mg sample of low density polyethylene (PE) sample and a milligram sample of polylactide (PL), a commonly used pharmaceutical excipient. The samples are placed in the bottom parts of standard aluminum DSC pans. To further reduce thermal lag, the pan mass was reduced by substituting a foil disk punched from aluminum wrap for the standard lid. After crimping, the pans are further flattened to improve thermal contact. Prior to each heating scan, the PE sample was cooled from above the melt to below –80 ºC using a nominal cooling rate of 20 ºC/min using the RCS mechanical refrigerator. This ensures that the sample is cooled at a known, constant cooling rate over the fusion temperature region.

RESULTS AND DISCUSSION

To obtain useful data, the DSC must quickly stabilize at the rapid heating rate. The Q Series DSC achieves substantially improved temperature control and equilibration from a redesign of its furnace/cooling system (3). Figure 2 shows the derivative of the sample temperature for fast heating rate analyses of indium. With Advanced Tzero Technology this heating rate is that of the sample pan and hence, the sample, for a small, well-coupled sample specimen, (not merely the heating rate of a control sensor, as is commonly displayed in some DSCs.) For precise temperature measurement, the temperature sensor must be as close to the sample as is physically possible without actually being in the sample (a necessary condition for heat flow measurements) (4). The temperature of the sample pan provided by Advanced Tzero Technology satisfies this condition. Figure 2 shows that heating rate equilibrium is achieved in about 30 seconds after starting the scan even without the use of exotic purge gasses or non-standard sample pans.

Useful heat flow data may be obtained only after the transient heat flow effects of switching from isothermal control to constant scanning control are dissipated. A steady state, straight, baseline needs to be achieved prior to the onset of the transition. A steady baseline indicates that the temperature gradients in the DSC cell have reached a steady state. But asymmetry in the cell manufacture delays the time required to reach a steady state. Because Tzero technology compensates for the cell asymmetry, the Q series DSCs quickly reach a straight baseline without subtracting empty-pan baseline data. Figure 3 contrasts the pre-melting baseline obtained from the Tzero-compensated circuit of the Q1000^{TM} DSC (T4P) with that obtained from the ΔT circuit from the traditional DSC (T1).

At a 100 ºC/min heating rate the temperature of the sample specimen and pan lags behind the temperature of the sensor surface up to 10 Celsius degrees, due to the thermal resistance between the pan and sensor. While temperature calibration may correct this potential error for a given set of conditions, this correction is only exact for the same pan type, weight of sample and scanning rate used for calibration. At rapid heating rates the uncertainty in the temperature of the sample specimen can easily reach several Celsius degrees.

Advanced Tzero Technology explicitly compensates for the temperature gradients in the DSC cell induced by the sample and pan heat capacity. Figures 3, 4 and 5 (the same data at different levels of scale expansion) show that the extrapolated onset of indium is independent of the heating rate (5).

The phase rule holds that when a pure sample undergoes a first order transition, the temperature of the sample remains constant. At scanning rates of 100 ºC/min or more, temperature gradients between the sample and DSC cell reach tens of Celsius degrees. This, in turn, creates temperature gradients within the DSC cell since only one side of the DSC is thermally restrained. These temperature gradients change the heating rate on one side of the DSC cell (Figure 2) distorting the peak shape, smearing it over a wider temperature range and diminishing the peak sharpness. The dashed lines of Figures 3 and 4 show the shape of the DSC peak using the T1 signal, the conventional ΔT signal used in DSC. Without correction to the data, analysis of this T1 signal leads to errors in the assessment of the sample characteristics.

Again, Advanced Tzero Technology compensates for this effect is shown in Figure 4 and 5 in the indium T4P data. ("T4P" means pan considered four term heat flow equation data.) The data in Figure 5 indicates that the accuracy possible with fast rate DSC analysis using the Q Series is as good as a $\pm$ 0.2 °C and a few percent in the energy of melting in going from 50 to 150 °C/min. Moreover, the integrity of the peak shape is clear, while the peak shape for the conventional DSC output is clearly distorted.

