Isothermal Crystallization Using the Q Series™ DSC and Liquid Nitrogen Cooling System

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ABSTRACT

The Q Series™ Differential Scanning Calorimeters (DSC's), when used with the closely coupled Liquid Nitrogen Cooling System (LNCS), provide the high cooling rates, rapid temperature equilibrium and accurate specimen temperature measurements needed to perform isothermal crystallization. The availability of user settable PID values for individual method segments yields heater control that is optimally "tuned" for each heater action whether it is isothermal, temperature ramp or ballistic cooling. When this superior instrument performance is joined with easy-to-use kinetics software, the Q series DSC becomes the preferred thermal analysis system for isothermal crystallization and other time-to-event experiments.

INTRODUCTION

Isothermal crystallization is a member of the class of experiments known as time-to-event (TTE) experiments. TTE experiments are used to study kinetic processes that are dependent both on time and temperature and involve fixing the temperature and then measuring time to constant sample conversion, such as peak onset or peak maximum.

TTE experiments involve "conditioning" of the test specimen at some initial temperature, followed by a rapid, step change to the selected test temperature where the sample is isothermally held until the reaction is nearly complete. In isothermal crystallization, this process involves conditioning the test specimen at a temperature about 30 °C above the melting temperature, then cooling the specimen to the isothermal test temperature below the melting temperature.

TTE experiments are best used to study two-step processes, the first of which is slow followed by a much faster process. In isothermal crystallization (IC), the initial "slow" process is the formation of nucleation or "seed" sites, followed by the "fast" crystallization process that results as the polymer crystallizes around the seeds.

The isothermal crystallization test may be used to meet both quality assurance and research needs. IC experiments are very sensitive to subtle changes in the test specimen. They are very useful to observe subtle changes in formulation or in lot-to-lot variations common to quality assurance needs.

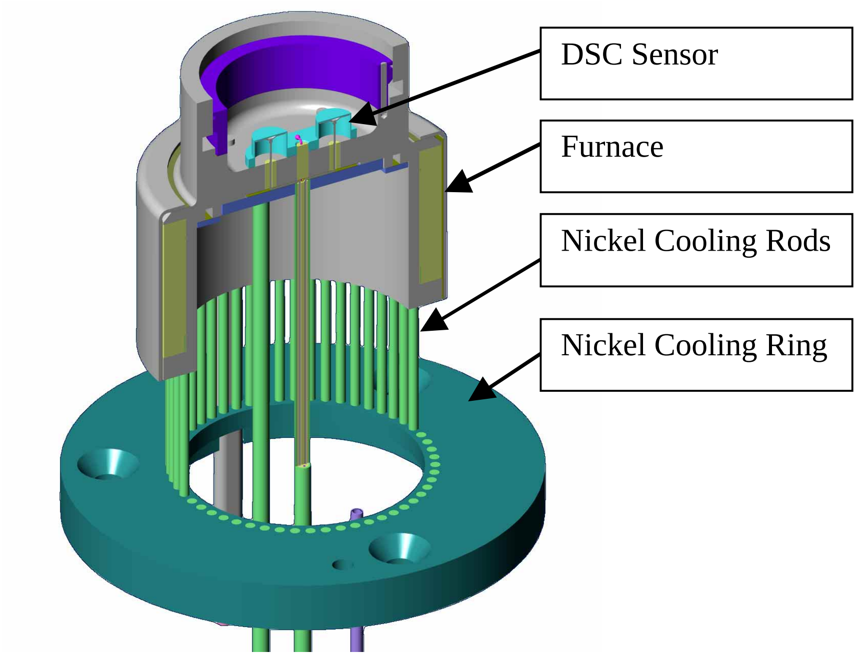

Figure 1 - DSC Cell Schematic

Isothermal crystallization is also used in research where determined kinetic parameters are used to predict performance at temperatures and time conditions unable to be reached by actual experimentation. This involves fitting experimental data to some kinetic model and then using the model to "predict" performance at different time/temperature conditions.

Rapid Cooling

Most reactions follow the Arrhenius expression and are exponentially dependent upon the (reciprocal) of absolute temperature. This means that the reaction is facilitated by a rapid temperature change to the test temperature and then rapid equilibrium at that temperature (with a minimum of over and undershoot).

