Differential Scanning Calorimetry

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Agenda

- Brief overview of polymers
- DSC Basics
- Applications
  - Melting transitions, T_m
  - The glass transition, T_g
  - Thermal Stability
- Modulated DSC, MDSC
- Variations in DSC

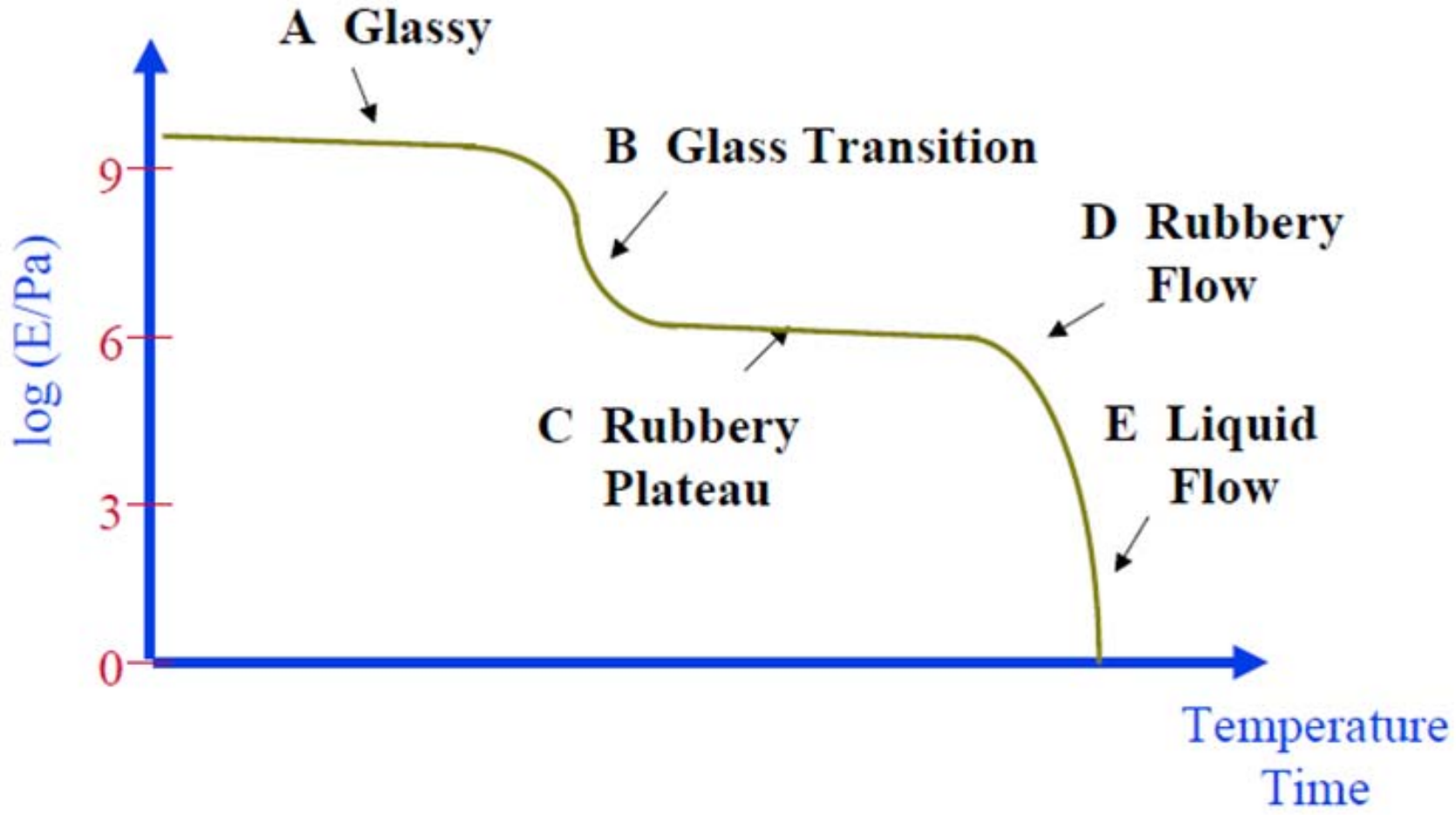
Thermal Analysis Useful For

- Quality Control
- Characterization
- Processing
- End Use Application

Most Commonly Used Thermal Analysis Techniques

Technique	Parameter Measured
DifferentialScanning Calorimetry(DSC)	dH/dT
Thermogravimetry (TGA)	Mass
Derivative Thermogravimetry (DTGA)	dM/dT
Thermomechanical Analysis (TMA) (Dilatometry; Penetration)	Deformation, Volume or Length
Dynamic Mechanical Analysis(DMA)	Modulus/ Damping
Dielectric Analysis (DEA)	Permitivity/ Loss Factor

Major Polymer Transitions



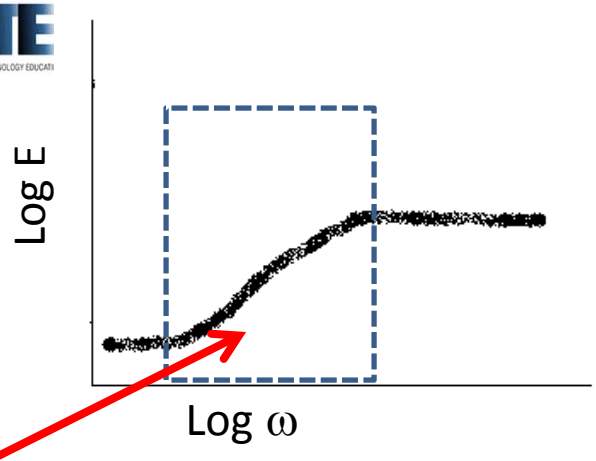
Two Main Transitions in Thermoplastic Polymers

- Glass Transition, Tg
  - Indicates minimum/maximum service temperature
  - Very important in amorphous polymers
- Melting temperature, T_m
  - Defines minimum processing andmaximum service temperature

Transitions and Relaxations Why Important?

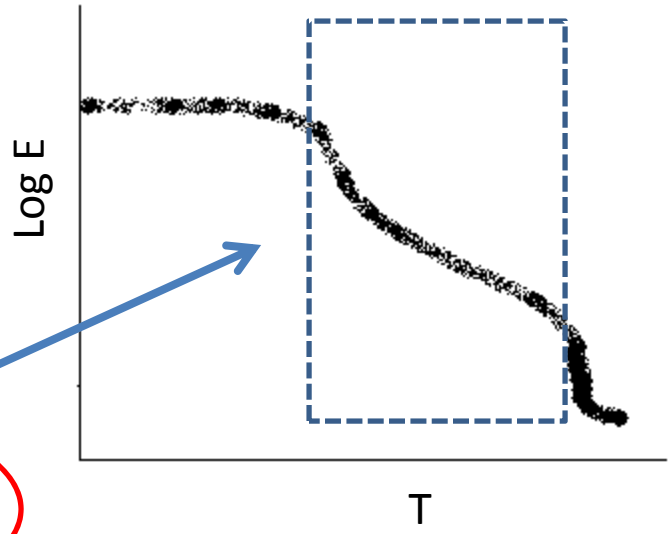
- Range at which properties change
  - Modulus
  - Brittleness
  - Impact strength
  - Wear
  - Permeability
  - Thermal conductivity
  - Strength
  - Dielectric constant
  - Stress-strain properties
  - Electrical conductivity

Transitions and Relaxations



If we examine polymer properties with respect to temperature and/or frequency
we find that there is a range over which the properties change(eg., Silly Putty)

- At high frequencies no motion -> unrelaxed
- At low frequencies it flows -> relaxed



If T is changed instead of ω, same features result.

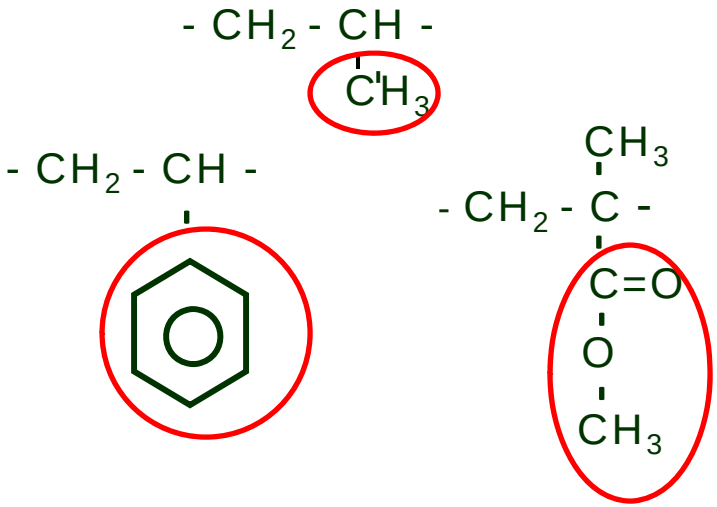
Relaxation – significant "sharp" or "steep" change in properties in a relatively narrow temperature or frequency range.

Transitions and Relaxations

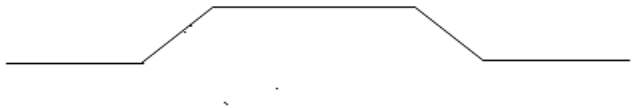
Relaxation – significant “sharp” or “steep” change in properties in a relatively narrow temperature or frequency range.

Can be related to various types of polymer motion :

1. Side chain rotation (PP, PMMA or PS)



2. Small segments as in PE :



3. Longer segments(20-30 carbon atoms, as at T_g)

Transitions and Relaxations

Transition – a discontinuous change in thermodynamic properties of a material.

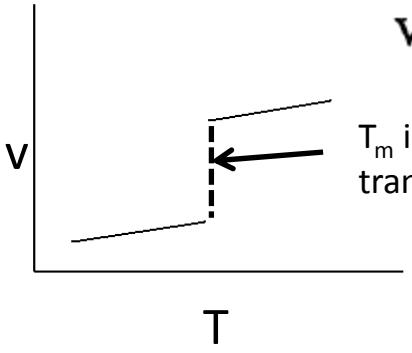
- Includes changes of state:
  - Crystalline-to-amorphous- T_m
  - Crystalline$_1$-to-crystalline$_2$ – polymorphism
  - Amorphous-to-glass – T_g

  - At a transition there will be a discontinuous change in thermodynamic properties, which can be observed to define the transition temperature.
    - Specific volume
    - Heat capacity
    - Specific heat(Enthalpy)

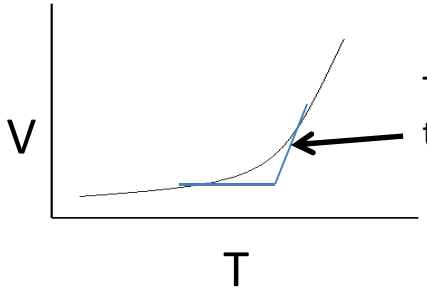
Transitions and Relaxations

1st Order Transition – Transition for which the first order derivative of free energy is a thermodynamic function that is discontinuous when plotted vs. temperature.

$$V = \left(\frac{\partial G}{\partial P}\right)_T$$

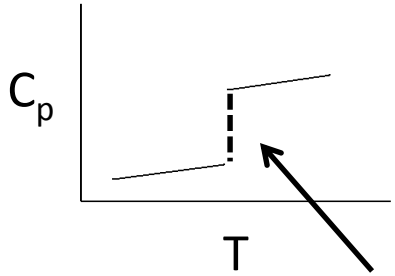


T_m is a first order transition



T_g is a second order transition

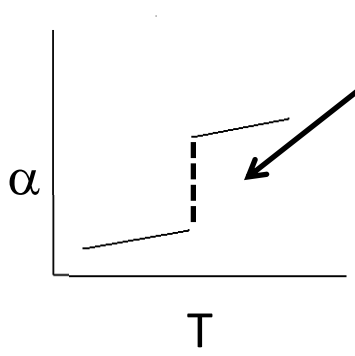
2nd Order Transition – Transition for which the second order derivative of free energy is a thermodynamic function that is discontinuous when plotted vs. temperature.



$$\frac{-C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

$$\frac{\alpha}{V} = \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial T \partial P}$$

T_g is a second order transition



$$\frac{1}{L}\frac{\partial V}{\partial T} = a$$

$$\frac{1}{V}\frac{\partial v}{\partial T} = a$$

Transitions and Relaxations

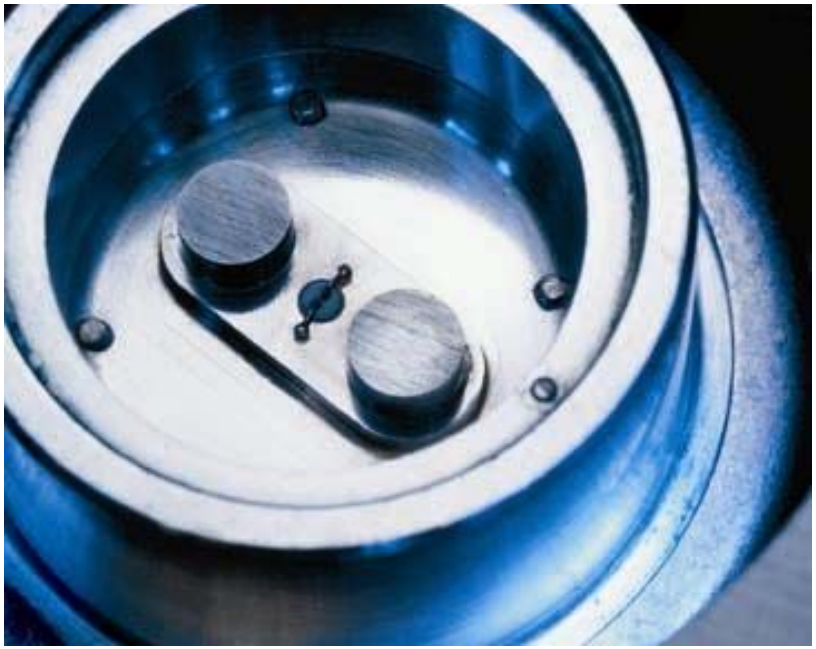
- Change is greatest at T_m and T_g, and less so at lower temperature relaxations.
  - Many polymers become brittle below Tg- no means to absorb energy of impact(PS, PMMA)
  - Some remain ductile(PC, PET), because of a large secondary relaxation at T < Tg which can absorb energy and become brittle at much lower T, below the secondary relaxation.

Relative Sensitivity of Thermal Analysis Instruments

Technique	Property Measured	Relative Signal Change at Tg
Differential Scanning Calorimetry	Heat flow(heat capacity)	0.2
Thermomechanical Analysis	Expansion Coefficient; Dimension Change or Softening	3
Dielectric Analysis	Permittivity and dielectric loss	100
Dynamic Mechanical Analysis	Mechanical strength and energy loss	200

What Does a DSC Measure?

