



Modulated DSC[®] Paper #1
Why Modulated DSC[®]? ; An Overview and Summary
of Advantages and Disadvantages Relative to Traditional DSC

Leonard C. Thomas
TA Instruments, 109 Lukens Drive, New Castle, DE 19720, USA

ABSTRACT

This paper outlines the basis for the Modulated DSC technique and shows its value in solving analytical problems that cannot be readily tackled by traditional DSC.

INTRODUCTION

Differential Scanning Calorimetry (DSC) has been a highly successful analytical technique for over 4 decades. Before then, material scientists used the similar, but non-quantitative, Differential Thermal Analysis (DTA) technique to study changes (transitions) in structure for a broad range of materials, including polymers, chemicals, foods products, composites and drugs. The success of DSC in solving material problems is attested to by the approximately forty-to-fifty thousand models in worldwide use today, with some larger laboratories having five or more instruments. The reasons for the commercial success of DSC are numerous and include:

- It is a relatively fast technique with most analyses taking less than thirty minutes.
- Sample preparation is easy. Solids, liquids, powders, films and fibers of essentially any shape are encapsulated in metal pans and placed into a temperature and atmosphere-controlled environment where the measurement occurs.
- The wide temperature operational range of -180 to 725 °C permits the analysis of transitions in a broad range of materials.
- Sophisticated, easy to use software permits a quantitative analysis of transitions as a function of temperature and time.

Despite these positive features, standard DSC still has some well-known limitations, which can complicate analysis of the results and also reduce measurement accuracy and precision. The more serious limitations are discussed below and include:

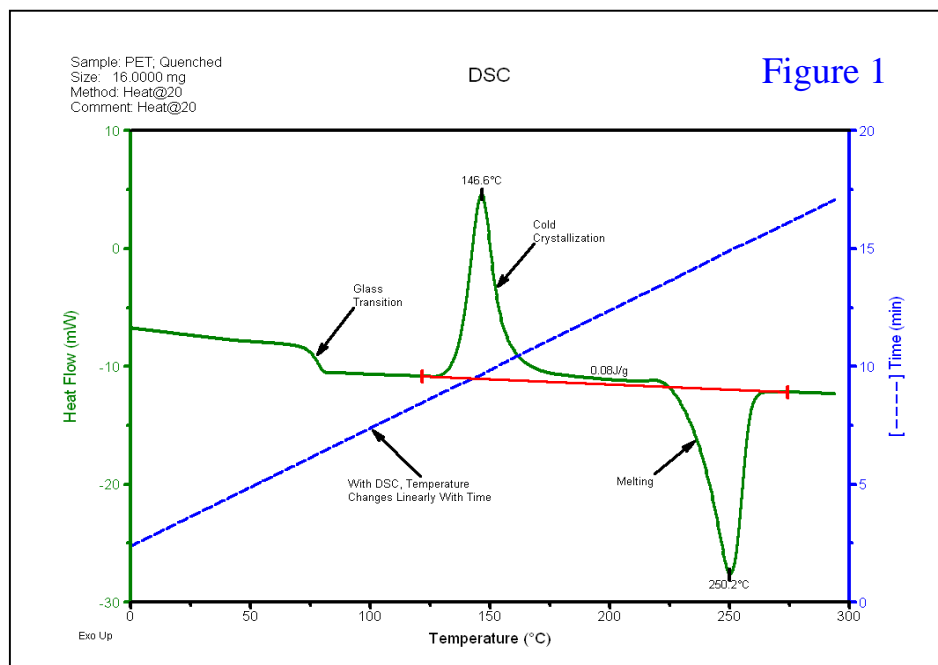
- Interpretation of results is often difficult since most modern commercial materials are made from blends of different components. The temperature range for transitions in the different materials often overlap and experience is required to create methods, which can assist with interpretation of results.
- DSC measures only the sum or average value of the heat flow rate from overlapping processes. This makes quantitative analysis of the individual processes impossible.
- For any DSC, the only way to improve sensitivity for detecting low energy transitions is to increase sample size and / or heating rate. This however decreases resolution (the ability to resolve transitions that occur close in temperature). DSC thus cannot optimize both sensitivity and resolution in a single experiment.

