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## **Modulated DSC<sup>®</sup> Paper #6 Measurement of Initial Crystallinity in Semi-crystalline Polymers**

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### **ABSTRACT**

This paper shows that under the correct operating conditions, MDSC is a very powerful and reliable technique for the measurement of polymer initial crystallinity.

### **INTRODUCTION**

Differential Scanning Calorimetry (DSC) has been used to measure the heat of crystalline melting (J/g) in polymers for over 40 years and is the most widely used technique in the polymer industry. However, results on semi-crystalline polymers and blends are often hard to interpret and typical analyses can be in error by as much as 50 %.

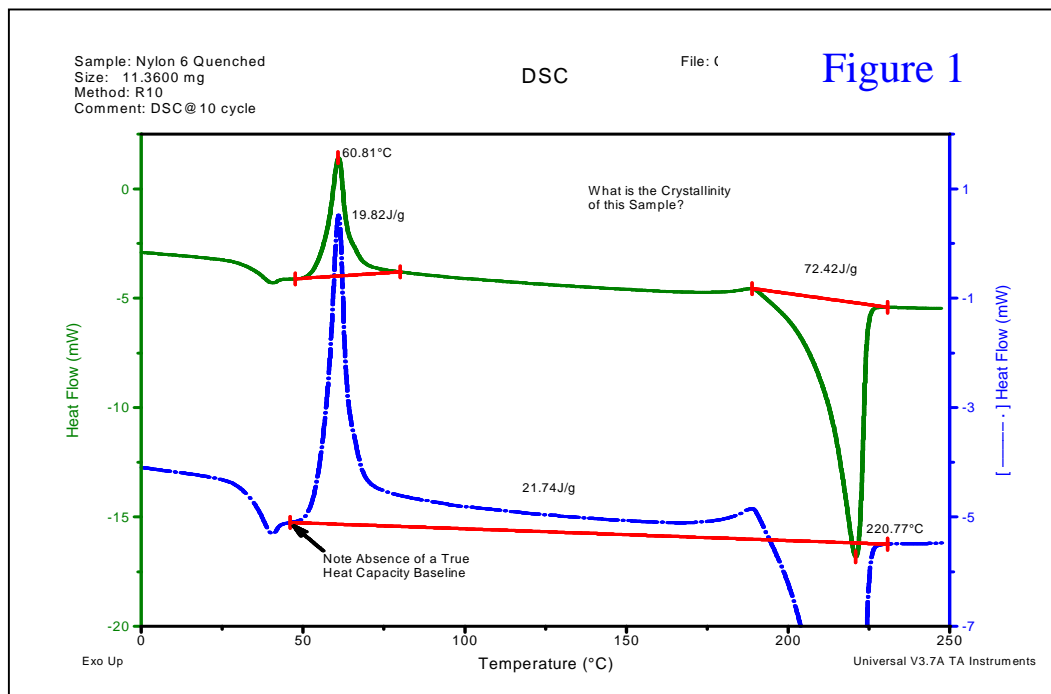
A 1997 article by Y. P. Khanna and W. P. Kuhn (1) summarizes the causes of the significant errors obtained by DSC. It also describes how a combination of analytical techniques such as DSC, XRD and NMR, when combined with extensive experience, can be used to obtain more reliable "initial crystallinity" values, which can be viewed as the crystallinity of the sample prior to heating it in the DSC.

The purpose of this paper is to show that MDSC is a very reliable technique for the measurement of polymer initial crystallinity. This will be accomplished as follows:

- Illustrating the problems associated with measuring crystallinity by standard DSC
- Reviewing the process of selecting optimum MDSC experimental conditions for polymer crystallinity measurement as discussed a previous paper in this series (2)
- Showing that MDSC can measure more accurate values of crystallinity than can be obtained by DSC
- Discussing two issues / concerns of the use of MDSC for analysis of melting and showing that they do not affect MDSC results