It is generally thought that very high cooling rates (on the order of 100's of °C/min) are required for isothermal crystallization experiments. In the past, DSC's based upon the power compensation design were preferred for isothermal crystallization experiments due to their high rate of cooling. However, the high cooling rates promoted by equipment manufactures are seldom achievable in the low temperature range of isothermal crystallization experiments. Most isothermal crystallization experiments are actually carried out at cooling rates of approximately 80 °C/min. Moreover, it has been shown, that only the most rapid crystallizing materials required cooling rates greater than ca. 20 °C/min (*1*).

To achieve a high rate of cooling, the temperature difference between the DSC cell and the temperature "sink" must be as large as possible necessitating the use of liquid nitrogen as the coolant. Secondly, this cooling must be closely coupled to the DSC cell so that energy may flow quickly from the sample to the sink. Such close coupling is difficult to achieve as most DSC sensors are insulated to their surroundings to avoid heat losses and the baseline curvature that results.

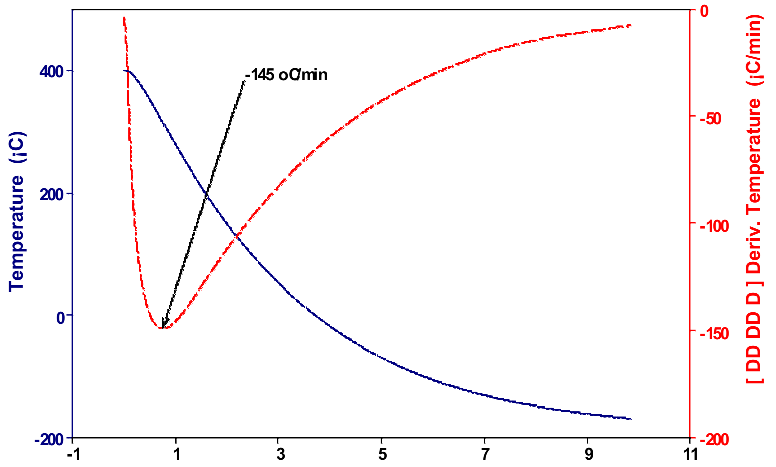

Figure 2 - Ballistic Cooling

This ability to cool rapidly is achieved in the Q series DSC's through the design in which the DSC is directly and efficiently coupled to the cooling accessory. This close coupling may be seen in Figure 1 where the DSC cell is connected by 54 high conductivity nickel rods to the cooling ring that the Liquid Nitrogen Cooling System holds at a constant cryogenic temperature.

The temperature range usable with the LNCS is from -180 to 550 °C. (Temperatures up to 725 °C are achievable with the Finned Air Cooling System.) Figure 2 shows a typical ballistic temperature cooling profile and cooling rate for the Q Series DSC/LNCS from 400 °C where a maximum cooling rate of ca. 145 °C/min is achieved. As in all DSC's, this maximum cooling rate declines as lower temperatures are reached but 5 °C/min cooling is still available at -150 °C.

The maximum cooling rates achievable depends on the particulars of the DSC itself and upon the efficiency of the cooling system to which it is affixed and varies from instrument to instrument. To overcome this difference, the designers of isothermal crystallization methods prefer to use linear cooling rates rather than ballistic cooling. This linear rate achievable is often much lower than that maximum ballistic rate due to the thermal inertia of this system. Figure 3 shows this type of cooling profile where a 100 °C/min cooling rate is achieved down to 120 °C.