A DSC measures the difference in heat flow rate (mW = mJ/sec) between a sample and inert reference as a function of time and temperature



Popularity of DSC Technique

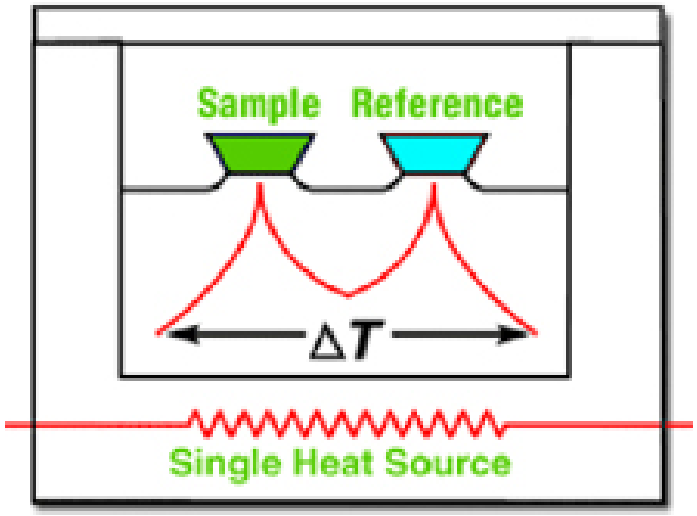
- Speed of operation
- Ease of operation
- Small sample size

Information Obtained from DSC

- Glass Transition temperatures
- Melting points and boiling points
- Crystallization time and temperature
- Percent crystallinity
- Heats of fusion and reaction
- Specific heat
- Oxidative stability
- Rate of cure
- Degree of cure
- Reaction kinetics
- Purity
- Thermal stability

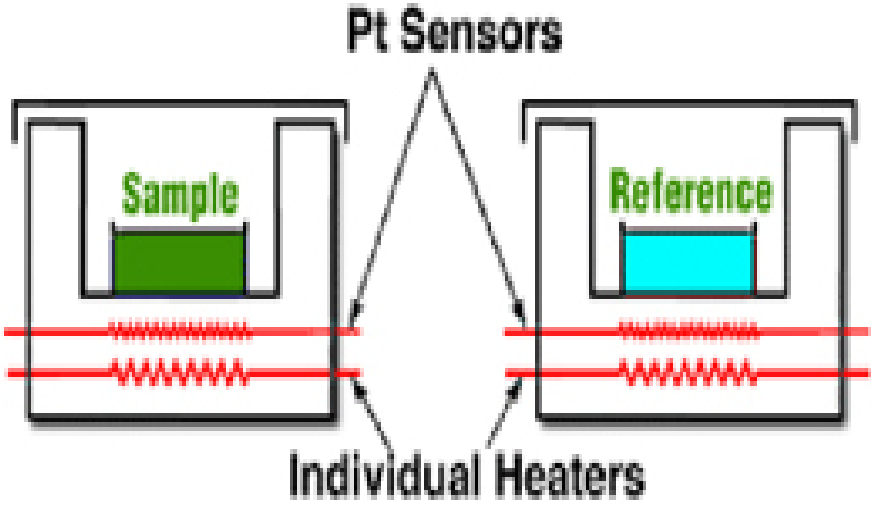
Types of DSC

Heat Flux



Same heat flows into both samples; $\Delta T = 0$. When a change occurs(endo or exo) a ΔT signal is generated which is proportional to the heat flow difference.

Power Compensation



When a ΔT is detected, an additional circuit will increase or decrease heating power Of sample furnace. This compensating heating power, ΔP, is proportional to heat absorbed or released.

DSC Heat Flow

$\frac{dH}{dt}$ = DSC heat flow signal

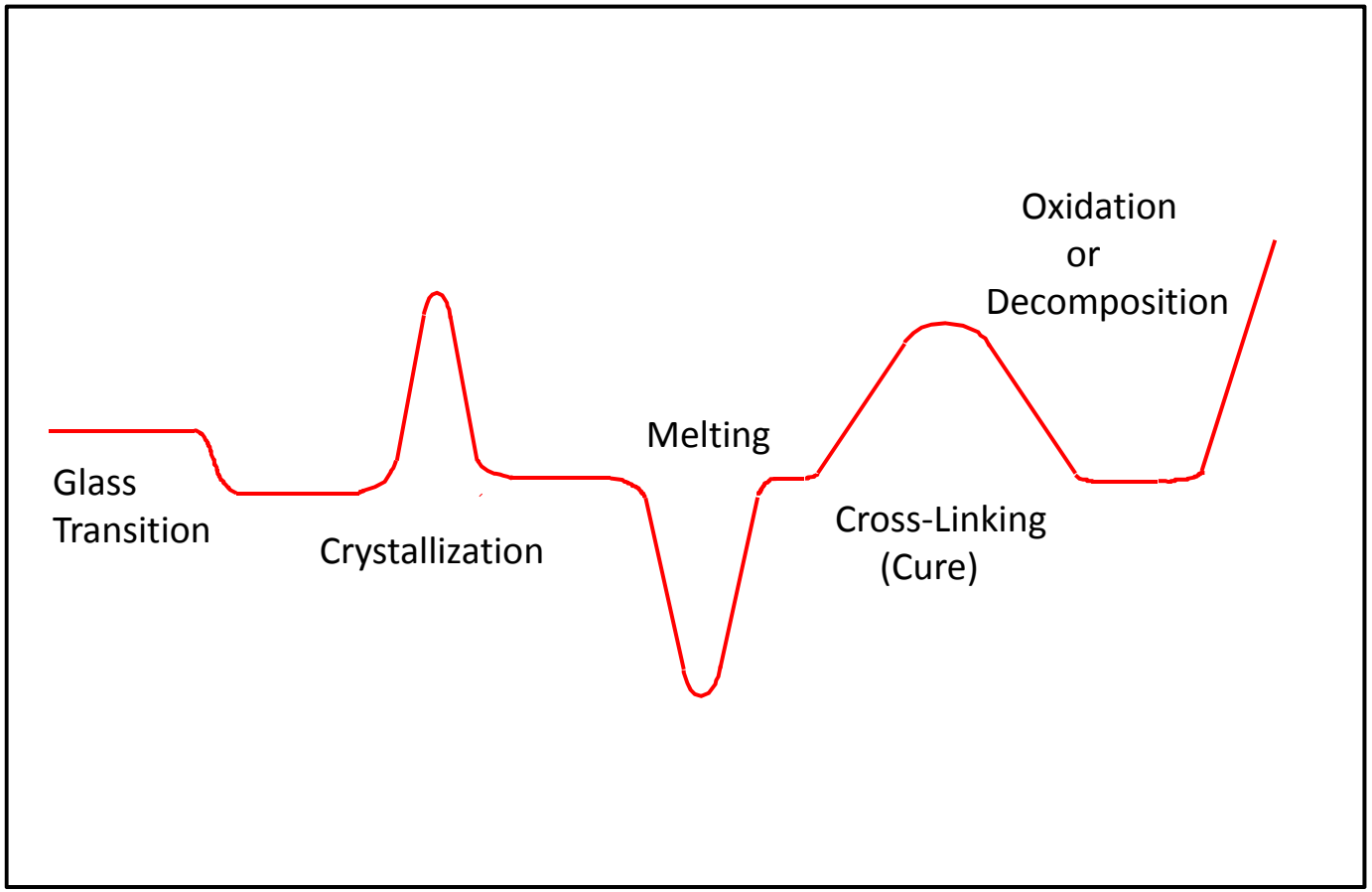
Cp = Sample Heat Capacity
= Sample Specific Heat x Sample Weight

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

$\frac{dT}{dt}$ = Heating Rate

$f(T,t)$ = Heat flow that is function of time at an absolute temperature (kinetic)

Typical DSC Output:
Transitions of Interest in a DSC



DSC Signals

DSC measures the difference in heat flow rate (mW = mJ/sec) between a sample and inert reference as a function of time and temperature

- Heat Flow
  - Endothermic: heat flows into the sample as a result of either heat capacity (heating) or some endothermic process (Tg, melting, evaporation, etc.)
  - Exothermic: heat flows out of the sample as a result of either heat capacity (cooling) or some exothermic process (crystallization, cure, oxidation, etc.)

DSC: Terminology

- **Amorphous Phase** - The portion of material whose molecules are randomly oriented in space. Liquids and glassy or rubbery solids. Thermosets and some thermoplastics.
- **Crystalline Phase** - The portion of material whose molecules are regularly arranged into well defined structures consisting of repeat units. Very few polymers are 100% crystalline.
- **Semi-crystalline Polymers** - Polymers whose solid phases are partially amorphous and partially crystalline. Most common thermoplastics are semi-crystalline.
- **Endothermic** - A transition which absorbs energy.
- **Exothermic** - A transition which releases energy.
- **Melting** - The endothermic transition upon heating from a crystalline solid to the liquid state. This process is also called fusion. The melt is another term for the polymer liquid phase.
- **Crystallization** - The exothermic transition upon cooling from liquid to crystalline solid. Crystallization is a function of time and temperature.
- **Cold Crystallization** - The exothermic transition upon heating from the amorphous rubbery state to the crystalline state. This only occurs in semi-crystalline polymers that have been quenched (very rapidly cooled from the melt) into a highly amorphous state.
- **Enthalpy of Melting/Crystallization** - The heat energy required for melting or released upon crystallization. This is calculated by integrating the area of the DSC peak on a time basis.

Physical Origins of Peaks in DSC

	Endothermic	Exothermic
Crystalline Transition	X	X
Fusion	X	
Crystallization		X
Vaporization	X	
Sublimation	X	
Adsorption		X
Desorption	X	
Glass Transition	Baseline Change,	No peaks
Liquid Crystal transition	X	
Physical Aging	X	

Chemical Origin of Peaks in DSC

	Endothermic	Exothermic
Chemisorption		X
Dehydration	X	
Decomposition	X	X
Oxidative Degradation		X
Oxidation in Gaseous Atmosphere		X
Adsorption		X
Solid State reaction	X	X
Combustion		X
Polymerization		X
Curing		X

Sample Size

- 5 to 15 mg for thermoplastics or elastomers
- Might no be able to determine TG of highly crosslinked sample
- Melting/Crystallizing
  - Less than 10 mg
  - Heat of reaction
    - As small as can be accurately measured
- Composites: Depends on filler loading

General Experimental Setup

- **Calbration:** ASTM E967, E968, D3417, D3418
  - Same heating rate as experiment
  - Same atmosphere and purge flow rates(50cc/min)
  - Same temperature range as experiment
- **Pan:**
  - Flat bottom
  - Good sample –to-pan contact
  - Inert to reactive samples
- **Reference:**
  - Same pan as sample, but it should be empty
- **Pan-Cell Contact:**
  - **Symmetric placement of reference and sample**

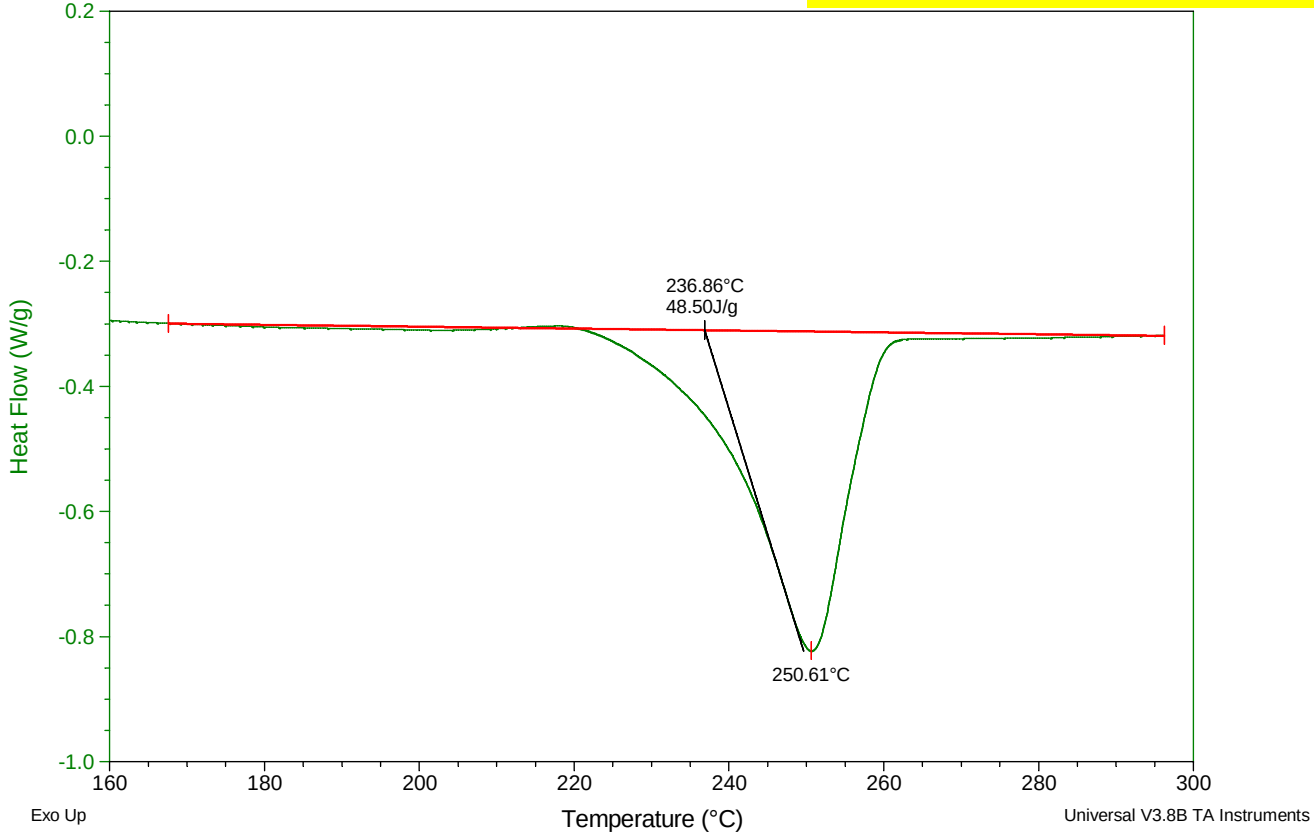
Reporting DSC Data
ASTM E472, D3418

- Identification of all substances and their sources
- Details of material histories, pretreatments, purities, etc.
- Calibration procedures, temperatures, cell constants used.
- Details of any preconditioning
- Temperature program
- Method for detrmining Tg, Tm
- Instrument used

T_m and Crystallinity Measurement by Differential Scanning Calorimetry, DSC

% Xtallinity = $\Delta H_{exp} / \Delta H_o$
Where ΔH_{exp} is Heat of fusion for the polymer

