Modulated DSC® Paper #3
Modulated DSC® Basics; Optimization of MDSC® Experimental Conditions

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

ABSTRACT

This paper, the third in a series on Modulated Differential Scanning Calorimetry (MDSC), reviews the optimum experimental conditions for obtaining best quality data.

INTRODUCTION

Since its inception in 1992, MDSC has proven to be a significant advancement in the science of differential scanning calorimetry (DSC) with hundreds of publications in refereed technical journals. By far the majority of these papers have developed using TA Instruments Modulated DSC instrumentation.

Selection of MDSC experimental conditions is well documented and should be the easiest aspect of MDSC to understand and implement. It is for some, however, a topic that is misunderstood and is the largest single cause of poor quality results. The main reason for errors in the selection of experimental conditions appears to be a lack of understanding of the principles of the technique.

As discussed in the first two papers in this series (1,2), MDSC does not measure the reversibility or non-reversibility of transitions, nor is it based on heating and cooling of the sample. The guiding principle of MDSC is to apply two heating rates simultaneously and measure how they affect the rate of heat flow. The underlying or average heating rate provides the same information (Total Heat Flow) as standard DSC, while the modulated heating rate permits the measurement of both the heat flow that responds to heating rate (Reversing signal) and the heat flow that responds to absolute temperature/time (Nonreversing signal). Heat capacity (Cp), changes in heat capacity and crystalline melting are all contained in the Reversing signal, while kinetic processes, such as crystallization, decomposition, evaporation, molecular relaxation and chemical reactions, contribute to the Nonreversing signal.

The secret to obtaining the best possible results from MDSC experiments is to choose optimum values for the average and modulated heating rates. This is done by first selecting the average heating rate directly, and then choosing the temperature modulation period and amplitude, which define the modulated heating rate. This paper will describe how to select all three MDSC experimental conditions. Key considerations in this process are as follows:

- The modulation period (seconds) must be long enough so that there is enough time for heat to flow between the sensor and the sample.
- The modulation amplitude (± °C) must be large enough to provide good sensitivity but not so large that it will reduce resolution.

- The average heating rate (°C/min) must be slow enough to provide a sufficient number of modulation cycles over transitions of interest.

SELECTING THE TEMPERATURE MODULATION PERIOD

The temperature modulation period is the time, in seconds, to complete one modulation cycle. MDSC uses a sine wave as the form of the periodic cycle but other periodic forms could also have been chosen. The instrument control software of the DSC / MDSC instrument permits the user to select values between 10 and 200 seconds for the modulation period. Depending on the sample (weight, thickness and thermal conductivity), sample pan, and type of measurement being made, any one the modulation period values between 10 and 200 seconds could be optimum. However, selecting the wrong value for the modulation period could result in data that is poor quality and not interpretable. The answer to the question of how to select the best or a suitable period for a particular experiment, given the number of variables listed above, is found in the following to two key points:

1. The modulation period (seconds) must be sufficiently long so that there is enough time for a quantitative measure of heat to flow between the sensor and the sample.
2. The modulation period should not be much longer than necessary for quantitative heat flow; otherwise, it will require a reduction in the average heating rate and an increase in the length of the experiment.

Fortunately, the operator can use the instrument and actual sample (in the desired type of pan) to determine the minimum modulation period for quantitative heat flow. However, because of the vast amount of experience obtained with MDSC, optimum conditions are well known and the following modulation periods are recommended. The user can verify these values using the technique described below if desired.

