Impact of Tzero™ Technology on the Measurement of Weak Transitions

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ABSTRACT

Tzero™ Technology is a fundamental improvement in DSC technology that will have a profound impact on the work of the Thermal Analyst. The innovative design of the Tzero™ DSC cell and the increased sophistication of the Tzero™ measurement results in a more accurate representation of the actual heat flow occurring in a sample. As a result of this new technology, the traditional sources of DSC baseline curvature during an experiment have been essentially eliminated. By dramatically reducing baseline curvature, the measurement of weak material transitions, which result in only a few microwatts of heat flow, is now readily possible. These benefits will be illustrated by specific measurements of glass transitions in semi-crystalline polymers and phase transitions in microgram samples that are extremely difficult or impossible to make using traditional DSC designs.

INTRODUCTION

The Q series DSC and Tzero™ Technology is a significant new development by TA Instruments that further advances the ability of the thermal analyst to make sensitive heat flow measurements. Without any preconceived design restrictions, a fundamentally new DSC was developed. A dramatic improvement in baseline performance has been achieved, while at the same time Tzero™ Technology has also improved sensitivity and resolution, which are usually compromised by improvements in baseline performance.

The improved design and manufacturing process of the Q series DSC minimizes the traditional inherent imbalance of current generation DSC cells. (1) The performance of this basic design is superior to conventional heat flow measurements. Tzero™ Technology (2) utilizes a DSC Heat Flow measurement model frequently described (3-5), but until now never implemented in a commercial device. Effects typically assumed to be insignificant and ignored are now included in the heat flow measurement. It is these effects, incorrectly assumed to be insignificant, that are responsible for the non-ideal behavior of conventional DSC measurements.

The result is a level of performance superior to conventional DSC. Baseline curvature has been dramatically decreased and at the same sensitivity and resolution have been improved. There is a saying in the thermal analysis community, ***"Give me a flat baseline and I can detect anything!"*** This paper will describe the level of baseline performance and sensitivity attained and illustrates a few examples of its impact on the measurement of weak transitions.

EXPERIMENTAL

A TA Instruments (New Castle, Delaware) Q100 Differential Scanning Calorimeter was used in these experiments. A Refrigerated Cooling System (RCS) and the Finned Air Cooling System (FACS) were both used as cooling devices. In all cases, the instrument was purged with dry Nitrogen. After installing and conditioning the cooling device, instrument calibration was performed using the Advantage for Q Series Calibration Wizard over the temperature range of –90 to 400°C at a heating rate of 20°C/min. Temperature calibration was performed using high purity Indium, also at a heating rate of 20°C/min.

The baseline performance data was based on a series of 8 consecutive empty cell baseline cycles acquired using an RCS as the cooling device, a temperature range of –90 to 400°C, a heating rate of 20°C/min, and the maximum data sampling rate of 10 points per second.

The Polypropylene analysis utilized a 40µm thick film of Polypropylene film obtained from Goodfellow (Cambridge, England.) A single ply, nominal 1mg, was encapsulated in a standard crimped Aluminum pan. The sample was given a known thermal history by heating the sample to 180°C and cooling the sample slowly to -90°C. This maximized the degree of crystallinity and minimized the level of the amorphous phase, making the analysis of the glass transition that much more challenging. The sample was then heated at 20, 10 and 5°C/min from –90°C through the glass transition. A data sampling rate of 10 points per second was also used.

The microgram Indium analysis utilized a high purity sample of Indium obtained from TA Instruments. A small piece of Indium was pressed flat and, while working under a stereomicroscope, a much smaller piece was cut using a razor and transferred to a preweighed standard crimped Aluminum pan using a sharpened dental pick. The pan was weighed using a Cahn C-33 Microbalance and found to be 1.0±0. 5µg. The sample was analyzed by equilibrating the sample at 180°C, then 50°C and then heating at 1°C/min through the melt transition.

The TAWN test specifies very precisely the test conditions to be used. The test utilized a 0.25±0.02mg sample of 4, 4'-Azoxyanisole, 98%, obtained Aldrich Chemical. The sample was weighed into a standard crimped Aluminum pan, heated to 130°C, held isothermal for 5 minutes and then heated at 0.1°C/min to 140°C. A data sampling interval of 1sec/pt was used rather that the 10sec/pt specified by the TAWN test. The faster sampling rate was required because, as measured by the Q100, the peak was too narrow to be adequately resolved at the slower data sampling rate.