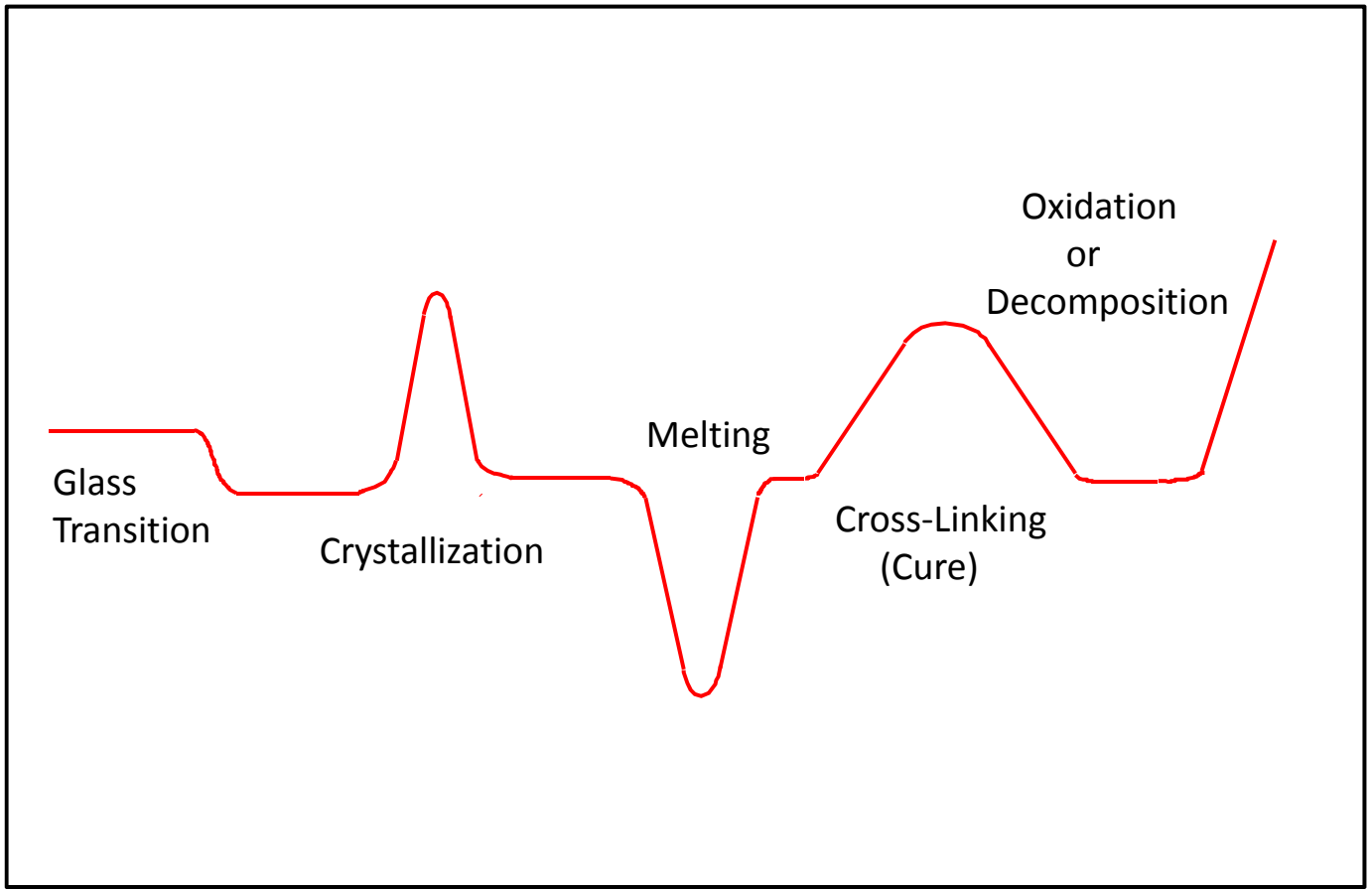
ΔH_0 is Heat of fusion for 100% crystalline polymer



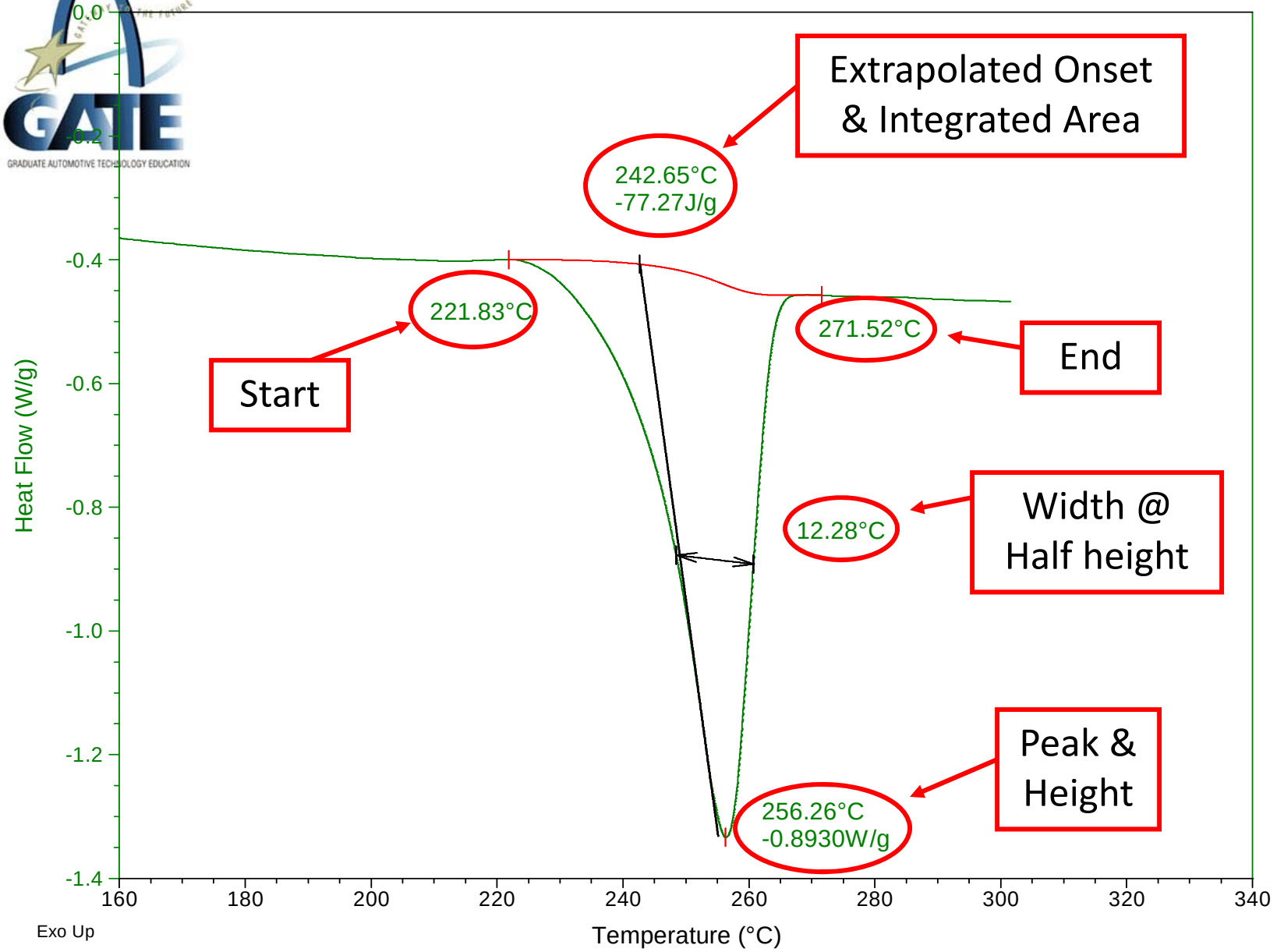
Melting and Crystallization

- Melting is the endothermic transition from a crystalline solid to a liquid amorphous state
- Crystallization is the exothermic transition from amorphous to crystalline (normally from liquid to solid during cooling)
- Cold-Crystallization is the exothermic transition during heating from a solid amorphous state to a solid crystalline state.

Typical DSC Output:
Transitions of Interest in a DSC



Measurement of Melting



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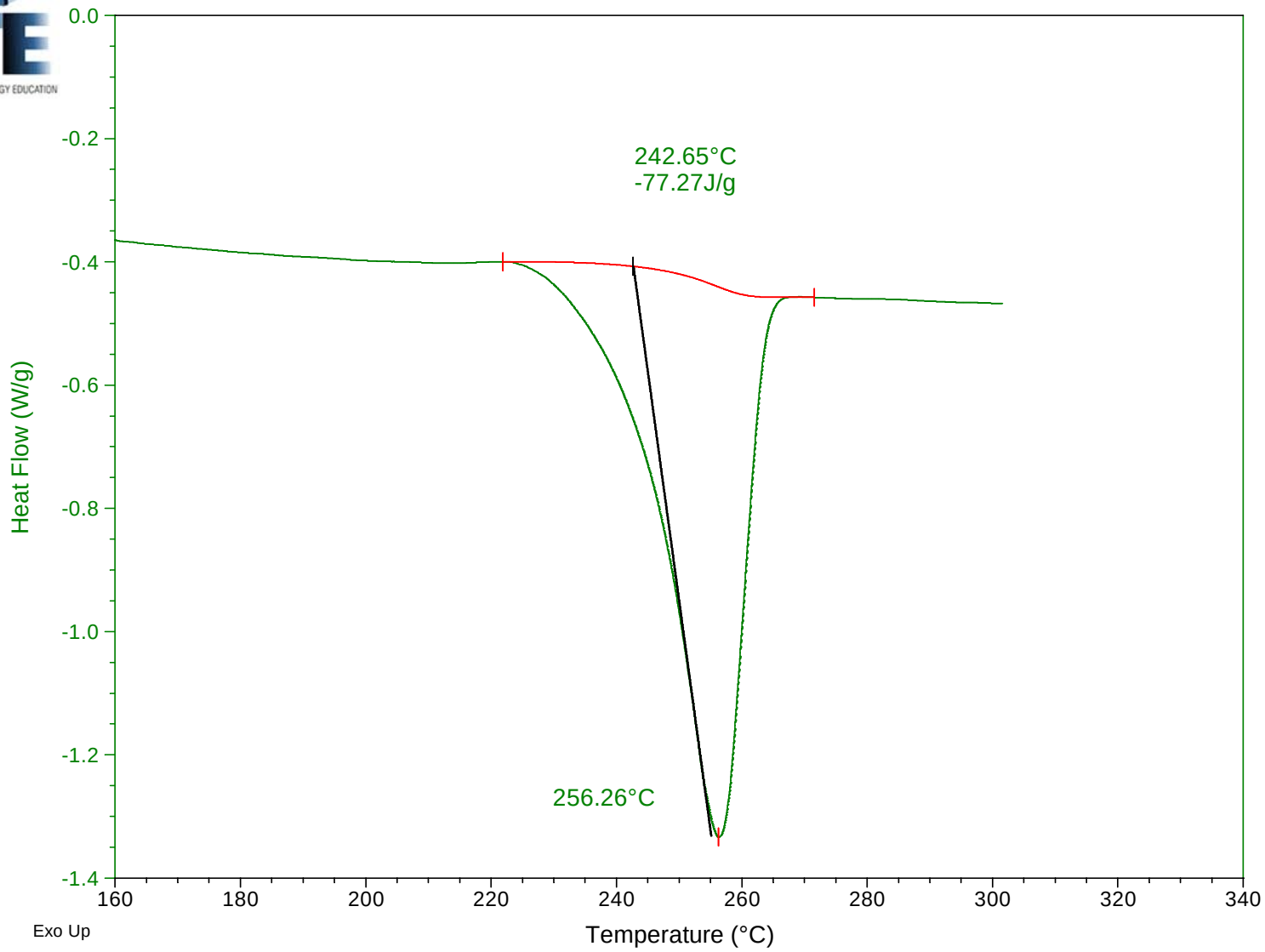


DSC Melting

- Polymers
  - The peak temperature is the melt point
  - Between the extrapolated onset and the peak, crystal perfection may be occurring
  - Between the peak and the end the sample is finished melting and returning to the DSC temperature
- Pure, low molecular weight materials (mw<500g/mol) (small molecules)
  - The extrapolated onset is the melting temperature
  - All of the crystals are melted at the peak
  - Between the peak and the end the sample is finished melting and returning to the DSC temperature

T_m is affected by:

- Mwt
- Chemical Structure
- Additives
  - Can disrupt packing of serve as nucleating sites
- Effect of heating/cooling rate

- Crystallization kinetics

- Effects of polymer structure/composition

- Effects of thermal/mechanical processing

Effect of Aromaticity on Melting

Polymer	% Aromatic	Melting Range
$-CH_2 - CH_2 -$	0	105 - 135°C
PET	39	250 - 275°C
-(Ph)-O-	62	300 - 315°C
-(Ph)-S-	70	300 - 360°C

Effect of Branching on Melting

Polyolefin	Branching	T_m
LDPE	irregular random lengths	~ 105°C
LLDPE	irregular fixed lengths	~ 127°C
HDPE	none	~ 135°C
PP	regular fixed lengths	~ 150°C

Effect of Polymer Type on Melting

Class	Structure	Melting Range
Polyolefins	-CH_2-CH_2-	85 - 174°C
Polyamides	-CH_2-NH-C(O)-CH_2-	190 - 265°C
Polyesters	-CH_2-O-C(O)-CH_2-	220 - 270°C
Polyphenylene Sulfides	-Ph-S-	300 - 360°C

Effect of Molecular Weight on Melting

Olefin Formula	Mole. Wt. (g/mol)	T_m (°C)
$C_{12}H_{26}$	170	-10
$C_{24}H_{50}$	339	54
$C_{30}H_{62}$	423	66
$C_{35}H_{72}$	493	75

Effect of Hydrogen Bonding on Melting

Polyamide	T_m	H Bonding
Nylon 12,2	236	Least
Nylon 10,2	242	
Nylon 8,2	279	
Nylon 6,2	326	Most