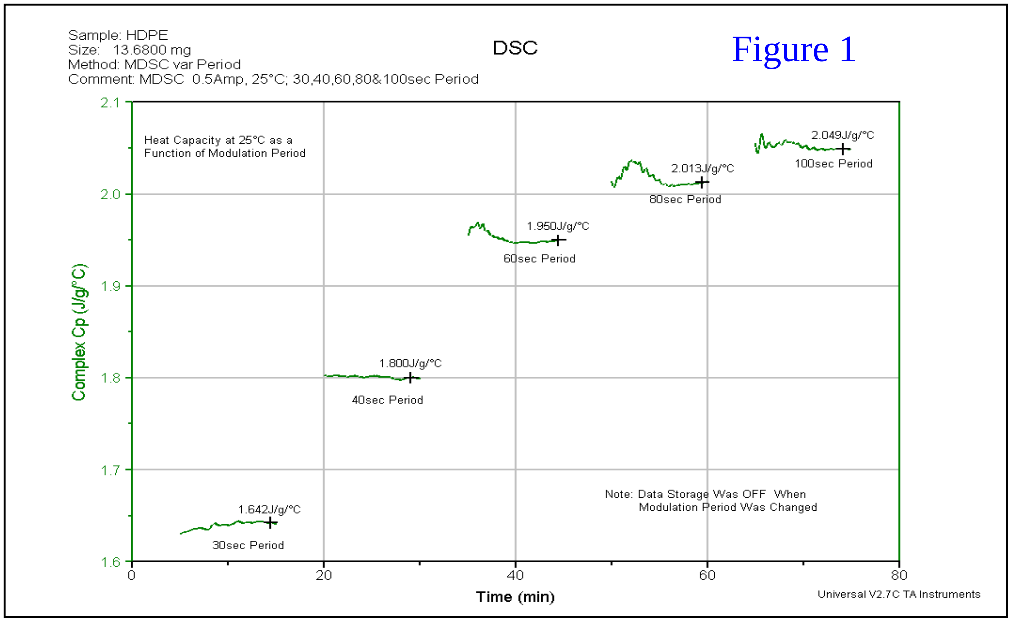
- 45 seconds to analyze transitions in samples up to 15mg contained in crimped aluminum pans. For older instruments, such as the TA Instruments DSC 2910 or 2920, the minimum recommended period is 60 seconds
- 60 seconds to analyze transitions in samples up to 15mg contained in hermetic aluminum pans. Increase the period to 70 seconds for older instruments
- 100 seconds to measure the absolute heat capacity of materials
- 200 seconds to analyze transitions in samples contained in large volume, stainless steel hermetic pans

Technique for Determining Minimum Modulation Period

As stated above, the modulation period must be sufficiently long for quantitative heat transfer to occur between the sample and the sensor. The reason for this is seen in the calculation of the Reversing Heat Capacity or Reversing Heat Flow signals. As shown in the second paper in this MDSC series (1), these signals are calculated by dividing the total change in heat flow (heat flow amplitude) by the total change in heating rate (heating rate amplitude).

$$\text{Rev Cp} = \frac{\text{Heat Flow Amplitude}}{\text{Heating Rate Amplitude}} \text{ x KCp Rev}$$

If the modulation period is too fast (shorter time), there will not be enough time for heat to flow between the sensor and sample. This will reduce the heat flow amplitude, which will result in a low value for the Reversing heat capacity and Reversing heat flow signals. Therefore, the operator can use the measured value of the Reversing Heat Capacity signal to determine how much time (modulation period) is required for quantitative heat flow. This is illustrated in Figure 1, an experiment run on an older generation DSC 2920.



In the above figure, the sample is 13.7mg of high-density polyethylene (HDPE) contained in a crimped pan with lid. The entire experiment was performed at 25 °C with a fixed temperature modulation amplitude of ± 0.5 °C. During the experiment, the temperature modulation period was increased to 30 and sequentially to 40, 60, 80 and 100 seconds respectively in ten-minute steps. As can be seen in Figure 1, the measured Complex Cp (Reversing Cp in the newer TA Instruments Q-Series 1000 or 100 models) increases by approximately 20 % as the period is increased from 30 to 60 seconds. However, it only increases by about 5 % as the period is increased from 60 to 100 seconds. This indicates that 60 seconds is a reasonable period for this combination of sample and pan. Any period longer than 60 seconds has very little affect on the accuracy of the heat capacity measurement or detection of transitions in the material. It does, however, increase the length of the experiment due to the need to have a sufficient number of modulation cycles over the temperature range of the transitions of interest.