- Flat, straight baselines are required for detection of small transitions, especially glass transitions. Unfortunately, the absolute value of the DSC heat flow signal is affected by instability in instrument electronics and cooling systems, and environmental changes such as temperature and humidity in the laboratory. This limits the real sensitivity even more than short-term noise in the heat flow signal.

The ideal calorimeter would have all of the advantages of traditional DSC and none, or fewer, of its disadvantages. With the exception of the need to use lower heating rates, and therefore use longer experimental times, Modulated DSC[®] is that ideal calorimeter. Hence, the purpose of this paper is to provide a general introduction to the technique of Modulated DSC[®] (MDSC[®]) and to illustrate its advantages over traditional DSC. A detailed discussion of how MDSC[®] signals are calculated and calibrated is provided in a following paper in this series (1).

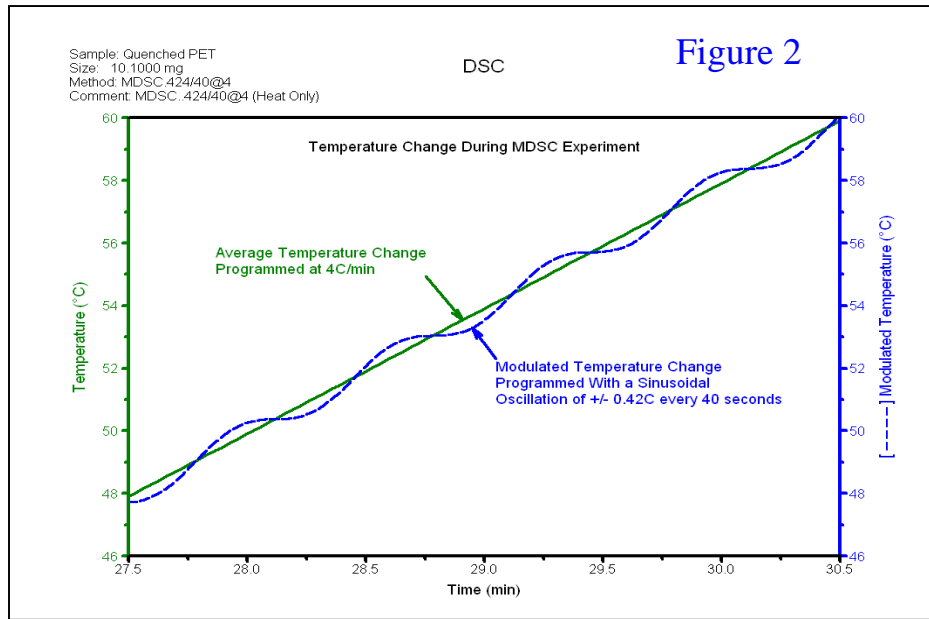
OPERATING PRINCIPLES OF MDSC[®]

With traditional or standard DSC, the difference in heat flow rate between a sample and an inert reference is measured as the sample is heated, cooled or held at an isothermal temperature. The resulting differential heat flow rate signal is typically plotted in milliwatts (mJ/sec) versus temperature or time. With standard DSC, temperature is always changed linearly and the operator must specify the rate in degrees per minute (°C/min). With a single heating rate, a single heat flow rate signal is produced, which is the sum of all heat flows occurring at any point in temperature or time. An example of such a DSC experiment is shown in Figure 1 for a sample of Polyethylene Terephthalate (PET) that had been quench-cooled from a temperature above its melting point.