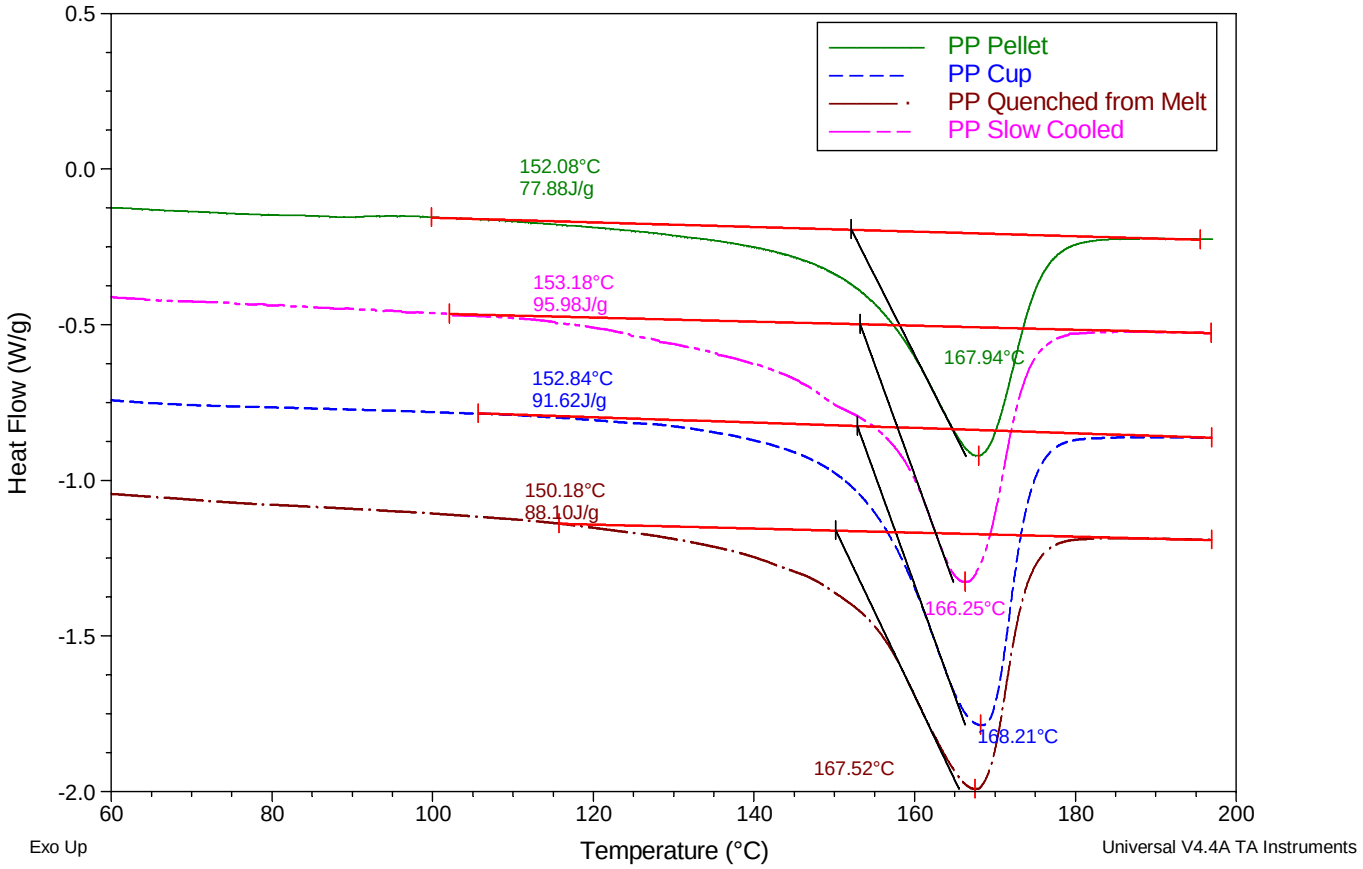
Nylon x,y where:

x = carbons in diamine section

y = carbons in diacid section

Effect of Processing on Crystallinity for PP

First heat vs. second heat



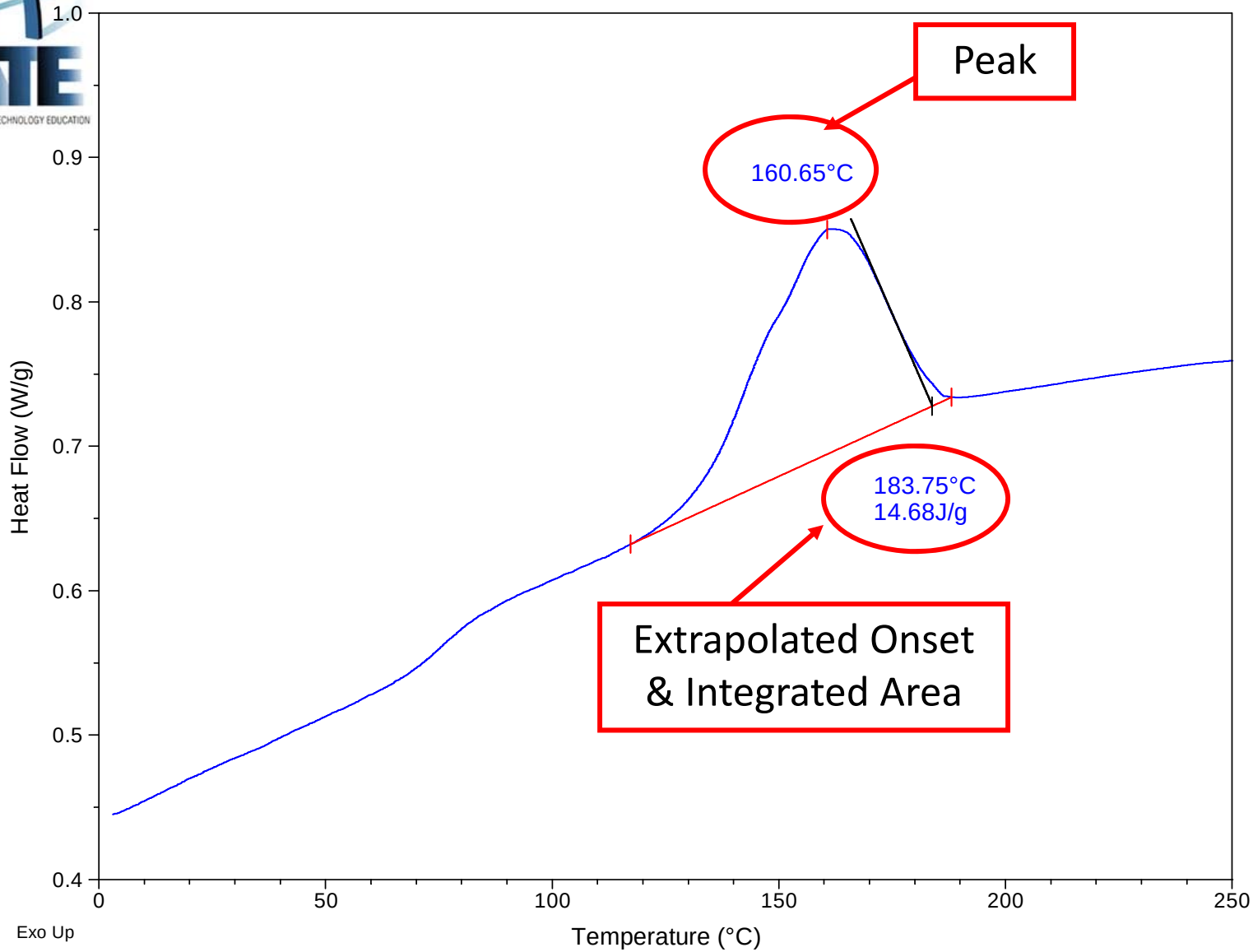
Observation of Crystallization

- Crystallization is a two step process:
  - Nucleation
  - Growth

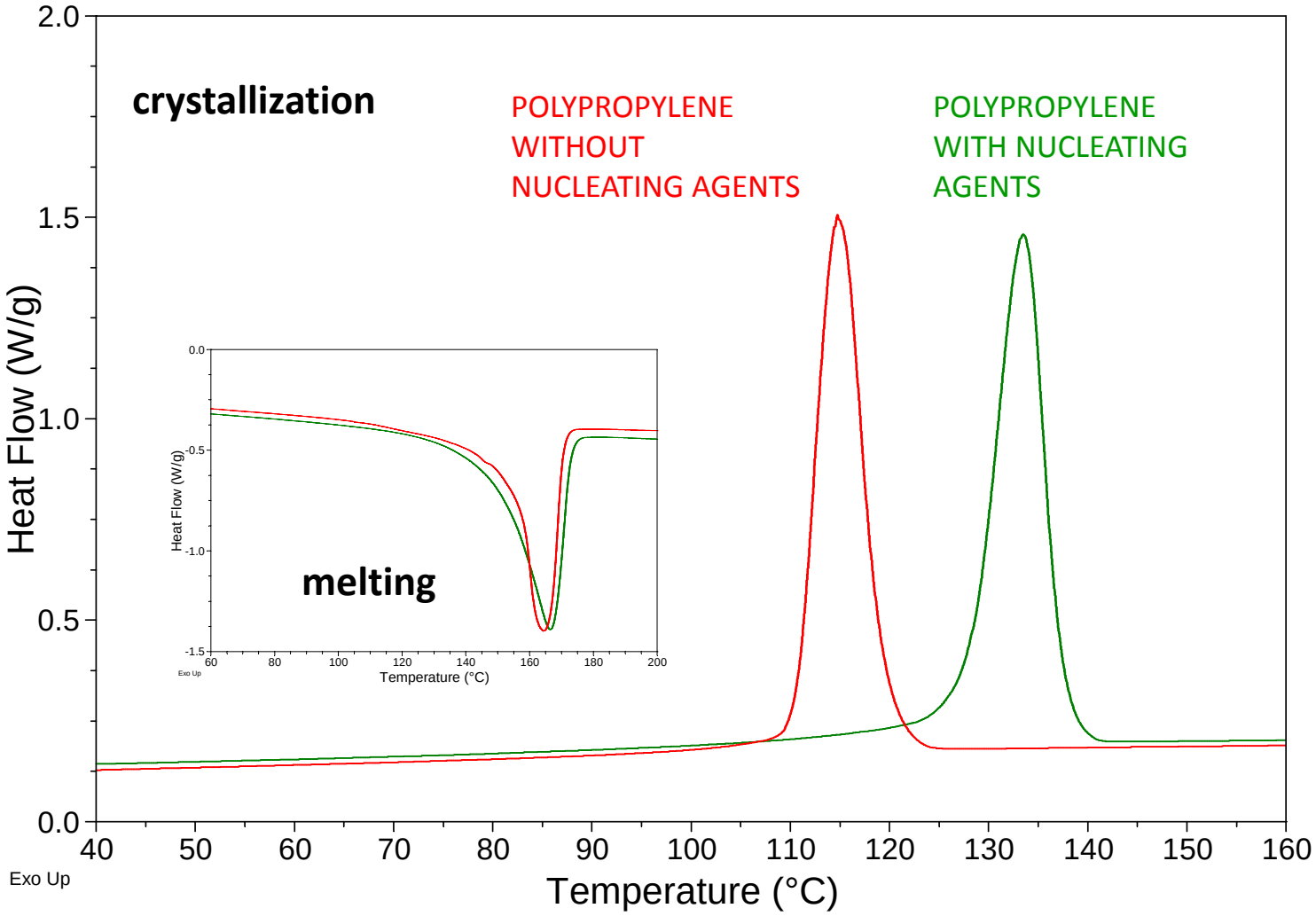
- The extrapolated onset is the nucleation temperature

- The peak maximum is the crystallization temperature

Observation of Crystallization



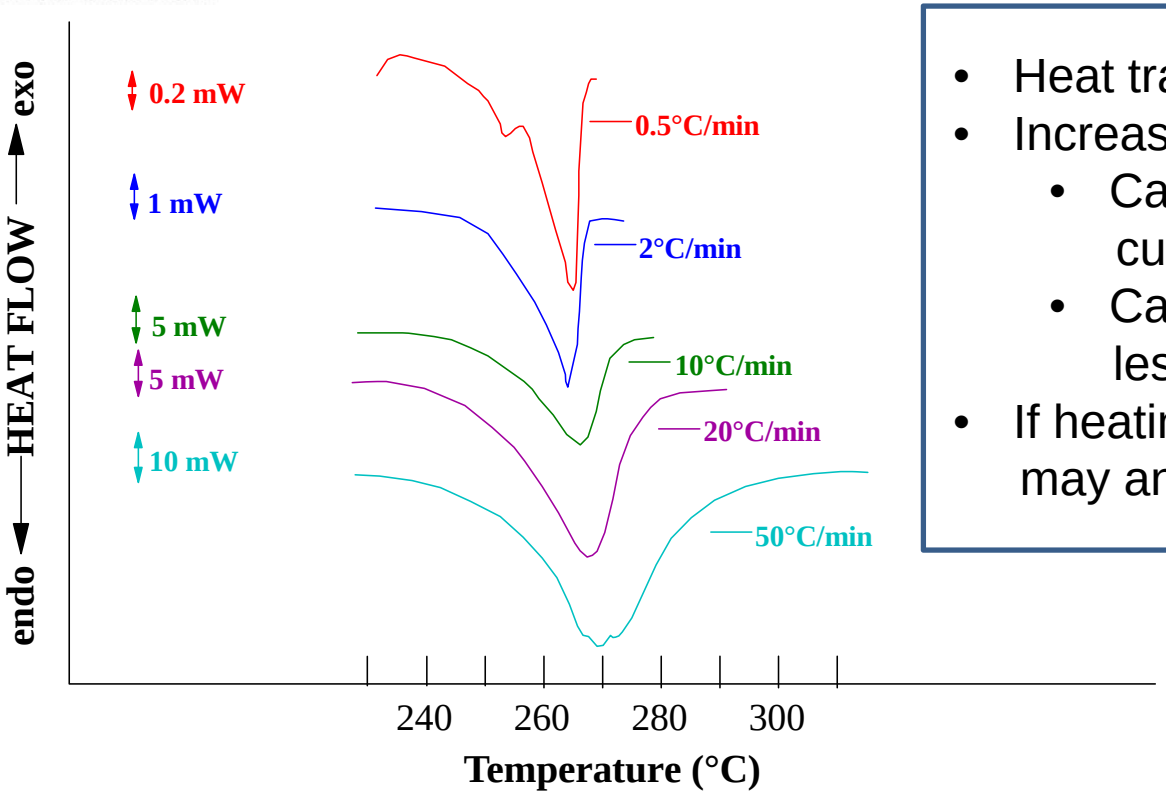
Effect of Nucleating Agents



DSC: Applications

- Effect of heating/cooling rate
- Crystallization kinetics
- Effects of polymer structure/composition
- Effects of thermal/mechanical processing

DSC: Effect of Heating Rate on Nylon 66 Melting Behavior



- Heat transfer rates; thermal gradients
- Increased heating rate causes:
  - Can change appearance of curve
  - Can cause T_m increase and be less accurate
- If heating rate is low, sample may anneal as it is tested.