In the above experiment, an older model DSC was used because the measured Reversing Cp signal changes more with period than with the newer Q-Series instruments, and the purpose of the figure is to illustrate the effect. The improved stability of Reversing Cp in the Q-Series instruments is the result of an improved sensor (flatter) and a slightly different approach to calculating the signal. That approach is discussed in the next paper in this series (2). The lower the measured value of the Reversing Cp signal, the larger the required calibration constant (KCp Rev). Ideally, the calibration constant would remain close to 1.0 regardless of the period used. Figure 2 shows the significantly improved performance of the Q1000 and Q100 DSCs over the older DSC2920.

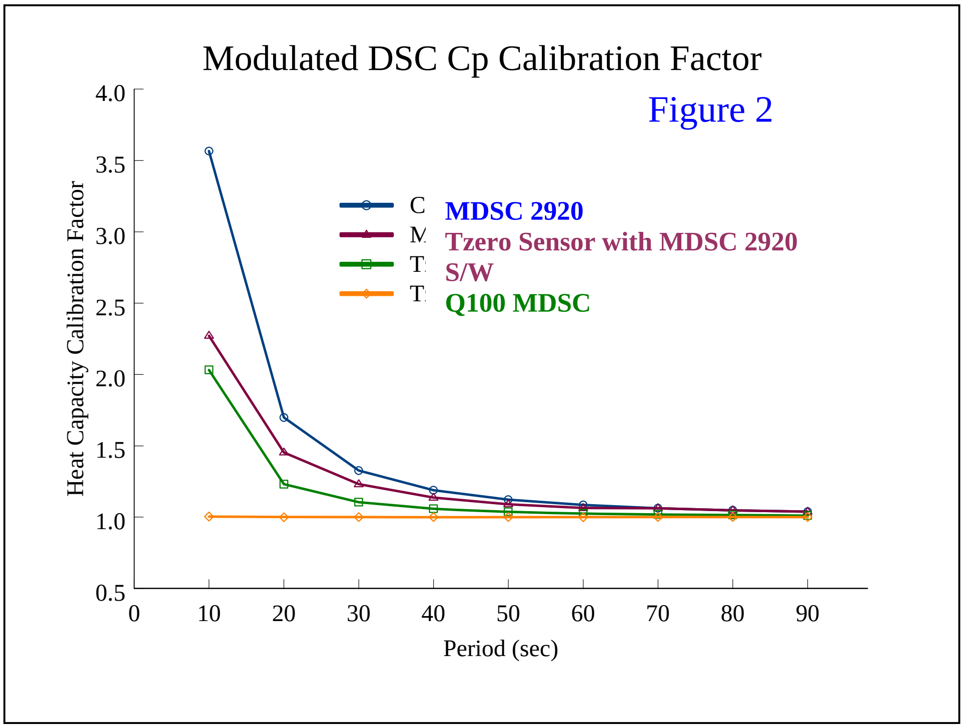


Figure 2 was created using a sapphire disk. Real samples are not as flat and have lower thermal conductivity. Therefore, the shortest recommended period for crimped pans and relatively small (<5mg) samples is 30 seconds, with best results obtained at periods of 40 seconds or longer.

SELECTING THE TEMPERATURE MODULATION AMPLITUDE

The temperature modulation amplitude is the sinusoidal temperature change (± °C) superimposed on the average temperature change. The time-based derivative of this temperature change gives the modulated heating rate (°C/min). With standard DSC, high heating rates provide increased sensitivity because they create larger heat flow signals. With MDSC, larger temperature modulation amplitudes give larger changes in heating rate and this provides increased sensitivity for transitions involving a change in heat capacity. Unlike the modulation period, the modulation amplitude has no affect on MDSC calibration as seen in Figure 3, where the measured heat capacity remains constant over the modulation amplitude range from ± 0.2 to 3.2 °C. This experiment is similar to that shown in Figure 1 and is conducted at the isothermal temperature of 25 °C. In this experiment the modulation period is fixed at 60 seconds and the modulation amplitude is increased every 10 minutes as shown.