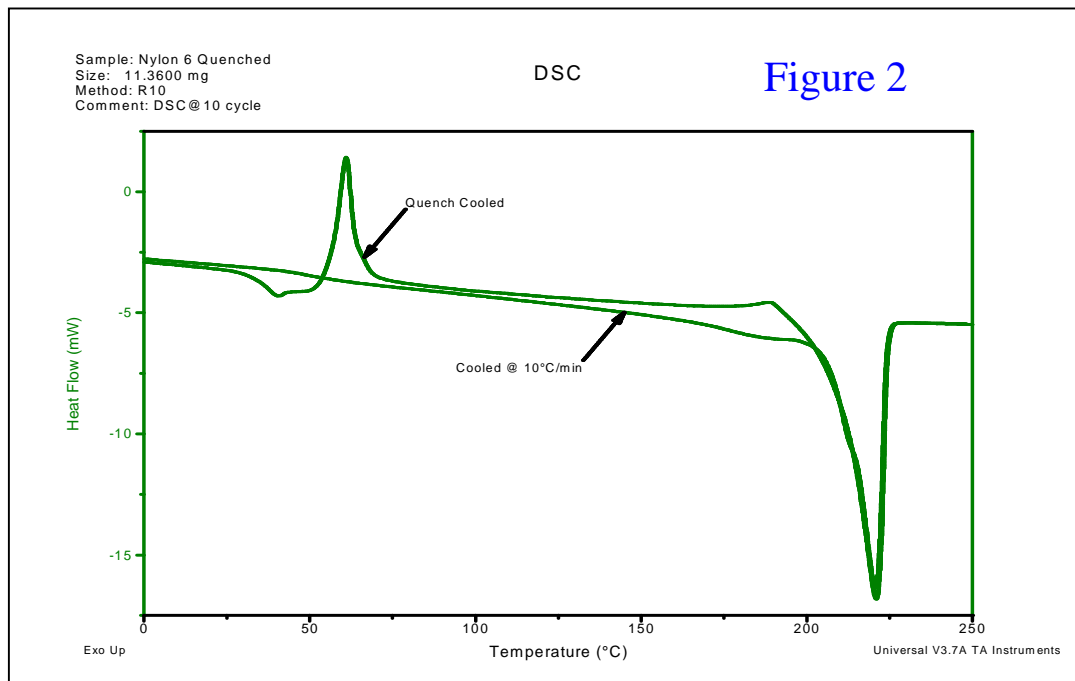
### **PROBLEMS OF STANDARD DSC**

In order to be able to measure the energy associated with any transition in DSC, it is necessary to be able to identify the baseline before and after the transition and use it to set analysis limits. This "baseline" region in the data is where there is no transition occurring and the heat flow signal is due only to the heat capacity of the sample. With this in mind, consider the DSC results on a Nylon 6 sample in Figure 1 that are similar to those given in the paper by Khanna (1).



The data in Figure 1 shows a DSC heat flow signal for Nylon 6 plotted at two different sensitivities. The plot illustrates two possible approaches to measuring the crystallinity of the sample. The top example (green trace) assumes that the region between about 75 °C and 175 °C is a baseline where there is no transition. The relative crystallinity in J/g would be calculated by subtracting the area of the cold crystallization peak (19.8 J/g) from the melting enthalpy of 72.4 J/g. This produces a crystallinity value of 52.6 J/g. The lower example assumes that the region between the cold crystallization and melting peaks is not a baseline region but the heat capacity baseline is linear over the temperature range from about 35 °C to 230 °C. Using this baseline to integrate the sum of the crystallization and melting peaks produces a crystallinity of 21.7 J/g, which is only 40 % of the value obtained in the first approach. Which approach is correct? The answer is that neither are correct but the value of 21.7 J/g is much closer to the real value, as will be illustrated later using MDSC®.

There are at least two causes for the large difference in results. The first is due to the fact that most semi-crystalline polymers undergo what Khanna terms “silent crystallization” as they are heated. Secondly, DSC has the ability (or limitation) of being able to measure only the sum of all heat flow events occurring at a particular time and temperature. This means that the endothermic melting of some crystals hides the exothermic crystallization of others. An experienced analyst using a DSC that has a stable baseline can often determine if a sample is developing additional crystallinity as it is heated by comparing results of the as-received sample with those of the same sample after it has been slowly cooled ( $\leq 10$  °C/min) from a temperature above the melt. This is illustrated in Figure 2, which compares results on the Nylon 6 sample from Figure 1 with those obtained after cooling it at 10 °C/min.



