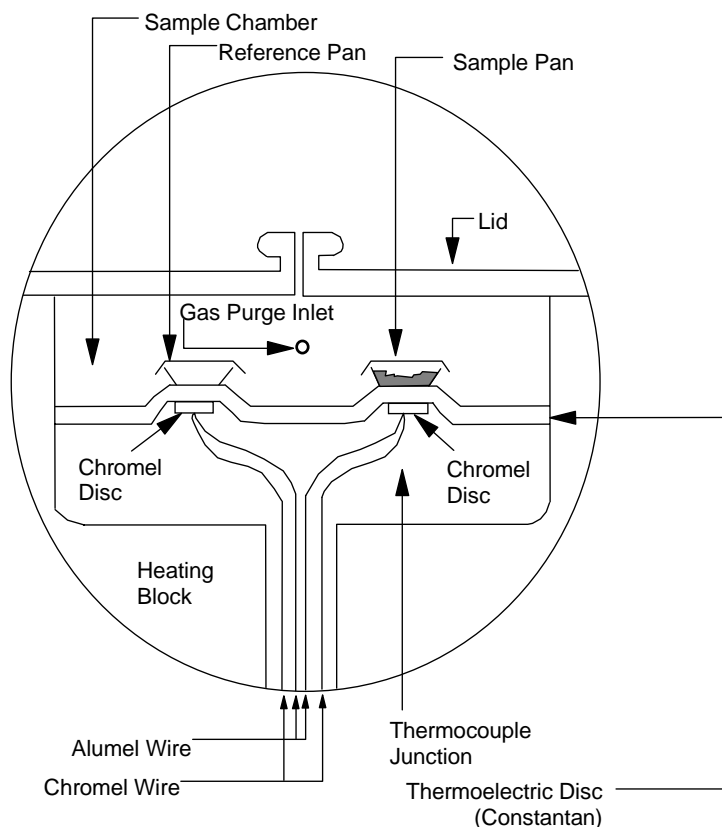# TA Instruments

Thermal Analysis & Rheology

THERMAL ANALYSIS REVIEW
MODULATED DSC™ THEORY

Modulated DSC (MDSC) can be easily understood by comparing it to its well-established precursor, differential scanning calorimetry (DSC). Conventional DSC is an analytical technique in which the difference in heat flow between a sample and an inert reference is measured as a function of time and temperature as both the sample and reference are subjected to a controlled environment of time, temperature, atmosphere and pressure. The schematic of a typical "heat flux" DSC cell is shown in Figure 1. In this design, a metallic disk (made of constantan alloy) is the primary means of heat transfer to and from the sample and reference. The sample, contained in a metal pan, and the reference (an empty pan) sit on raised platforms formed in the constantan disk. As heat is transferred through the disk, the differential heat flow to the sample and reference is measured by area thermocouples formed by the junction of the constantan disk and chromel wafers which cover the underside of the platforms. Chromel and alumel wires attached to the chromel wafers form thermocouples which directly measure sample temperature. Purge gas is admitted to the sample chamber through an orifice in the heating block wall midway between the raised platforms. The gas is preheated by circulation through the block before entering the sample chamber. The result is a uniform, stable thermal environment which assures excellent baseline flatness and exceptional sensitivity (signal-to-noise). In conventional DSC, the temperature regime seen by the sample and reference is linear heating or cooling at rates from as fast as 200°C/minute to rates as slow as 0°C/minute (isothermal).

Figure 1: HEAT FLUX DSC SCHEMATIC

Sample Chamber
Reference Pan
Sample Pan
Lid
Gas Purge Inlet
Chromel Disc
Chromel Disc
Heating Block
Alumel Wire
Chromel Wire
Thermocouple Junction
Thermoelectric Disc (Constantan)

TA-211B

Modulated DSC is a technique which also measures the difference in heat flow between a sample and an inert reference as a function of time and temperature. In addition, the same "heat flux" cell design is used. However, in MDSC a different heating profile (temperature regime) is applied to the sample and reference. Specifically, a sinusoidal modulation (oscillation) is overlaid on the conventional linear heating ramp to yield a heating profile (solid line in Figure 2) in which the average sample temperature still continuously increases with time but not in a linear fashion. The net effect of imposing this more complex heating profile on the sample is the same as if two experiments were run simultaneously on the material - one experiment at the traditional linear (average) heating rate [dashed line in Figure 2] and one at a sinusoidal (instantaneous) heating rate [dashed-dot line in Figure 2]. The actual rates for these two simultaneous experiments is dependent on three operator-selectable variables:

·   Underlying heating rate (range 0-10°C/minute; see next page for recommended conditions)
·   Period of modulation (range 10-100 seconds; see next page for recommended conditions)
·   Temperature amplitude of modulation (range ±0.01-10°C; see next page for recommended conditions)

Figure 2: MDSC HEATING PROFILE
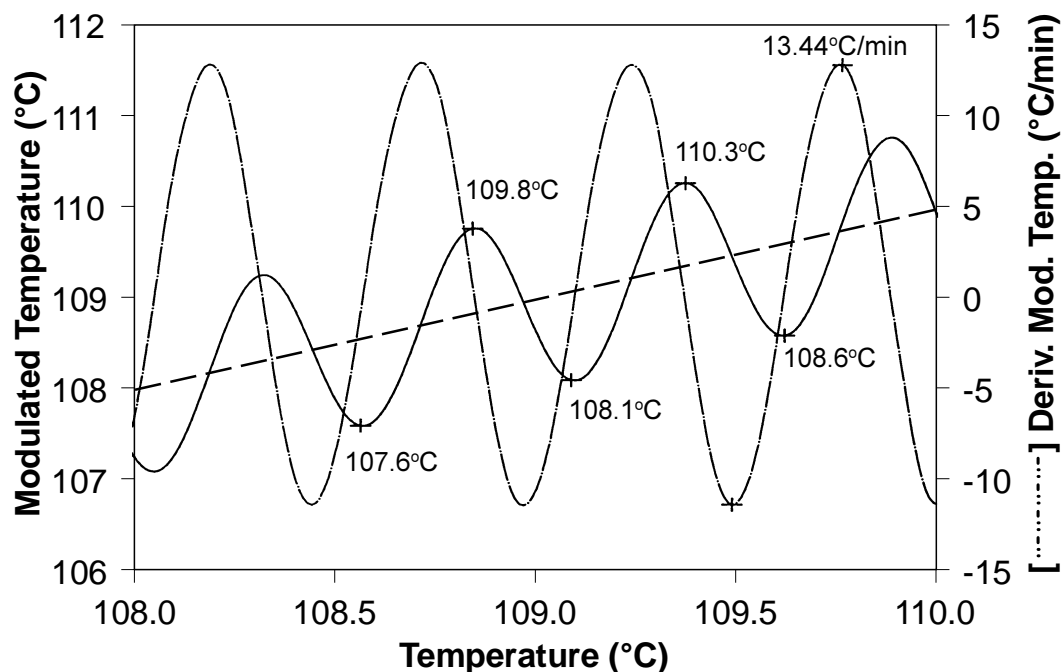
In the example shown in Figure 2, the underlying heating rate is 1°C/minute, the modulation period is 30 seconds, and the modulation amplitude is ±1°C. This set of conditions results in a sinusoidal heating profile where the instantaneous heating rate varies between +13.44°C/minute and -11.54°C/minute (i.e., cooling occurs during a portion of the modulation). Although the actual sample temperature changes in a sinusoidal fashion during this process (Figure 3), the analyzed signals are ultimately plotted versus the linear average temperature which is calculated from the average value as measured by the sample thermocouple (essentially the dashed line in Figure 2). [Note: As in conventional DSC, MDSC can also be run in a cooling rather than heating mode.]