One of the applications for fast scan DSC is the rapid characterization of small quantities of polymer blends and copolymers produced by "shotgun" synthesis techniques, such as combinatorial analysis. To evaluate this rapid characterization technique, a sample of low-density polyethylene (PE), displaying both broad and sharp melting regions, was analyzed at rapid heating rates after imposing a controlled thermal history. Figure 6 shows the analysis of the peak maximum, onset and energy are independent of scan rate. This indicates that the Tzero signal is properly compensating for the thermal lag permitting the operator to choose which heating rate to use for the analysis.

For easy comparison of data obtained at different heating rates, it is convenient to display results in heat capacity units. This is possible due to the DSC cell balancing effect of the Tzero capability and is shown in Figure 7. One of the unique characteristics of the Q1000 with Advanced Tzero Technology is that the displacement from zero is proportional to the scanning rate. Thus, by dividing by the scanning rate (and sample weight), the sample specific heat capacity is directly obtained. The Q1000 offers the specific heat capacity as one of the choices of output signal, and any data from a weighed sample can be displayed in specific heat capacity units, without subtracting empty pan baseline data. Figure 8 shows the PE data taken at 50, 75 100 and 150 ºC/min in heat capacity units. It is clear that the temperature distribution of melting is the same at these rates, and that temperature dependent crystallinity could equally well be obtained from any of these curves. This also indicates that there is very little crystallization occurring on heating at any of these rates.

One potential use of the fast rate DSC is in characterizing systems in metastable states. For example, when an unstable amorphous material is heated at normal DSC rates crystallization begins above the glass transition and is followed by the crystalline melt. Amorphous polyethylene terephthalate (PET), such as used in PET bottle performs, is a familiar example. When such an amorphous material is heated at rates above 100ºC/min there is little or no crystallization that occurs before the temperature of the specimen is above the normal melting range. By suppressing crystallization, low levels of crystallinity can be more accurately measured, and the DSC analysis gives a more accurate characterization

To demonstrate this capability a sample of polylactide was repeatedly put into an amorphous state, and then run at a series of heating rates. From Figure 8 it can be seen that at 10ºC/min the polylactide crystallizes, and then melts; whereas at 100 or 150ºC/min

there is no apparent crystallization and very little melting. This behavior can also be observed with PET. However, other materials crystallize so rapidly above Tg that these rates, and higher, are still insufficient to suppress crystallization.

In this analysis the polylactide specimen was put into an amorphous state by ballistic cooling in the DSC using a refrigerated cooling system (RCS) to cool the DSC cell. For other materials it is necessary to quench cool more vigorously by manually removing the sample from the DSC cell above the melt and placing it on a room temperature surface. Alternatively, this quenching step may be carried out automatically by using the Q Series autosampler to remove the encapsulated sample at a temperature above the melt and place it in the room temperature autosampler. It can then re-load the sample into the DSC cell at a temperature below Tg where it can be cooled to the subambient and analyzed at a rapid scan rate. This is similar to the manually manipulated procedure illustrated by the data above.

Another cooling option for placing the samples in a metastable state is that of using a constant programmed cooling rate to give a more specified thermal history. For this application a cooling rate of 100°C/min is achievable over the necessary temperature range with the liquid nitrogen cooling accessory.

Some experimentalists suggest that data is improved by the use of neon-helium mixture purge gas, foil encapsulation and thermally conductive grease to improve the coupling of the sample pan to the DSC (*1*). These procedures may indeed help, but they each have drawbacks and it is clear that they are not necessary when using Advanced Tzero Technology. Moreover the procedures used in this work are compatible with an autosampler recommended for high throughput operation. The data shows that rates up to 150 °C/min can be used. However, experience shows that unless there is a real need for this fast rate, heating rates of 100 °C/min or less are adequate. Rates faster than 100 ºC/min increase the likelihood of errors related to encapsulation, such as sample swelling which may change the value of R_0 in Equation 1 thus leading to baseline artifacts.

One additional feature of the TA Advantage instrumentation control is the availability of user-selected heater control PID values to optimize the heater control for each type of method segment. This feature is used here to optimize performance for the high heating rates. Because of the demanding conditions required by fast rate DSC, the default PID values were replaced by user-selected values that optimized scanning equilibration (*6*). This is achieved experimentally with a simple addition to the DSC method that specifies the desired PID values shown in Figure 9 (*3*).