BASELINE PERFORMANCE

The baseline performance of conventional DSC is limited by fundamental assumptions made concerning the imbalance of the DSC when measuring and calculating heat flow. The truly significant feature of Tzero™ Technology is that even though the imbalance is minimized through design and manufacturing improvements, the remaining imbalance is not assumed to be insignificant. On the contrary, the residual imbalance is actually measured during calibration and those effects are included in the heat flow measurement. The result of this effort is a dramatic decrease of most if not all of the instrumental artifacts present in conventional DSC baselines.

As it pertains to the detection of weak transitions, baselines that are flat and without significant curvature, are extremely important. Traditionally, baseline subtraction was required to obtain an adequately flat baseline. This required a baseline experiment using the precise conditions and preferably immediately before each experimental run.

The effectiveness of this baseline subtraction technique is often limited by the repeatability of the DSC baselines.

The Q series DSC and Tzero™ Technology generate a DSC baseline that is not only repeatable but also flat. Baseline bow, or curvature can be defined as the maximum deviation of the heat flow signal from a linear baseline drawn between two temperature limits, and has traditionally been used as a critical measure of DSC performance.

A typical result of a Tzero™ baseline cycling experiment as described is shown in figure 1. The average baseline curvature over a 250°C temperature range beginning at –50°C was found to be 10µW. This data was obtained during the development phase of the Q series DSC and represents average results and is not intended to represent a performance specification. Rather, these results are intended to illustrate the level to which baseline curvature can be reduced using Tzero™ Technology.

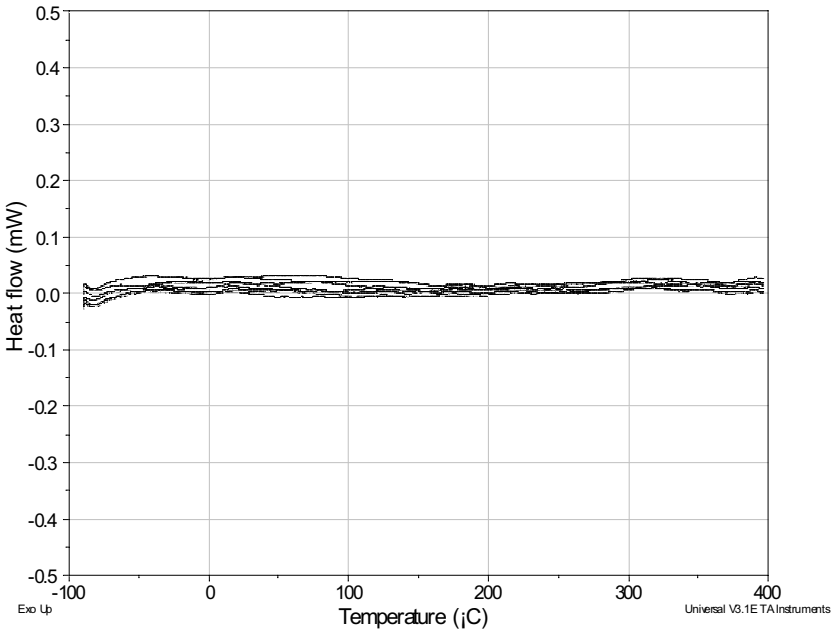

Figure 1.
Q series DSC Tzero™ Baseline Performance

POLYPROPYLENE ANALYSIS

Polypropylene is a widely used semi crystalline polymer and as such contains both an amorphous and a crystalline phase. The ability to detect and evaluate both of these phases can be extremely important. The amorphous phase can be characterized by the glass transition, which may be observed as a step change in the DSC heat flow signal. Unfortunately, in the case of polypropylene, the glass transition is rather challenging to detect and evaluate using DSC. Since the magnitude of the step change is rather small.

An overlay of the three curves obtained in the experiment described earlier is shown in Figure 2. In this experiment, the step change in the heat flow signal at the glass transition of the 40µm film of Polypropylene film was clearly observed. As expected, since sensitivity is proportional to the heating rate, the magnitude of the transition increased as the heating rate was increased. At 20°C/min, the step change was 37.8µW. However, at the slower heating rates, 10 and 5°C/min, the transition was only 13.4 and 9.8µW.

