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## How Tzero™ Technology Improves DSC Performance Part VI: Simplifying Temperature Calibration for Cooling Experiments

R. Bruce Cassel  
TA Instruments, Inc., 109 Lukens Drive, New Castle DE 19720, USA

### ABSTRACT

Because of thermal lag between DSC sample and temperature control sensors, most DSC's require calibration at the heating rate to be used. Alternatively, calibration at multiple rates is required to correct for the heating rate dependence of thermal lag. Without this calibration there is considerable error in the temperature data in going from one heating rate to another. This problem is especially troublesome when performing a cooling experiment due to the thermal lag being in the opposite direction as that of heating doubling its effect. This problem is solved with a new DSC sensor employing Tzero™ technology. With the Q Series DSC system an additional thermocouple on the DSC sensor allows complete calibration of the DSC cell and compensation for all thermal lags, including those caused by the encapsulated sample. The use of a liquid crystal sample is described to demonstrate that the calibration is independent of heating or cooling rate, even when using a non-ideal hermetic sample encapsulation.

### INTRODUCTION

Perhaps the most common DSC experiment performed is one using a heat-cool-heat temperature program. The first heating step gives information about the initial state of the sample "as received" and removes artifacts due to stresses caused by sample history or by specimen encapsulation. The cooling step quantifies the fusion, or gelation, characteristics, and puts the sample into a standardized state where it can be compared to other materials so treated. Then, the second heat allows the melting characteristics of the thermally defined specimen to be quantified.

One challenge with this approach is that the DSC is calibrated to give correct temperature data for the *heating* experiments. Unless a complex multiple rate calibration has been carried out using the appropriate experimental conditions (purge type, pan type and cooling system), there will be an error in the cooling run temperature readout of about *two times the thermal lag*. As discussed in a previous report (1), this thermal lag is proportional to heating rate, sample-plus-pan heat capacity and the thermal resistance between the sample specimen and the "sample temperature" sensor. The thermal lag is normally in the range of 0.4 to 0.9 °C (for 10 °C/min), so if it has been corrected for the heating experiment (by DSC temperature calibration at the heating rate to be used for the samples), it is off by one to two Celsius degrees for the cooling data (2, 3).

This problem is eliminated using Advanced Tzero™ Technology from TA Instruments. The Q1000 DSC cell provides an additional thermocouple sensor and an automated calibration routine that allows all the thermal characteristics of the cell -- both

those affecting the ordinate baseline, and those affecting the temperature scale -- to be addressed (4).

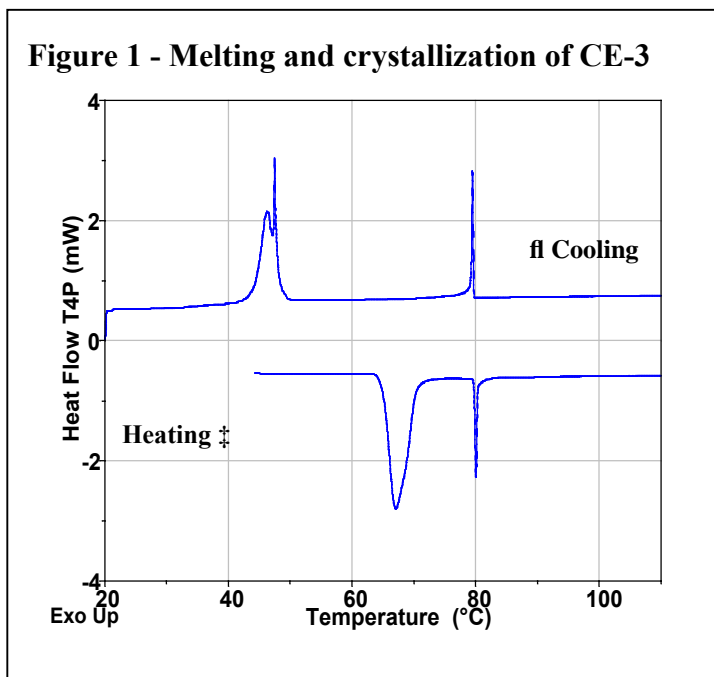
But how can one verify that this problem has been eliminated even for cooling experiments, given that most common temperature calibration materials super-cool making them unsuitable for calibration on cooling. A suitable tool is the use of certain liquid crystalline materials that do not super-cool.

## EXPERIMENTAL

The liquid crystal material used is {(+)-4-n-hexyloxyphenyl 4'-(2"-methylbutyl)-biphenyl-4-carboxylate}, known as CE-3. This material was obtained in purified form from a commercial vender (5), the use of which is described in ASTM standard E2069 for DSC calibration on cooling (6). 1.5 milligrams of a purified sample of CE-3 was encapsulated in a hermetically sealed pan.