SUMMARY

High heating rates, rapid temperature equilibrium, invariant temperature calibration with changing heating rate are proven to be practical with the use of Advanced Tzero Technology

Advanced Tzero Technology provides automatic compensation for thermal lag effects that are a major source of error in fast rate DSC. The use of the Q1000 with Tzero Technology, together with careful standard encapsulation, is shown to allow exceptional data to be obtained at heating rates of up to 150 ºC/min--without the need to use operator-intensive, foil-and-grease techniques.

REFERENCES

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KEYWORDS

differential scanning calorimetry, metals, polyolefins, thermoplastic polymers
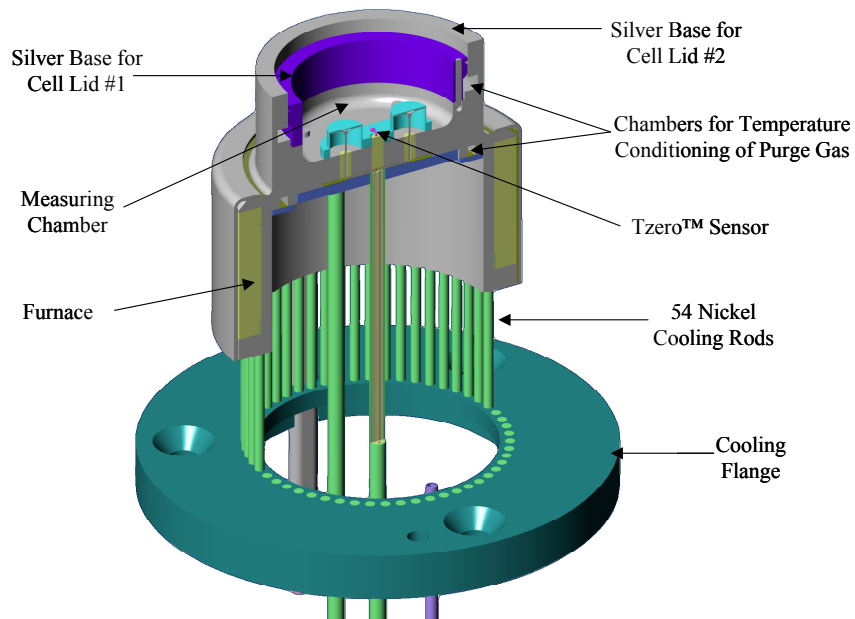
Figure 1 – Q Series DSC Cell
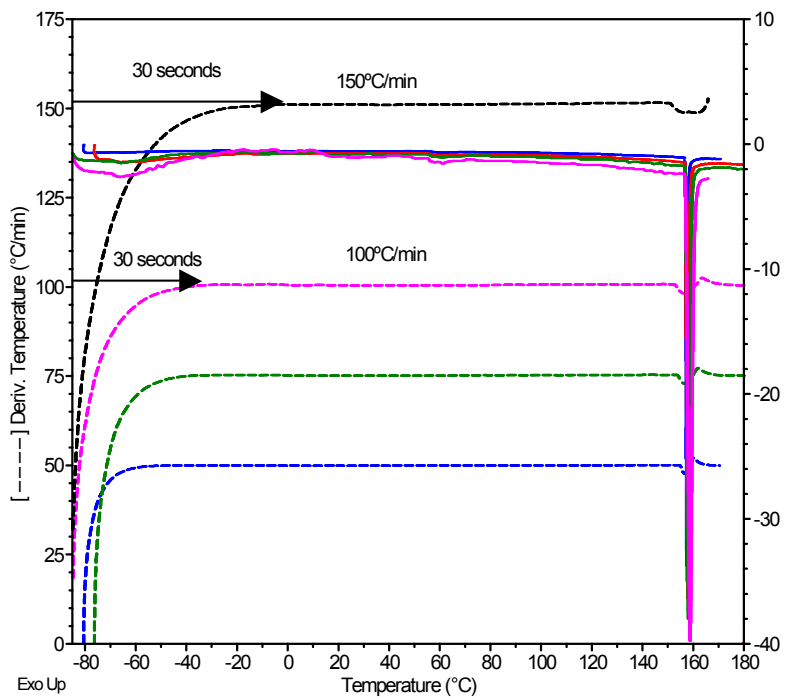
Figure 2 - Indium Melting at 50, 75, 100 and 150 ºC/min.
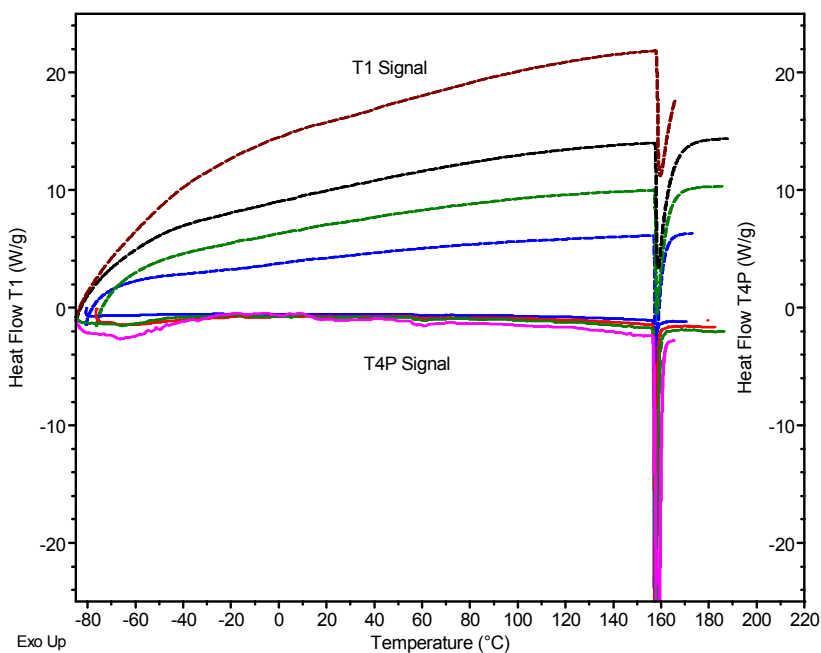Broken lines are heating rate *at the sample*