Experimental Parameters

The key to obtaining accurate and reproducible results is the same in both conventional and modulated DSC - the material being studied must be able to follow the temperature profile imposed on it. Obviously, in modulated DSC, since the material is being subjected to a more complex temperature profile, the operator must be careful in choosing experimental parameters. The following summary provides good guidelines for general modulated DSC studies [Note: The optimum conditions for a specific determination (e.g., qualitative evaluation of weak glass transitions) may be slightly different than those summarized here.]

Figure 3: THE EFFECT OF AMPLITUDE ON DISTORTION OF THE HEAT FLOW SINE WAVE
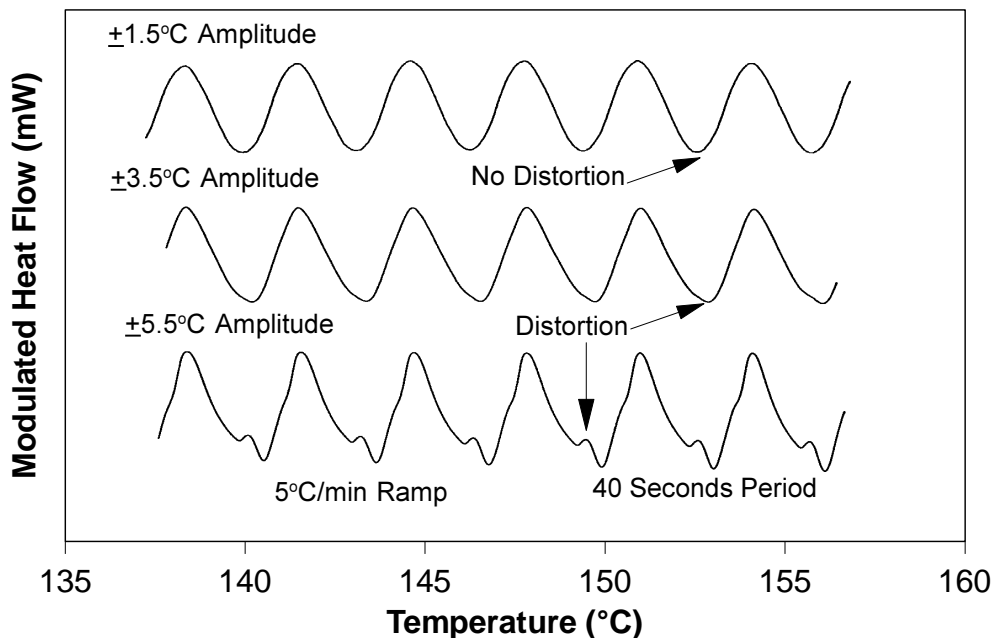
Sample Size: 10-20 mg Contact between sample material and DSC pan should be optimized by crimping. Flat, thin samples are best.

Underlying Heating Rate: 1-5°C/minute Slower heating rates than conventional DSC are preferred to allow sufficient modulations during a thermal event. At least 4-5 modulations are required.

Temperature Amplitude of Modulation: ±0.5 to 2°C The larger the amplitude, the larger the heat flow response since the instantaneous heating rate is directly related to amplitude.

$$\frac{dT}{dt} = \beta + A_T \, \omega \cos (\omega t)$$

where: dT/dt = instantaneous heating rate (°C/minute)
β = underlying heating rate (°C/minute)
A_T = modulation amplitude (°C)
ω = angular frequency = 2π/modulation period (min^{-1})
t = time (minutes)

Therefore, larger amplitudes increase sensitivity for transitions such as the glass transition. However, too large an amplitude may result in a situation where the material cannot follow the modulation. The easiest way to check if the amplitude is acceptable is examination of the raw modulated heat flow signal. Distortion from the expected sine wave (Figure 3) indicates the amplitude is too large.

The range of instantaneous heating rates seen by the sample during modulation can be controlled by adjusting amplitude so that

· only heating occurs,
· both heating and cooling occur (as seen previously in Figure 2), or
· the heating rate goes to 0 (isothermal) at one extreme of modulation.

This latter situation is particularly useful when evaluating crystalline perfection/melting processes and the table in Figure 4 provides a guide for selecting an amplitude which yields this situation.

Figure 4: MAXIMUM 'HEAT ONLY' AMPLITUDE (ºC)

Period (sec)	Heating Rate (°C/min)						
	0.1	0.2	0.5	1	2	5	10
10	0.003	0.005	0.013	0.027	0.053	0.133	0.265
20	0.005	0.011	0.027	0.053	0.106	0.265	0.531
30	0.008	0.016	0.040	0.080	0.159	0.398	0.796
40	0.011	0.021	0.053	0.106	0.212	0.531	1.062
50	0.013	0.027	0.066	0.133	0.265	0.663	1.327
60	0.016	0.032	0.080	0.159	0.318	0.796	1.592
70	0.019	0.037	0.093	0.186	0.372	0.929	1.858
80	0.021	0.042	0.106	0.212	0.425	1.062	2.123
90	0.024	0.048	0.119	0.239	0.478	1.194	2.389
100	0.027	0.053	0.133	0.265	0.531	1.327	2.654

$$T_{amp} = H_r * \left(\frac{P}{2\pi * 60} \right)$$

where: T_{amp} = maximum temperature amplitude for "heat only" (ºC)
H_r = Average heating rate (ºC/min)
P = period (seconds)
60 = converts seconds to minutes