Such a small transition would be difficult to observe using conventional DSC with significant baseline curvature. At the very least, baseline subtraction would be required, however the effectiveness of baseline subtraction is often limited by baseline

repeatability. Another challenging aspect of this analysis is the proximity of the transition to 0°C. The presence of any water artifacts introduced by the cooling system would interfere with this analysis.

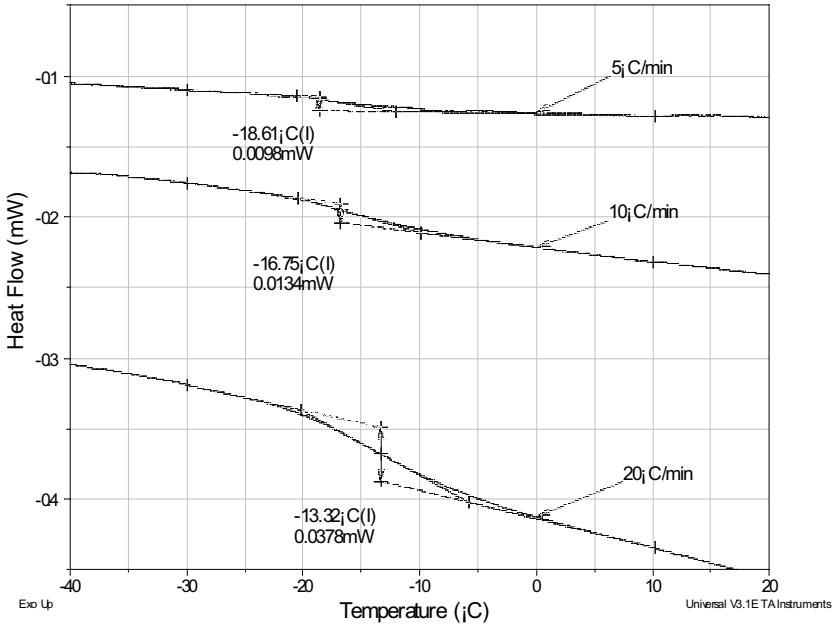

Figure 2.
Polypropylene Glass Transition as a Function of Heating Rate

MICROGRAM INDIUM ANALYSIS

In many situations, the ability to detect very small transitions can be extremely valuable. Often, only a very small amount of sample may be available, such as after the purification of a new compound under development. In other cases, the analyte may be present only as a minor component in the bulk sample and cannot be purified and concentrated. In these cases, when observing transitions in the µW range, flat baselines and high sensitivity become very important.

Figure 3 shows the analysis of a 1.0±0.5µg sample of Indium. The sample was carefully prepared as described earlier and then heated at 1°C/min through the melt transition. The result clearly shows that melt transition of a 1µg Indium sample is well within the detection limits of the Q100 DSC. The peak height of this transition was only 2.2µW. The s/n ratio was about 5, close to the quantification limits and the measured area, or the enthalpy of the melt only 0.040mJ. Given the uncertainty in the sample size due to the extremely small size, I would be hesitant to quantify this measurement, however, this example serves to illustrate the utility of high baseline performance and sensitivity when working with small transitions.

