Strategies for Better DSC Data

October 4, 2016 Leicester
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Outline

- ✓ Introduction
- ✓ Quantification of instrument performance
- ✓ Optimization of experimental parameters
- ✓ Proper interpretation of datacurves

DSC Technique

- ✓ **D**ifferential **S**canning **C**alorimetry is a technique that measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a *controlled atmosphere*.

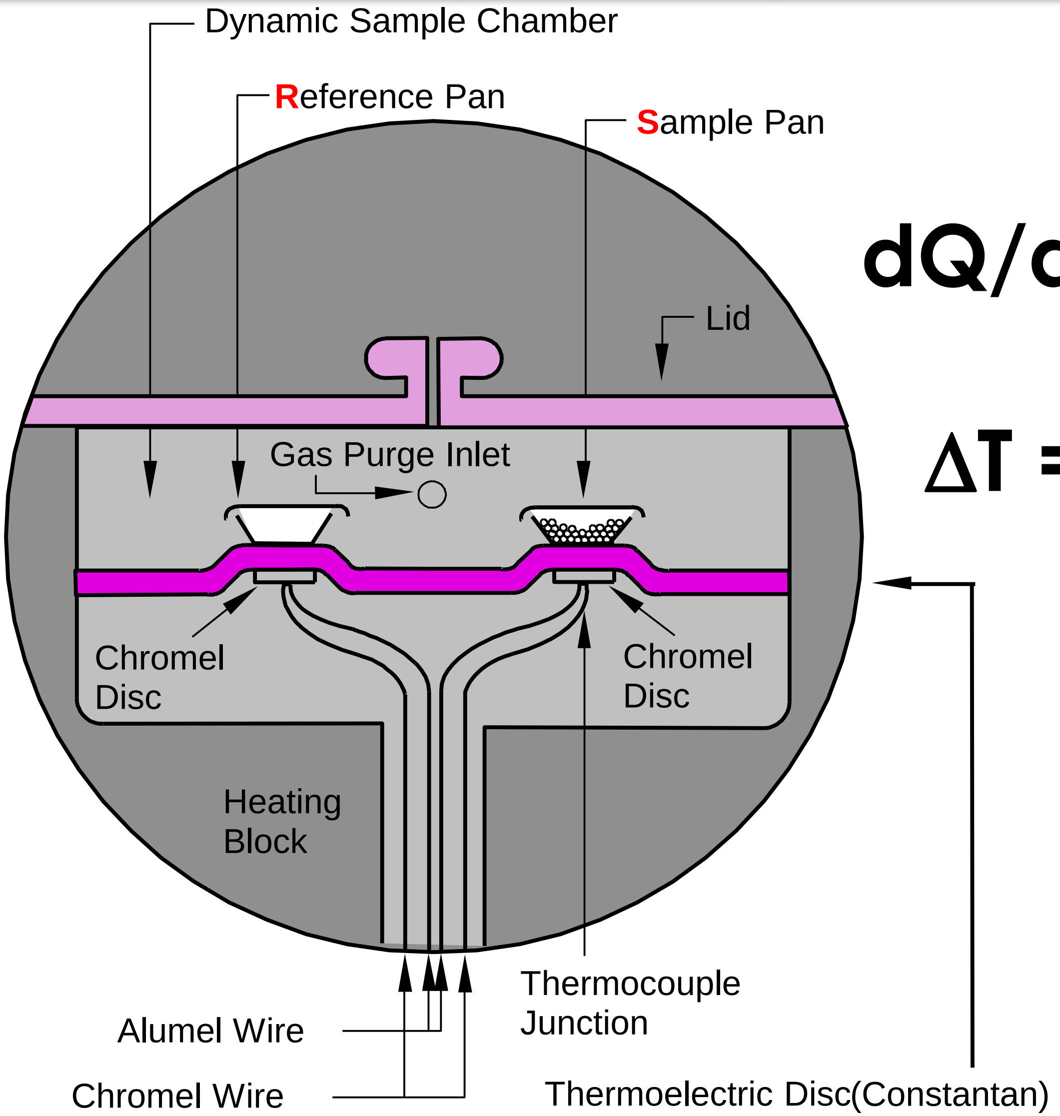
- ✓ These measurements provide quantitative and qualitative information about *physical* and *chemical changes* that involve ***endothermic*** or ***exothermic processes***, or ***changes in heat capacity***.

Know Your Instrument Capabilities by Measuring Them

- ✓ Baseline
  = empty cell run, without sample

- ✓ Cooling Rate

Heat Flux DSC Instrument (Q20 – Discovery DSC 25)

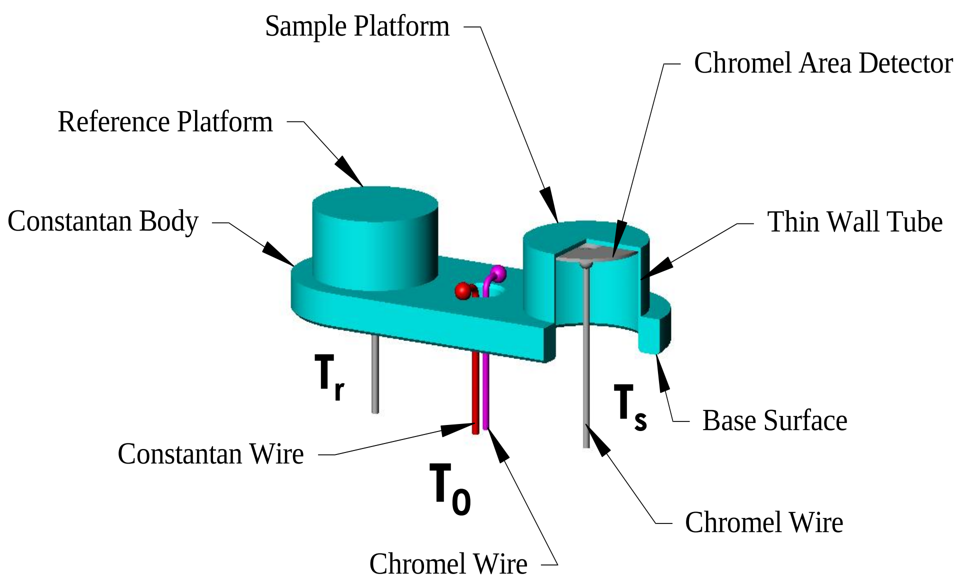


$$dQ/dt = -\Delta T/R$$

$$\Delta T = T_s - T_r$$

Assumes complete symmetry between sample side and reference side of the calorimeter !

Tzero DSC Instrument
(Q2000 – Discovery DSC 250 & 2500)



- Flatter baseline
- Better resolution
- Direct Cp

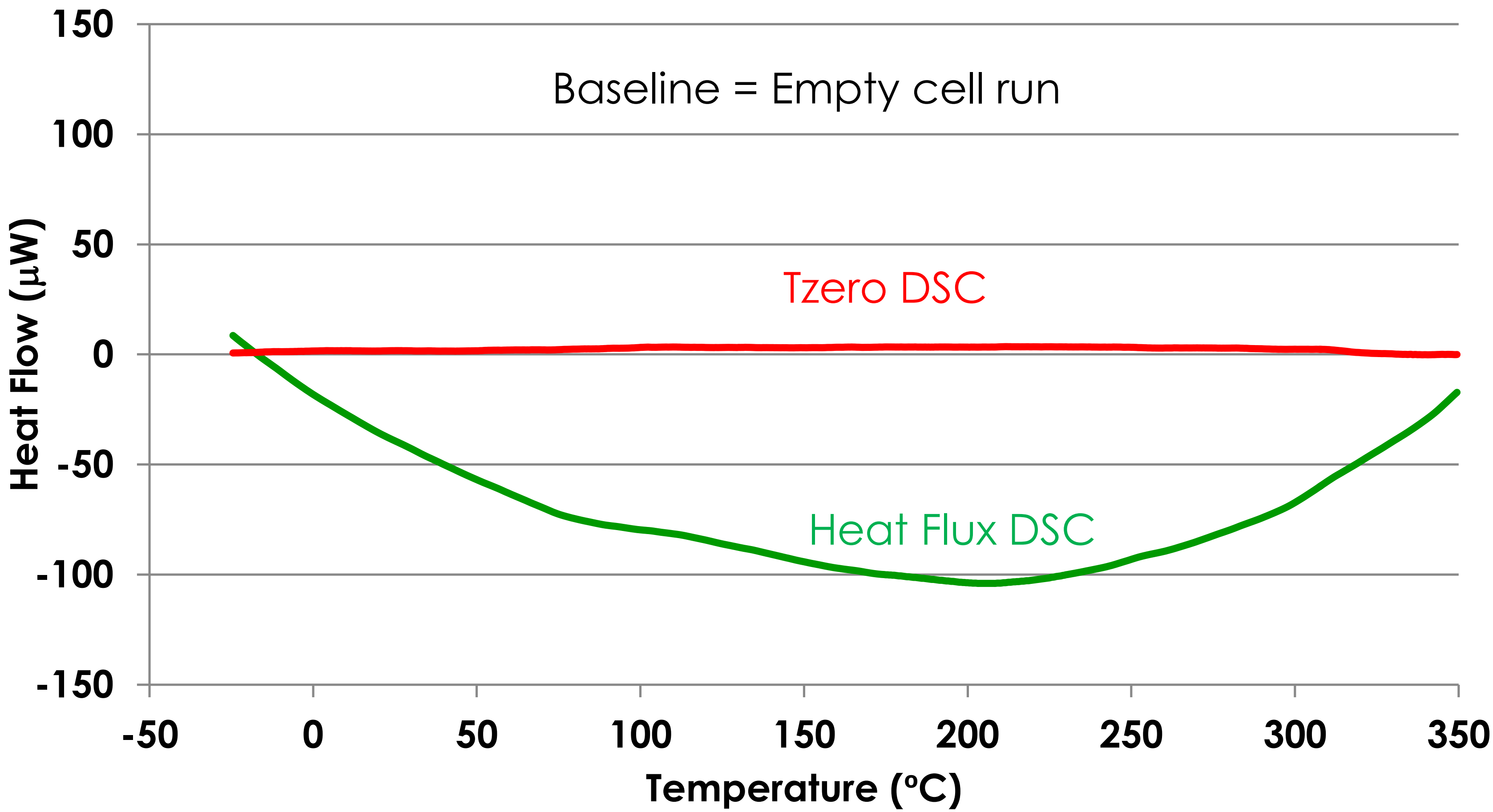
$$q = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{dt} - C_r\frac{d\Delta T}{dt}$$