When comparing the results in Figure 2, the assumption is that a sample cooled slowly from the melt is already highly crystalline and will not develop much additional crystallinity as it is heated in the DSC. There are at least two significant points to be made from this comparison.

- A quench-cooled sample should have lower crystallinity and, therefore, a higher heat capacity than a slow-cooled sample. This higher heat capacity should result in a more endothermic baseline. A comparison of the heat flow signals in the region between 50 and 200 °C shows that the quench-cooled sample has a less endothermic baseline over this entire region, which can only be caused by ongoing exothermic crystallization as the sample is heated.
- A sample cooled at 10 °C/min should have more perfect crystals than a quench-cooled sample and therefore, the onset of melting should be at a higher temperature. The results in Figure 2 show that the sample cooled at 10 °C/min begins to melt as low as 150 °C, which is as much as 50 °C lower than the quench-cooled sample. This is just the opposite of what is expected. Since DSC can only see the sum of all heat flows, it cannot detect the true onset of melting because it is hidden by the stronger, exothermic crystallization and crystal perfection which occur as the sample is being heated.

### SELECTING MDSC EXPERIMENTAL CONDITIONS

A more detailed discussion on the process of selecting optimum MDSC experimental conditions can be found in the third paper in this series entitled Optimization of MDSC Experimental Conditions (2). The key points for the analyst to remember include the following:

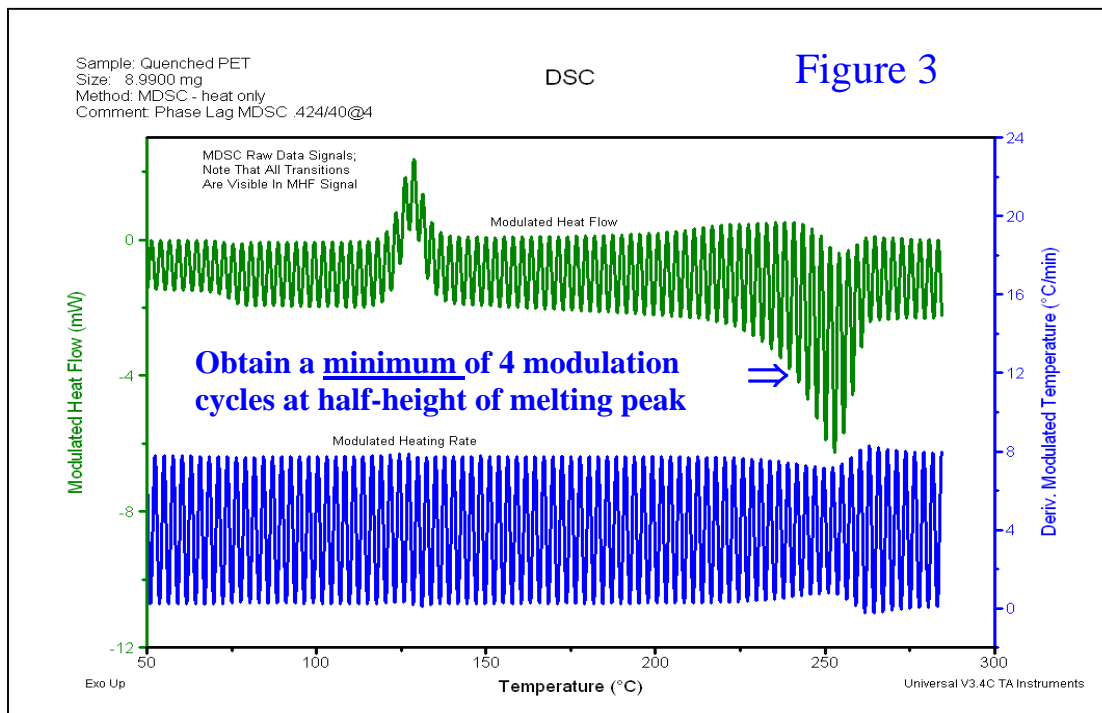
- The modulation period (seconds) must be sufficiently long so that there is enough time for heat to flow between the sensor and the sample.
- The modulation amplitude ( $\pm$  °C) must be sufficiently large to provide good sensitivity but not so large that it will reduce resolution.