Rapid Temperature Equilibrium

Rapid equilibrium at the test temperature is of more importance to the quality of the isothermal crystallization data than is rapid cooling. In order to assess the nature of "rapid equilibrium", the user must establish when isothermal temperature conditions have been achieved. Historically, isothermal conditions are thought to be achieved when the temperature is within ± 0.3 °C of the desired set temperature. This value is taken from ASTM Standard D3895 on Oxidation Induction Time (*2*). Similarly, ASTM standard E698 on Thermal Stability Kinetics calls for the heat flow to be less than 8 mW to achieve isothermal conditions (*3*) . This heat flow corresponds to 0.3 °C. Moreover, a

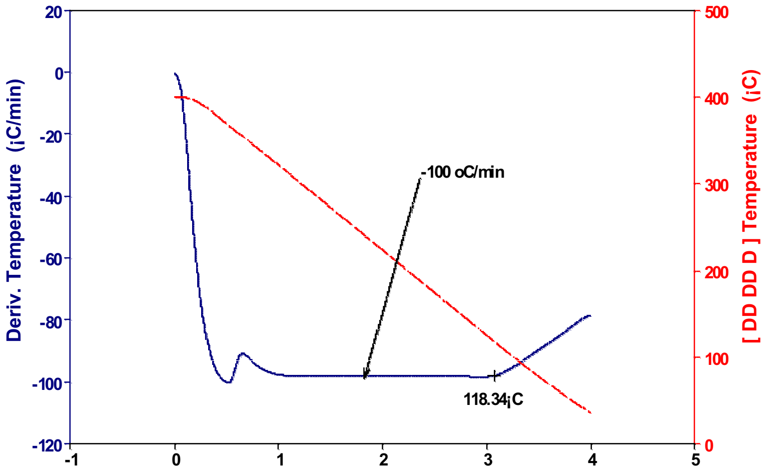

Figure 3 - Programmed Cooling at 100 °C/min to 120 °C

0.3 °C temperature difference results in less than a 2 % change in reaction rate and less than 0.1 % change in activation energy for 100 kJ mol^{-1} reactions.

Precise temperature control is achieved in differential scanning calorimeters through the use of proportional band feedback heater control systems. “Prop band” controllers use three control modes to provide the necessary control. These include the proportion band (or “gain”), integral (or “reset”) and derivative (or “rate”) modes. These three modes are identified by the acronym PID. The optimum PID values depend upon a wide variety of experimental conditions including how responsive the system is, the presence of any time lags, the load on the system and the desired rate of change.

Historical, DSC’s are designed using a single set of PID condition that is optimized for a linear temperature ramp at 10 to 20 °C/min. As it turns out, the PID settings required for a high rate of temperature change and those for tightly controlled isothermal temperature conditions are quite different from each other, are mutually exclusive and are different from those required for a linear ramp. These two extremes of temperature control (rapid cooling and tight temperature control) may not be satisfied with the same set of PID values. Inappropriate PID values cause the temperature to over- or undershoot the test temperature during isothermal crystallization experiments.

To overcome this control challenge, the PID values in the Q series DSC’s are operator settable as a method segment. The operator is thus able to “tune” the controller for each method segment whether it is a linear ramp, ballistic temperature change or isotherm temperature operation. For example, Figure 4 shows the temperature profile for a system tuned for isothermal crystallization experiments. Here a ballistic cooling profile with a rate of 125 °C/min achieves the isotherm test temperature within a 15 to 20 second time period with no over- or undershoot.

Polypropylene Example

There is no more difficult sample upon which to perform isothermal crystallization than polypropylene (PP). PP is a very fast crystallizing material with a