Thermal resistance & heat capacity imbalance

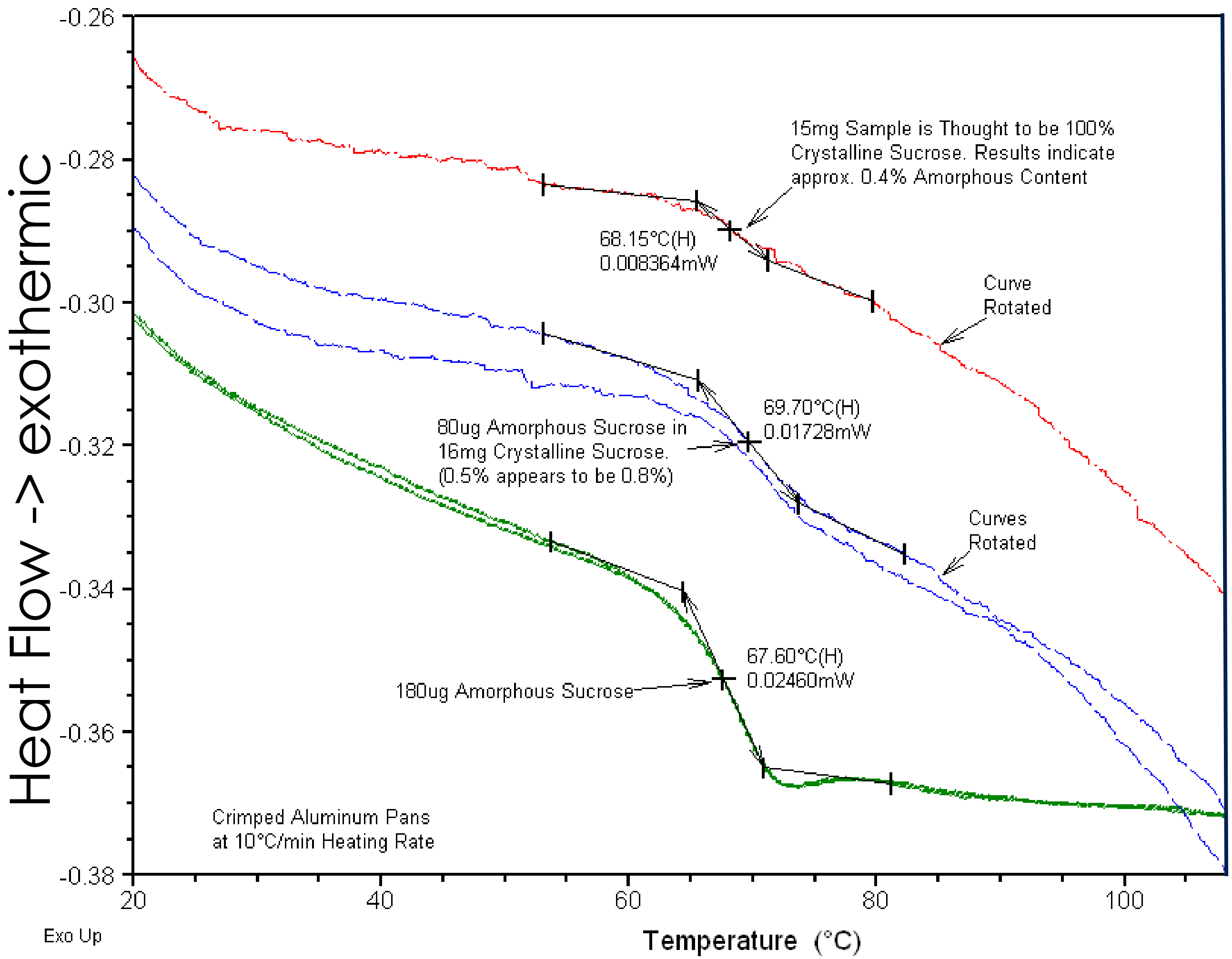
Heating Rate difference

Measure Your Instrument Baseline !

$$q = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{dt} - C_r\frac{d\Delta T}{dt}$$



Detecting Small Amounts of Amorphous Structure in "Crystalline" Sucrose



100% amorphous sucrose

180µg sample -> 24.6µW

"100% Crystalline" sample

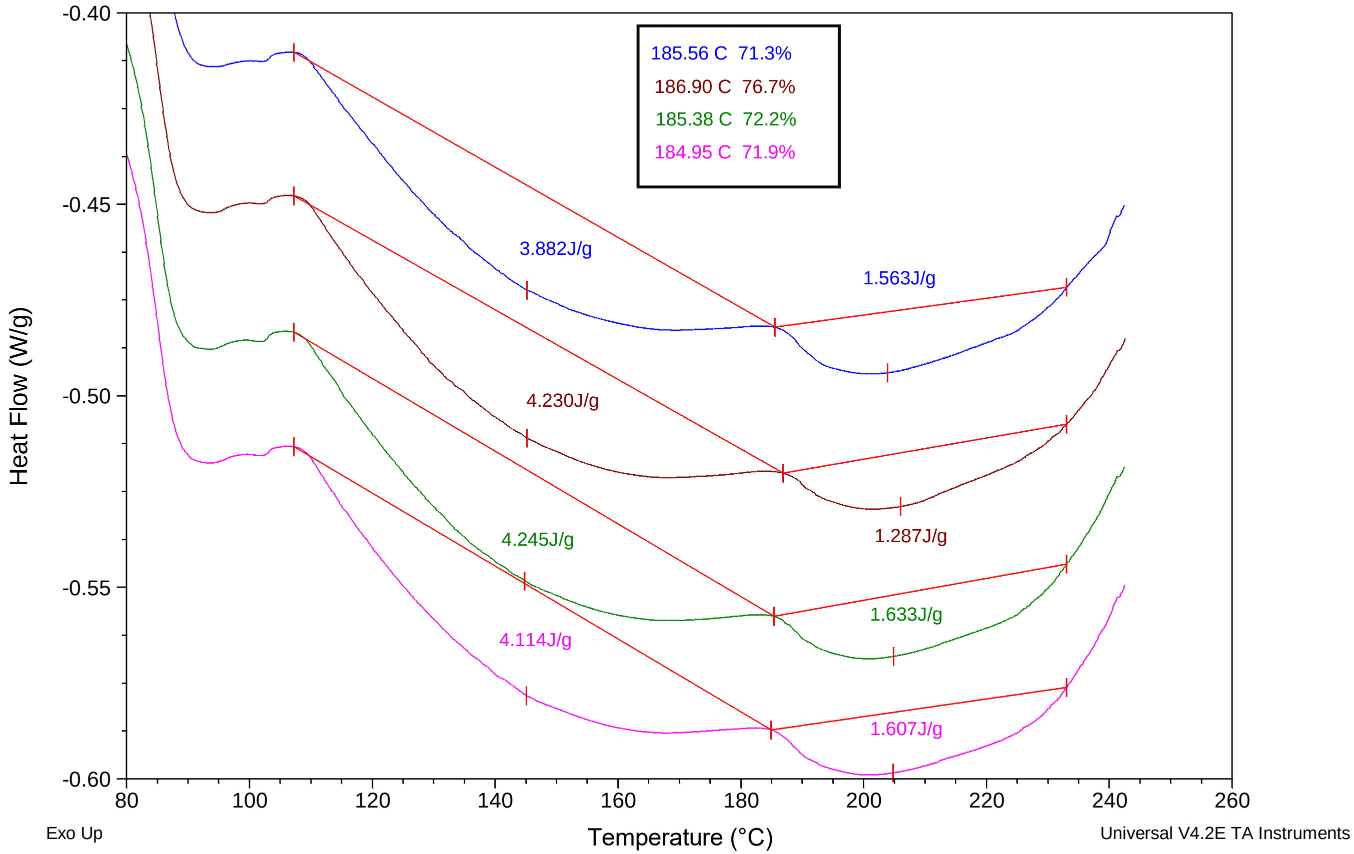
$$\frac{24.6\mu W}{180\mu g} = \frac{8.4\mu W}{x}$$

$$x = 61\mu g$$

$$\%\ \text{Amorphous Sucrose} =$$

$$\frac{61\mu g \times 100}{15{,}000\ \mu g} = 0.4\%$$

PVC Degree of Gelation



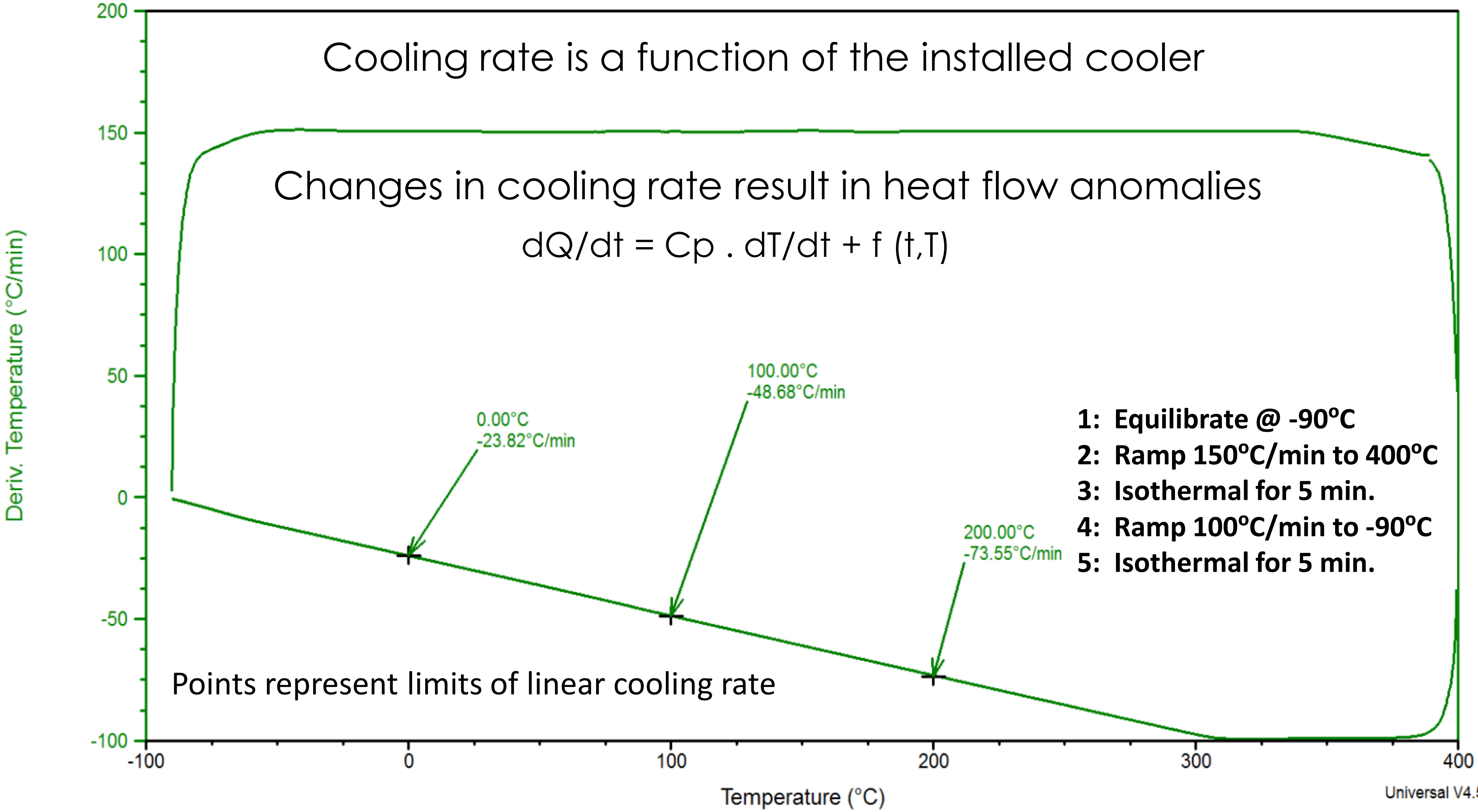
Perform repeatability test for each sample if you want to be sure that the small differences between the 4 different samples are 'real'