- The average heating rate ( $^{\circ}\text{C}/\text{min}$ ) must be slow enough to provide a sufficient number of modulation cycles over transitions of interest.

Applying these guidelines to the analysis of polymer crystallinity, the following conditions are recommended:

**Modulation Period:**

- Crimped pans: 40 seconds for the Q100 and Q1000 DSC and 60 seconds for the older 2910 and 2920 models.
- Hermetic pans: 60 seconds for Q100 and Q1000, and 80 seconds for the 2910 and 2920 models.
- Modulation Amplitude: Use the value indicated in the table below once an average heating rate is selected (or use a template provided in the software for the Q Series DSCs)
- Average Heating Rate: Sufficiently slow to obtain a minimum of 4 modulation cycles at half-height of the melting peak as illustrated in Figure 3.
- Sample Size: 10-15mg (keep sample thin)



## Table of Amplitude Values Used to Create Heat-Iso (No Cooling) Temperature Modulation

		Period (sec)						
		40	50	60	70	80	90	100
<i>H e a t i n g</i>	<b>0.1</b>	0.011	0.013	0.016	0.019	0.021	0.024	0.027
	<b>0.2</b>	0.021	0.027	0.032	0.037	0.042	0.048	0.053
	<b>0.5</b>	0.053	0.066	0.080	0.093	0.106	0.119	0.133
	<b>1.0</b>	0.106	0.133	0.159	0.186	0.212	0.239	0.265
	<b>2.0</b>	0.212	0.265	0.318	0.371	0.424	0.477	0.531
<i>R a t e</i>	<b>5.0</b>	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:**

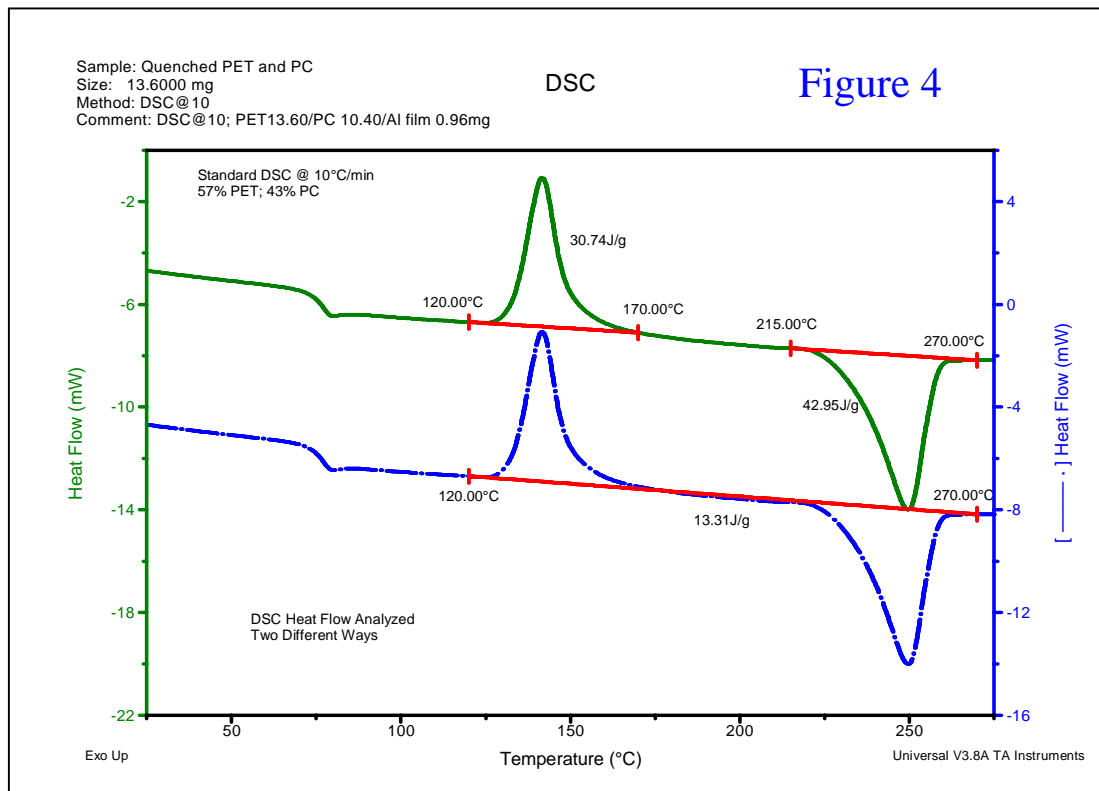
$$\text{Amplitude (40s, 2.5°C/min)} = 0.212 + 0.053 = \pm 0.265^\circ\text{C}$$