**Figure 5: THE EFFECT OF PERIOD ON THE MAXIMUM TEMPERATURE AMPLITUDE
(with LNCA as cooling source)**
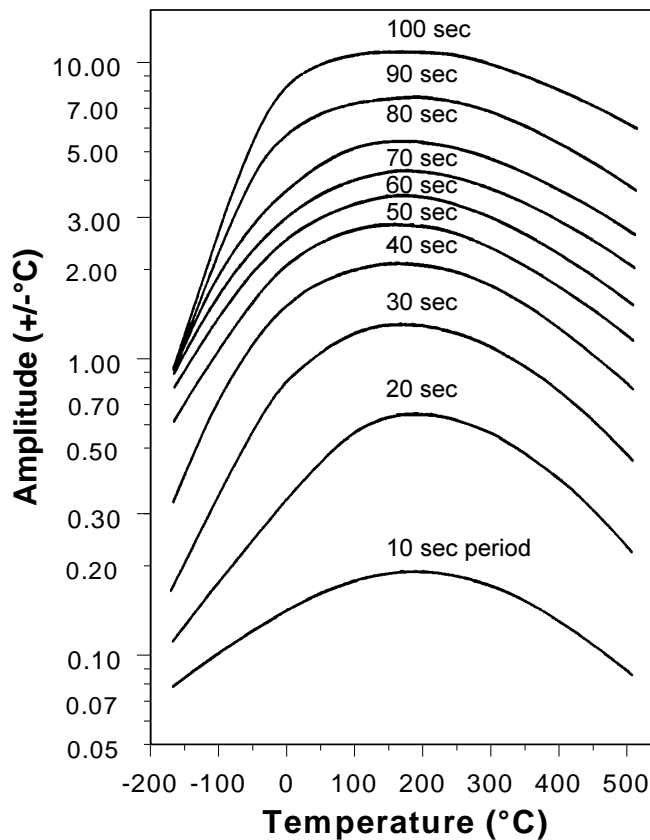
Period of Modulation: <u>40-100 seconds</u> The period and amplitude of modulation are interrelated terms. Figure 5 shows the range of acceptable amplitudes for a given period (with an LNCA as the cooling source). Obviously as the period of modulation increases, the material has longer to respond and the range of acceptable amplitudes increases. Note, however, that smaller amplitudes are still preferred even with longer periods for covering a reasonable tempeaure range.

The most sensitive measure of acceptable period is determination of heat capacity. Figure 6 (for example) illustrates the heat capacity for polyethylene as a function of period. It's easily seen that periods below 40 seconds in this case can result in significant errors. Remember, this range of acceptable period is affected by sample mass and heat transfer characteristics and hence may vary somewhat from material to material.

Purge Gas: <u>Helium</u> Purge gas conductivity influences heat transfer in DSC. Although nitrogen is acceptable for most MDSC evaluations, helium is preferred.

Figure 6: SPECIFIC HEAT CAPACITY OF POLYETHYLENE AS A FUNCTION OF PERIOD
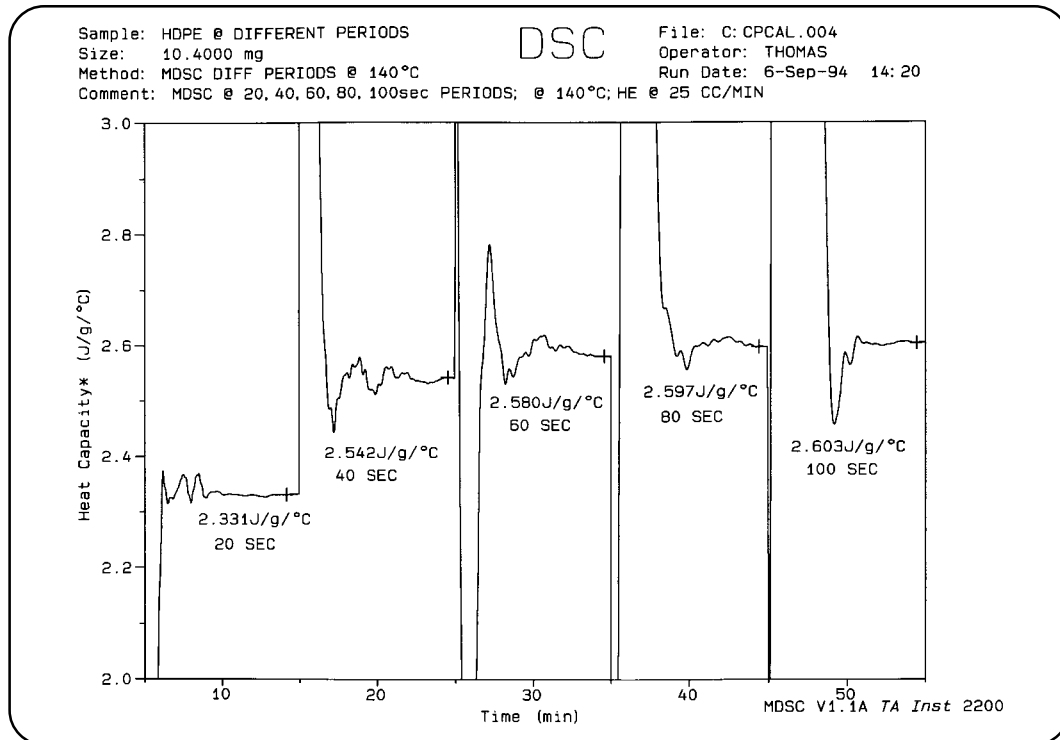
Heat Flow Components

A simplified equation which describes the resultant heat flow at any point in a DSC or MDSC experiment is:

$$\frac{dQ}{dt} = Cp\beta + f(T,t) \qquad\qquad [1]$$

where: $\dfrac{dQ}{dt}$ = total heat flow

Cp = heat capacity
β = heating rate
$f(T,t)$ = heat flow from kinetic (absolute temperature and time dependent) processes

As can be seen from the equation, the total heat flow (dQ/dt) which is the only heat flow measured by conventional DSC, is composed of two parts. One part is a function of the sample's heat capacity and <u>rate of temperature change,</u> and the other is a function of <u>absolute temperature and time.</u>

Modulated DSC determines the total, as well as these two individual heat flow components, to provide increased understanding of complex transitions in materials. MDSC is able to do this because it effectively uses two heating rates - the average heating rate which provides total heat flow information and a sinusoidal heating rate which provides heat capacity information from the heat flow that responds to the rate of temperature change.

The individual heat flow components are often referred to by different names as listed below. In the remainder of this paper they will be called "heat capacity component" ($Cp\beta$) and "kinetic component" (f(T,t)).

Heat Capacity Component	Kinetic Component
Reversing heat flow	Nonreversing heat flow
In-phase component	Out-of-phase component
Heating rate-related component	Time dependent component

MDSC Heat Flow Signals

All MDSC heat flow signals are calculated from three measured signals - time, modulated heat flow, and modulated heating rate (the derivative of modulated temperature). Figure 7 shows these signals for amorphous polyethyleneterephthalate (PET). Since these raw signals are visually complex, they need to be deconvoluted to obtain the more standard DSC heat flow curves. (Note: Although deconvolution is required to obtain the final quantitative results provided by MDSC, the raw signals, particularly the modulated heat flow, can still be used to obtain valuable insights regarding what is occurring in the material.) Hence, it is generally recommended that the raw modulated heat flow and modulated heating rate signals be stored as part of the MDSC data file.