Quantify the Heating and Cooling Envelope

Cooling rate is a function of the installed cooler

Changes in cooling rate result in heat flow anomalies

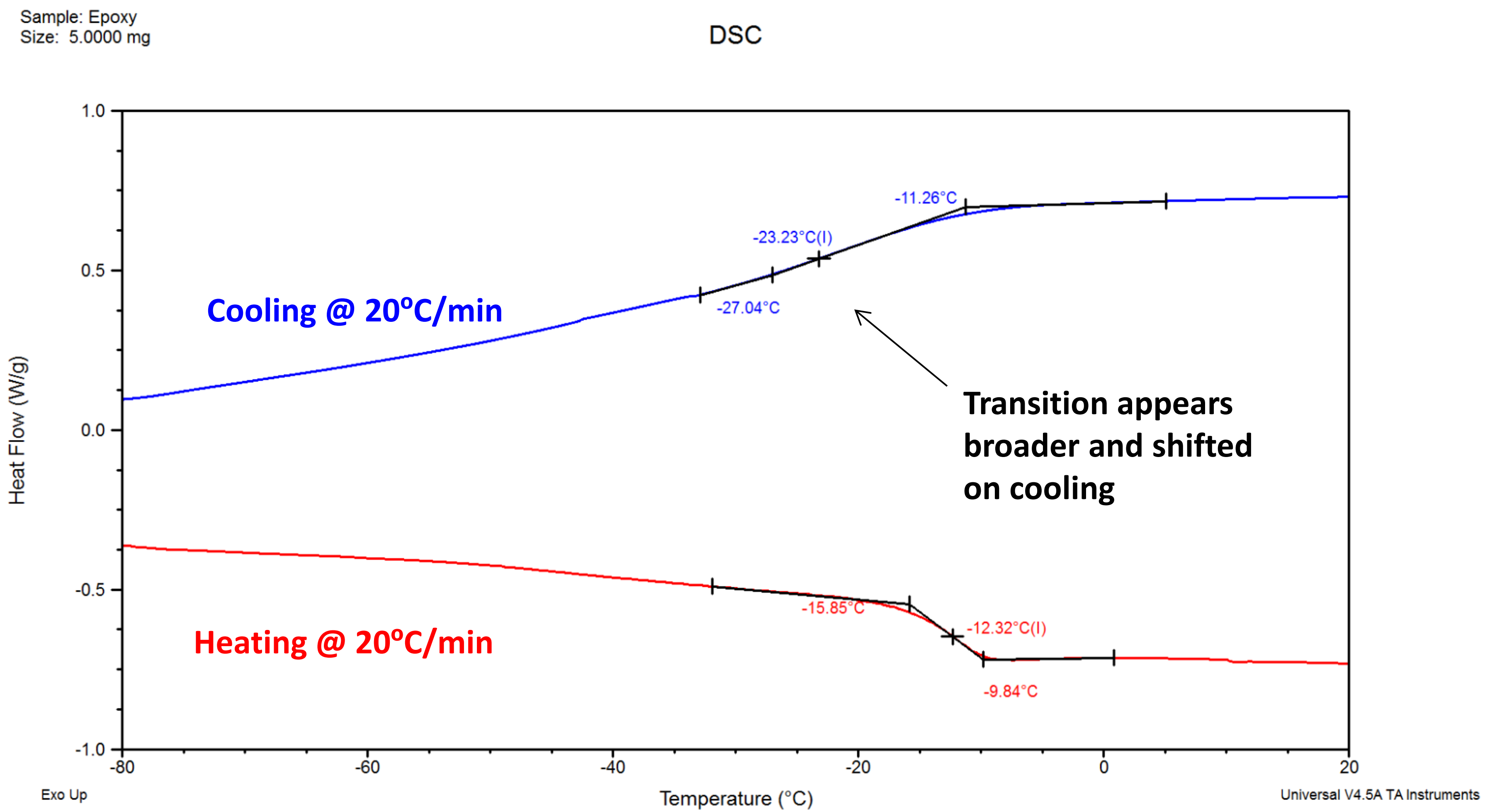
$$dQ/dt = Cp \cdot dT/dt + f(t,T)$$



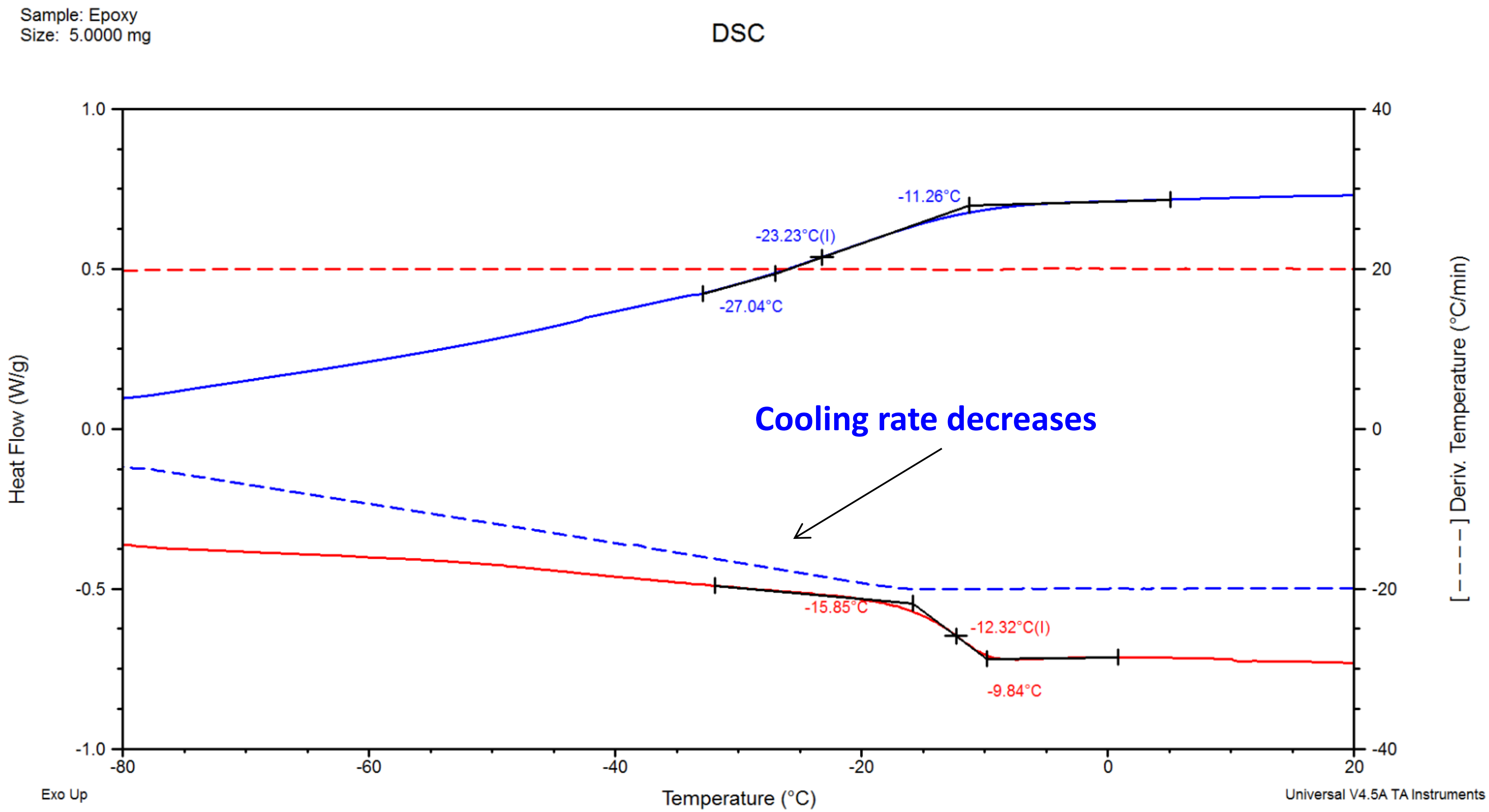
1: Equilibrate @ -90°C
2: Ramp 150°C/min to 400°C
3: Isothermal for 5 min.
4: Ramp 100°C/min to -90°C
5: Isothermal for 5 min.

Points represent limits of linear cooling rate

Glass Transition Analysis



Glass Transition Analysis, with Scanning Rates



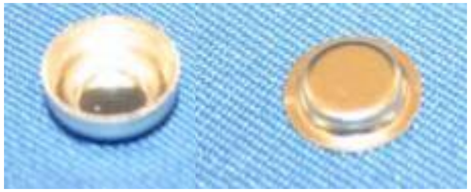
Optimize the Experimental Parameters

- ✓ Type of cup
- ✓ Sample preparation
- ✓ Reference cup
- ✓ Sample size
- ✓ Temperature program

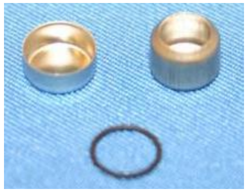
DSC Pan Types

- ✓ Standard Pans: Appropriate for most solid samples (films, powders, metals, polymer chip, etc)

- ✓ Hermetic Pans: Designed primarily for samples which may evolve volatiles during heating (P > 2 bar -> leaking !)
  - Can be used for small quantities of liquids as well

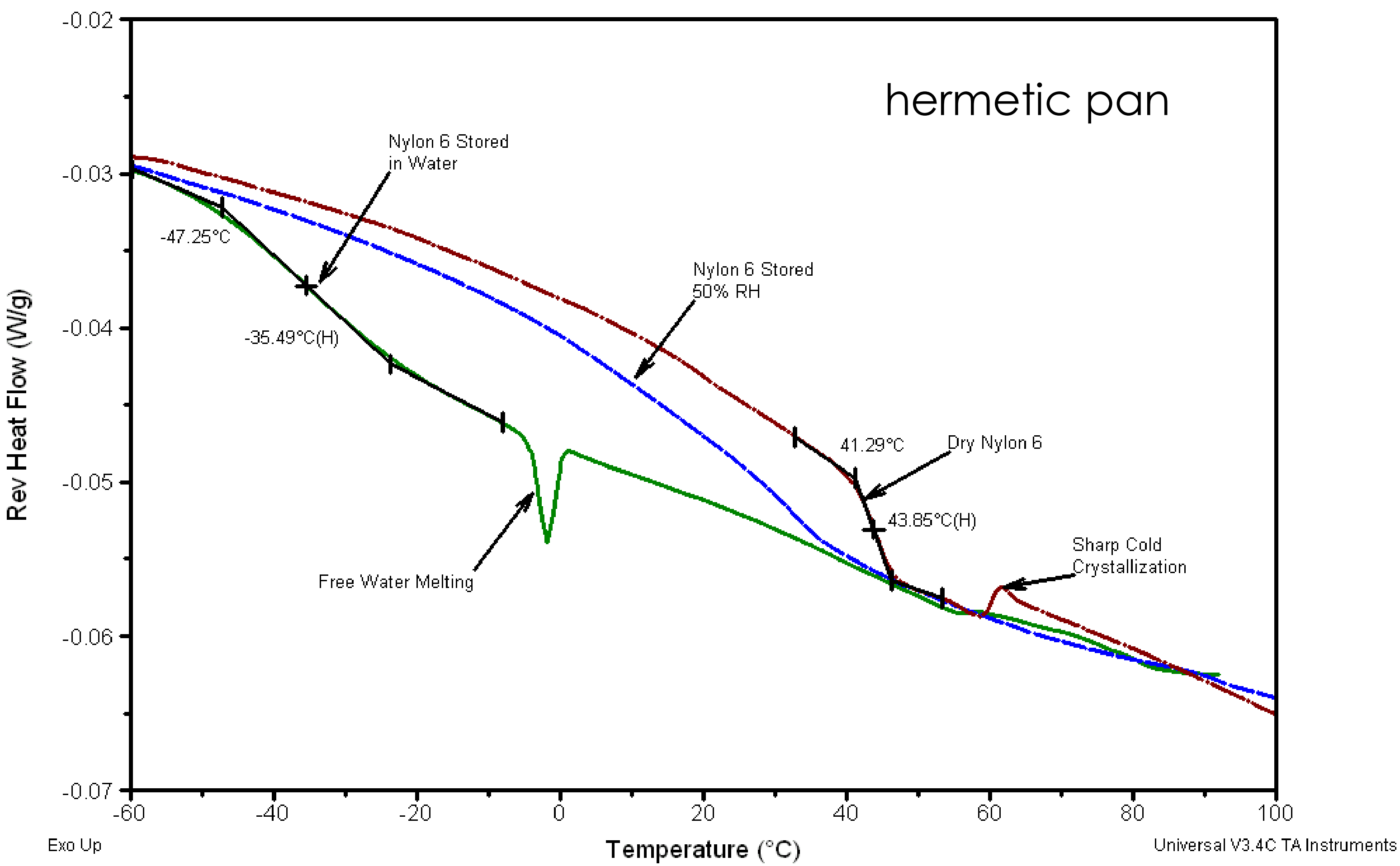


- ✓ Specialty Pans:
  - High Volume Pans: Used for larger quantities of liquids and solutions (up to 40 bar)