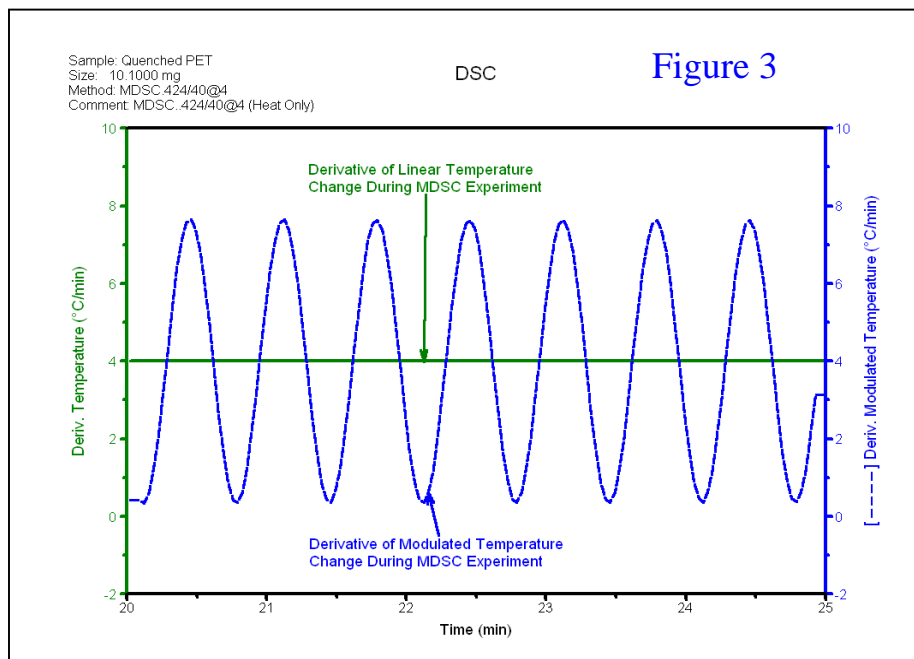


The operating principle of MDSC[®] differs from standard DSC in that MDSC[®] uses two simultaneous heating rates - a linear heating rate that provides information similar to standard DSC, and a sinusoidal or modulated heating rate that permits the simultaneous measurement of the sample's heat capacity. Creation of the sinusoidal

temperature change requires the operator to select a modulation period (seconds) and modulation temperature amplitude (\pm °C). Figure 2 shows the temperature profile from an MDSC[®] experiment.