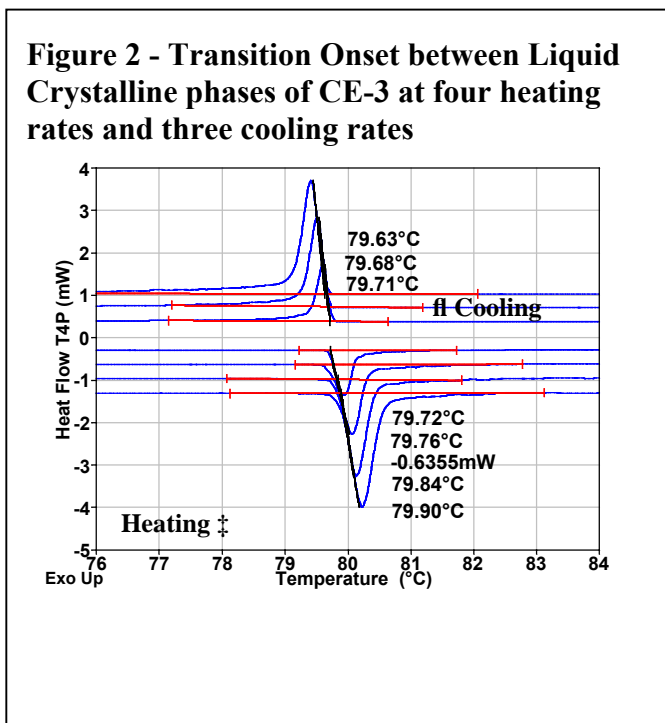
Figure 1 shows a thermal curve showing two-phase transitions of this material. Note that while the solidification of the sample into a solid shows considerable super-cooling, the onset of the higher temperature peak (just under 80 °C) appears at the same temperature. It is this transition that allows for a more carefully examination of the scanning-rate invariance of the Advanced Tzero temperature data.

The DSC used to demonstrate this was a Q1000 DSC from TA Instruments. The Advanced Tzero Technology capability comes standard with this model. This capability allows the thermal characteristics of the sample pan, as well as those of the DSC sensor itself, to be addressed in the output signals. This is accomplished using a cell calibration that does not require the use of any particular sample pan. Once calibrated, the system properly compensates for thermal lag caused by heat flow within the DSC sensor, and into the capsule containing the sample. As a result, one can consider that the temperature displayed on the X-axis is the *sample pan temperature*, the temperature at the surface of the sample specimen itself. This is a considerable improvement over reporting the temperature solely based on a sensor embedded in a DSC disk, sample holder, or yet farther removed from the sample (7). The Q1000 DSC was calibrated using only sapphire heat capacity standard scanning at 20 °C/min and indium metal for a melting standard, encapsulated in a standard aluminum pan. No special care was taken in calibration, or to "fine-tune" the instrument.



## RESULTS

Figure 2 shows the results of heating and cooling the CE-3 system through a liquid crystal phase change transition. This peak corresponds to the transition between two liquid crystalline phases, the chiral smectic phase and the cholesteric phase. The correct transition temperature for this single valued point is obtained by extrapolating the peak onset back to the isothermal baseline, the zero heat capacity line (which on the Q Series is zero milliwatts). This can be seen to be 79.7 °C as measured either heating or cooling. Using the standard method of onset from the peak baseline gives a maximum temperature offset of 0.2 °C when using heating rates up to 30 °C/min or cooling rates up to 20 °C/min. Moreover, when using standard aluminum pans for encapsulation, this offset will be even less.



## CONCLUSIONS

Some liquid crystal transitions are known to exhibit very little super-cooling. Therefore, the onset of this transition should appear at the same temperature as it is heated or cooled at normal DSC scanning rates. That this is demonstrated using the Q-Series DSC shows that the compensation provided by Advanced Tzero Technology is effectively addressing all thermal lag in the DSC/sample pan system. To make this proof even more convincing, the experiment was carried out in the less-than-ideally-coupled hermetic sample pans often used for the analysis of organic materials containing volatile components.

What does this mean for ordinary heat-cool-heat analysis, or any other routine cooling experiment? It means that for all practical purposes you can calibrate the DSC at any reasonable heating rate, and the DSC temperature data will be correct within a few tenths of a Celsius degree for data taken at other heating *or cooling* rates. Because advanced Tzero compensates for the effect of pan thermal mass and coupling, it is possible to calibrate using one pan type and then use another pan type (as was done in this report) without incurring substantial error. In short, because Tzero technology utilizes more information about the DSC itself in its measurement, it is safe to run under a wider range of conditions without calibrating under those specific conditions.

## REFERENCES

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2. J. D. Menczel and T.M. Leslie, "Temperature Calibration of a Power Compensation DSC on Cooling", *Thermochimica Acta*, **1990**, 166, pp. 309-317.

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4. R. B. Cassel, "Technology Improves DSC Performance, Part V: The Reduction of Thermal Lag in the Reporting of Peak Temperature", TA Instruments Applications Brief TA282.
5. 99.9% Purity from Chromophore, Inc., Huntsville, AL.
6. ASTM E2069, "Temperature Calibration on Cooling of Differential Scanning Calorimeters", American Society for Testing and Materials, West Conshohocken, PA.
7. Some DSCs even report the sample temperature based on the output of a sensor in the furnace. Often, DSC manufacturers do not explain where the temperature signal is measured.

## **KEYWORDS**

differential scanning calorimetry, organics