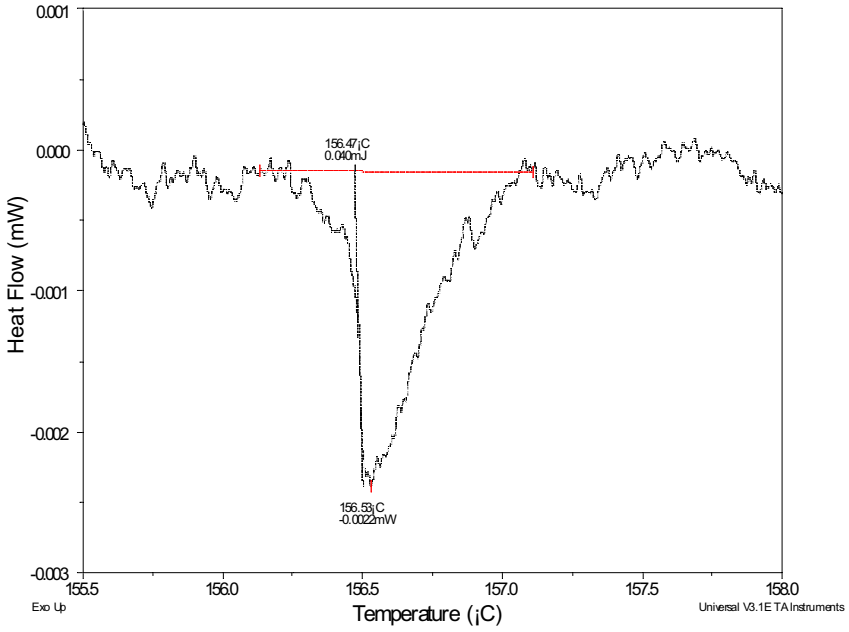

Figure 3.
Melt Transition of 1 Microgram of Indium at 1°C/min

TAWN SENSITIVITY TEST

The Dutch Society for Thermal Analysis (TAWN) developed a comparative test of the resolution and sensitivity of DSC instruments (6). The test uses a small sample of 4, 4'-Azoxyanisole, which has a pair of endothermic transitions spaced ~17°C apart. The first is a large solid-liquid crystal transition at about 117°C and the second is a small liquid crystal-isotropic liquid transition at about 134°C. The sensitivity test heats and cools the sample at a very slow heating rate (0.1°C/min) through the second, smaller transition and evaluates the peak height measured compared to the peak-peak baseline noise level.

This experiment was carried out as described earlier and the result is shown in Figure 4. The small liquid crystal-isotropic liquid transition (delta H ≈ 2J/g) was clearly detected with a peak height of 16µW. Given the magnitude of the transition, ~2J/g, and the very slow heating rate, 0.1°C/min, this measurement is clearly within the detection and probably the quantification limits.

The TAWN procedure specifies precisely how the data is to be presented and analyzed. The data was plotted and a linear baseline was drawn between 132°C and 136°C. The peak height was determined and the maximum peak-peak variation of the baseline was also determined. The sensitivity is quantified by dividing the peak height by the peak-peak variation of the baseline over the temperature range. Using the TAWN definition, the sensitivity was found to be 8, indicative of the excellent sensitivity of the Q Series DSC.

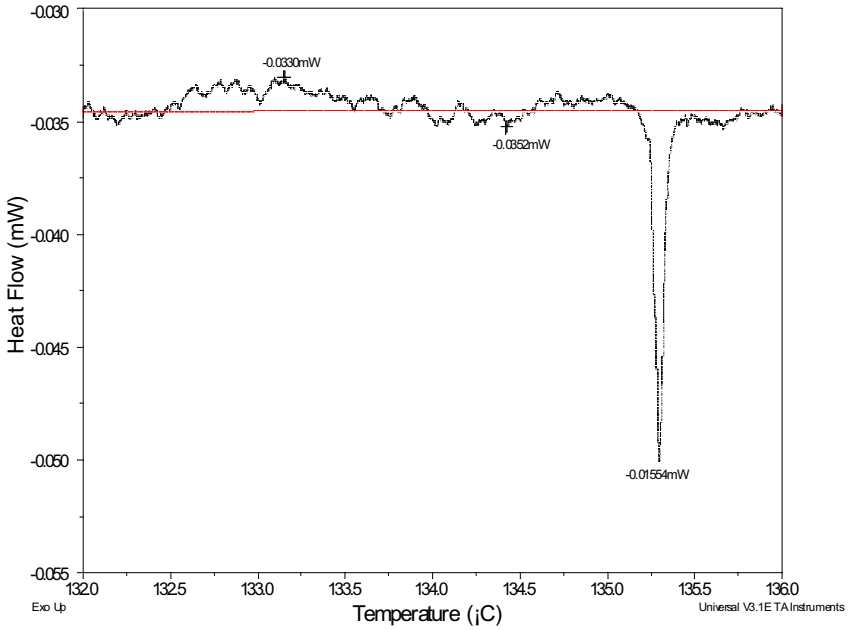

Figure 4
TAWN Sensitivity Test

CONCLUSION

The Q Series DSC and Tzero™ Technology is an exciting new development by TA Instruments that will be of great benefit to the thermal analyst. Tzero™ Technology addresses the fundamental issues causing baseline curvature in conventional DSC measurements and at the same time improves the sensitivity and resolution of the measurement of transitions.

An example of a typical Q Series DSC Tzero™ baseline was presented. With an essentially flat baseline, several examples of the sensitivity achieved using Tzero™ Technology were shown. Specific examples included the glass transition in slow cooled polypropylene, the melt of a 1µg sample of Indium heated at 1°C/min and a 2J/g Azoxyanisole transition at 0.1°C/min.

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