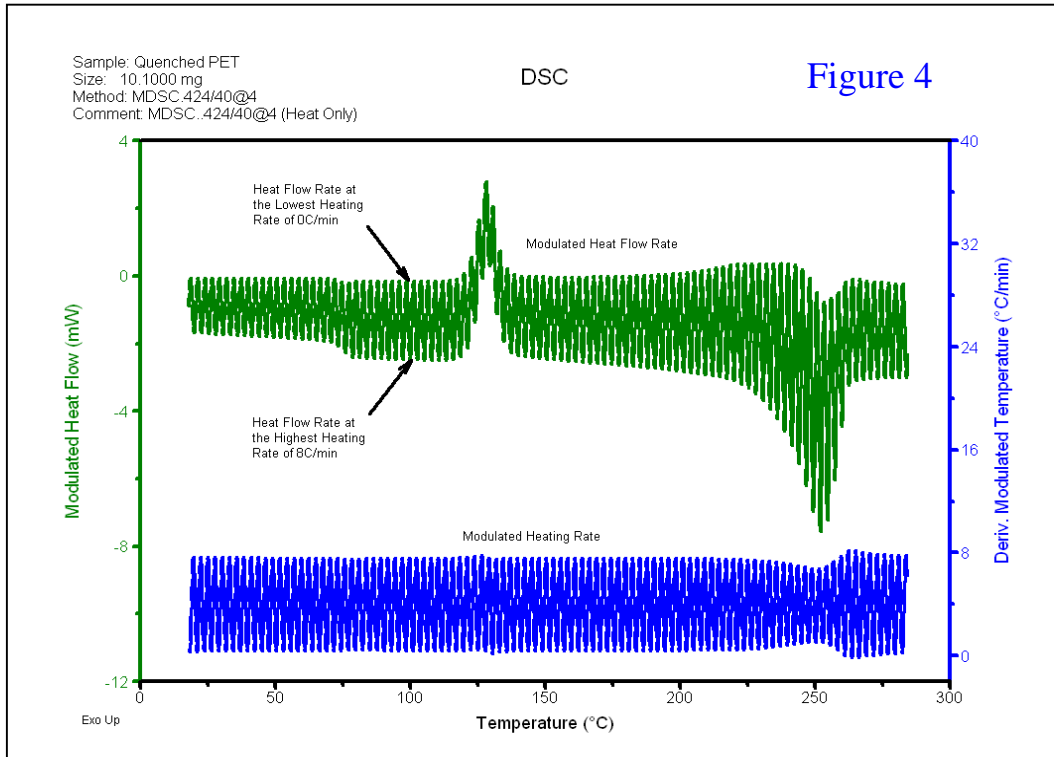


The easiest way to understand the effect of these temperature changes on the heat flow rate is to plot the time-based derivative of temperature, which is the heating rate in units of °C/min. Figure 3 shows the time-based derivatives for the temperature profiles shown in Figure 2.



Before viewing the MDSC[®] heat flow signals, a common misunderstanding of the technique needs clarification. From the appearance of the modulated heating rate in

Figure 3, MDSC has been incorrectly viewed just as a heat-cool technique. In fact it only requires that there be a periodic change in heating rate. The user is free to pick heat-only or heat-cool conditions and as seen in Figure 2 the temperature never decreases during the modulation. The sinusoidal heating rate causes a similar response in the measured heat flow rate from the calorimeter (Figure 4), which is termed the Modulated Heat Flow (MHF). Selection of optimum MDSC experimental conditions is covered in another in this series of papers on MDSC (2).



Applying simultaneous heating rates (linear and modulated) provides further information on sample heat capacity or structure. The equation that describes the heat flow signal from a DSC or MDSC[®] experiment shows the benefit of this technique.

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)$$

Where:

$\frac{dH}{dt}$ is the Total Heat Flow due to the underlying or linear heating rate. It is equivalent to standard DSC at the same average heating rate

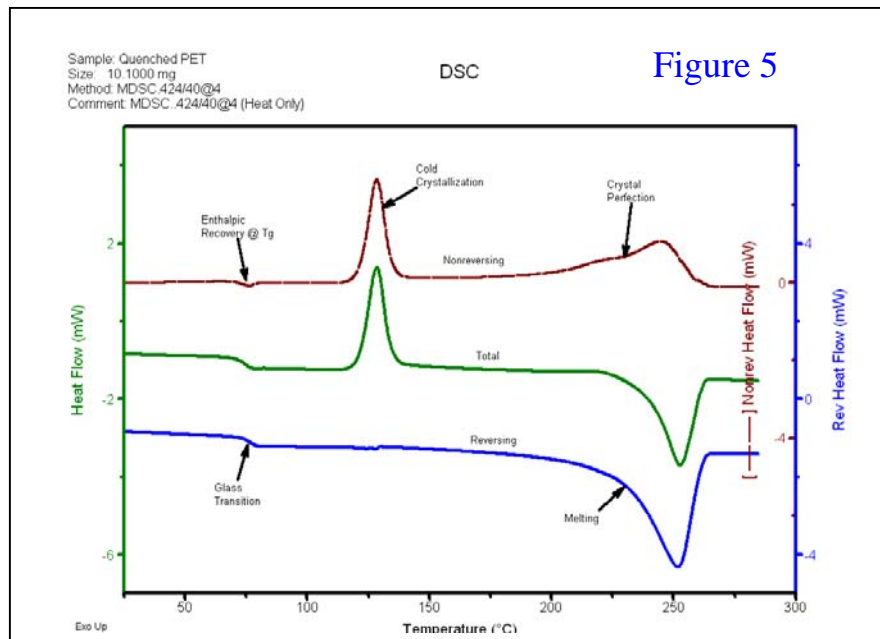
C_p is the Heat Capacity Component of the Total heat flow and is calculated from just the heat flow that responds to the modulated heating rate

$\frac{dT}{dt}$ is the measured heating rate, which has both a linear and sinusoidal (modulated) component

$f(T,t)$ is the Kinetic Component of the Total heat flow and is calculated from the difference between the Total signal and Heat Capacity Component.