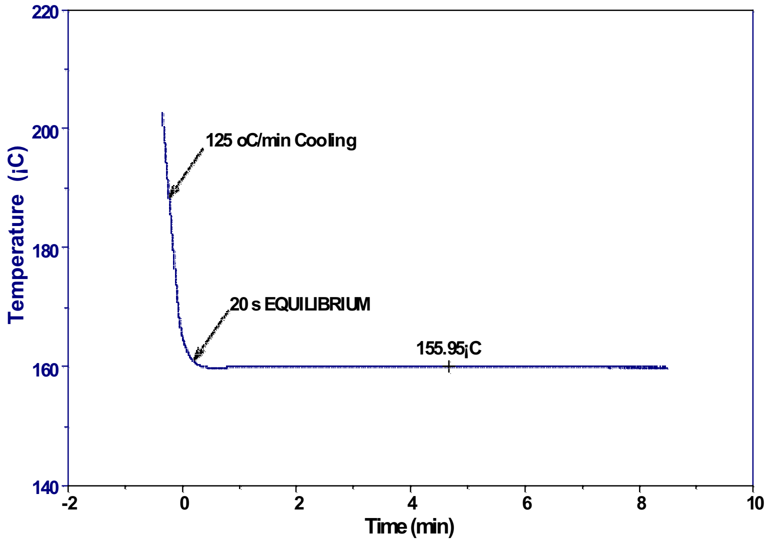

Figure 4 - Rapid Equilibrium with Tuned Controller

very high activation energy. It is a bellwether material used to explore isothermal crystallization capabilities since success achieved with PP results in success for virtually all other polymers to be tested. Figure 5 shows a family of isothermal crystallization thermal curves for a polypropylene reference material (*4*) where the same test specimen is evaluated at a series of closely spaced temperature intervals.

For qualitative comparisons, the elapsed time is measured from the establishment of the isothermal test temperature to the peak of the crystallization exotherm and compared with other “bench mark” materials for the same temperature. Figure 5 shows that the crystallization exotherm for PP goes from a high, narrow peak with an elapsed time of less than 1 minute to a low, broad peak of more than 4 minutes all within a few Celsius degrees. This rapid change of elapsed time with temperature is why IC experiments of PP are so difficult.

<u>Kinetics</u>

For a more thorough understanding of the nucleation and crystallization processes, a detailed look at the kinetics of the respective reactions is used. Activation energy, the kinetic tool that tells how the reaction rate changes with temperature, may be derived from a series of time-to-event measurements at a series of isothermal test temperatures. In its simplest form, the “kinetics” of the slow nucleation formation step is examined by observing the elapse time (Δt) to the exothermic peak for each of several isothermal temperature (T) conditions. The equation for this evaluation is a special form of the Arrhenius equation taken from ASTM Standard D2070, Method B (*5*) :

$$\ln [\Delta t] = E/RT + c \qquad \text{(eq. 1)}$$

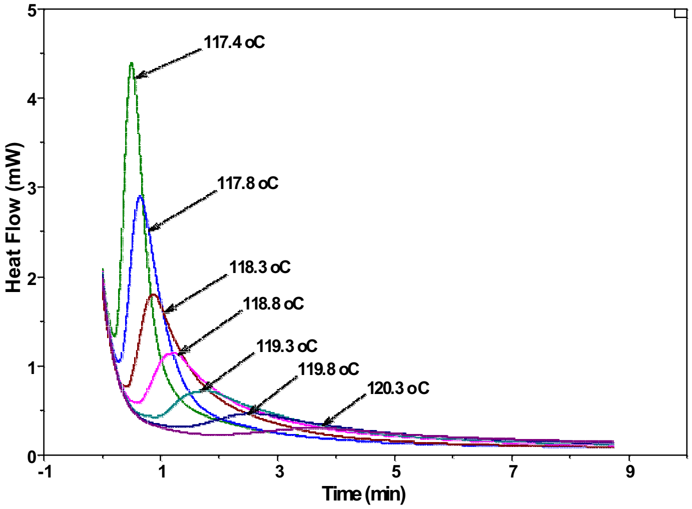

Figure 5 - Isothermal Crystallization of Polypropylene

where E is the activation energy, R is the gas constant (= 8.314 J mol^{-1} K^{-1}), and T is the absolute temperature. This equation has the form of Y = mX + b and may be solved using least squares linear regression analysis. If Y = ln [Δt] is plotted versus X = 1/T, then the activation energy is the slope (m) of the resultant straight line times the gas constant. The activation energy determined by this process is for the nucleation process and not for the crystallization process itself.

Figure 6 shows the resultant least squares best fit to the data taken for the isothermal crystallization times for polypropylene. The slope of the straight line yields an activation energy of -948 kJ mol^{-1}. A closer look at the individual data points shows that the mid-range points fall close to the best-fit line but those at the high and low temperature (short or long elapsed times) do not fit the line quite so well. This is because at long elapsed times, the crystallization peak is very shallow and quite broad. This makes the determination of the actual peak time difficult. Similarly, at short elapsed time the imprecision in the elapsed time measurement increases making the value unreliable.