Effect of Sample Mass

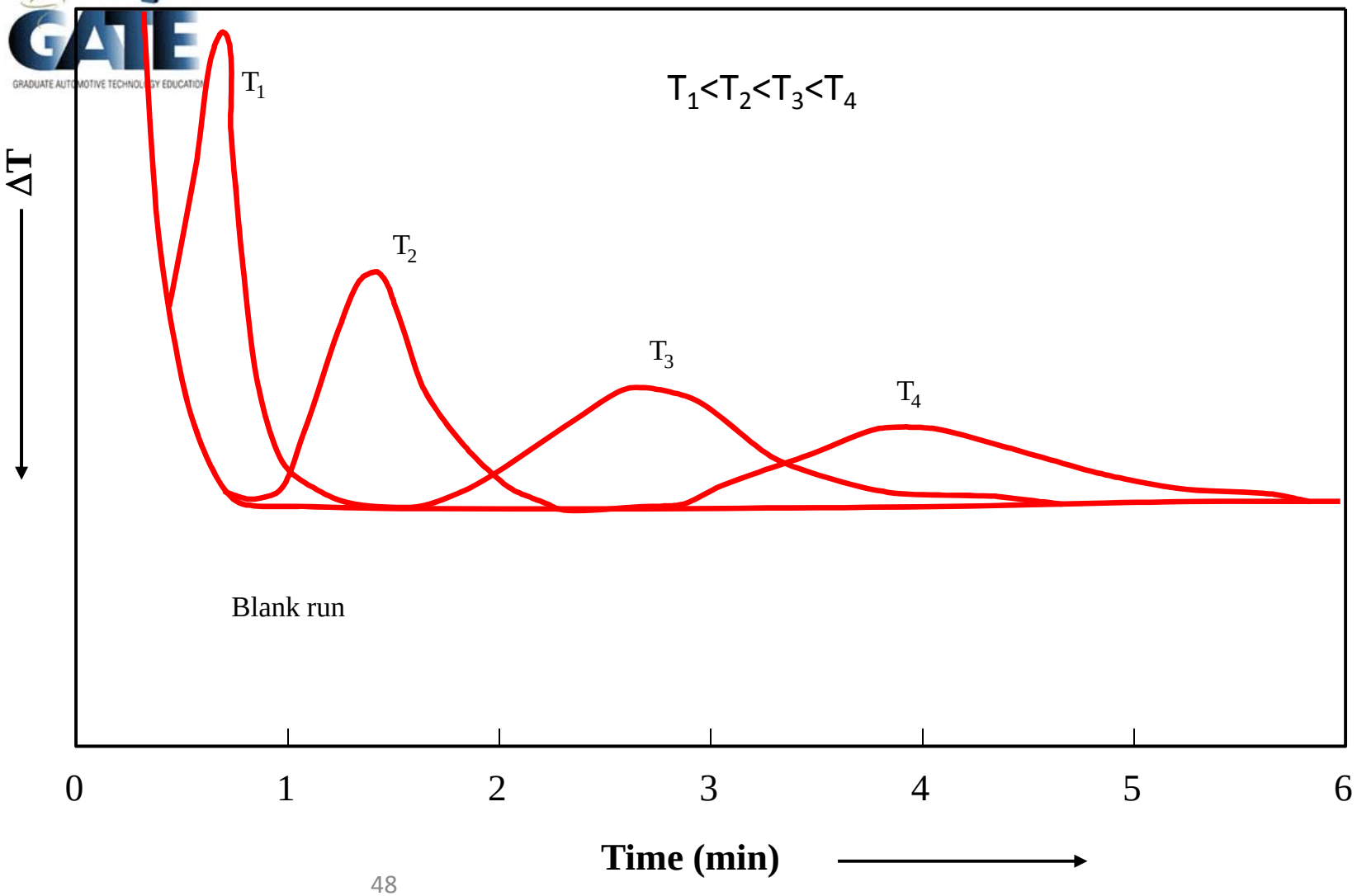
DSC: Crystallization Kinetics

- Two step process
  - Nucleation
  - Crystal growth
- Nucleation may be
  - Natural
  - Induced (using nucleation agents)
- Thermally influenced process
  - Natural nucleation
  - Crystal growth
  - Modeled by Isothermal Kinetics using the Autocatalytic Model

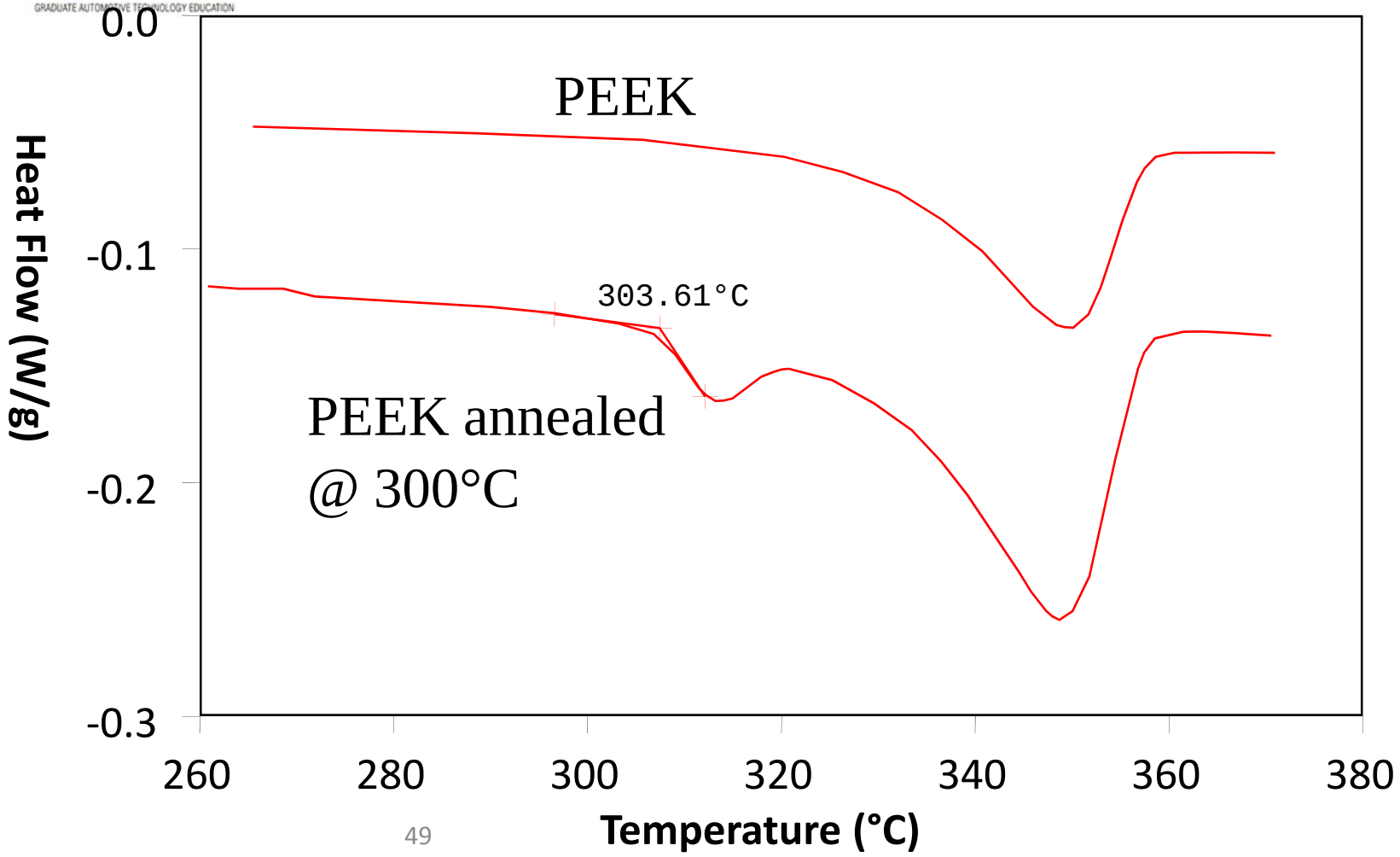
DSC:
Isothermal Crystallization Procedure

- Heat to 10°C above T_m
- Hold for 5 minutes to remove local order
- Cool rapidly to below melt onset (DO NOT OVERSHOOT TEMP)
- Hold isothermally
- Record time to crystallization peak (t)

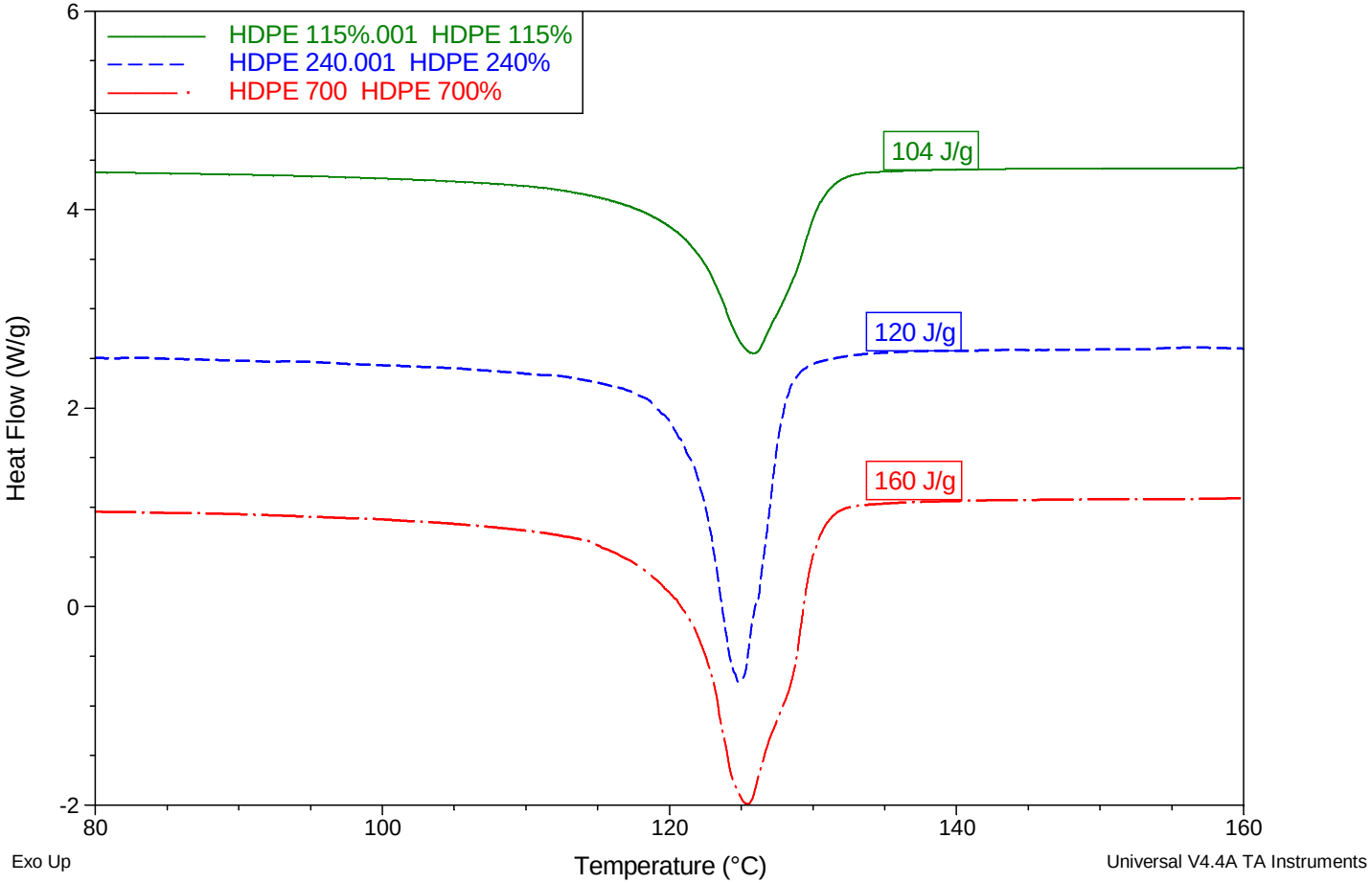
DSC: Isothermal Crystallization of Polyethylene Terephthalate



Effect of Annealing Poly(ethyletherketone) (PEEK) on Melting



Effect of Draw Ratio on Crystallinity for HDPE Fibers



Melting and Crystallization - Summary

- Melting and crystallization are phase changes from organized solid to amorphous phases and vice-versa.

- Melting is a one-step process while crystallization involves nucleation and crystal growth.

- The enthalpy of melting can be used to measure crystallinity or filler.

- Any process that makes it easier for molecules to be organized will raise the melting temperature.

The Glass Transition Temperature, T_g

- Observed in amorphous thermoplastics but not all semicrystalline thermoplastics
- Observed in thermosets
  - Exceptions:
    - Extremely high crosslink densities
    - Very rigid backbones

The Glass Transition

- The Glass Transition is 1.) the reversible change of the amorphous region of a polymer from, or to, a viscous or rubbery condition to, or from, a hard and relatively brittle one. 2.) onset of large scale, cooperative motion of the polymer chains.