Figure 7: MDSC RAW SIGNALS
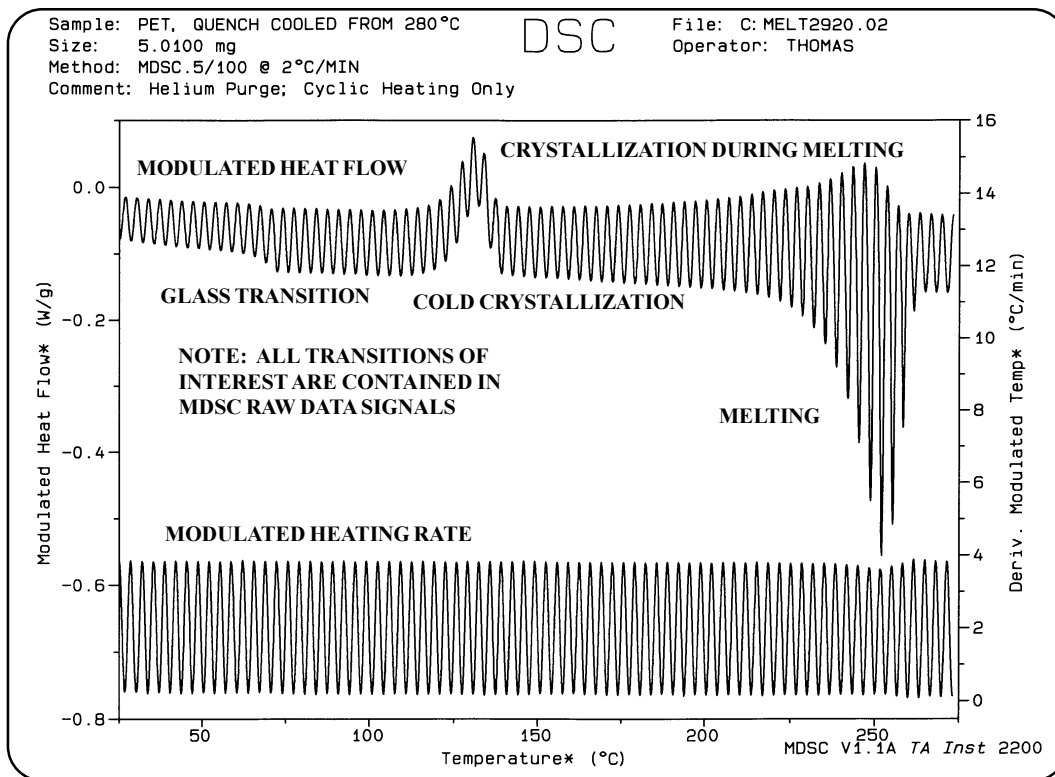
The **heat capacity (Cp)** of the sample is continuously determined by dividing the modulated heat flow amplitude by the modulated heating rate amplitude. The validity of this approach can be proven by considering the well-accepted procedures for determining Cp in conventional DSC. In conventional DSC, Cp is generally calculated (equation [2]) from the difference in heat flow between a blank (empty pan) run and a sample run under identical conditions including heating rate. Curves 1 and 2 in Figure 8 show typical curves for sapphire.
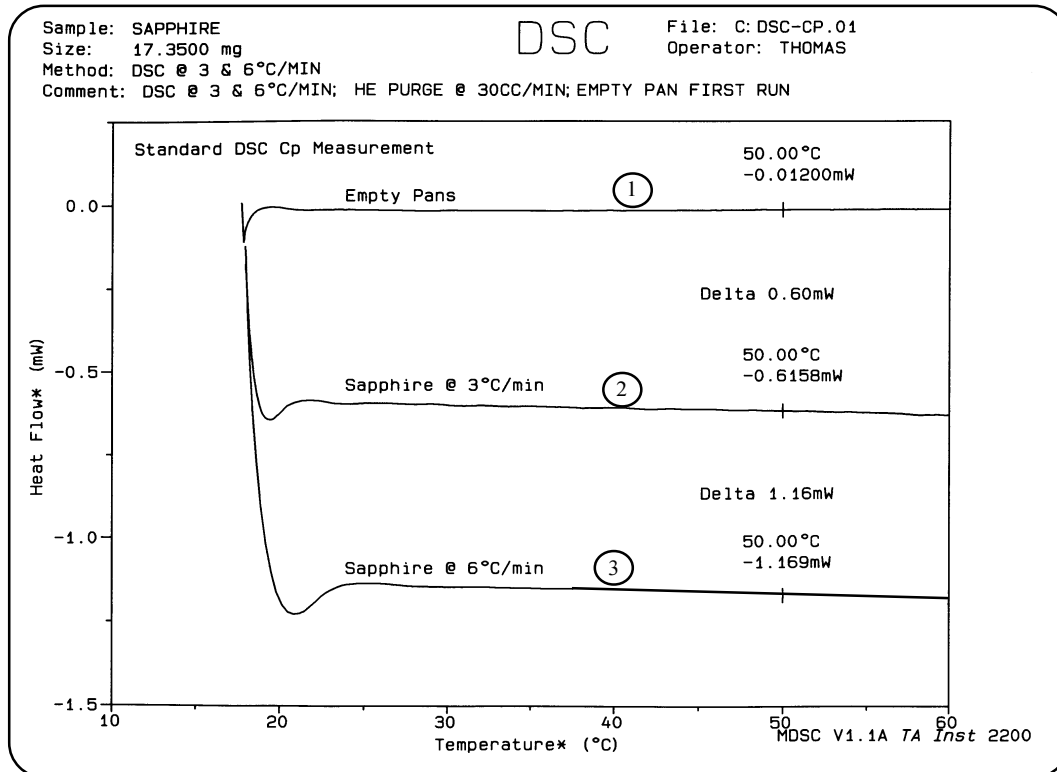
$$Cp = KCp \ x \ \frac{\text{Heat Flow (Sample)} \ - \ \text{Heat Flow (Blank)}}{\text{Heating Rate}} \qquad [2]$$

where KCp = calibration constant

Cp can also be calculated, however, by comparing the difference in heat flow between two runs on an identical sample at two different heating rates. Curve 3 in Figure 8 represents the same sapphire sample as curve 2 run at a higher heating rate. In this case:

$$Cp = KCp \ x \ \frac{\text{Heat Flow at Heat Rate 2} \ - \ \text{Heat Flow at Heat Rate 1}}{\text{Heating Rate 2} \ - \ \text{Heating Rate 1}} \qquad [3]$$

Figure 8: DSC Cp MEASUREMENT


```
Sample: SAPPHIRE                         DSC      File: C:DSC-CP.01
Size:   17.3500 mg                                Operator: THOMAS
Method: DSC @ 3 & 6°C/MIN
Comment: DSC @ 3 & 6°C/MIN; HE PURGE @ 30CC/MIN;EMPTY PAN FIRST RUN
```

In MDSC, the heating rate changes during the modulation cycle. In Figure 9 the MDSC conditions are chosen so that the modulated heating rate varies between two heating rates which are essentially the same as those chosen for curves 2 and 3 in Figure 8. If the resultant modulated heat flow curve from Figure 9 is then overlaid on curves 2 and 3 in Figure 8, it is easily seen (Figure 10) that taking the difference in modulated heat flow and dividing it by the difference in modulated heating rate is equivalent to the conventional DSC approach using two different heating rates and equation [3].