A more complete approach to the determination of the kinetics of the crystallization reaction is through the use of the Sestak-Berggren equation (*6*, *7*) formalized as method A for ASTM Standard E2070 (*5*). The Sestak-Berggren equation is a more general form of the traditional form of the kinetic equation and may be related to the Avrami Equation (*8*). The Sestak-Berggren equation has the form:

$$d\alpha/dt = Z\,\alpha^{m}\,(1 - \alpha)^{n} \exp\,[\,E/RT] \qquad \text{(eq. 2)}$$

where α is the fraction reacted, $(1 - \alpha)$ the fraction left unreacted, $d\alpha/dt$ is the rate of the reaction, Z the Arrhenius pre-exponential factor, m is the reaction order for the induction period and n is the reaction order for the crystallization reaction. In practice, a series of partial fractions across the isothermal crystallization peak are taken to evaluate the terms

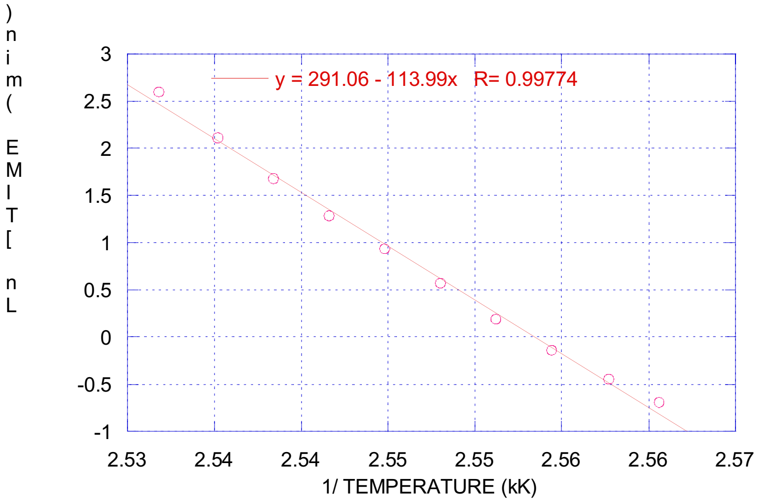

Figure 6 - Polypropylene Crystallization Kinetics by ASTM E2070 (Method B)

of this equation. α is obtained by the ratio of the enthalpy of reaction up to a particular time divided by the total enthalpy of reaction.

A comparison of the results for the two approaches to isothermal kinetics parameters for polypropylene is shown in Table 1. The numerical values for the two approaches are slightly different but within the confidence limits of each other. A more useful and practical approach is to compare these results to the values for the reference material itself. The value of 119.4 °C is in excellent agreement with the reference value of 120 °C for the 2-minute isothermal crystallization time.

Table 1 - Polypropylene Comparison Data

ASTM E2070 (Method B)

E = -948 kJ mol^{-1}

ASTM E2070 (Method A)

E = -1090 ± 140 kJ mol^{-1}
Log Z (min) = -144 ± 19
m = 0.62 ± 0.15
n = 0.94 ± 0.29

Isothermal Crystallization 120 °C Reference Material

2 min IC = 119.4 °C

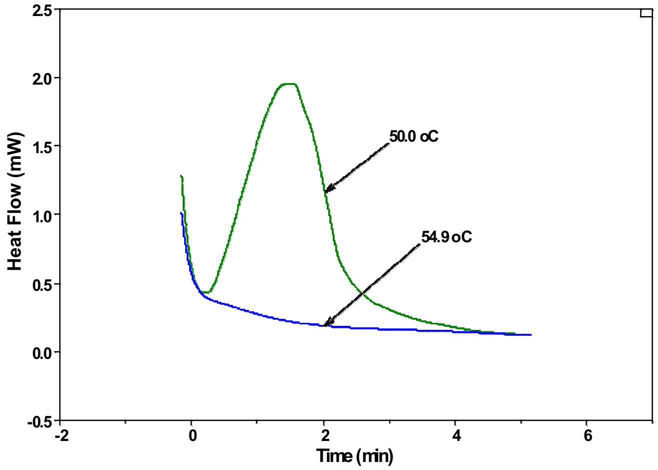

Figure 7 - Polyethylene Oxide with Curve Subtraction

DISCUSSION

There are several difficulties associated with the use of isothermal crystallization time less than one minute. The first of this is the establishment of the "baseline" associated with the crystallization exotherm. Due to its thermal conductivity, the test specimen will more slowly achieve temperature equilibrium than the DSC apparatus. The best criterion for this temperature equilibrium is the attainment of a baseline before the onset to the crystallization exotherm. As is shown in figure 5, this usually requires an isothermal crystallization time of 3 minutes or more.