Figure 3 - Melting Indium at 50, 75, 100 and 150 ºC/min
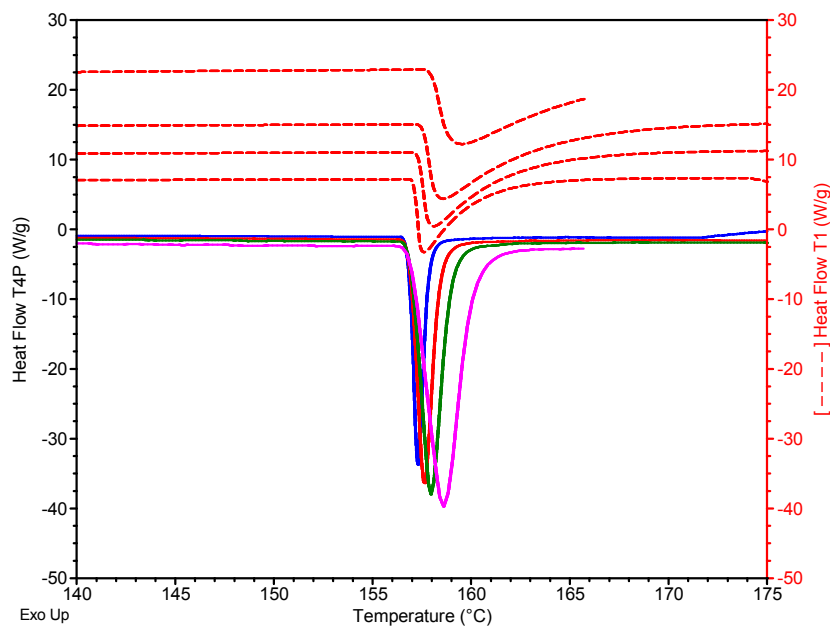with (T4P) and Without (T1) Advanced Tzero Capability.