The **heat capacity (reversing) component** of total heat flow is calculated by converting the measured heat capacity into heat flow using equation [1] where β is the average (underlying) heating rate used in the experiment. Reversing Heat Flow = (- Cp) x Average Heating Rate [Note: -Cp is used in the actual calculation so that endotherms and exotherms occur in the proper downward and upward directions respectively. See Figure 11.]
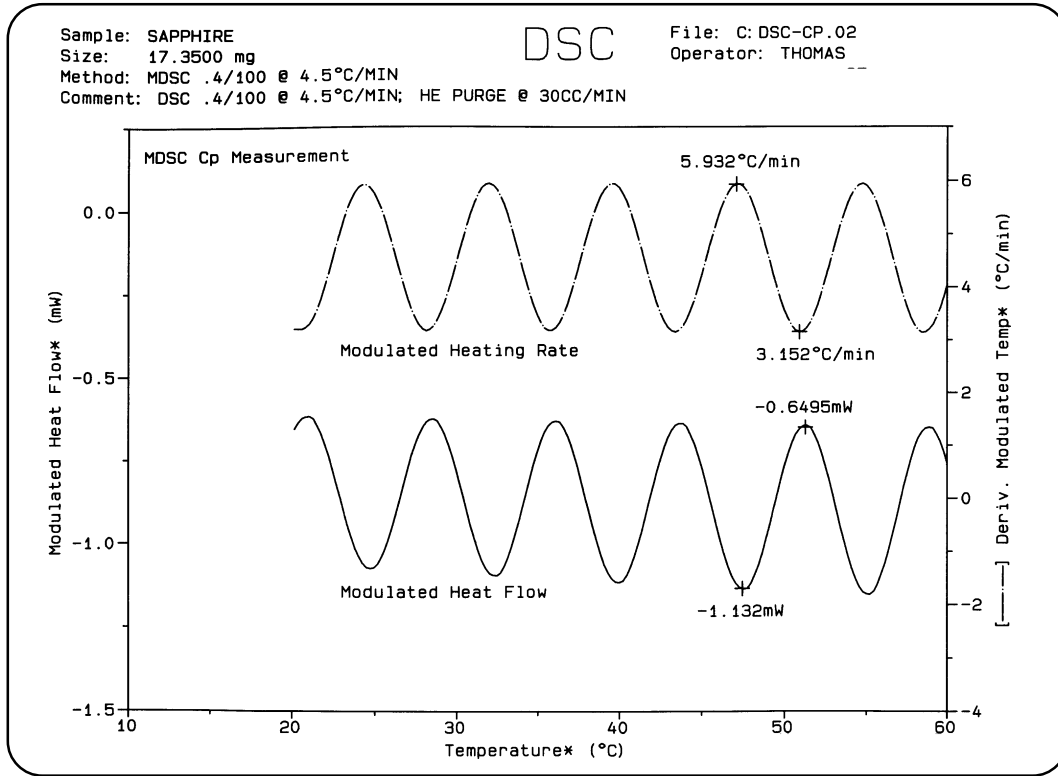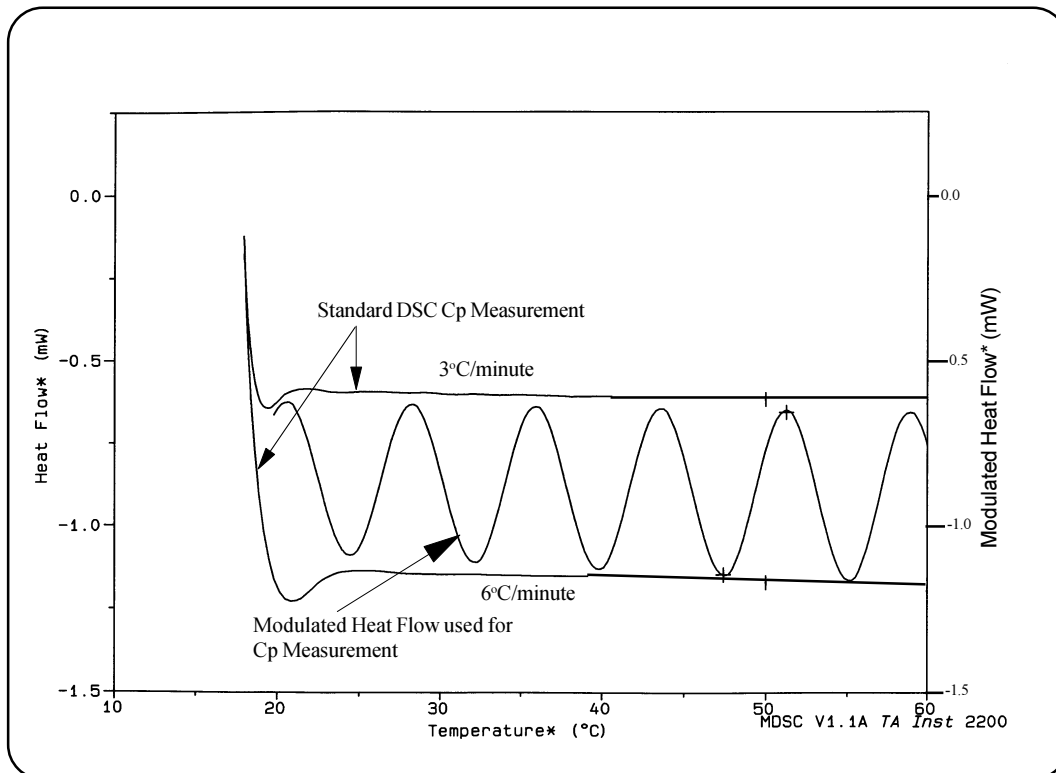
Figure 9: MDSC Cp MEASUREMENT

Sample: SAPPHIRE
Size: 17.3500 mg
Method: MDSC .4/100 @ 4.5°C/MIN
Comment: DSC .4/100 @ 4.5°C/MIN; HE PURGE @ 30CC/MIN

DSC

File: C:DSC-CP.02
Operator: THOMAS

MDSC Cp Measurement

5.932°C/min

Modulated Heating Rate

3.152°C/min

-0.6495mW

Modulated Heat Flow

-1.132mW

Modulated Heat Flow* (mW)

Temperature* (°C)

Deriv. Modulated Temp* (°C/min)