- The Glass Transition Temperature is a temperature taken to represent the *temperature range* over which the glass transition takes place

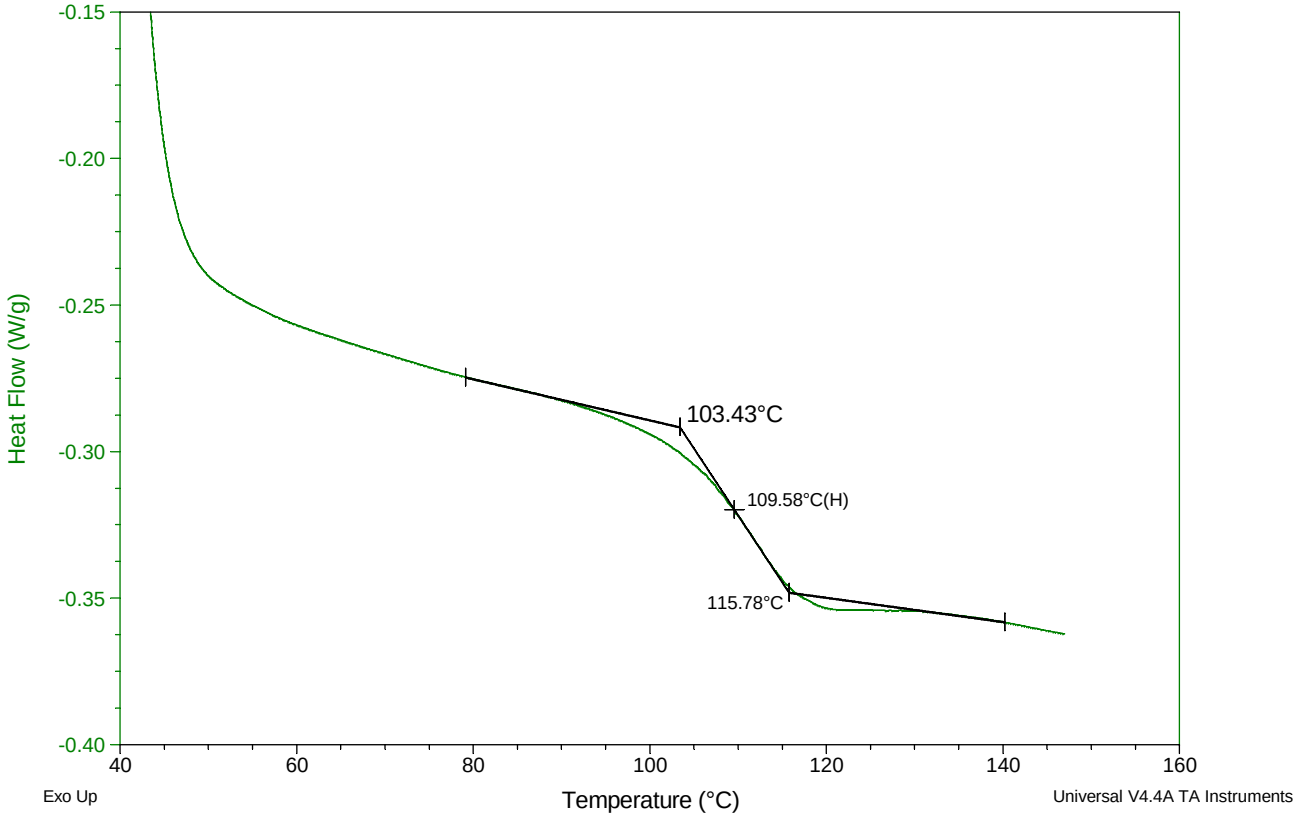
- Detected by DSC as an increase in Cp

Tg Measurement by DSC
Tg of PMMA

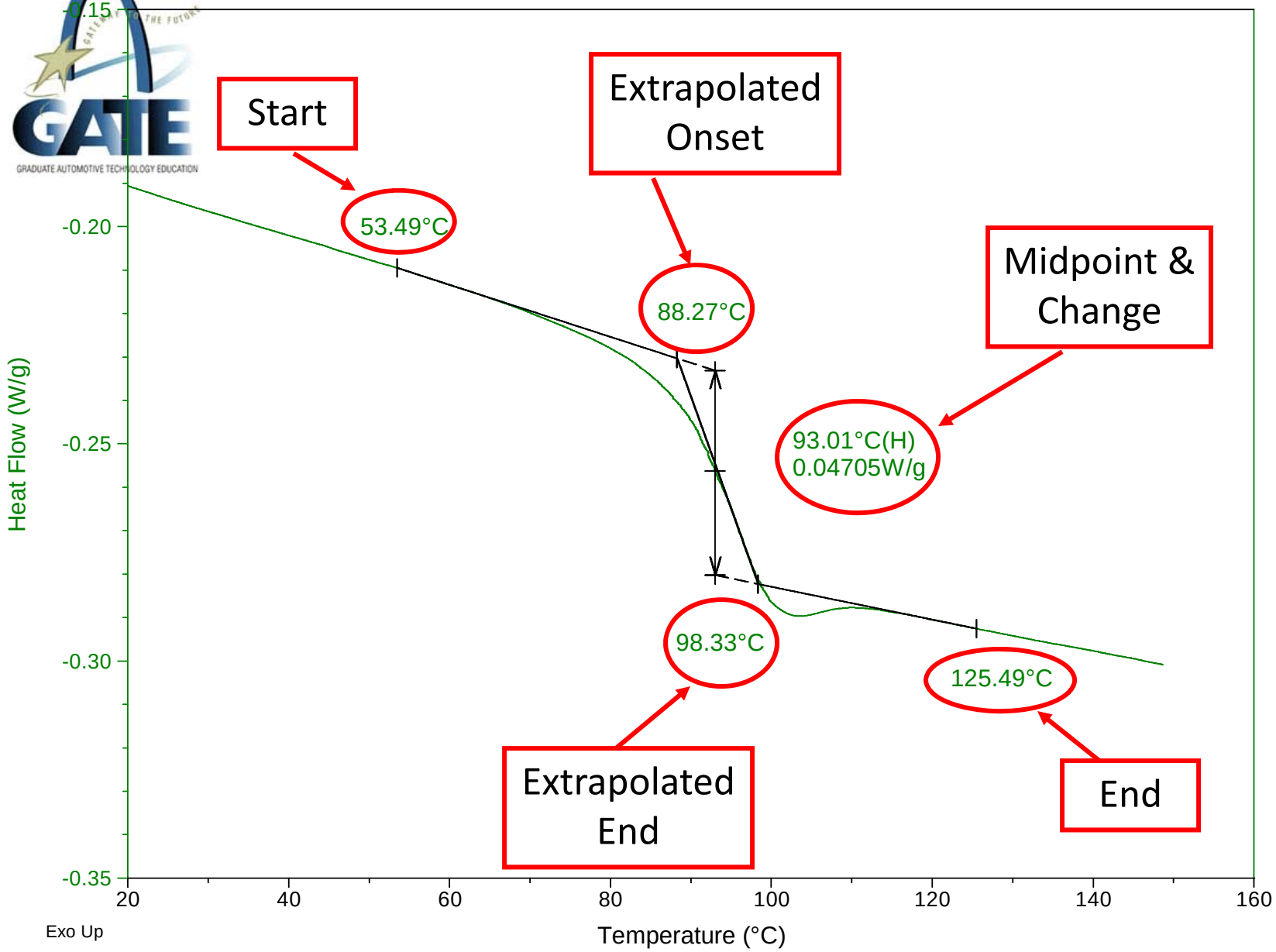
Sample: PMMA sample
Size: 10.6500 mg
Method: Ramp

DSC

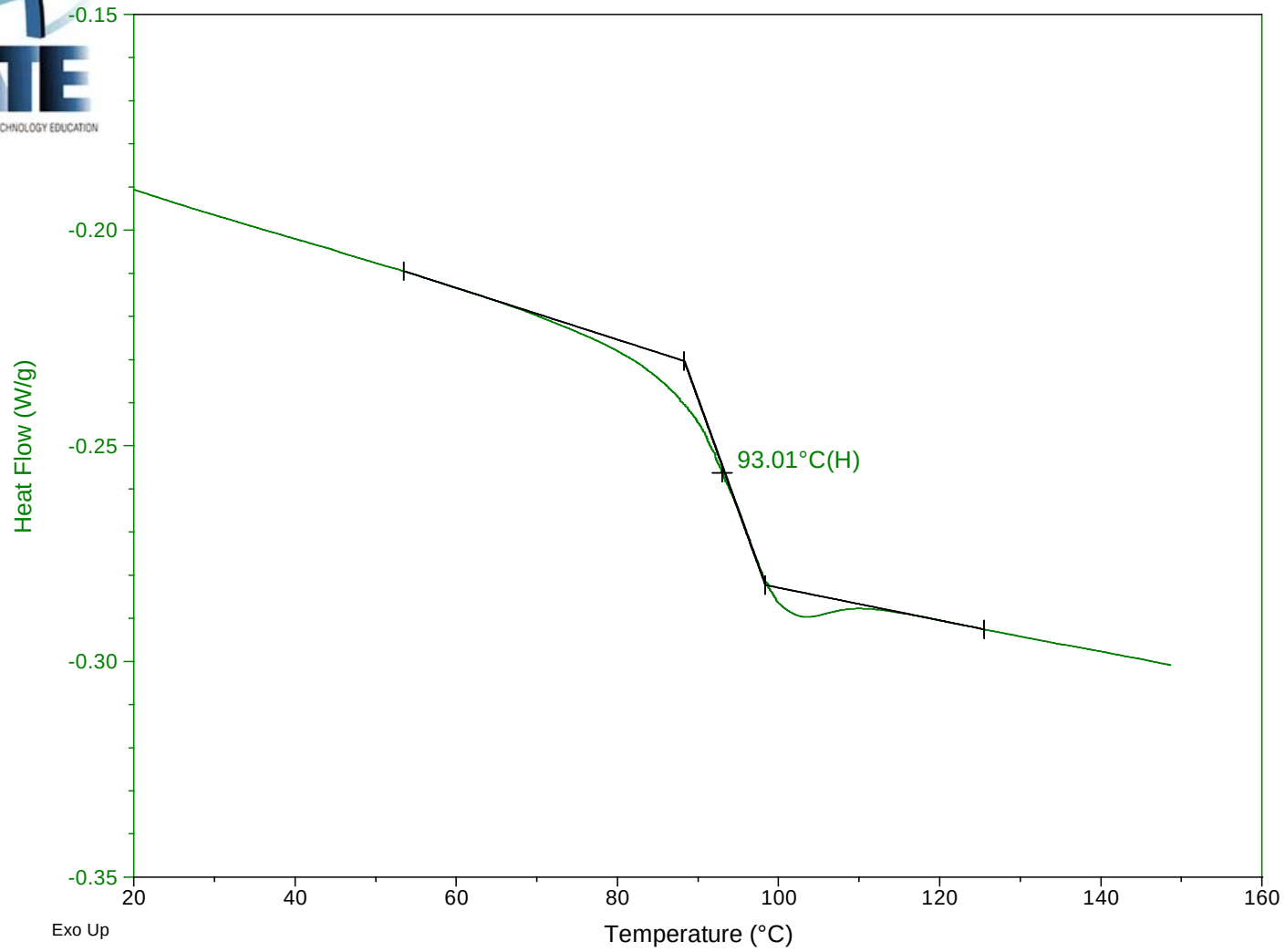
File: J:...\MSE 430-Fall 2010\Team 2\PMMA.001
Operator: AH
Run Date: 01-Oct-2010 12:51
Instrument: DSC Q100 V9.8 Build 296



Measurement of Tg

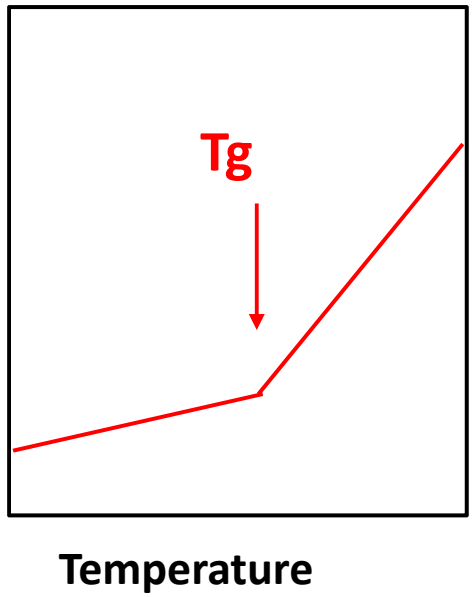


Measurement of Tg



Some Properties Affected at Tg

Physical property	Response on heating through Tg	
Specific Volume	Increases	V,
Modulus	Decreases	1/E,
Coefficient of thermal expansion	Increases	CTE
Specific Heat	Increases	Cp
Enthalpy	Increases	H &
Entropy	Increases	S



Tg is Affected by:

- Heating rate
- Molecular weight
- Chemical structure
- Crystallinity
- Crosslinking
- Plasticizer
- Physical Aging
- Blends/copolymers
- Composites

Anything that effects the mobility of the molecules, affects the Heat Capacity, which in turn affects the Tg

DSC: Heating Rate

Heating Rate (°C/min)	Sensitivity	Reproducibility
5	poor	very good
20*	good	good
40	very good	poor

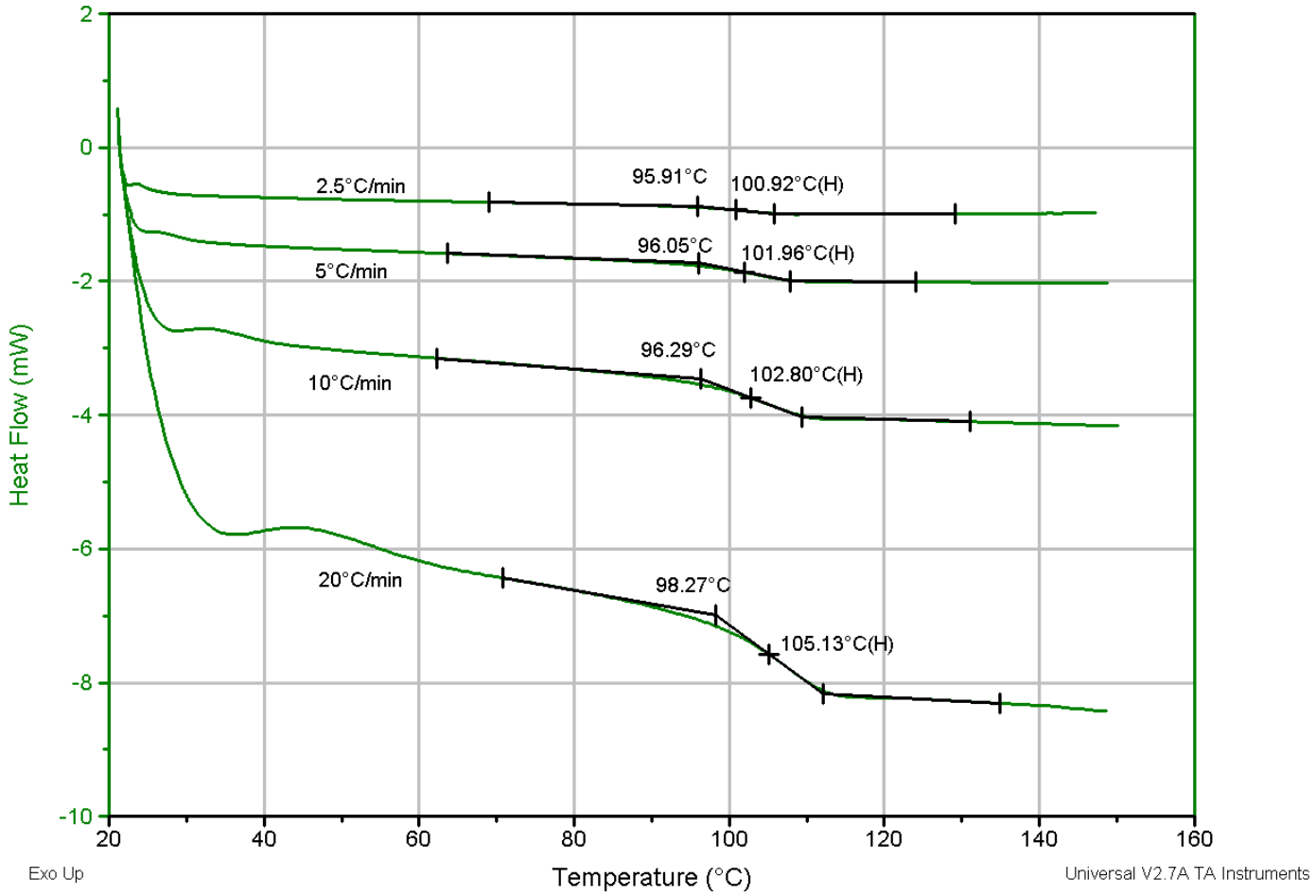
* Recommended heating rate for measuring Tg.