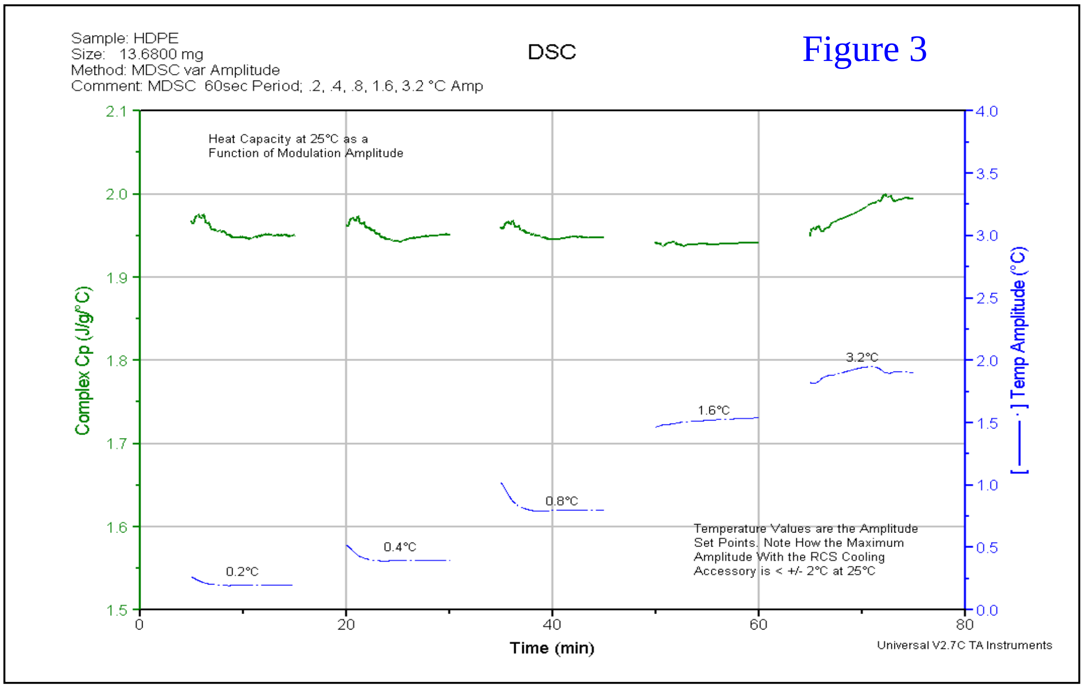
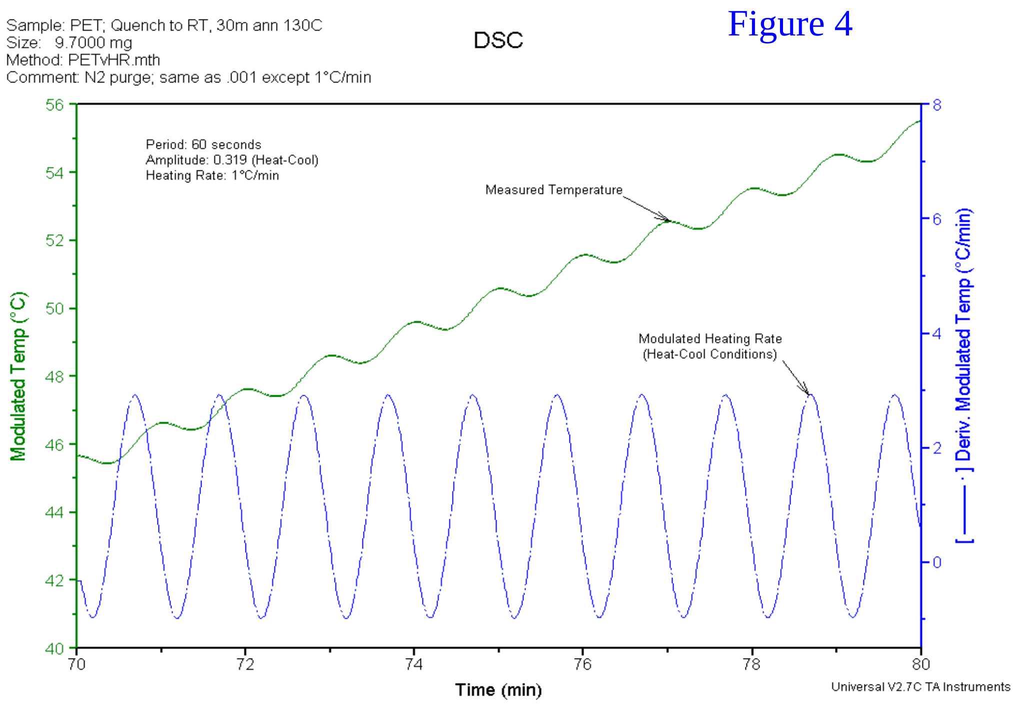