The experimental conditions used for the data in Figure 3 were a period of 40 seconds, a heating rate of 4 °C/min and an amplitude of 0.424 °C. Note that the above table does not list a 4 °C/min heating rate. However, the table is linear as indicated and the value provided for 2 °C/min was doubled and used. These conditions provide only a positive heating rate with no cooling as can be seen in the heating rate signal of Figure 3.

### ACCURACY OF THE MDSC CRYSTALLINITY MEASUREMENT

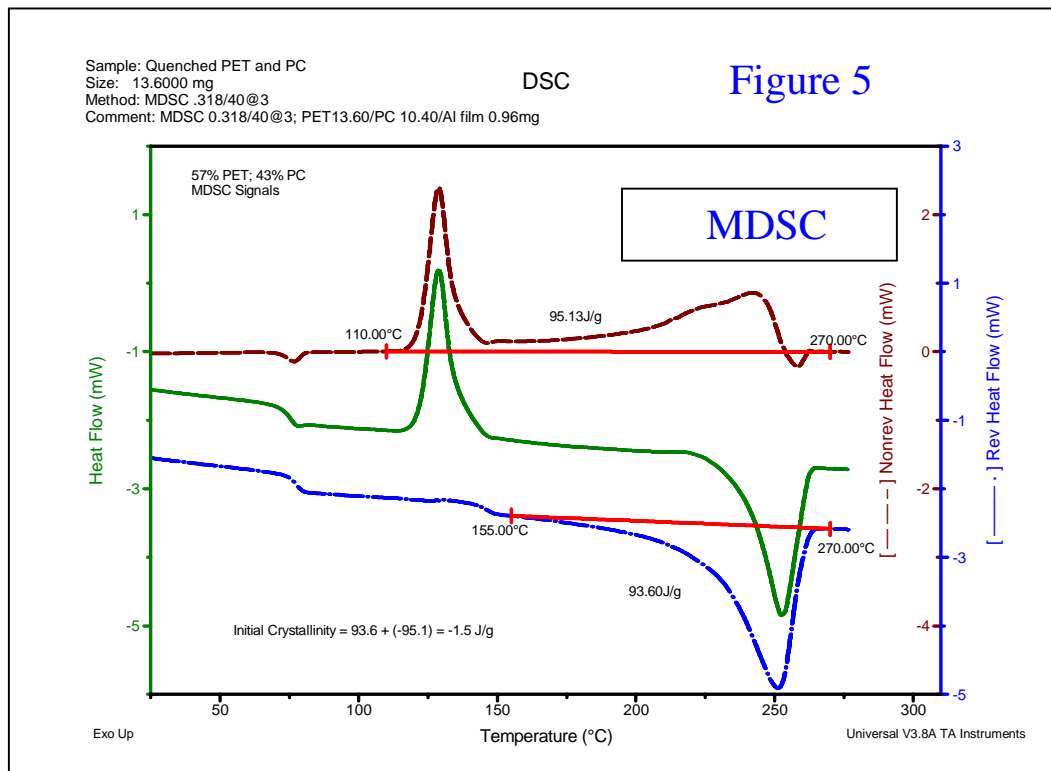
One of the difficulties in illustrating the problems of standard DSC or the improved capability of MDSC is that there are no polymer standards for crystallinity. However, this problem is easily overcome by using two polymers that are known to have no crystallinity. These are Polycarbonate (PC) and quench-cooled Polyethylene Terephthalate (PET). The sample is "quench-cooled" by heating it to 275 °C for 5 minutes and then removing it from the DSC cell at that temperature and placing it on a metal surface at room temperature. This provides an effective cooling rate of several thousand degrees per minute to a temperature below the PET Tg that is near 70 °C.