$C_p \frac{dT}{dt}$ is the Reversing Heat Flow Component of the Total Heat Flow

Figure 5 shows the three most often used MDSC signals and the benefits of the dual heating rates. The Total signal (green) is equivalent to standard DSC; the Reversing signal (blue) provides information on heat capacity and melting, while the Nonreversing signal (brown) shows just the kinetic processes of enthalpic recovery at T_g, cold crystallization and crystal perfection.



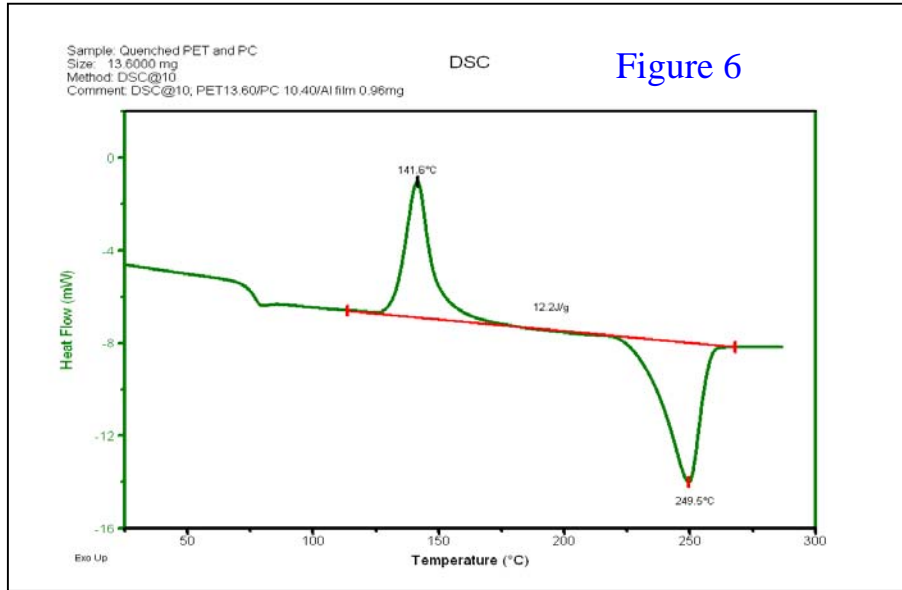
Before viewing examples of MDSC benefits, a second misunderstanding must be addressed. MDSC measures neither reversibility nor non-reversibility of transitions. The term "Reversing" was chosen because true heat capacity (heat associated with increasing or decreasing a materials temperature) is reversible. However, a heat capacity change during a transition is almost never reversible. While a transition in the Reversing signal is associated with a heat capacity change, it may or may not be reversible.