Figure 10: DSC & MDSC Cp MEASUREMENTS

Standard DSC Cp Measurement

3°C/minute

6°C/minute

Modulated Heat Flow used for
Cp Measurement

Heat Flow* (mW)

Modulated Heat Flow* (mW)

Temperature* (°C)

MDSC V1.1A *TA Inst* 2200

Figure 11: REVERSING HEAT FLOW FROM MDSC RAW SIGNALS

Sample: PET; QUENCHED FROM 280°C
Size: 5.5000 mg
Method: MDSC 1/100 @ 2°C/MIN
Comment: HE @ 25CC/M; MDSC 1/100 @2°C/MIN; CRIMPED PAN
DSC
File: C:N6.14
Operator: APP LAB

HEAT CAPACITY

REVERSING HEAT FLOW
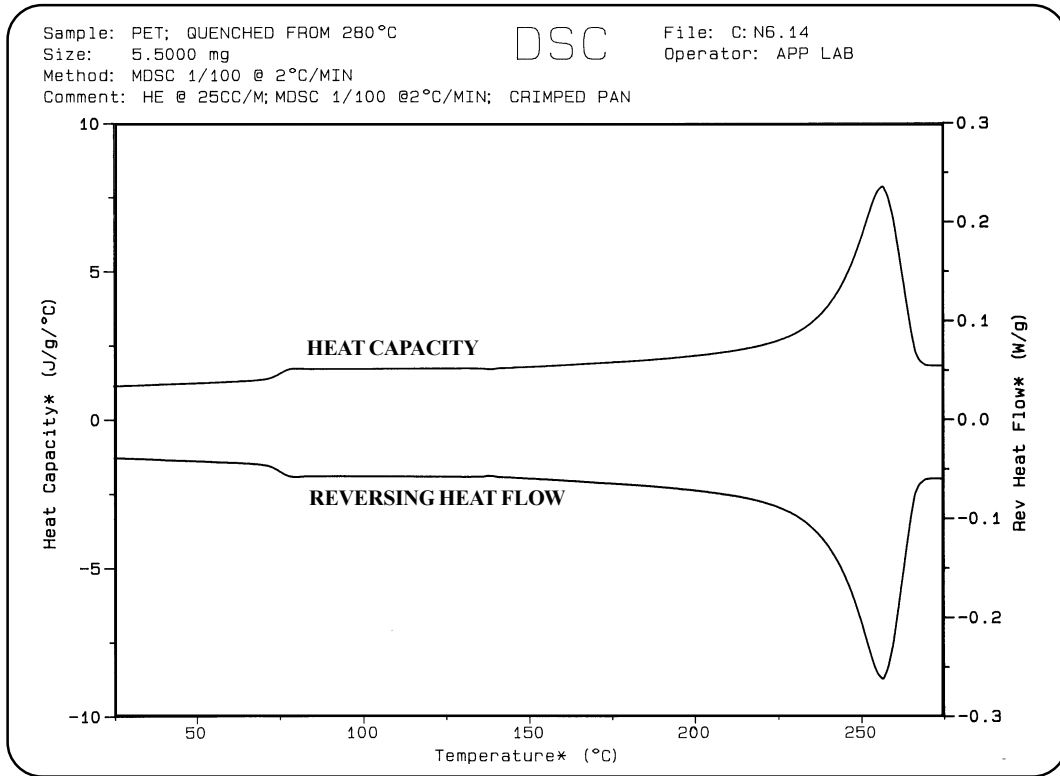
Figure 12: TOTAL HEAT FLOW FROM MDSC RAW SIGNALS

Sample: PET; QUENCHED FROM 280°C
Size: 5.5000 mg
Method: MDSC 1/100 @ 2°C/MIN
Comment: HE @ 25CC/M; MDSC 1/100 @2°C/MIN; CRIMPED PAN
DSC
File: C:N6.14
Operator: APP LAB

TOTAL HEAT FLOW IS CALCULATED
AS THE AVERAGE VALUE OF THE
MODULATED HEAT FLOW SIGNAL
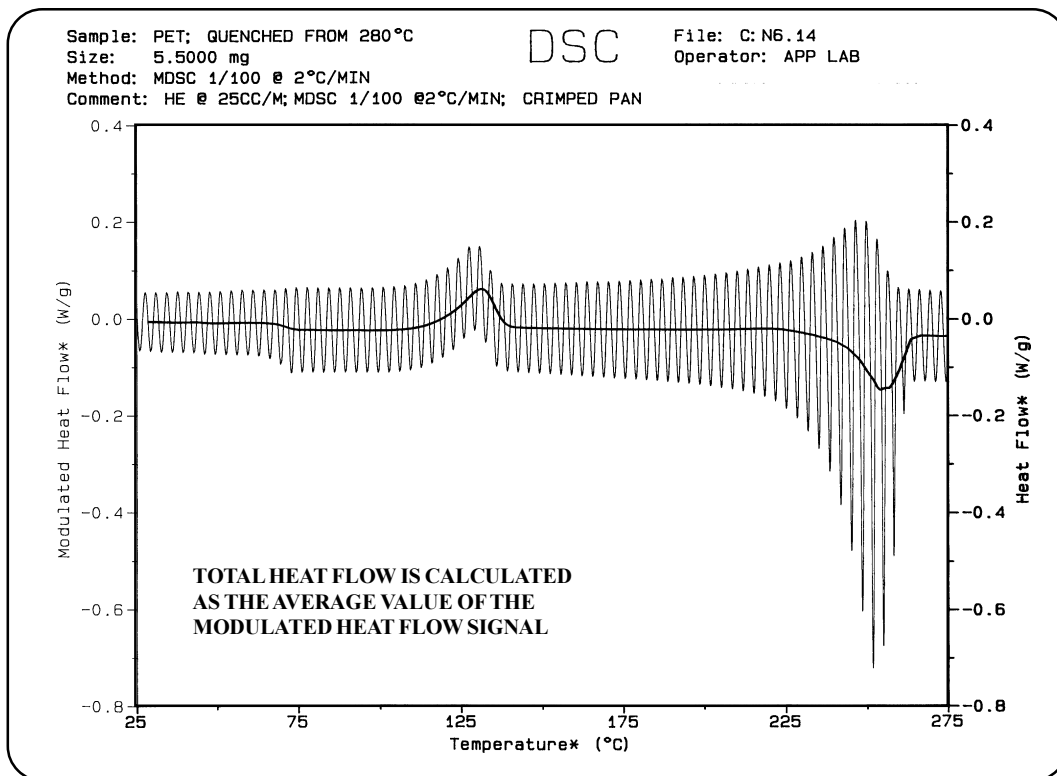
The **total heat flow** in MDSC is calculated as the average value of the raw modulated heat flow signal (Figure 12) using a Fourier Transformation analysis. This approach is used to <u>continuously</u> calculate the average value rather than using only the two points per cycle (maximum and minimum). Use of the Fourier Transformation provides much higher resolution because up to 5 points per second can be calculated for both the average and amplitude values. <u>Note</u>: As Figure 12 shows, the raw modulated heat flow is not corrected for temperature by the current software and hence transitions appear to occur lower in temperature in this raw signal than in the calculated signals. This difference is a result of the time delay associated with "real-time" deconvolution (about 1.5 cycles).