Effect of Heating Rate on the Tg

Sample: PMMA
Size: 10.0400 mg
Method: Heat@2.5,5,10,20
Comment: DSC@ 2.5,5,10&20°C/min

DSC

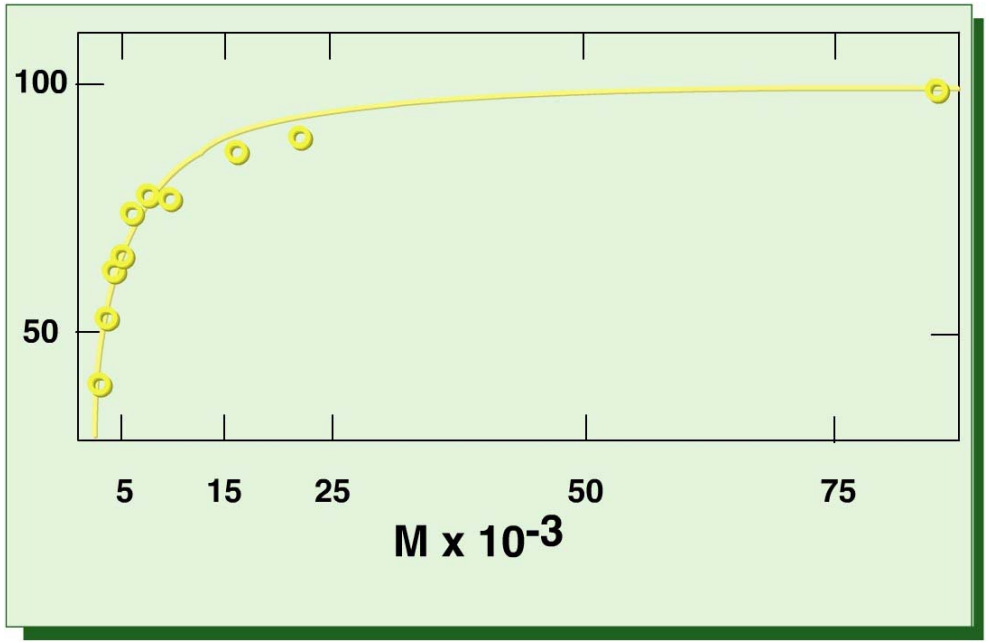
File: C:\TA\DATA\DSC\W-pmma.001
Operator: Thomas
Run Date: 20-Jan-00 09:58



Optimizing Measurement of Tg

- If Tg is hard to see:
  - Use larger sample weight
  - Use higher heating rate
  - Use MDSC®

Factors that Affect the Tg
Molecular Weight



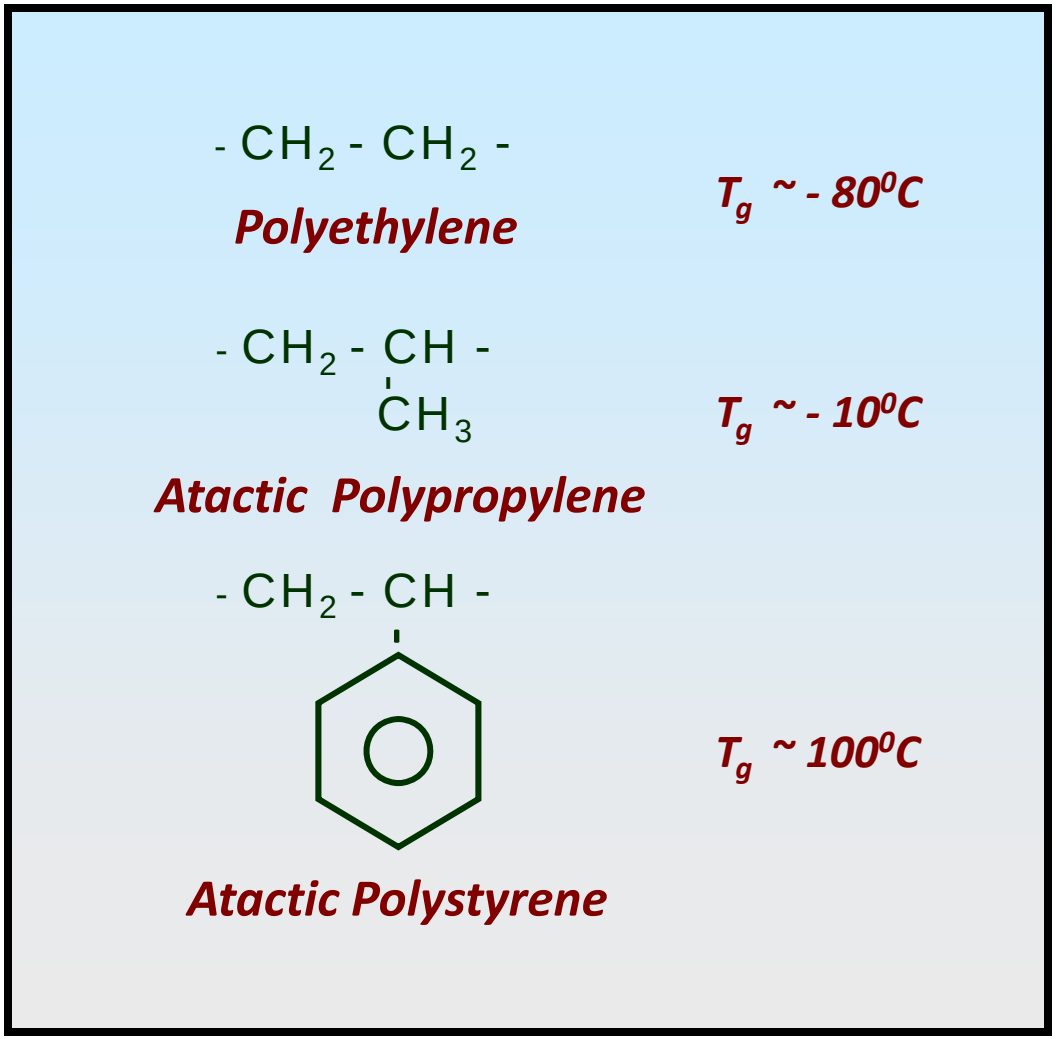
Redrawn from the data of T.G. Fox and P.J. Flory,
J.Appl. Phys., 1950, 21, 581

Effect of Molecular Weight on the Tg (for Styrene Oligomers/Polymers)

Molecular Weight	Tg
104	-138°C
524	- 40°C
2,210	40°C
3,100	62°C
15,100	86°C
36,000	94°C
170,000	100°C

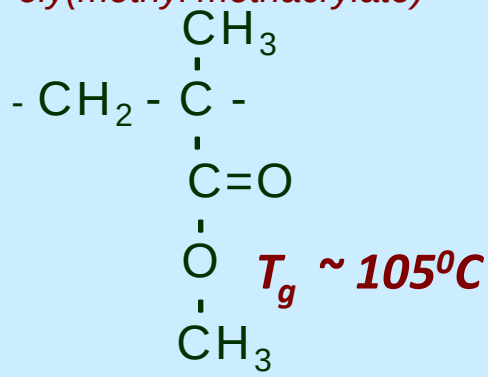
Turi, pg 249 **Kumler, 1977**

Bulky Substituents

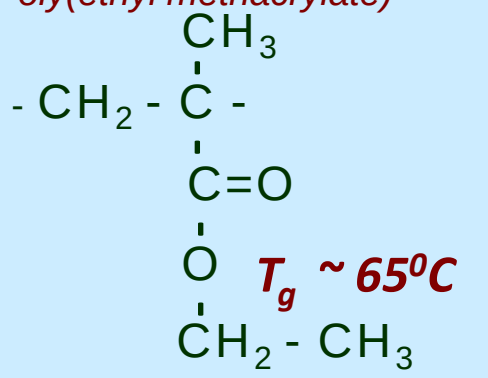


Flexible Substituents

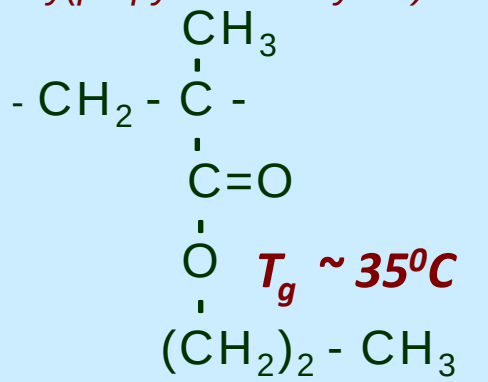
Poly(methyl methacrylate)



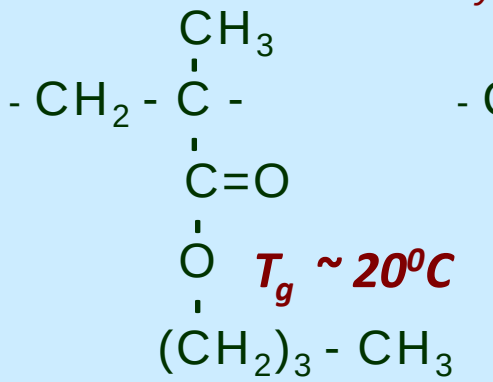
Poly(ethyl methacrylate)



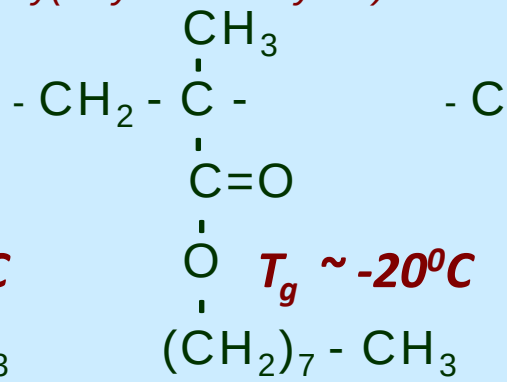
Poly(propyl methacrylate)



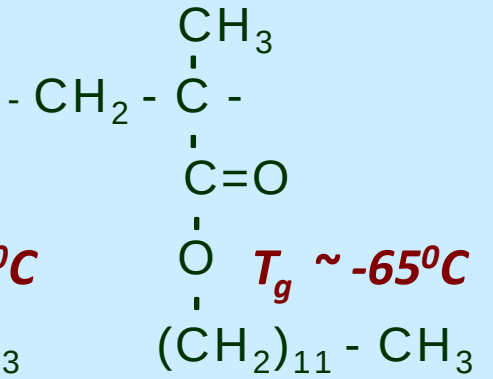
Poly(butyl methacrylate)



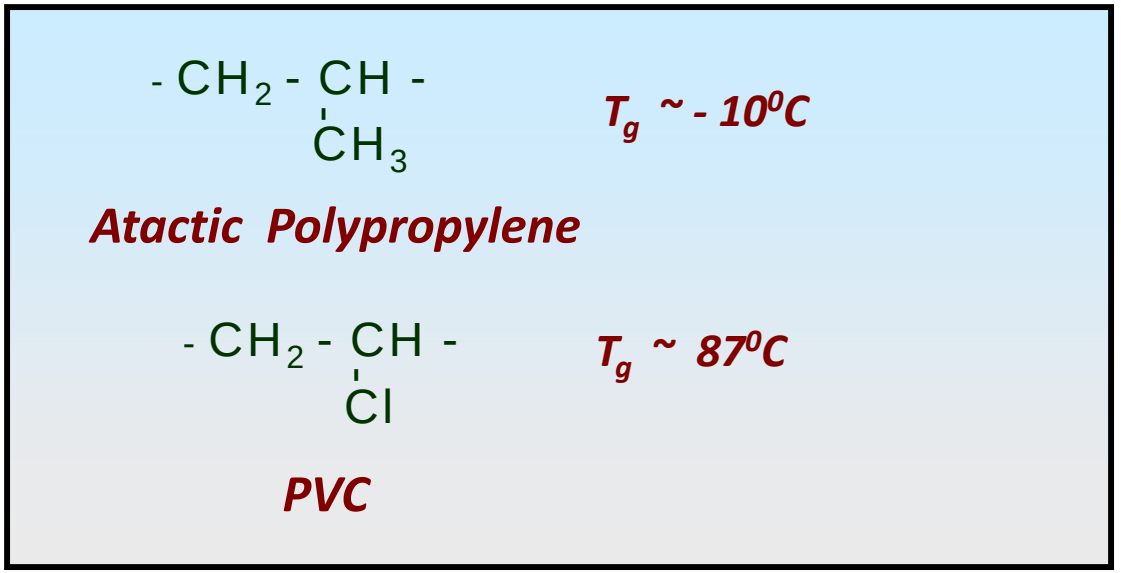
Poly(octyl methacrylate)



Poly(dodecyl methacrylate)