EXAMPLES OF THE BENEFITS OF MDSC

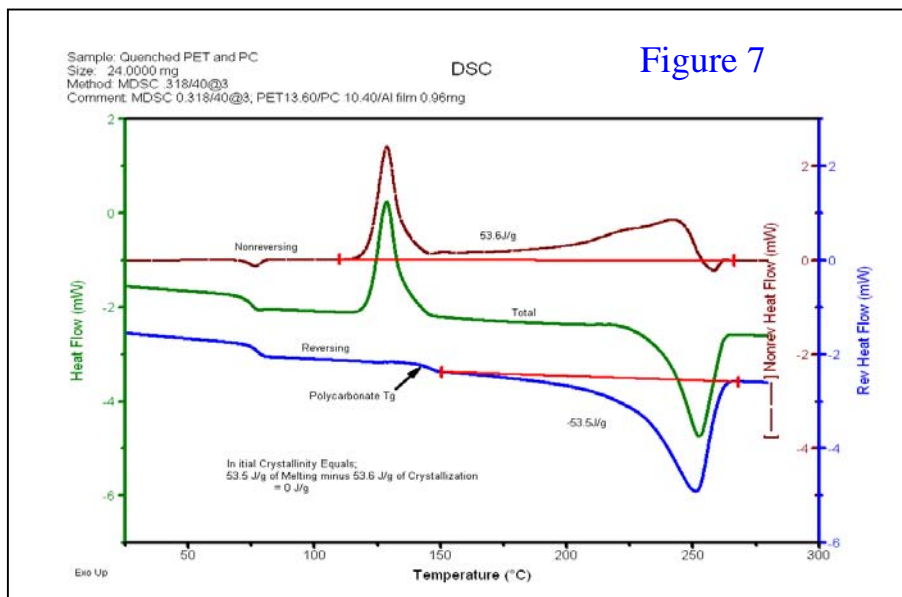
Traditional DSC provides a single signal (dH/dt) that is the sum of all thermal events occurring at a specific temperature or time during the experiment. This often causes difficulty in detection of small transitions or in data interpretation. MDSC improves upon traditional DSC since it measures the Total heat flow plus its Heat Capacity Component and obtains the Kinetic Component from their difference. Its ability to resolve complex transitions into specific components improves data interpretation.

The previous examples discussed all used a single, unblended, polymer (PET). Another sample with slightly different physical properties was analyzed by DSC and the

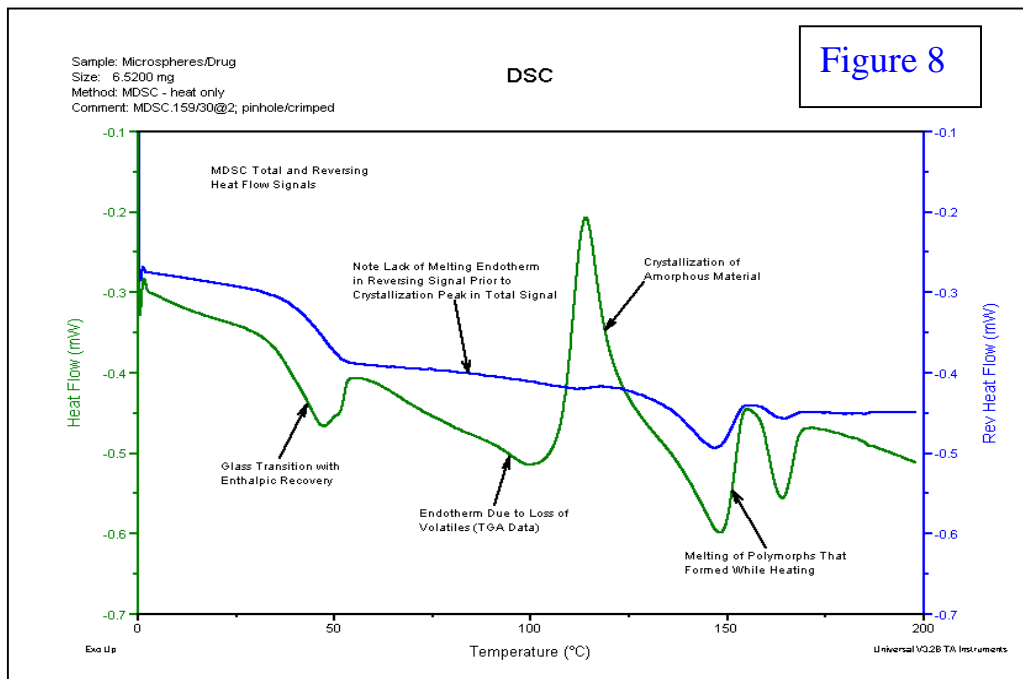
data (Figure 6) might incorrectly lead to the conclusion that the material was only PET. However, this sample was a known mixture of PET and Polycarbonate (PC). PC is amorphous with a T_g near $140\text{ }^\circ\text{C}$. In this sample, however, the T_g is undetected by traditional DSC since the heat flow due to cold crystallization in the PET occurs at the same temperature. This interpretation error would also cause an incorrect calculation of PET crystallinity (12.2 J/g from Figure 6). In fact it should be zero J/g for a quench-cooled sample.