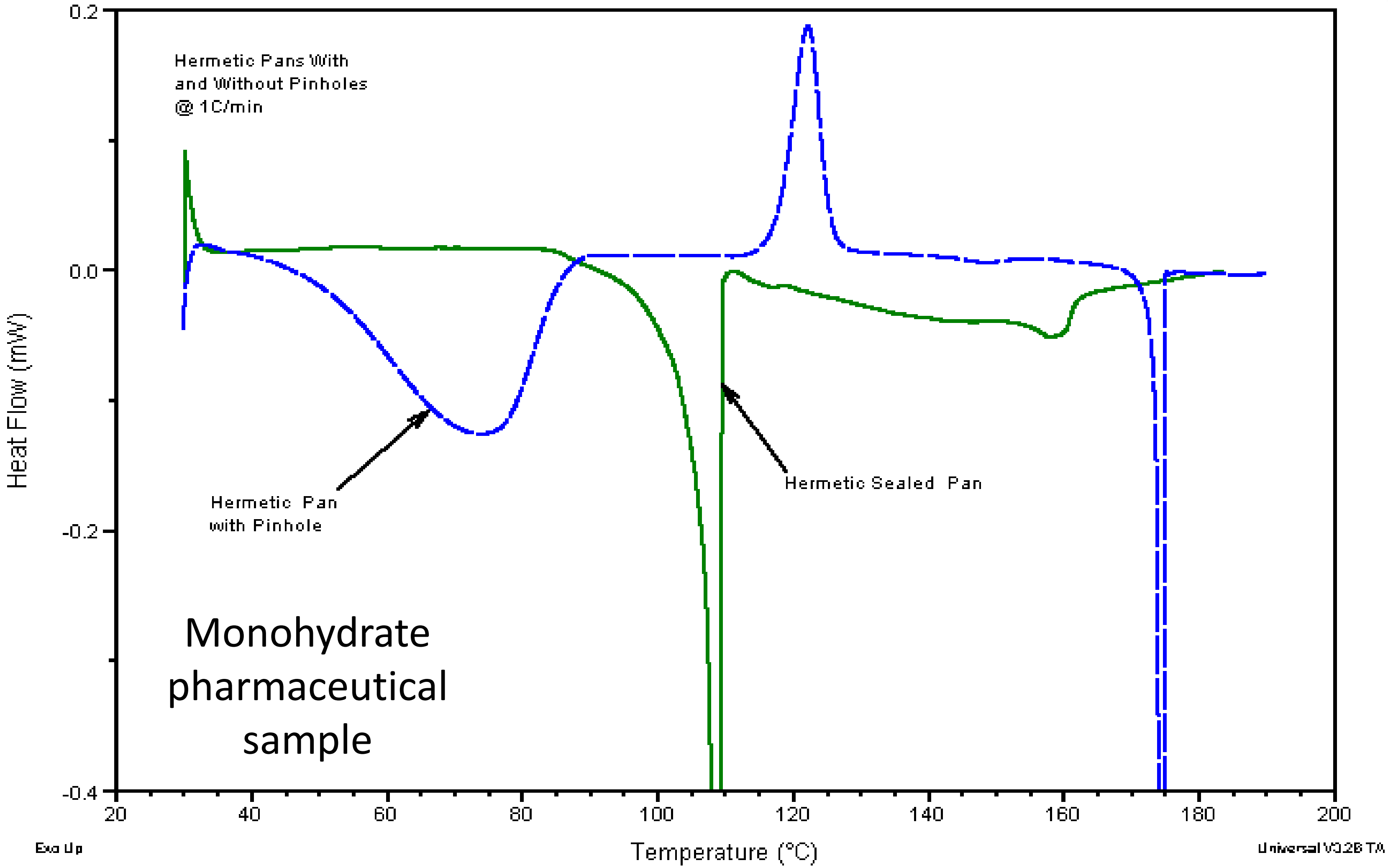


  - High Pressure Pans: Used for energetics or materials which evolve large quantities of gas (up to 100 bar)

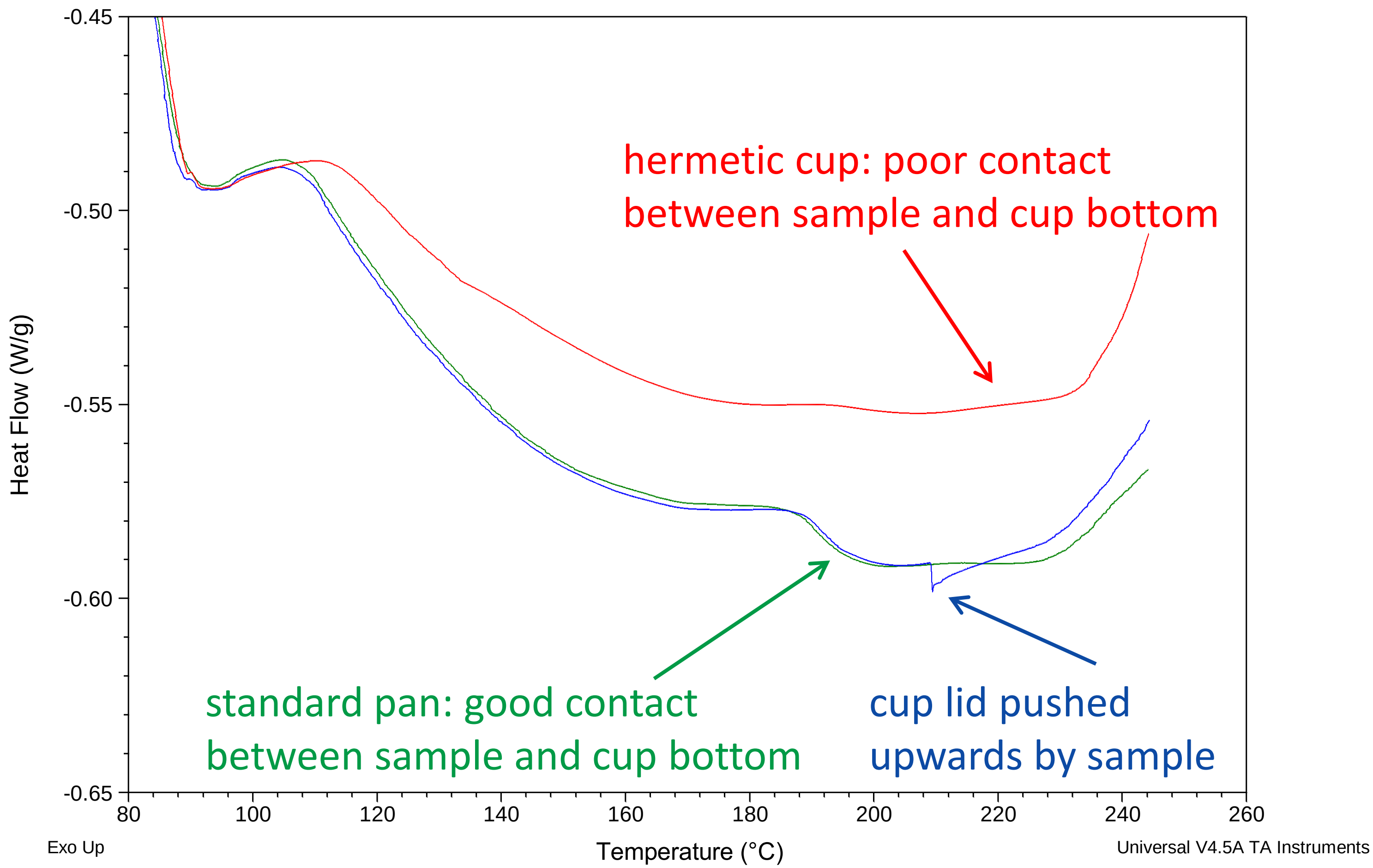
Effect of Water (Plasticizer) on Tg of Nylon 6



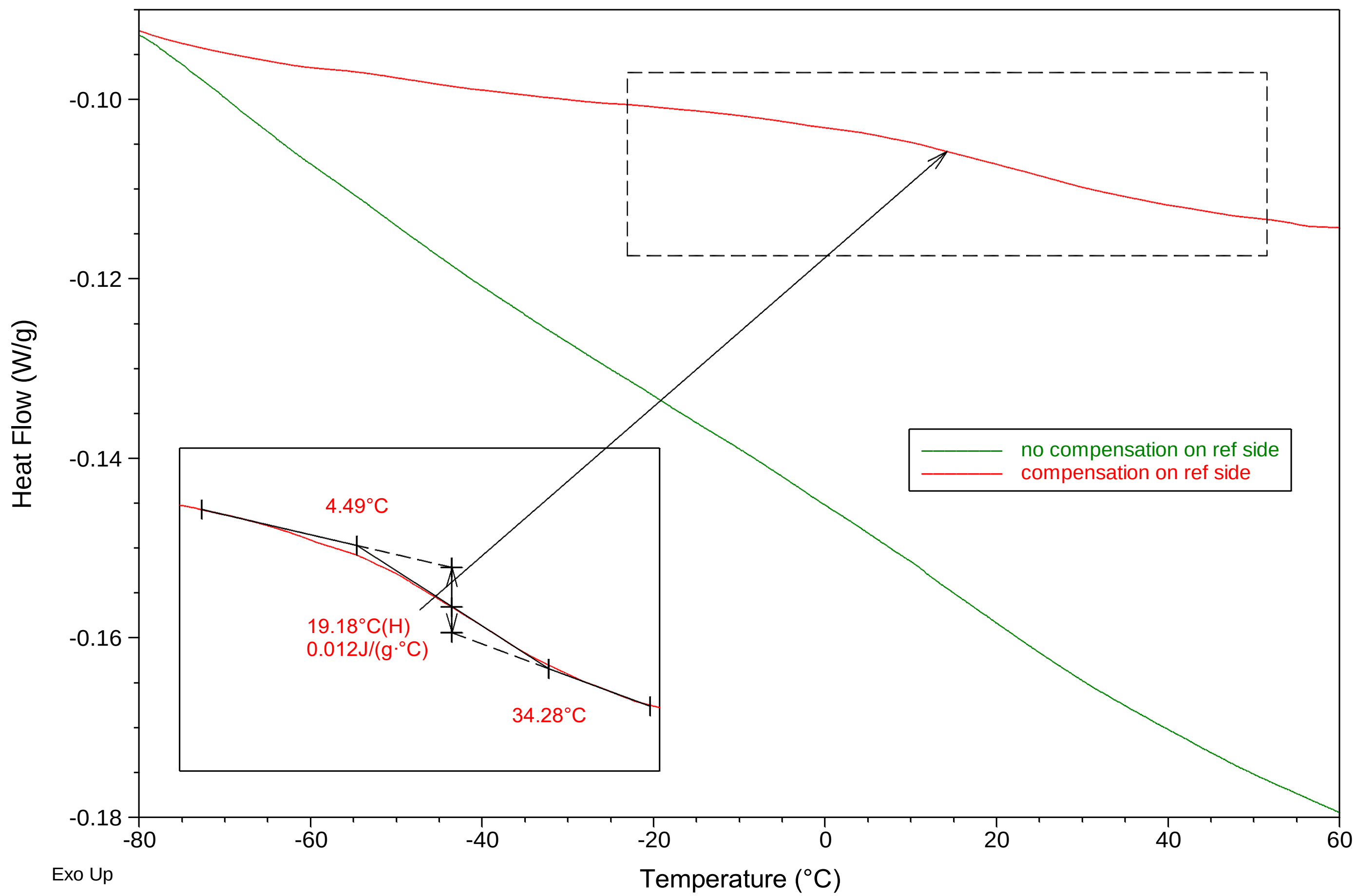
It Can Matter a Lot What Pan You Use



PVC Degree of Gelation: Influence of Sample Shape and Cup



Tg of Coating on Glass with Compensation on Reference Side (Uncoated Glass)