Figure 4. Melting indium at 50, 75, 100 and 150ºC/min showing the
output of the Advanced Tzero signals and the conventional ΔT signals
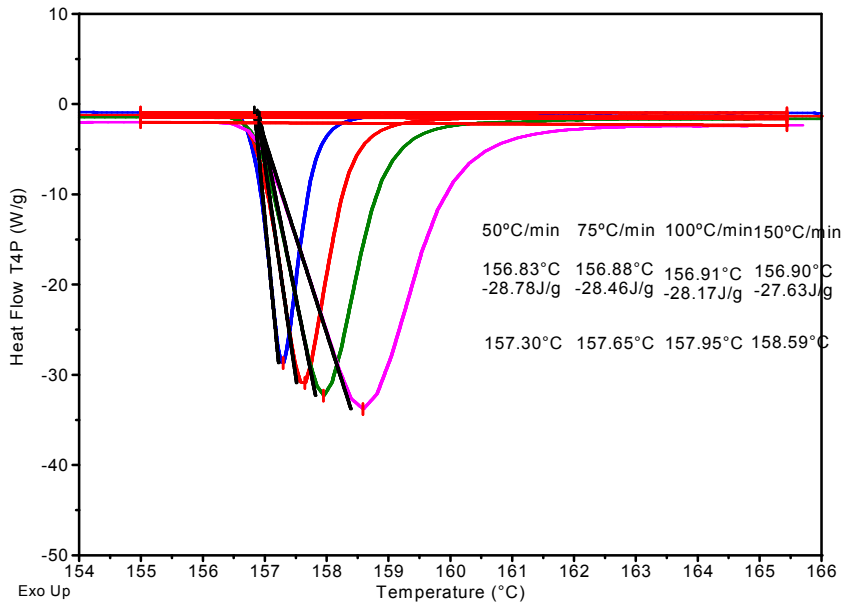(broken lines) at an expanded scale

Figure 5 - Melting Indium at 50, 75, 100 and 150 ºC/min
showing onset, energy and peak max calculations
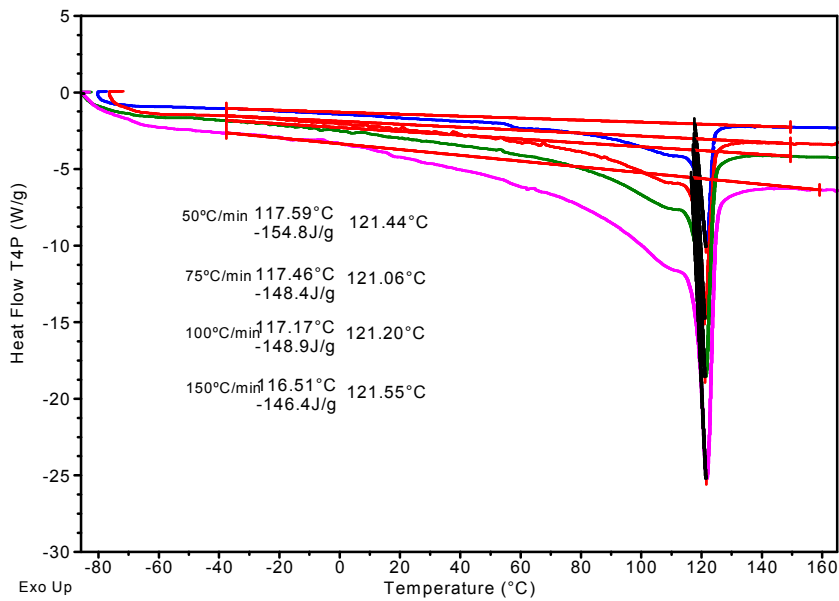
Figure 6 - T4P Heat Flow data for PE at heating rates from
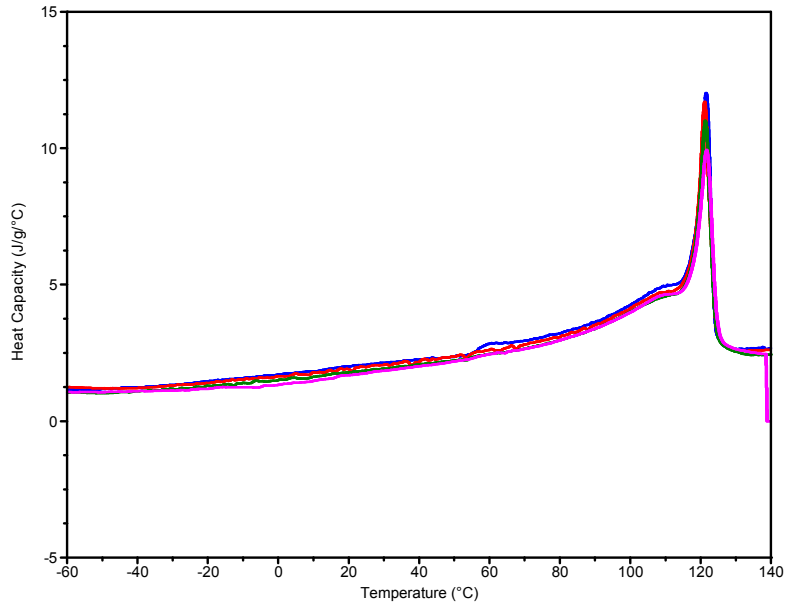50 to 150 ºC/min showing onset, energy and peak max calculations