Figure 3

As with the modulation period, extensive practical experience with MDSC has shown that there is an optimum range of values for the modulation amplitude. Amplitudes less than ± 0.1 °C are not recommended for use because they give poor sensitivity, while amplitudes greater than ± 2.0 °C have been found to decrease resolution. The operating software permits selection of amplitude values from ± 0.001 to 10 °C. In practice, the useful range is much narrower and there are very specific recommendations on how to select the optimum modulation amplitude for a given experiment.

For most experiments, the amplitude is selected to provide or not to provide cooling during the modulation. The latter conditions result in the heating rate never going below 0° C/min. An example of such experimental conditions designed to cause cooling during the temperature modulation is shown in Figure 4 with Polyethylene Terephthalate (PET) as the sample. Here, the average heating rate is 1.0 °C/min. with a modulation period of 60 seconds and modulation amplitude of ± 0.319 °C.



As shown in Figure 4, the modulated temperature is seen to increase and decrease as the average temperature increases. The time-based derivative of this signal shows that the average heating rate is 1.0 °C/min, while the modulated heating rate ranges from approximately -1.0 to 3.0 °C/min. This overall range of 4.0 °C/min is the result of the selected period and amplitude. Conditions of this type, where the selection has provided for both heating and cooling during the temperature modulation, are found to be best for measuring heat capacity or changes in heat capacity. As such, they are ideal for identifying events such as a glass transition (Tg).

The data displayed in Figure 5 results from selection of conditions involving the same modulation period (60 seconds) and same modulation amplitude (± 0.319 °C) as the for that shown in Figure 4. The difference is that the average heating rate has been increased to 2 °C/min. Under these conditions, there is still a range of 4 °C/min involved (0 to 4 °C/min), but now there is no cooling during the modulation as seen in the modulated temperature signal. These experimental parameters are often referred to as "heat-iso" conditions because the heating rate is intended to go to zero (isothermal) with no cooling. Heat-iso conditions are recommended as the method of choice for the measurement of crystallinity. The reasons for this are discussed in more detail in the sixth paper in this MDSC series, which covers the measurement of initial crystallinity in semi-crystalline polymers (3).