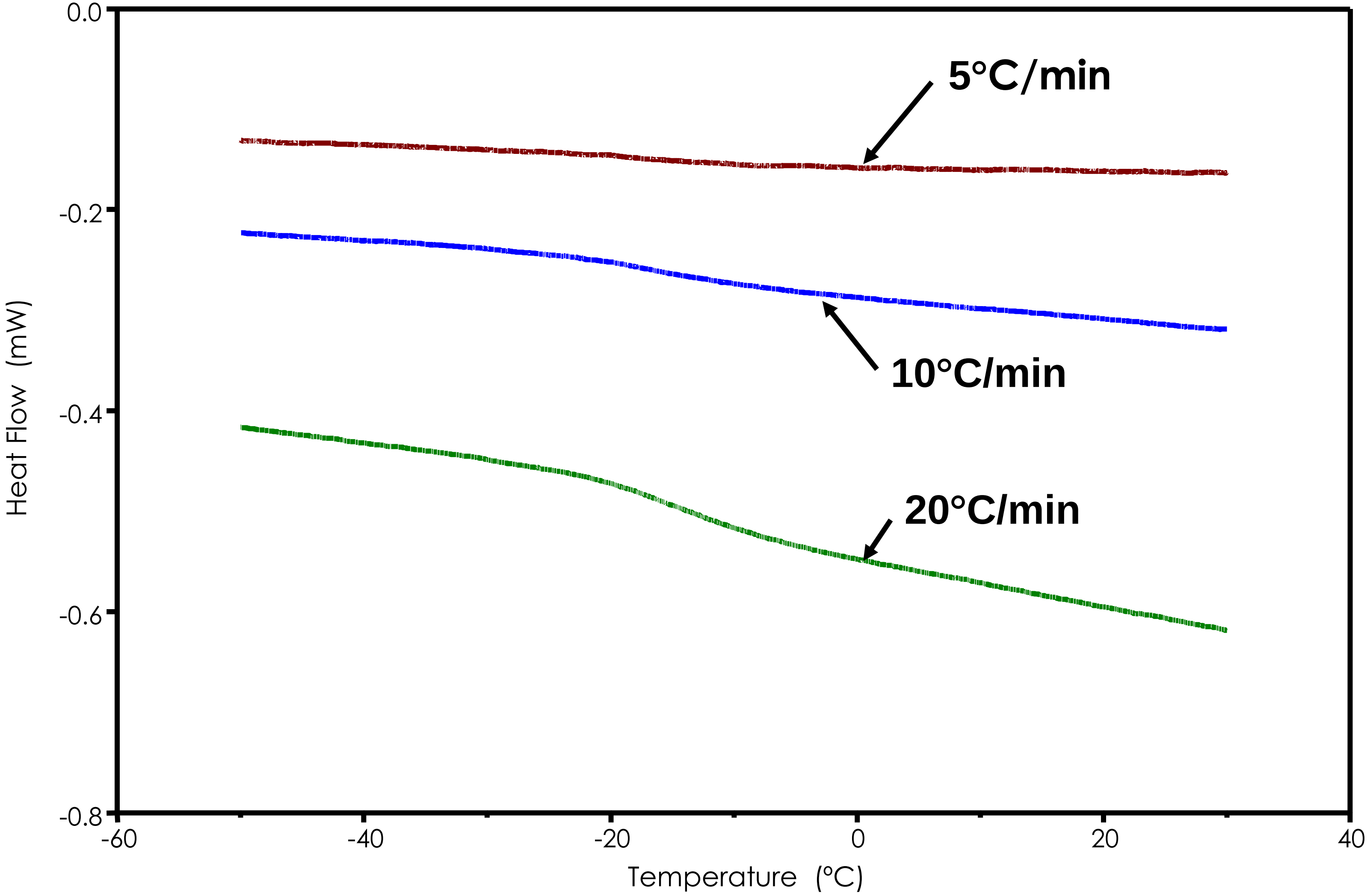
Sample Size & Heating Rate

$$dQ/dt = Cp \cdot dT/dt + f(t,T)$$

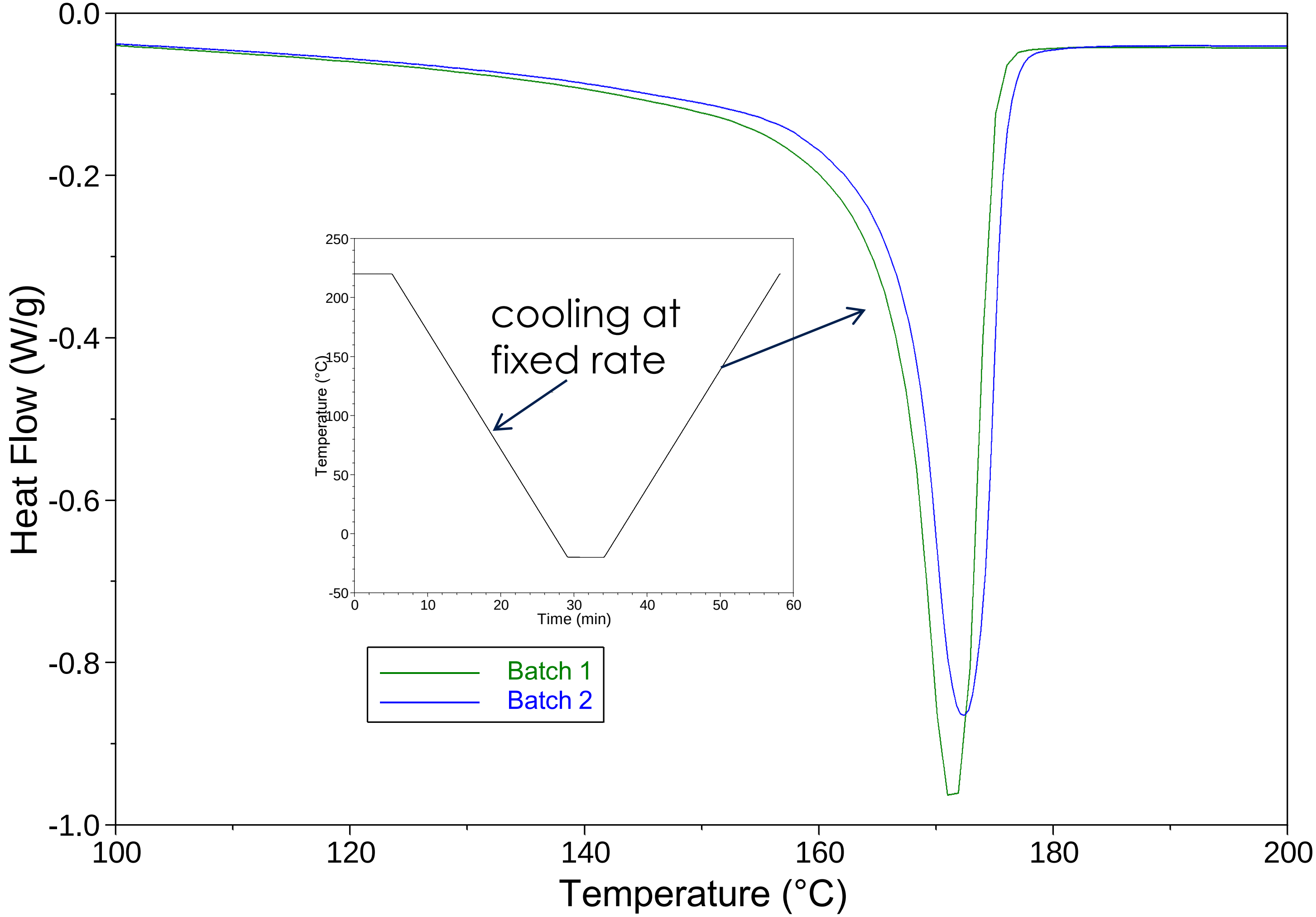
- ✓ **Sample size** is a trade off between sensitivity and resolution
  - ✓ Larger samples = more sensitivity
  - ✓ Smaller samples = better resolution
- ✓ **Heating rate** is a trade off between sensitivity and resolution
  - ✓ High heating rate = more sensitivity
  - ✓ Low heating rate = better resolution
- ✓ Use the smallest sample size which does not compromise the required sensitivity. Smaller sample means less thermal gradients.
- ✓ Start with a heating rate of 10°C/min, good compromise between minimizing thermal gradients & fast result.

TA

Effect of Heating Rate on Tg of PP



Fingerprinting of PVDF after Different Polymerization Conditions



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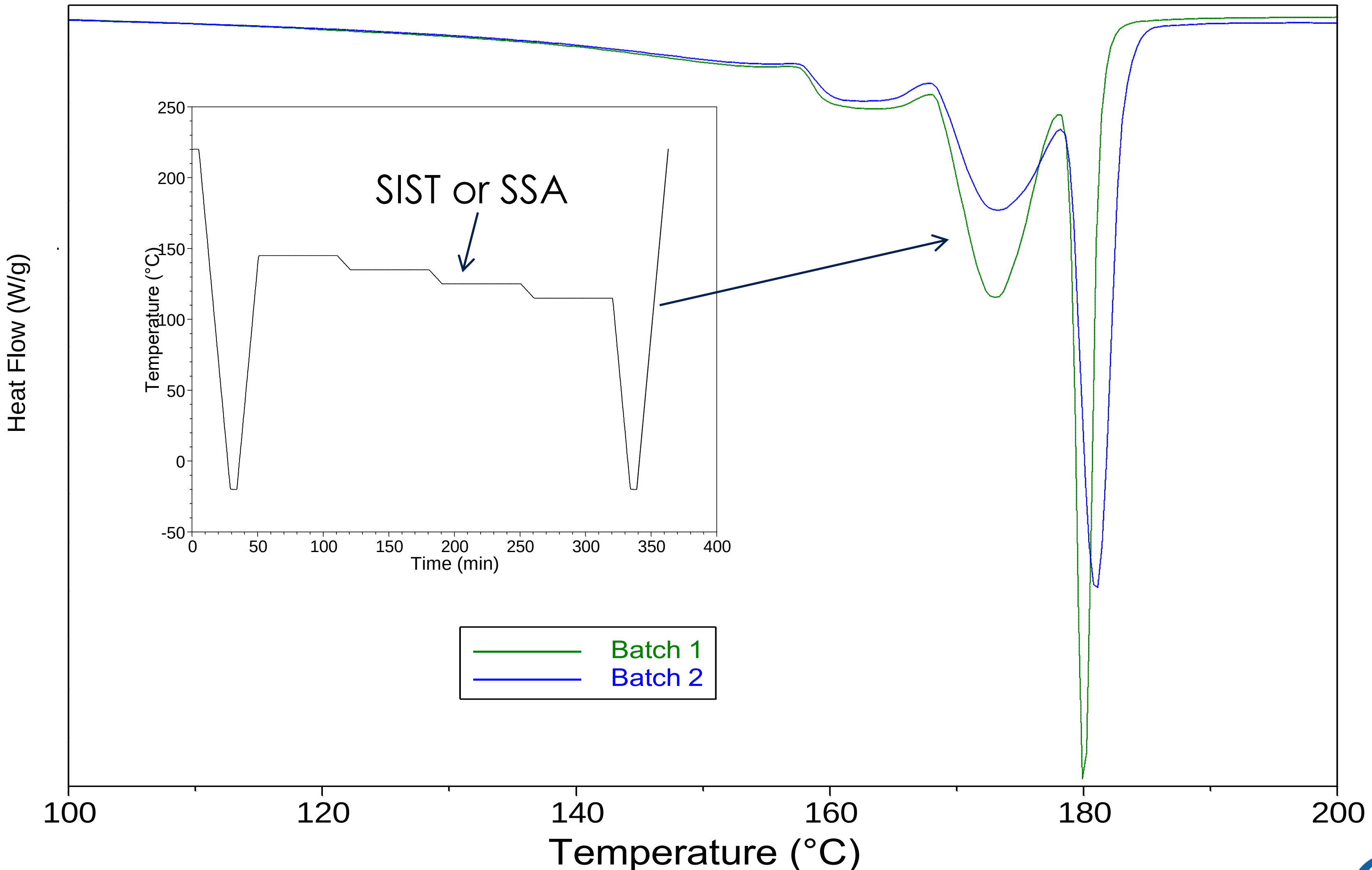
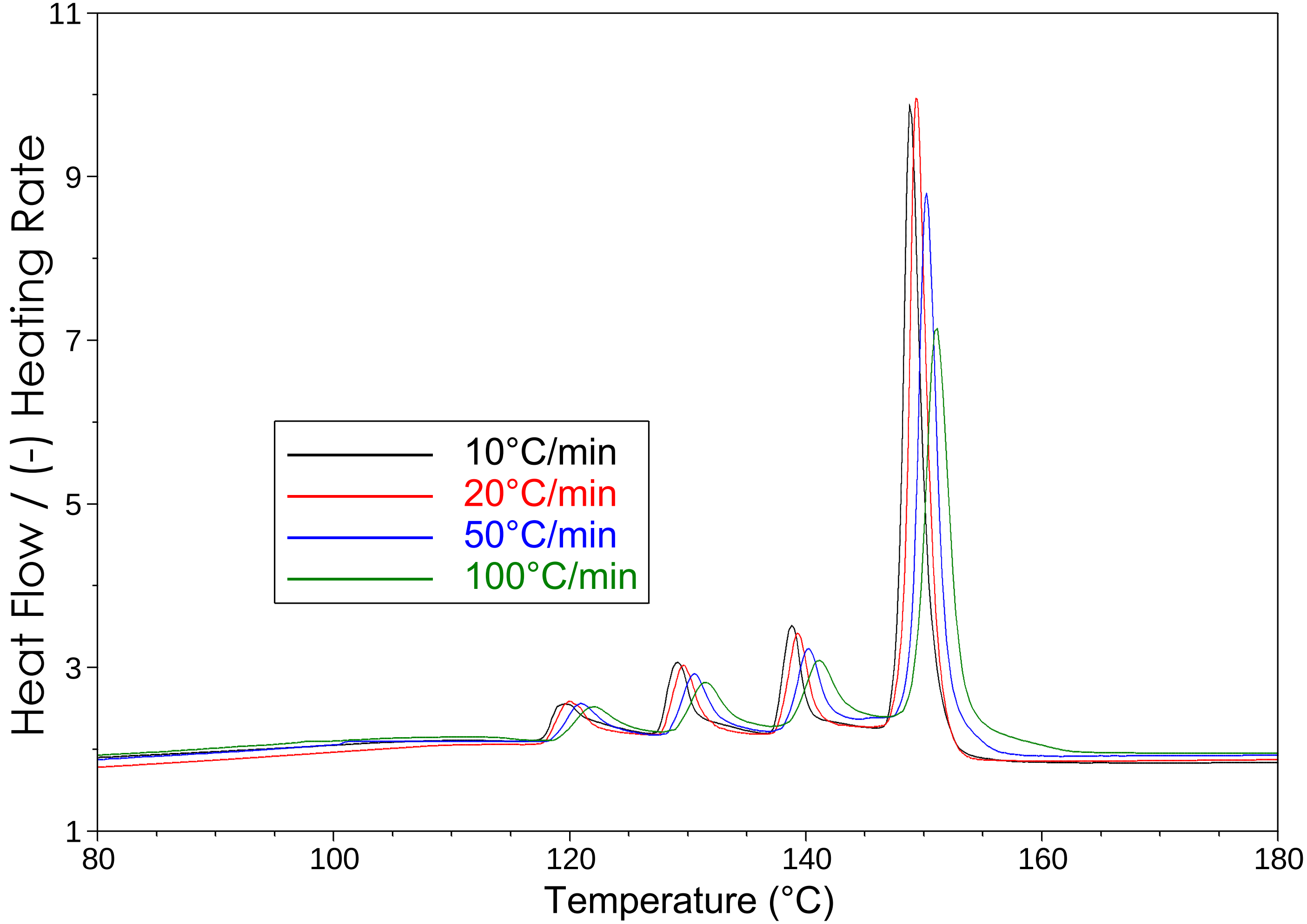