Since the PET crystallizes as it is being heated, it shows a very clear melting peak above 200 °C as seen in Figure 4. In this particular example, the sample pan contains both PC (10.40mg) and PET (13.60mg), which are separated with a 1mg piece of aluminum foil. The PC is amorphous and has a glass transition is near 140 °C. This transition is not seen in the DSC data in Figure 4 because of the cold crystallization peak in the PET that occurs over the same temperature range. Remember, DSC can only measure the sum of all heat flows.



As with Figure 1, the data is plotted twice and analyzed in two different ways. In both cases, a crystallinity value of 12-13 J/g is obtained. This is a very large error since the crystallinity of the mixture of PC and PET is known to be zero. It is not surprising that such a large error would occur with DSC because it cannot even detect the glass transition of the PC near 140 °C.

MDSC analysis of the same sample is shown in Figure 5. The MDSC Total signal (green) is essentially identical to that from standard DSC and shows only the sum of all heat flow. The Reversing signal (blue) contains heat capacity, changes in heat capacity (i.e. glass transitions) and most melting. Clearly seen are the glass transition of the PET around 70 °C, the glass transition of the PC near 140 °C, and melting of the PET between 150 and 270 °C respectively. The Nonreversing signal (brown) contains time-dependent or kinetic processes. It shows enthalpic recovery at the PET glass transition, cold crystallization of the PET starting just above 110 °C and "crystal perfection" from just above the cold crystallization to the end of the melting peak near 270 °C. "Crystal Perfection" is the process of the smallest, least perfect crystals melting at temperatures below the thermodynamic melting point and then crystallizing and melting one or more times as sample temperature increases.