MDSC is superior to DSC since it can separate kinetic events (e.g., a cold crystallization) from changes in heat capacity (e.g., a T_g). Figure 7 shows MDSC data for the above sample. It clearly reveals the T_g for PC in the Reversing Heat Flow signal and allows the correct calculation of crystallinity for quench-cooled PET from the sum of crystallization and melting (sum of Nonreversing and Reversing signals).



Similar, or more complex analyses can occur with pharmaceutical materials. Drug delivery systems are usually mixtures of the drug and other excipient materials. The drug can be amorphous or exist in multiple crystal forms called polymorphs. It can also be anhydrous or a hydrate, solvate or salt. As with polymers, the ability of MDSC to enhance resolution of overlapping events while maintaining high sensitivity can greatly simplify interpretation or eliminate errors in analyses. Figure 8 shows the analysis of a drug delivery system based on amorphous, biodegradable polymer microspheres. Here, the Total signal, which is the analog of standard DSC, makes it very hard to find the polymer T_g. The MDSC Reversing signal has the kinetic processes (enthalpic recovery and water evaporation) removed and permits an easy analysis of the polymer's T_g.



SUMMARY

Modulated DSC is an option with most TA Instruments DSC products. As seen above and in additional papers to follow, it has significant advantages over traditional DSC. Because the capability can be turned ON or OFF during an experiment, MDSC provides all of the benefits of DSC but is not limited by its natural limitations. In general, MDSC provides the following advantages:

- Separation of overlapping transitions
- Improved sensitivity for detecting weak transitions
- Improved sensitivity and resolution in a single experiment
- More accurate measurement of polymer initial crystallinity
- Direct measurement of heat capacity
- Quasi-isothermal measurement of heat capacity changes during reactions or kinetic processes

REFERENCES

1. MDSC Paper #2, Modulated DSC[®] Basics: Calculation and Calibration of MDSC Signals; TA Instruments Technical Paper TP 007.
2. MDSC Paper #3, Modulated DSC[®], Optimization of MDSC Experimental Conditions; TA Instruments Technical Paper TP 008

KEY WORDS

modulated differential scanning calorimetry, mdsc, differential scanning calorimetry, dsc, total heat flow, reversing heat flow, non reversing heat flow, heat capacity

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TA INSTRUMENTS

United States, 109 Lukens Drive, New Castle, DE 19720 • Phone: 1-302-427-4000 • Fax: 1-302-427-4001
E-mail: info@tainstruments.com

Spain • Phone: 34-93-600-9300 • Fax: 34-93-325-9896 • E-mail: spain@tainstruments.com

United Kingdom • Phone: 44-1-293-658900 • Fax: 44-1-293-658901 • E-mail: uk@tainstruments.com

Belgium/Luxembourg • Phone: 32-2-706-0080 • Fax: 32-2-706-0081
E-mail: belgium@tainstruments.com

Netherlands • Phone: 31-76-508-7270 • Fax: 31-76-508-7280
E-mail: netherlands@tainstruments.com

Germany • Phone: 49-6023-9647-0 • Fax: 49-6023-96477-7 • E-mail: germany@tainstruments.com

France • Phone: 33-1-304-89460 • Fax: 33-1-304-89451 • E-mail: france@tainstruments.com

Italy • Phone: 39-02-27421-283 • Fax: 39-02-2501-827 • E-mail: italia@tainstruments.com

Sweden/Norway • Phone: 46-8-594-69-200 • Fax: 46-8-594-69-209
E-mail: sweden@tainstruments.com

Japan • Phone: 813 5479 8418 • Fax: 813 5479 7488 • E-mail: nurayama@taij.po-jp.com

Australia • Phone: 613 9553 0813 • Fax: 61 3 9553 0813 • E-mail: steve_shamis@waters.com

To contact your local TA Instruments representative visit our website at www.tainst.com