The **kinetic (nonreversing) component** of the total heat flow is determined as the arithmetic difference between the total heat flow and the heat capacity component. Figure 13 shows the three heat flows for quenched PET.

Figure 13: QUENCH COOLED PET - MODULATED DSC
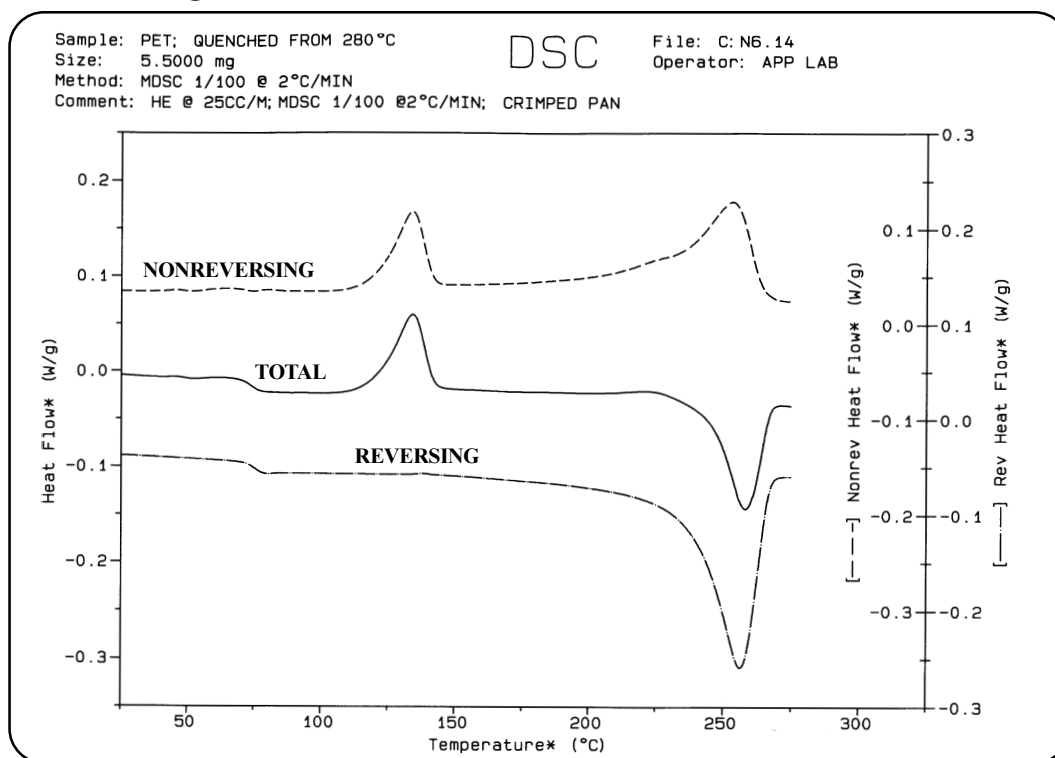
Phase Lag Considerations