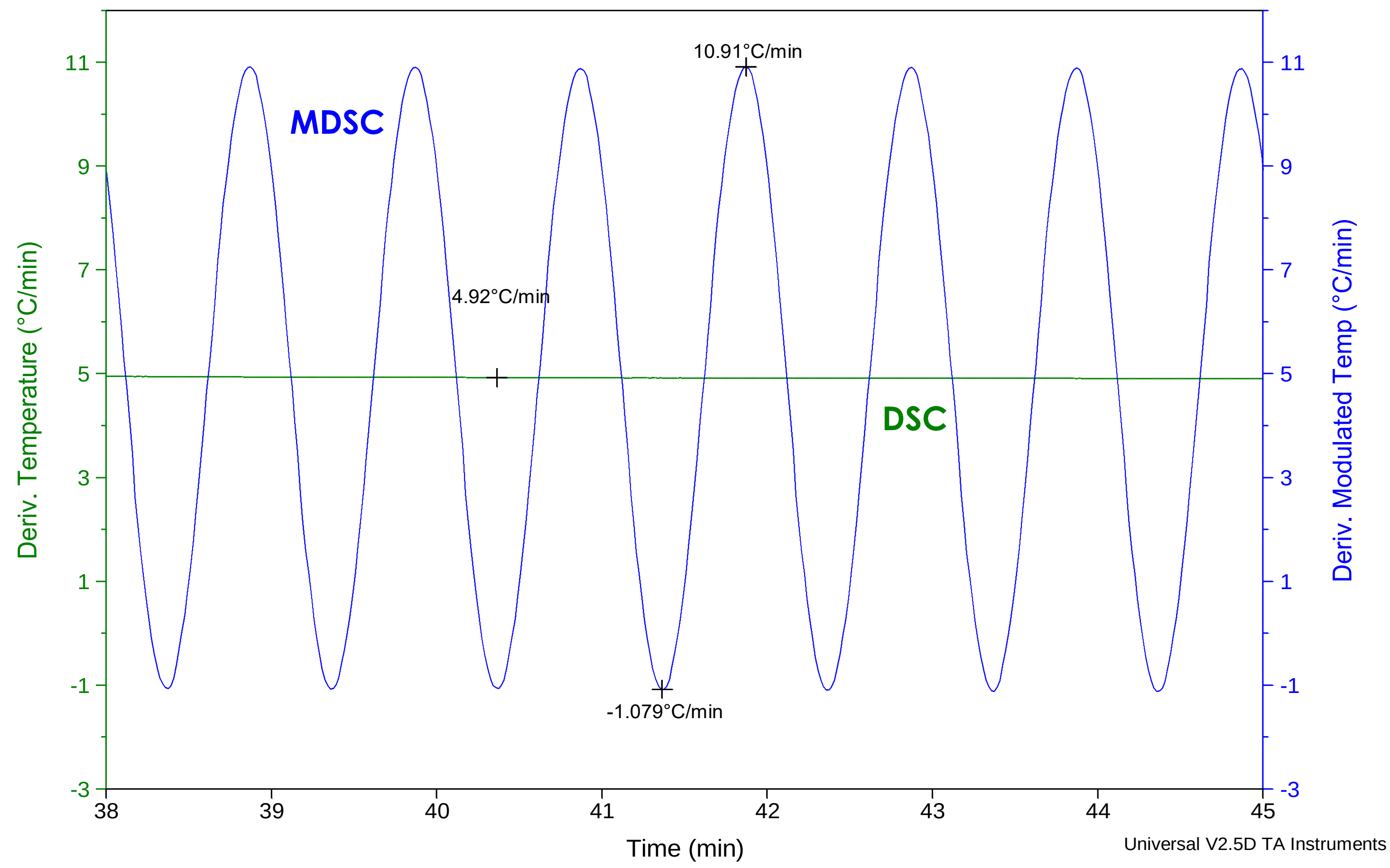
Fingerprinting of PVDF (Copolymer) Effect of DSC Heating Rate



Help in Proper Interpretation of Datacurves

- ✓ Modulated DSC
  MDSC
- ✓ Use of Derivative Curves

Modulated DSC Heating Rate

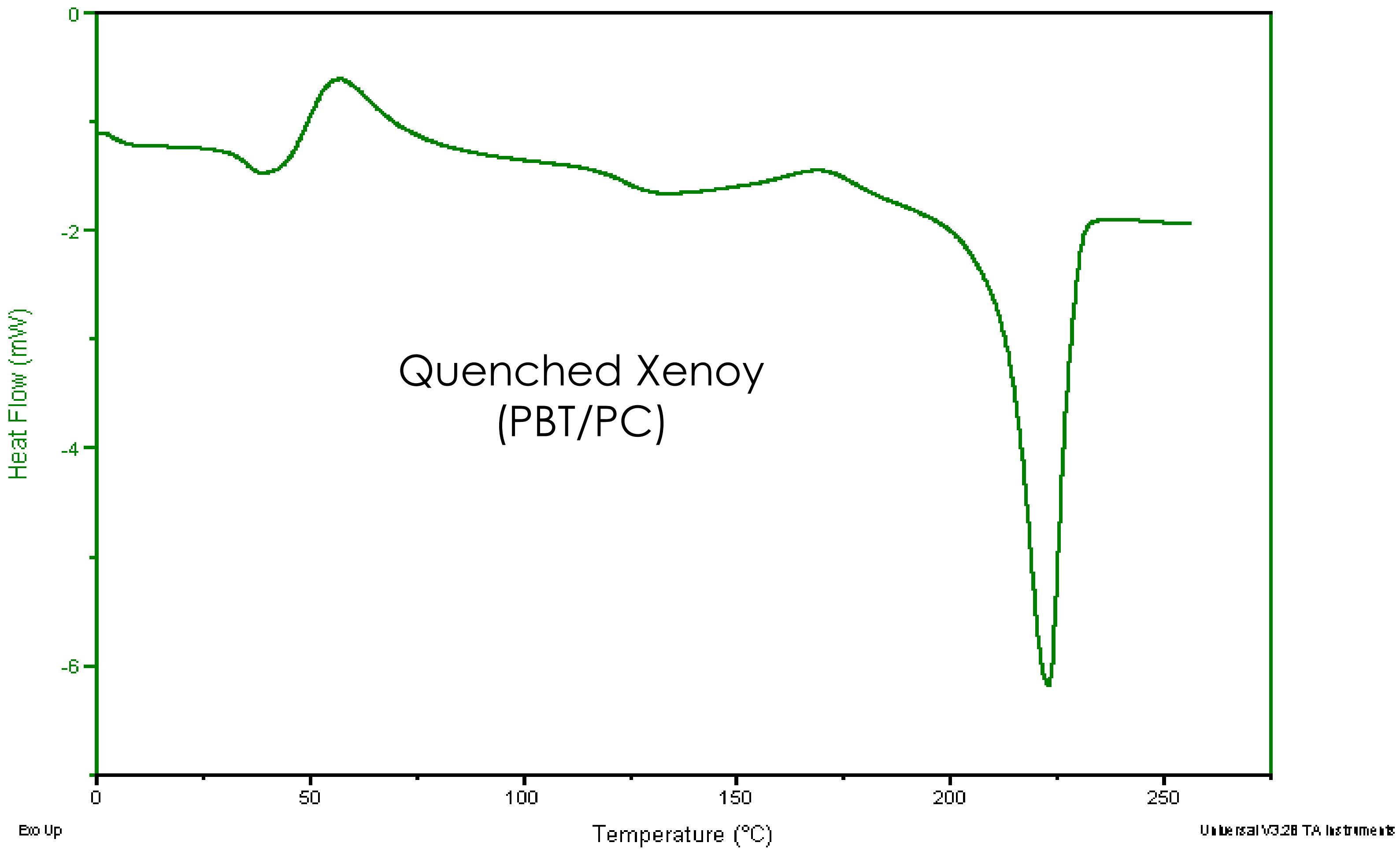


MDSC to Separate Overlapping Events

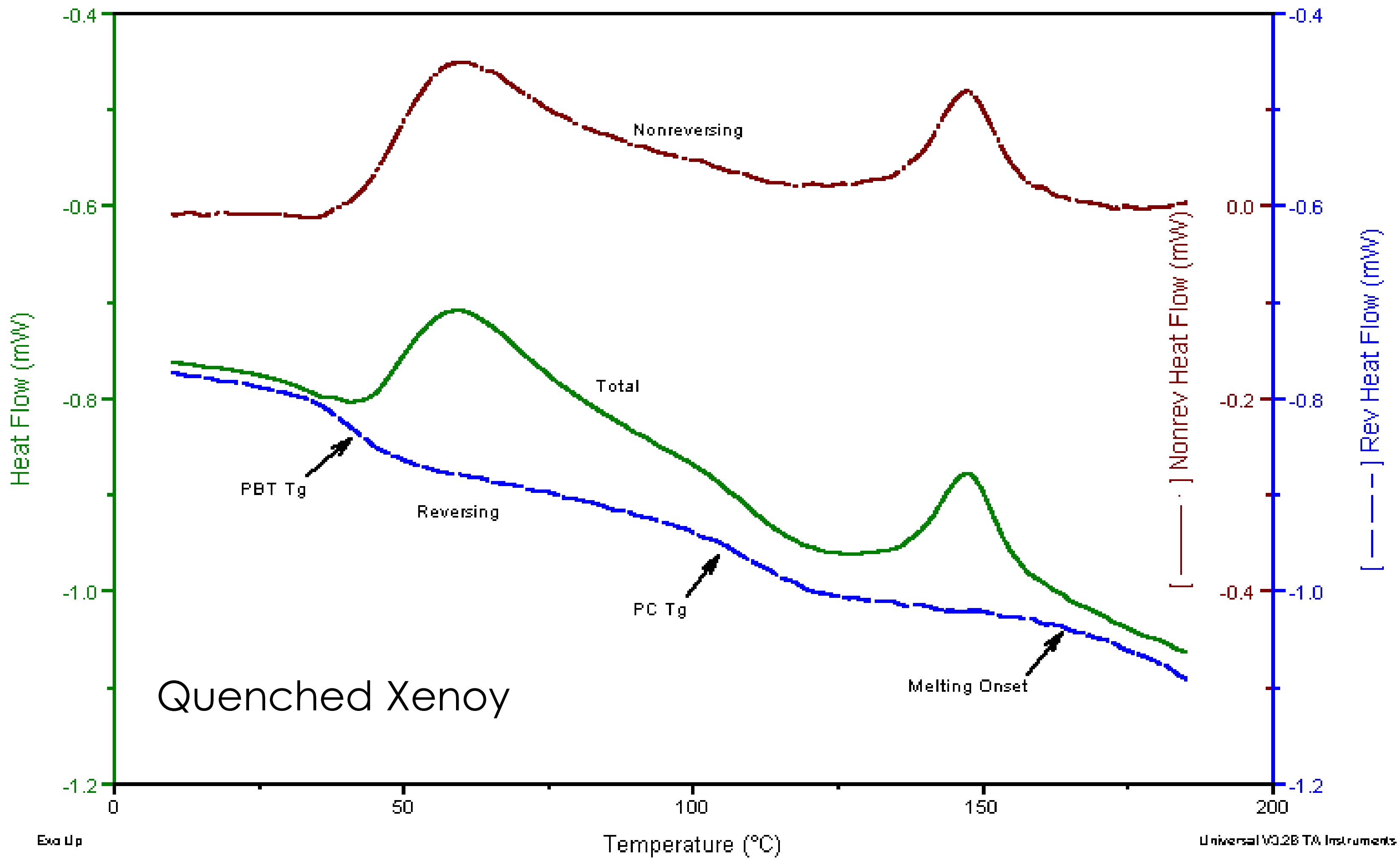
$$\frac{dQ}{dt} = Cp\frac{dT}{dt} + f(T,t)$$