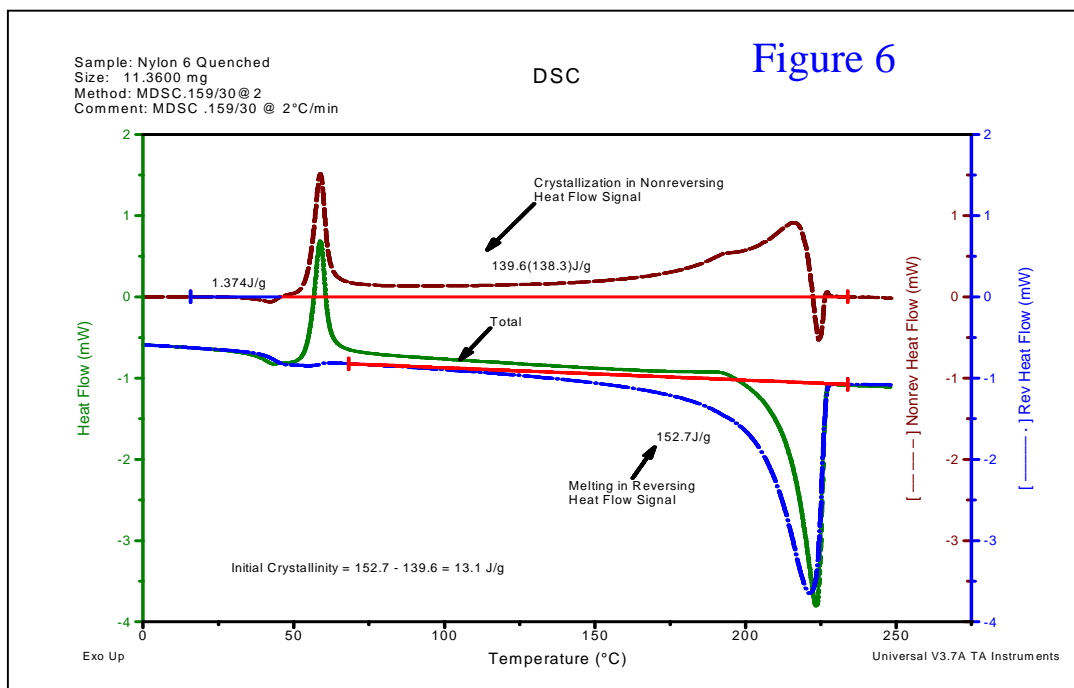


Initial crystallinity from MDSC data is always calculated from the sum of all melting and crystallization observed in the Reversing and Nonreversing signals. Therefore, there is no effect of some melting occurring in the Nonreversing signal as seen in Figure 5 near 260 °C. Integration of heat flow in the Nonreversing signal should begin at a temperature prior to any observed exotherm and end at a temperature above the melting peak. From Figure 5, this provides a value of 95.1 J/g. Integration of the Reversing signal should begin prior to any observed endothermic melting and end at a temperature above the melting peak. This provides a value of 93.6 J/g in Figure 5. Since crystallization is exothermic and melting is endothermic the sum of the integrations provides a value of just 1.5 J/g which is within experimental error of the known value of zero crystallinity.

Two additional points can be made from the MDSC data.

- Melting can be seen as low as 150 °C in the Reversing signal while it is not observed in the Total signal until almost 225 °C due to the crystal perfection process.
- Since crystal perfection starts when the smallest crystals begin to melt, the first sign of exothermic crystal perfection in the Nonreversing signal can be used to assist with detecting the onset of endothermic melting in the Reversing signal.

As shown in Figures 1 and 2, it is very difficult to use DSC for measurement of crystallinity of Nylon 6 that has been cooled rapidly from a temperature above its melting point. Possible DSC crystallinity results ranged from 21.7 to 52.6 J/g. The MDSC results in Figure 6 show a more accurate value of only 13.1 J/g and indicates that the melting process begins close to 100 °C in the Reversing signal as compared to 200 °C in the Total signal.



## TWO THEORETICAL ISSUES / CONCERNS ABOUT USE OF MDSC FOR THE MEASUREMENT OF INITIAL CRYSTALLINITY

### Sample Temperature Cannot Be Modulated During the Melting Process

This is true only for relatively pure materials that melt over a narrow (5-10 °C) temperature range (metals, chemicals and pharmaceuticals drugs). Polymers melt over a broad temperature range due to distributions in molecular weight and crystal size, and there is no problem with modulating sample temperature during the melting process.

### The Areas of the Crystallization and Melting Peaks in MDSC Results Change With Changes in MDSC Experimental Conditions

This is also true but has no effect on the measured initial crystallinity as long as it is calculated from the sum of all melting and crystallization observed in the Reversing and Nonreversing signals. Since the Nonreversing signal measures time dependent process, the amount of melting observed in the Nonreversing signal increases whenever:

- Sample weight or thickness are increased (time for heat flow increases)
- The modulation period (time of each modulation cycle) is decreased
- The modulation amplitude is increased to cause cooling during the temperature modulation (less time for heating during each modulation cycle)
- The average heating rate (time vs. temperature) is decreased

## SUMMARY

Modulated DSC is a very reliable technique for the measurement of initial crystallinity in polymers. The ability to separate the melting and crystallization processes into two different signals permits accurate selection of baselines and thus superior choice of integration limits for quantitative crystallinity measurements. MDSC overcomes the natural limitation of DSC, which has the ability to only measure the sum of all heat flows.



## REFERENCES

1. Y. P. Khanna and W. P. Kuhn (Journal of Polymer Science: Part B: Polymer Physics Vol. 35, No. 14, 1997); "Measurement of Crystalline Index in Nylons by DSC: Complexities and Recommendations"
2. MDSC Paper #3, Modulated DSC<sup>®</sup> Basics; Optimization of MDSC Experimental Conditions; TA Instruments Technical Paper (TP008)

## KEY WORDS

modulated differential scanning calorimetry, mdsc, dsc, polymers, crystallinity

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