There is one additional comment germane to the calculation of the modulated signals, namely the presence and importance of correction for phase lag. The general heat flow equation [1] used to describe modulated DSC assumes that in regions where the sample material has no time dependent (kinetic) phenomena, $dQ/dt = Cp\beta$ and that the sinusoidal modulated heat flow signal and the sinusoidal modulated heating rate are perfectly in-phase. That is, the sample responds instantaneously and directly tracks the sinusoidal heating profile. In reality, this assumption is not valid. As shown in Figure 14, there is actually a phase shift (lag) between the two measured raw signals due to non-instantaneous heat transfer between the DSC cell and the sample. In regions where no thermal events are occurring in the sample, this lag is due entirely to "instrumental" effects. In regions where the sample exhibits thermal events, this lag is a combination of instrumental and sample effects. As a result, the heat capacity measured in modulated DSC is actually the complex heat capacity (Cp*) which can be split into an in-phase, real component Cp' (usually considered the thermodynamic heat capacity) and an out-of-phase, imaginary component Cp". To obtain a quantitative measure of Cp", and hence Cp', it is first necessary to compensate (calibrate) for the instrumental lag. This is easily accomplished by selecting "baseline" areas outside the transition region and adjusting the phase angle to the theoretically expected $\pi/2$. [This is equivalent to adjusting the phase lag to 0° since the maximum in endothermic modulated heat flow should occur at the minimum in modulated heating rate (See Figure 9). Thus, when these two signals are perfectly in-phase, the sine waves differ by 90° ($\pi/2$).] Any remaining lag is then attributable to the sample and can be used to calculate Cp' and Cp". Figure 15 shows that the relative magnitude of Cp" at the glass transition for amorphous PET is <1%. Figure 16 shows, furthermore, that Cp" becomes significant for this material only in the melt. Correction for Cp" is hence currently only of interest academically. However, future work with suitable models may enable additional information about the material's structure and behavior to be obtained from quantifying Cp" particularly in the melt.
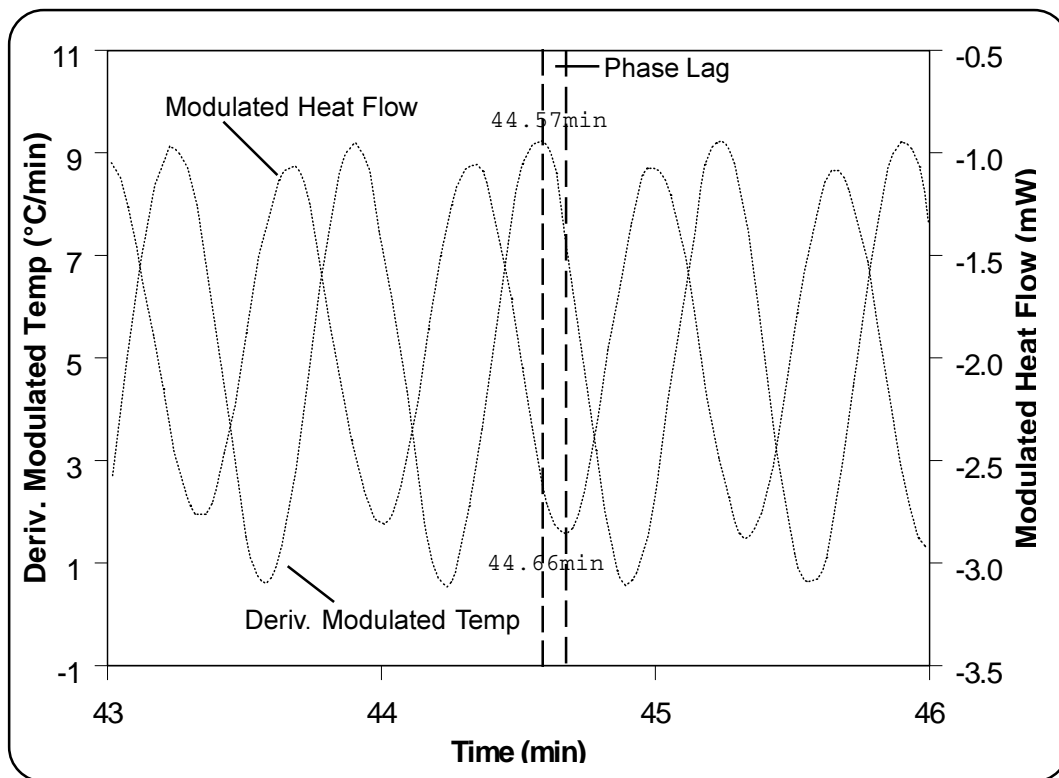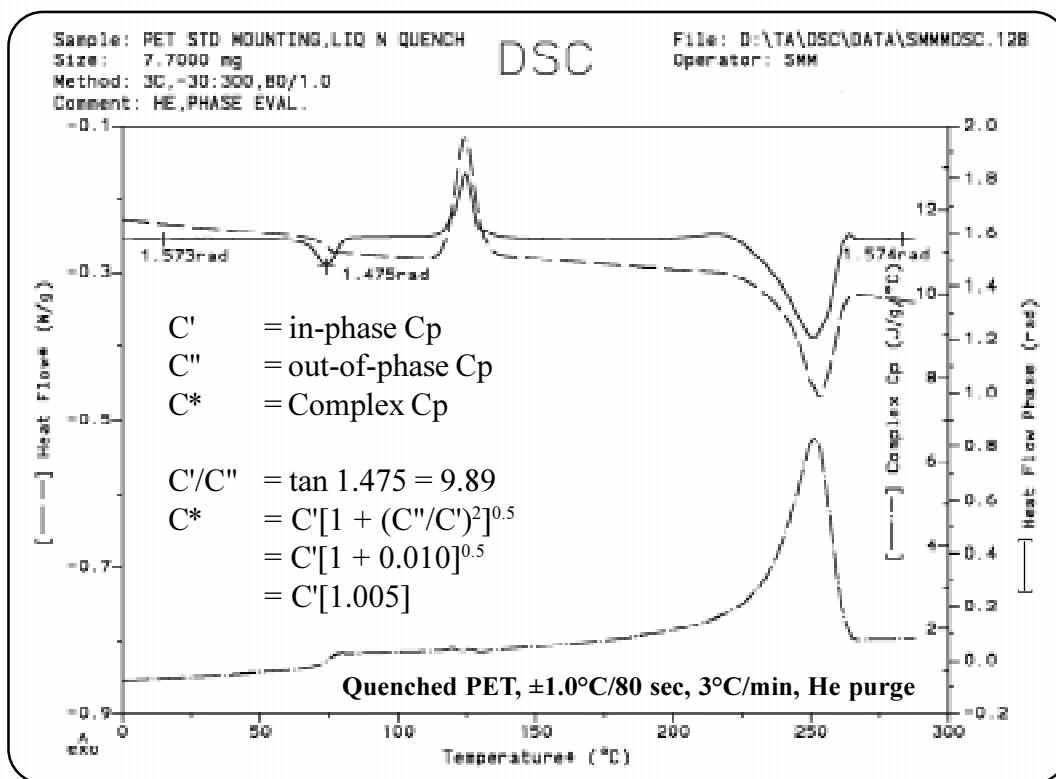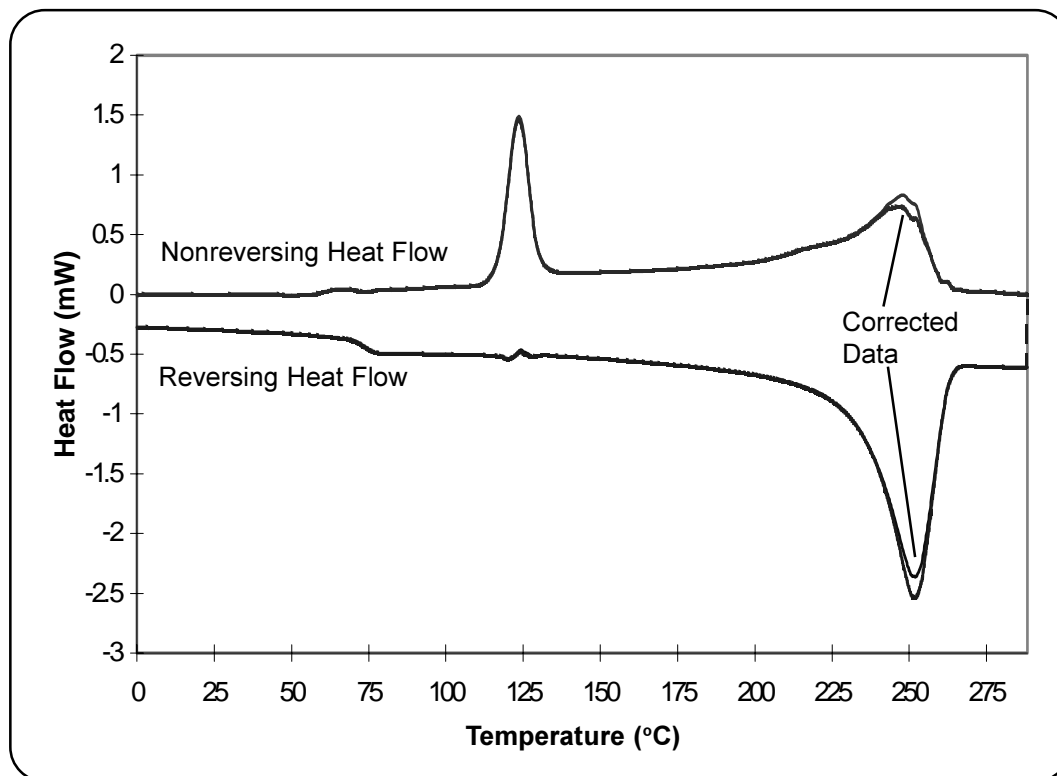
Figure 14: PHASE LAG

Figure 15: HEAT FLOW PHASE CONTRIBUTION

C'   = in-phase Cp
C"   = out-of-phase Cp
C*   = Complex Cp

C'/C"   = tan 1.475 = 9.89
C*   = C'[1 + (C"/C')^2]$^{0.5}$
            = C'[1 + 0.010]$^{0.5}$
            = C'[1.005]

Quenched PET, ±1.0°C/80 sec, 3°C/min, He purge

**Figure 16: PHASE-CORRECTED HEAT FLOW SIGNALS
QUENCHED PET**

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