Total Heat Flow	**Reversing Heat Flow**	**Non-Reversing Heat Flow**
• All Transitions	• Heat Capacity Cp • Glass Transition Tg • Most Melting	• Enthalpy Recovery • Evaporation • Crystallization • Thermoset Cure • Decomposition • Some Melting

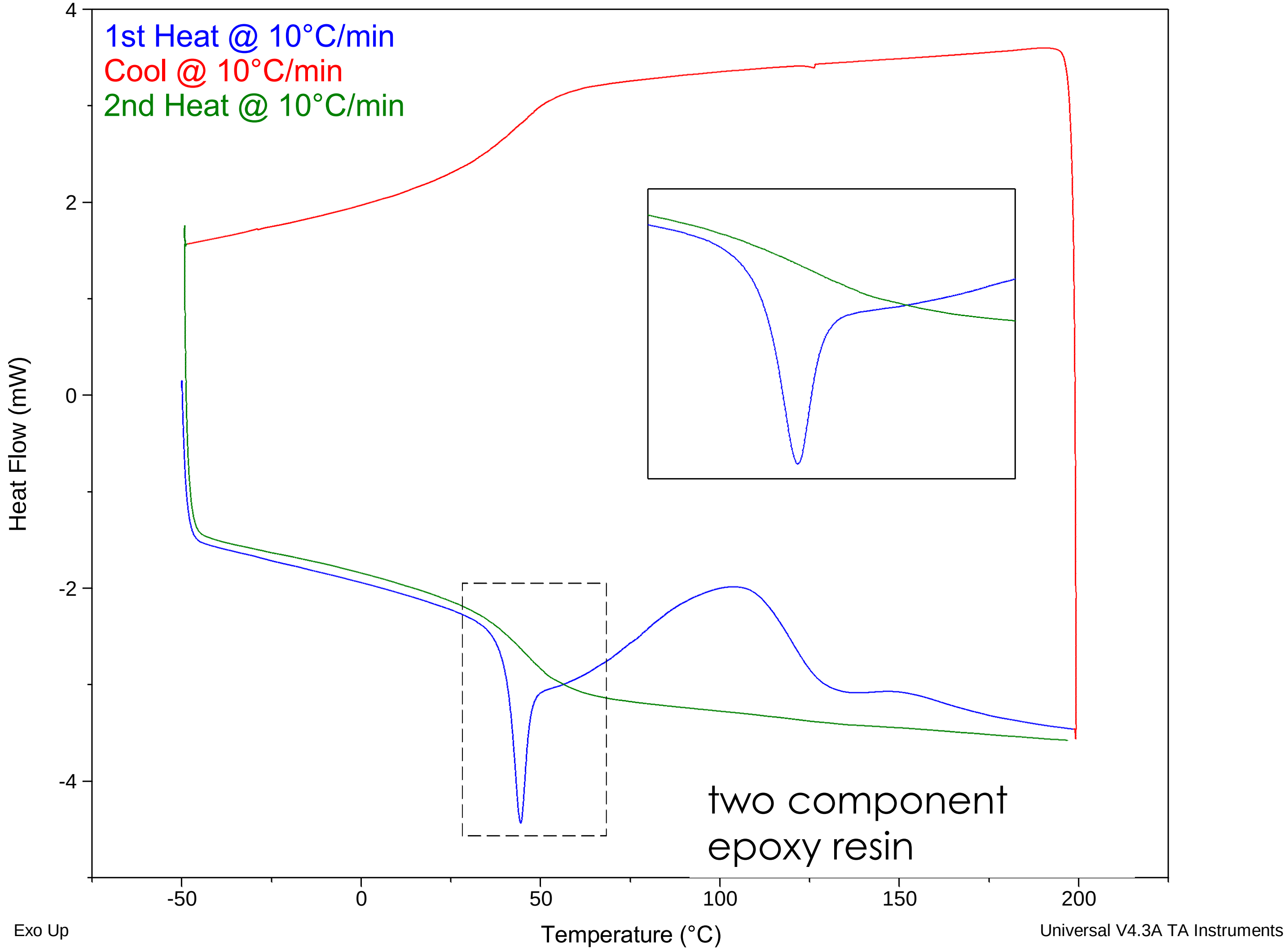
DSC of Polymer Blend



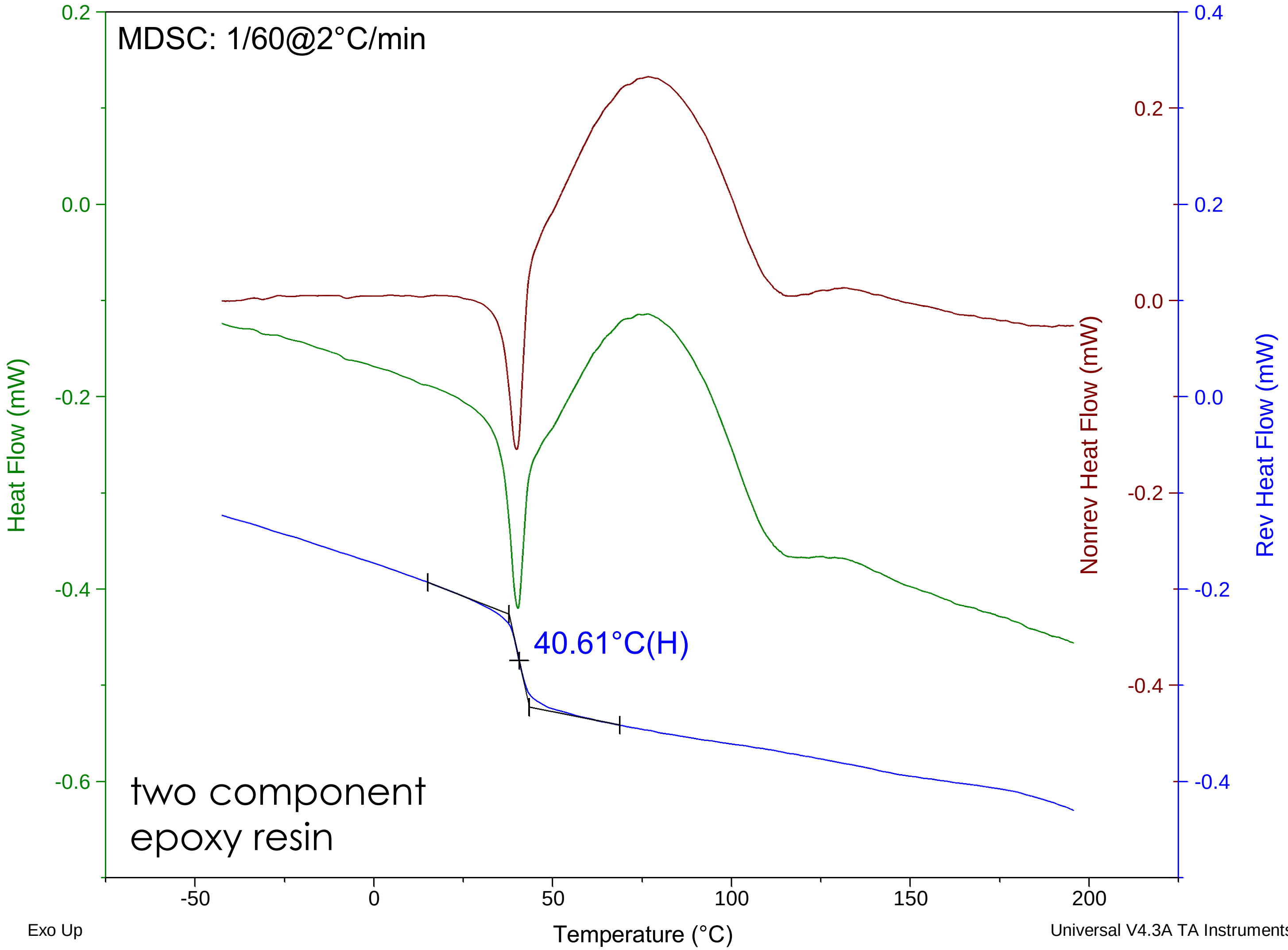
MDSC of Polymer Blend



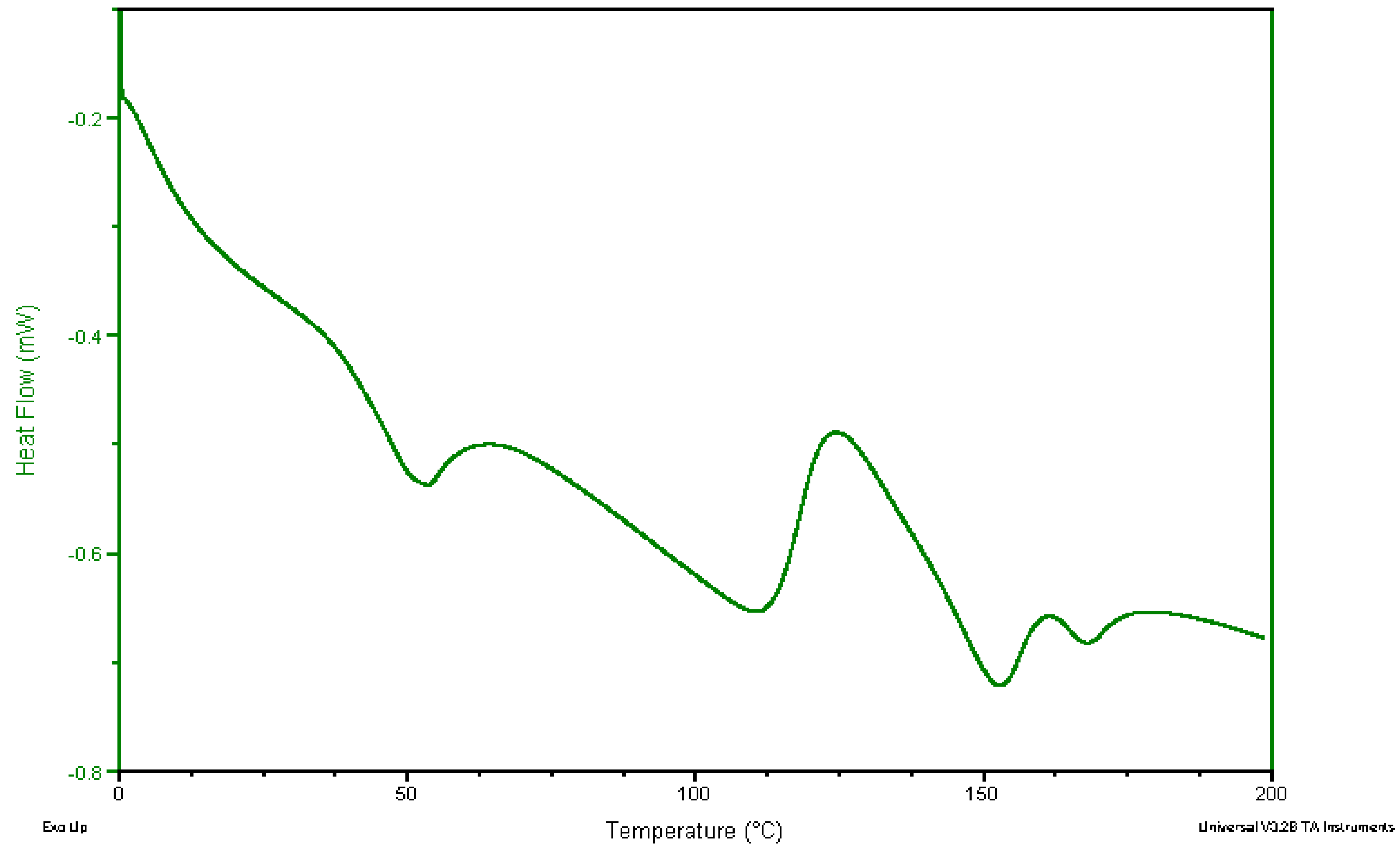
Tg Not Easily Determined on First Heat



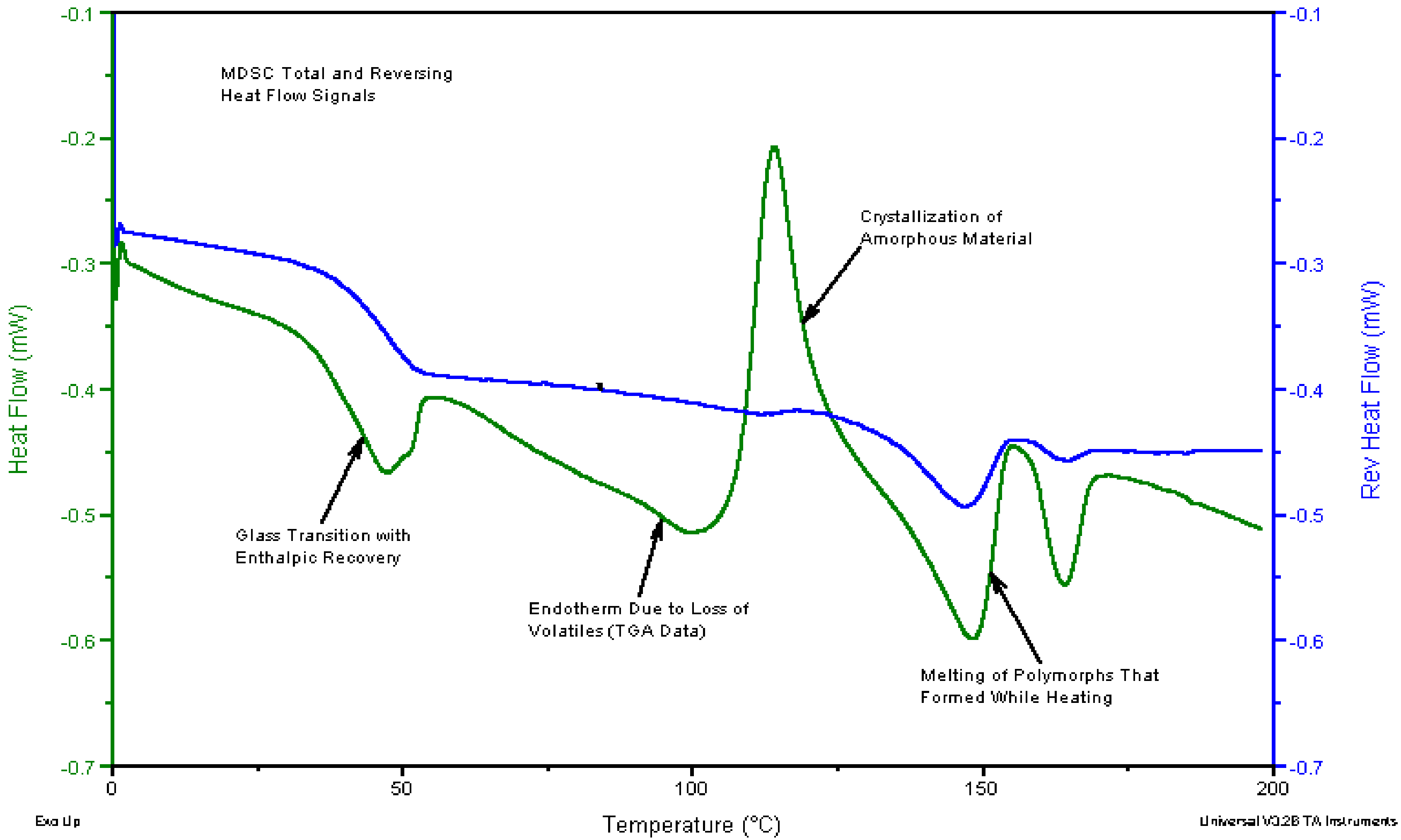
Reversing Heat Flow Easily Shows Tg



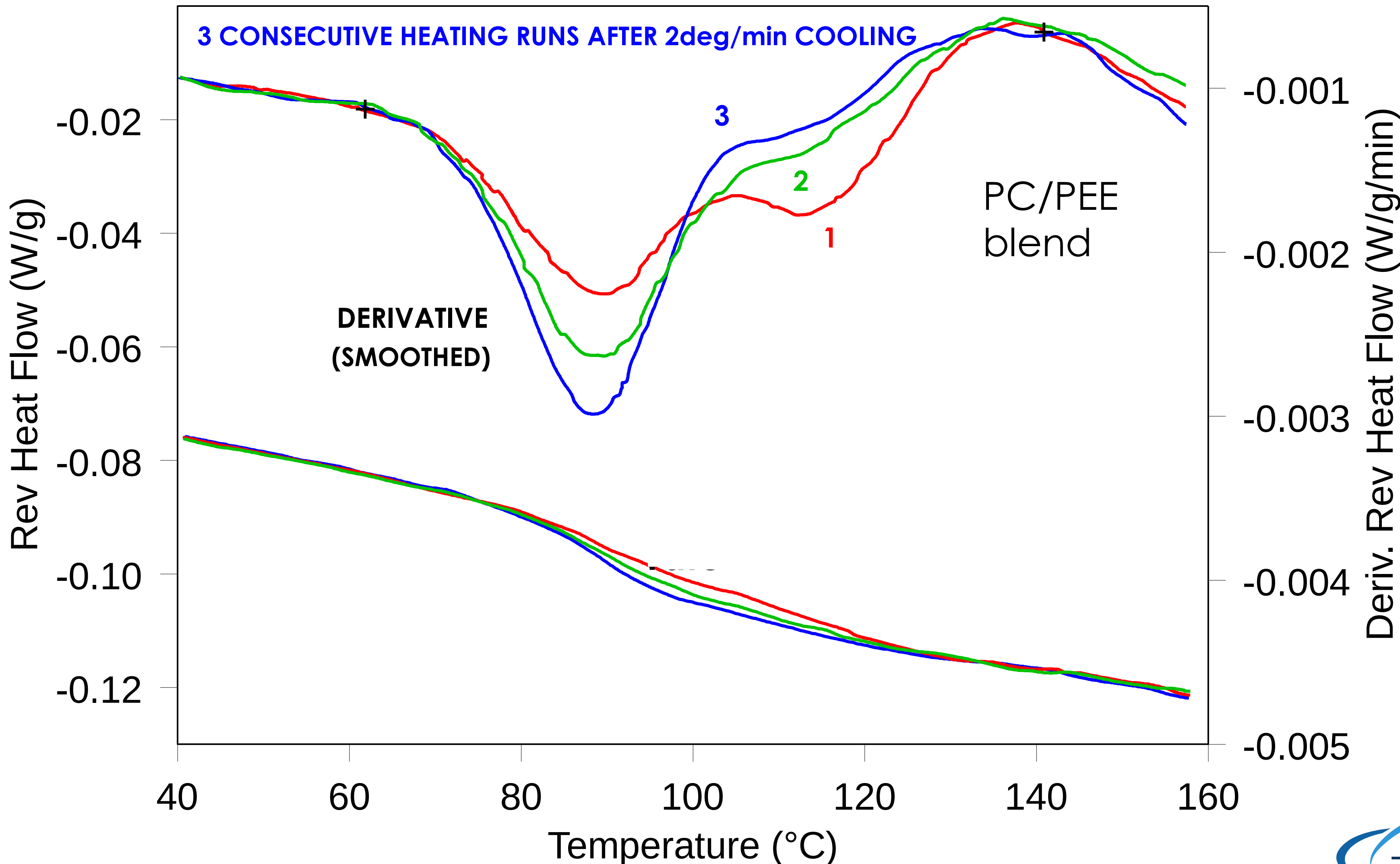
DSC for Drug Microspheres



MDSC for Drug Microspheres



Use of Derivative: Indicates 2 Tg's



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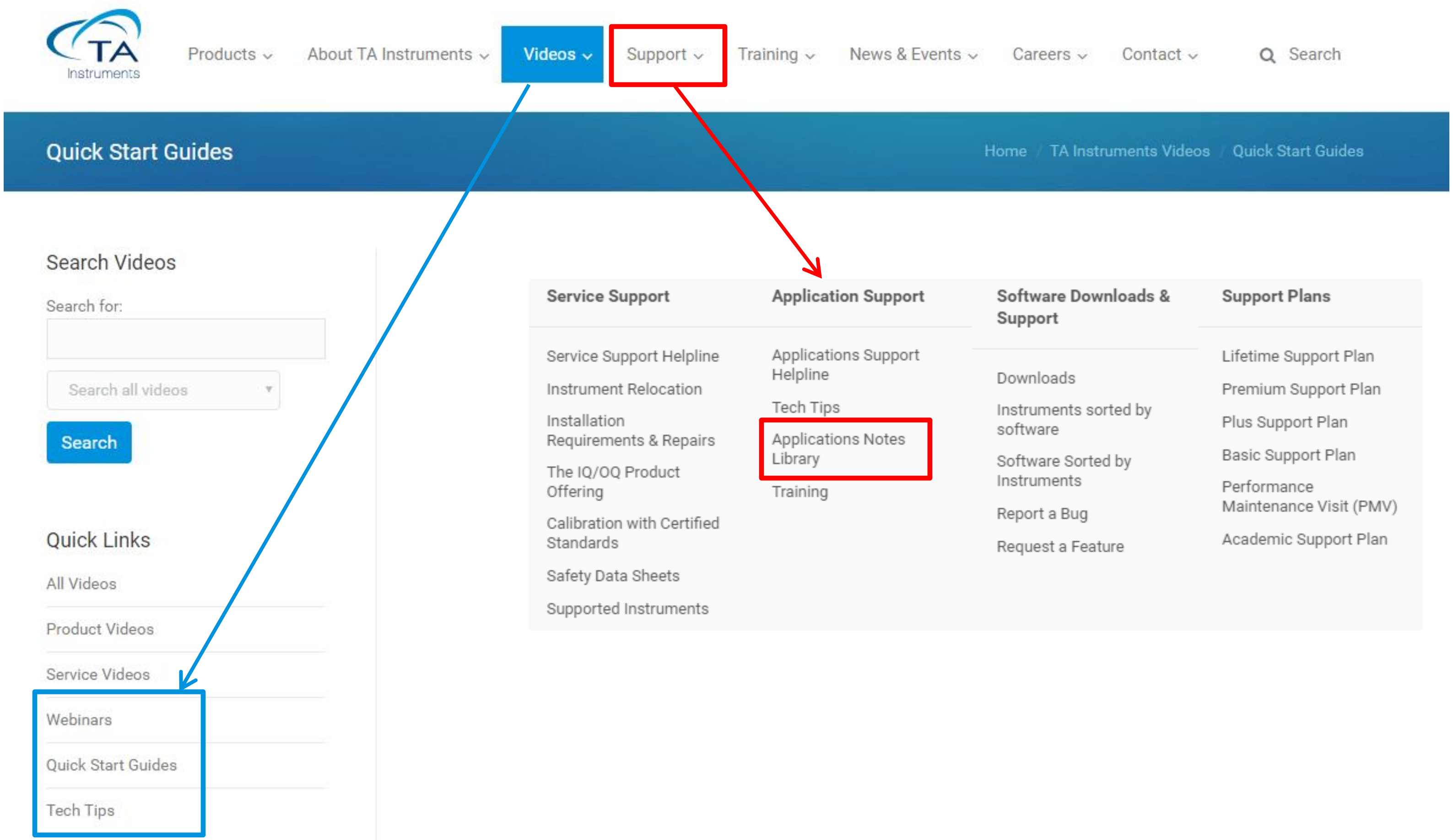

Welcome to New Line of Discovery DSC's

DSC2500, DSC250, DSC25

with AS

without AS

Overview of DSC's

model	technology	cell	MDSC	auto-sampler	direct Cp	reso-lution	base-line	software
Q20	Heat flux T1	Tzero cell	option	option no retrofit	no		flat	Advantage
Q200	Tzero T4	Tzero cell	option	option	no	better	flattest	Advantage
Q2000	Adv Tzero T4P	Tzero cell	option	option	yes	best	flattest	Advantage
Discovery	Adv Tzero T4P	Diffusion bonded	included	included	yes	best	flattest	Trios
DSC25	Heat flux T1	Fusion cell	included	option	no		**flat**	Trios
DSC250	Tzero T4	Fusion cell	included	option	no	**better**	**flattest**	Trios
DSC2500	Adv Tzero T4P	Fusion cell	included	included	**yes**	**best**	**flattest**	Trios

Thank you for your attendance