Figure 7. Melting of LDPE at 50, 75, 100 and 150ºC/min.
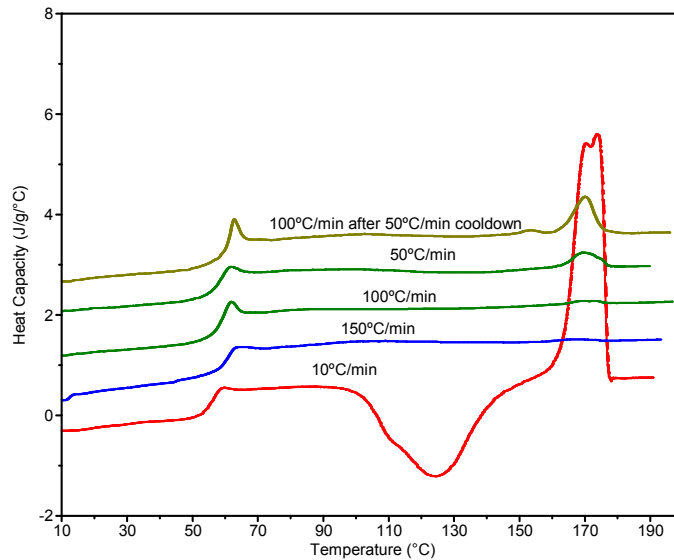Data is displayed in Cp units

Figure 8 - DSC of Rapidly Cooled Polylactide at Several Heating Rates.
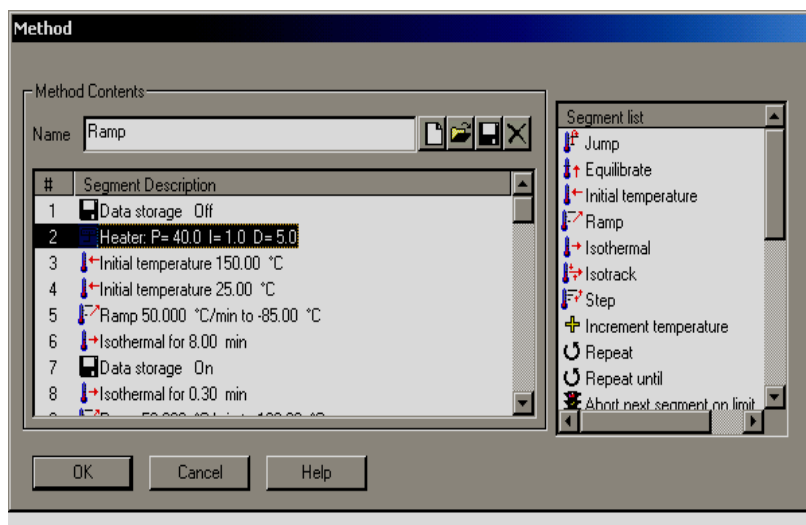(Data are in Cp units, but curves are offset for visual clarity.)

Figure 9. Universal Analysis Method Editor with PID step highlighted.
On the left are the method steps, on the right is a menu
of available method step choices.