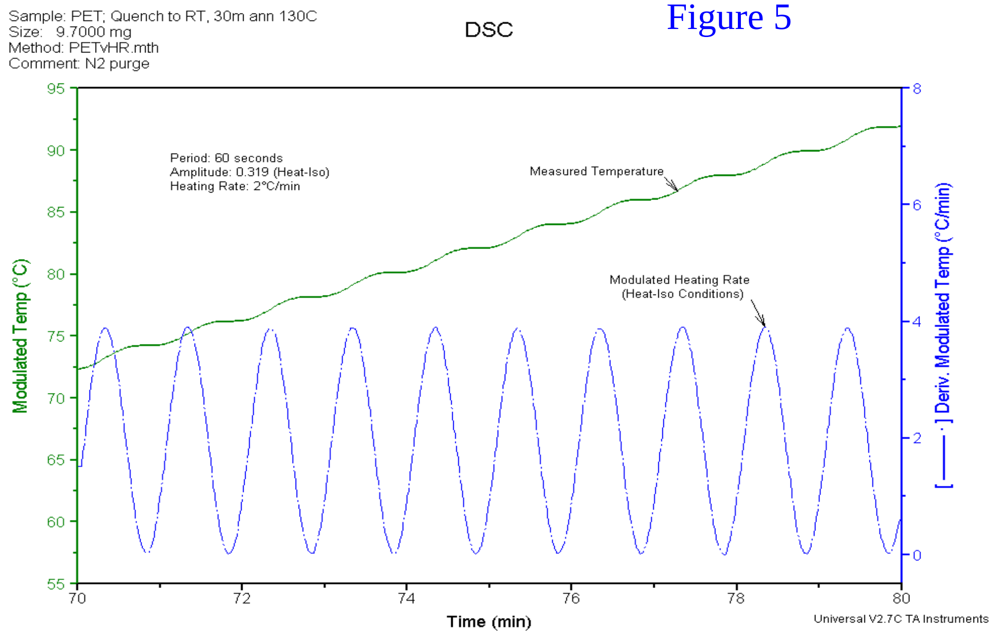


Figure 5

At this point, the reader may be thinking that all of this is easy to follow but "how is the amplitude actually selected to provide cooling or no cooling conditions. Fortunately, TA Instruments experience has resulted in production of the following table that makes the selection process very easy and it is shown in Figure 6.

Figure 6

Period (sec)

Heating Rate	40	50	60	70	80	90	100
0.1	0.011	0.013	0.016	0.019	0.021	0.024	0.027
0.2	0.021	0.027	0.032	0.037	0.042	0.048	0.053
0.5	0.053	0.066	0.080	0.093	0.106	0.119	0.133
1.0	0.106	0.133	0.159	0.186	0.212	0.239	0.265
2.0	0.212	0.265	0.318	0.371	0.424	0.477	0.531
5.0	0.531	0.663	0.796	0.928	1.061	1.194	1.326

This table is additive, i.e. the heat only amplitude for a period of 40 sec and heating rate of 2.5°C/min. is the sum of the values for 2.0°C/min and 0.5°C/min:

Amplitude (40s, 2.5°C/min) = 0.212 + 0.053 = ±0.265°C

The table in Figure 6 can be readily used in the following way. The operator first selects the modulated period and average heating rate that will be used for the experiment. If heat-iso conditions are desired, the amplitude value can be taken directly from the table. If heat-cool conditions are desired, then any amplitude greater than the indicated amplitude will produce cooling during the modulation. The amount of cooling and the sensitivity of the signal to changes in heat capacity increase as the amplitude is increased. Based on experience with MDSC, the amplitude value should be increased by the factors below, depending on the type of measurement.

Glass Transitions (Tg)

- For "standard Tg":
  Sample Size: 10 – 15 mg   Amplitude   2X Table
  Period: 40 seconds   Heating Rate: 3°C/min

- Tg is Hard to Detect (Figures 28 – 30)
  Sample Size: 10 – 20 mg   Amplitude: 4X Table
  Period: 60 seconds   Heating Rate: 2°C/min

Tg has Large Enthalpic Relaxation
  Sample Size: 5 – 10 mg   Amplitude: 1.5X Table
  Period: 40 seconds   Heating Rate: 1°C/min

Note; These are reasonable starting conditions which may need to be adjusted depending on the transition of interest

Note that sample sizes range from 5 to 20mg. above. For most experiments, a starting weight of ten (10) milligrams is recommended, and it can be increased for improved sensitivity or decreased for improved resolution.