For periods shorter than about 3 minutes, one must assumes a straight-line baseline between the valley before the onset to crystallization and the end of the peak. As the crystallization times get shorter than about 1 minute however, an appreciable error is induced into the measurement. One way to overcome this difficultly is through the use of curve subtraction. In this case, the baseline of the same sample run at a higher isothermal crystallization time (and thus longer crystallization time) may be subtracted from the shorter period. This concept is illustrated in figure 7 for polyethylene oxide for which the isothermal crystallization temperature is near 50 °C. The subtraction of the baseline due to thermal conductivity from the isothermal crystallization curve provides more accurate enthalpy of reaction information.

Another challenge for short isothermal crystallization periods is the self-heating that takes place with isothermal crystallization times of less than 1 minute. In such experiments, the energy associated with the crystallization process results in adiabatic self-heating due to the specific heat capacity of the specimen. This effect may be seen in figure 8 where the specimen temperature is recorded for a series of polypropylene samples of varying size. As the test specimen size gets bigger, the amount of self-heating increases. This figure shows that self-heating for a 4 mg test specimen exceed the ± 0.3 °C criterion for isothermal operation obtained earlier. Furthermore, it shows that samples with isothermal crystallization times of less than about 1.5 minutes are particularly vulnerable to this self-heat effect. For larger test specimens and shorter (than 1.5 minutes) isothermal crystallization times, this challenge is acerbated. If the temperature of the test specimen is measured, then this value (rather that the set temperature) may be used to produce more accurate results. Clearly measurement of the specimen's temperature is an important part of any isothermal crystallization experiment.

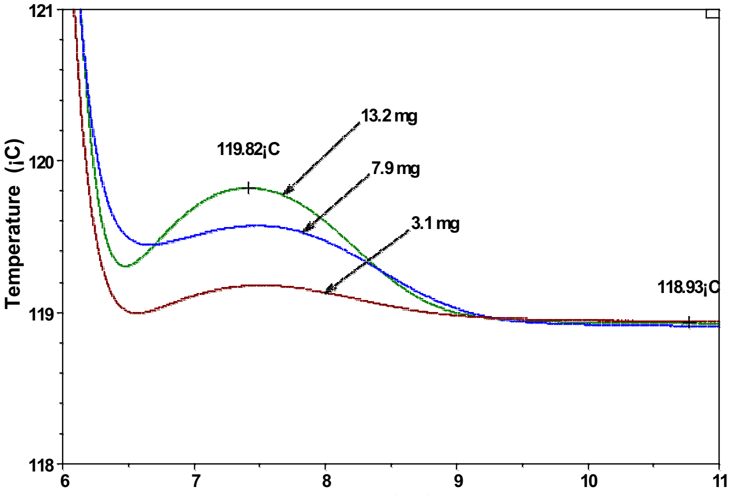

Figure 8 - Self-Heating of Polypropylene

CONCLUSIONS

It is demonstrated that the Q Series DSC apparatus from TA Instruments, equipped with the Liquid Nitrogen Cooling System (LNCS) produces reliable and accurate isothermal crystallization data, including kinetic parameters on the most difficult of test specimen, polypropylene. This ability is achieved through the combination of a highly efficient and closely coupled cooling system, individual segment heat tuning for each method segment and the availability of ASTM standard kinetic methods for evaluation of the resultant kinetic information. Moreover, the ability of the Q Series DSC to measure and record specimen temperature provides an unambiguous measurement of the primary independent parameter, temperature. This combination makes the Q Series DSC's coupled with the LNCS, to be the preferred tool for isothermal crystallization and other time-to-event experiments.

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KEYWORDS

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