SELECTING THE AVERAGE HEATING RATE

In general, the average heating rate should be as fast as possible to increase productivity **but must be sufficiently slow to obtain a minimum number of modulation cycles over the temperature range of the transition.** This minimum is four or more cycles over the critical range the thermal event under consideration (where the transition is changing the fastest). For transitions involving peaks, the minimum is determined at half-height of the peak as shown in Figure 7 for the melting of Polyethylene Terephthalate (PET).

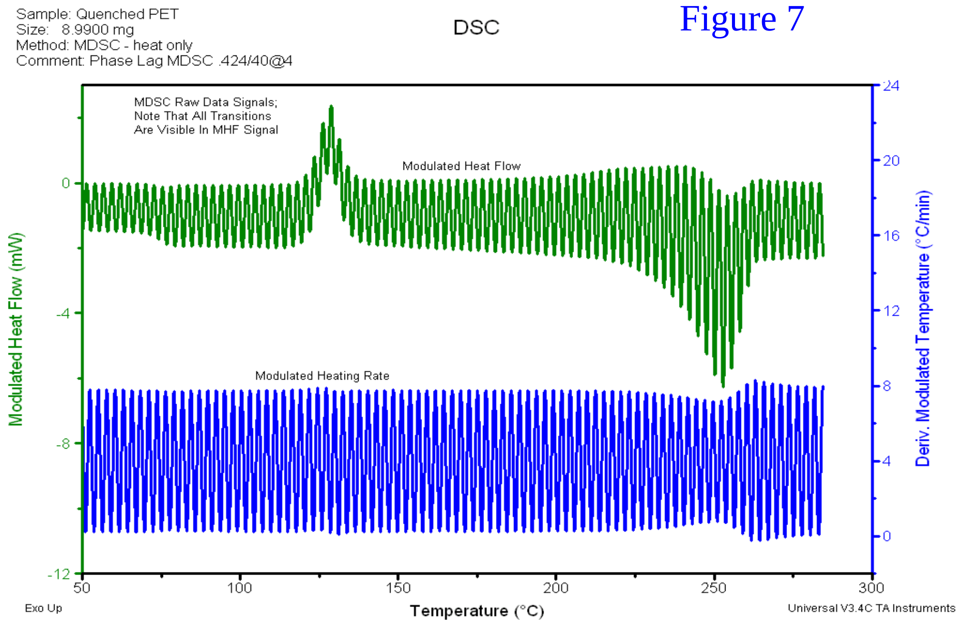


Figure 7

As can be seen in Figure 7, at half-height of the melting peak near 250 °C, there are approximately seven cycles, which meets the requirement of four (4) or more. However, there are only three cycles at half-height of the cold-crystallization peak and this indicates that the average heating rate is slightly too fast. This experiment was done at 4 °C/min and better results would be obtained at 3 °C/min because all transitions involving peaks would have four or more cycles at half-height of the peak. For glass transitions or other transitions involving a step-change in heat capacity, the minimum number of cycles is still four (4) and is determined between the extrapolated on-set and extrapolated end-set of the step.

SUMMARY

Optimum MDSC results are obtained when the analyst clearly understands what is being measured by the technique and selects experimental conditions that permit proper separation of the Total heat flow into the Reversing and Nonreversing components. Heat transfer in MDSC is very important because of the changing heating rate. The analyst must keep the sample as thin as possible and adjust the modulation period for the type of instrument and sample pan used in the experiment.

REFERENCES

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2. Modulated DSC Basics; Calculation and Calibration of MDSC Signals; TA Instruments Technical Paper TP 007.
3. Modulated DSC; Measurement of Initial Crystallinity in Semi-Crystalline Polymers; TA Instruments Technical Paper TP 011.

KEY WORDS

modulated differential scanning calorimetry, mdsc, dsc, modulation period, modulation amplitude

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