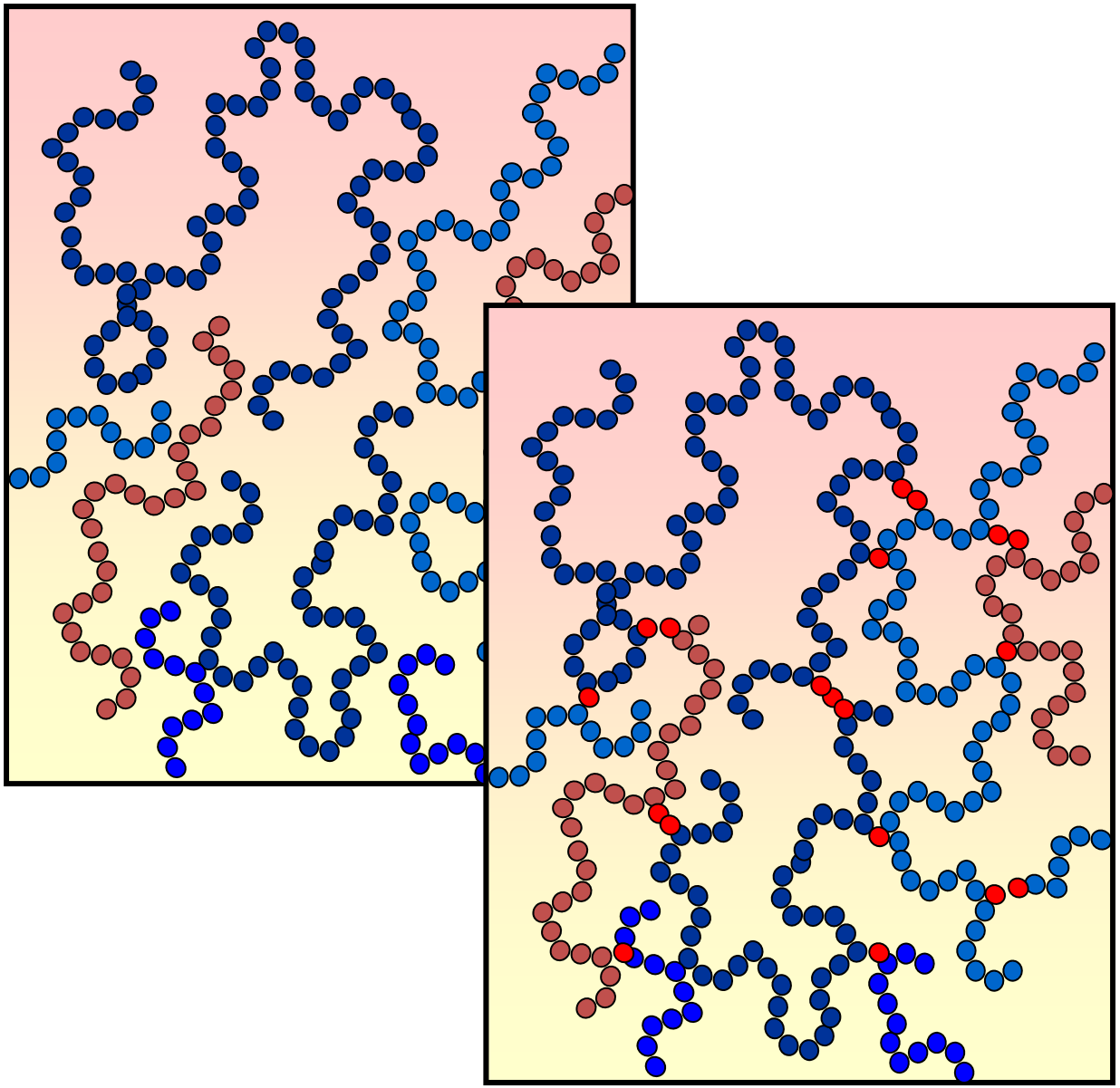
The Effect of Intermolecular Interactions



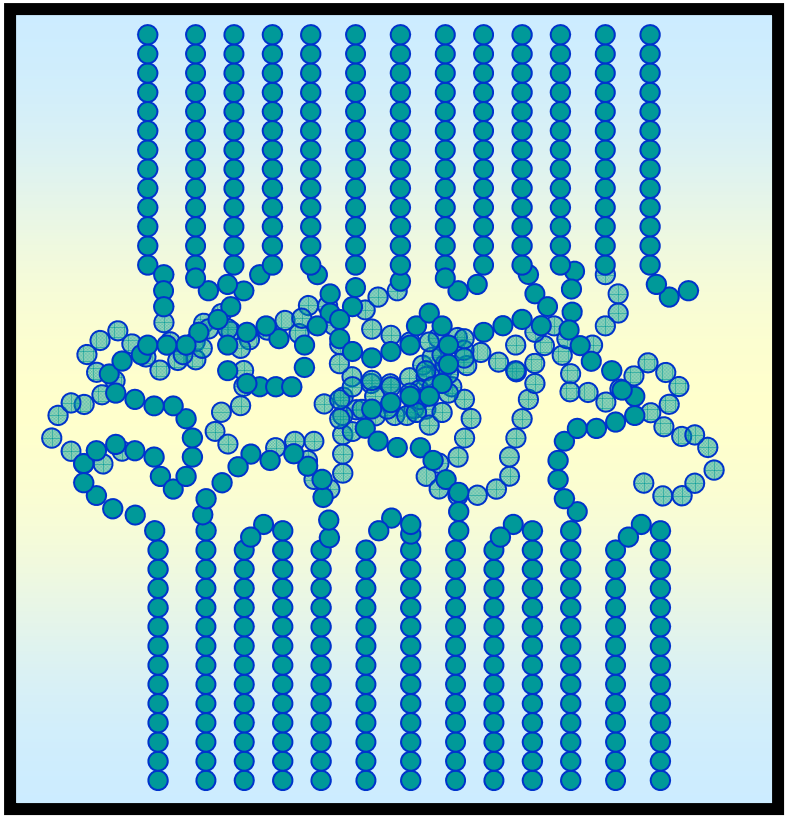
Effect of Hydrogen Bonding on the Tg

Polyamide	Tg (°C)	HBonding
Nylon 12,2	59	Least
Nylon 10,2	56	
Nylon 8,2	93	
Nylon 6,2	159	Most

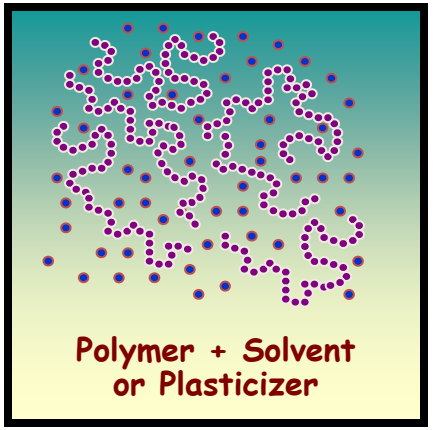
The Effect of Cross - Linking

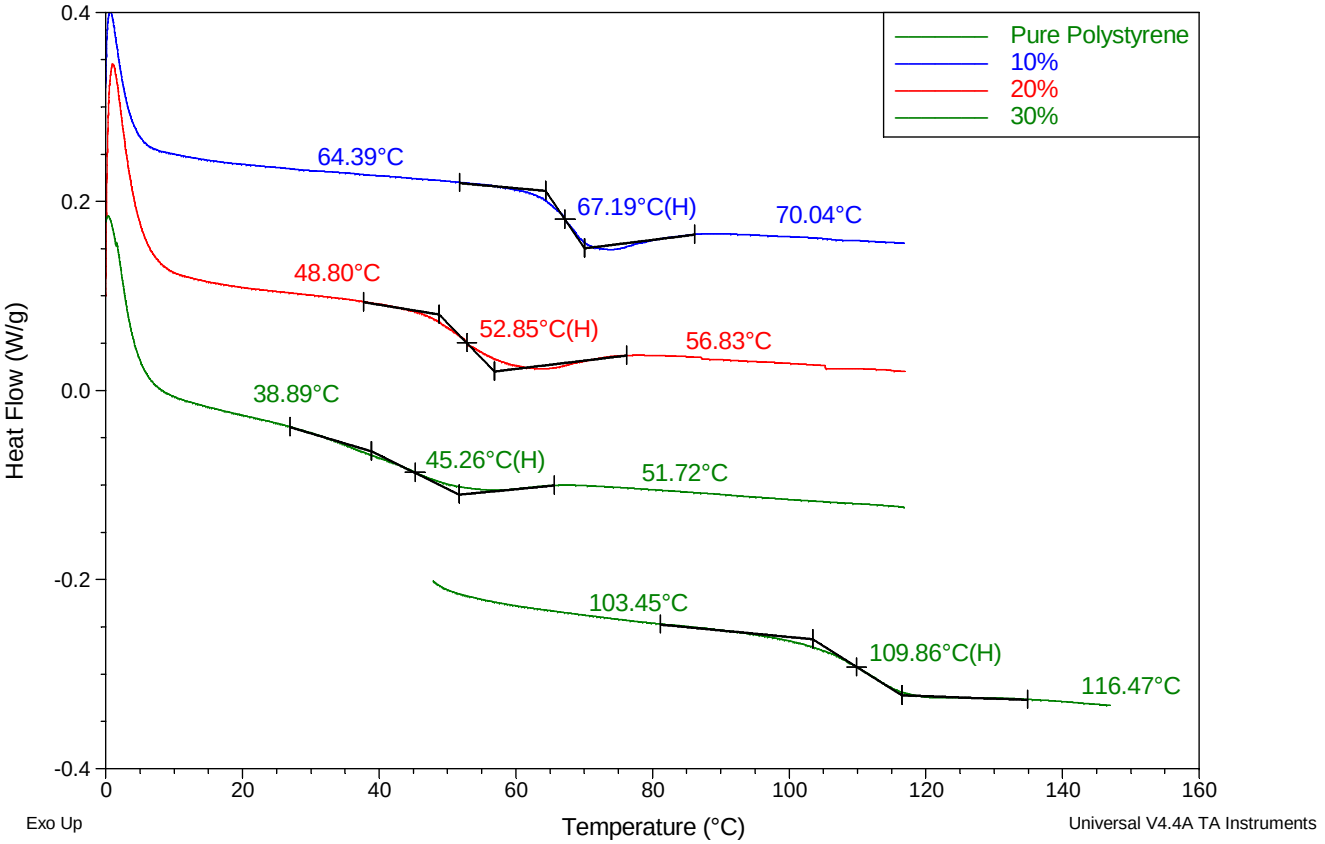


The Effect of Crystallization

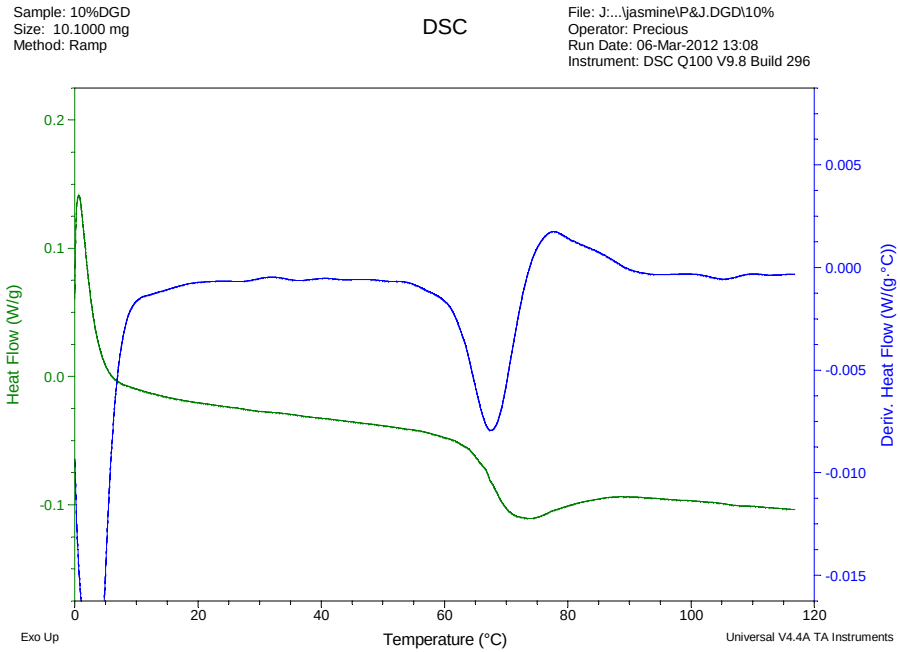


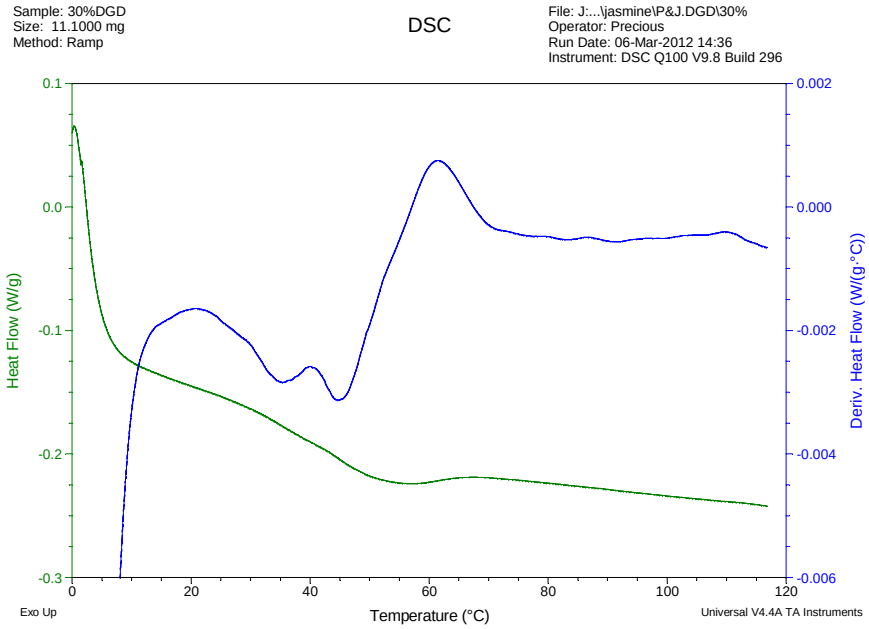
The Effect of Plasticizer on Tg





The Effect of Plasticizer on Tg



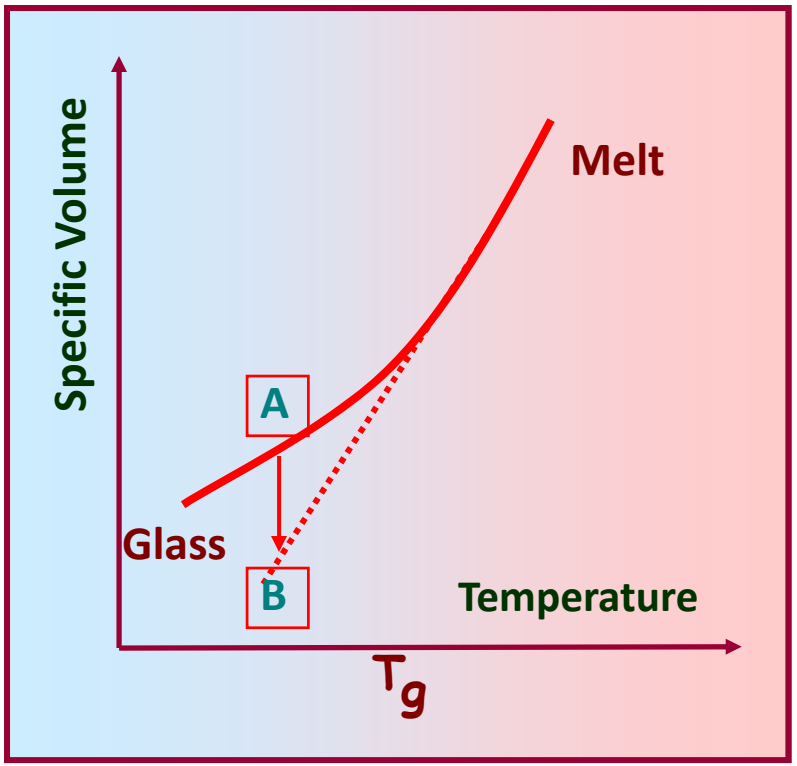


Effect of Plasticizer on the Tg

for Polyamides

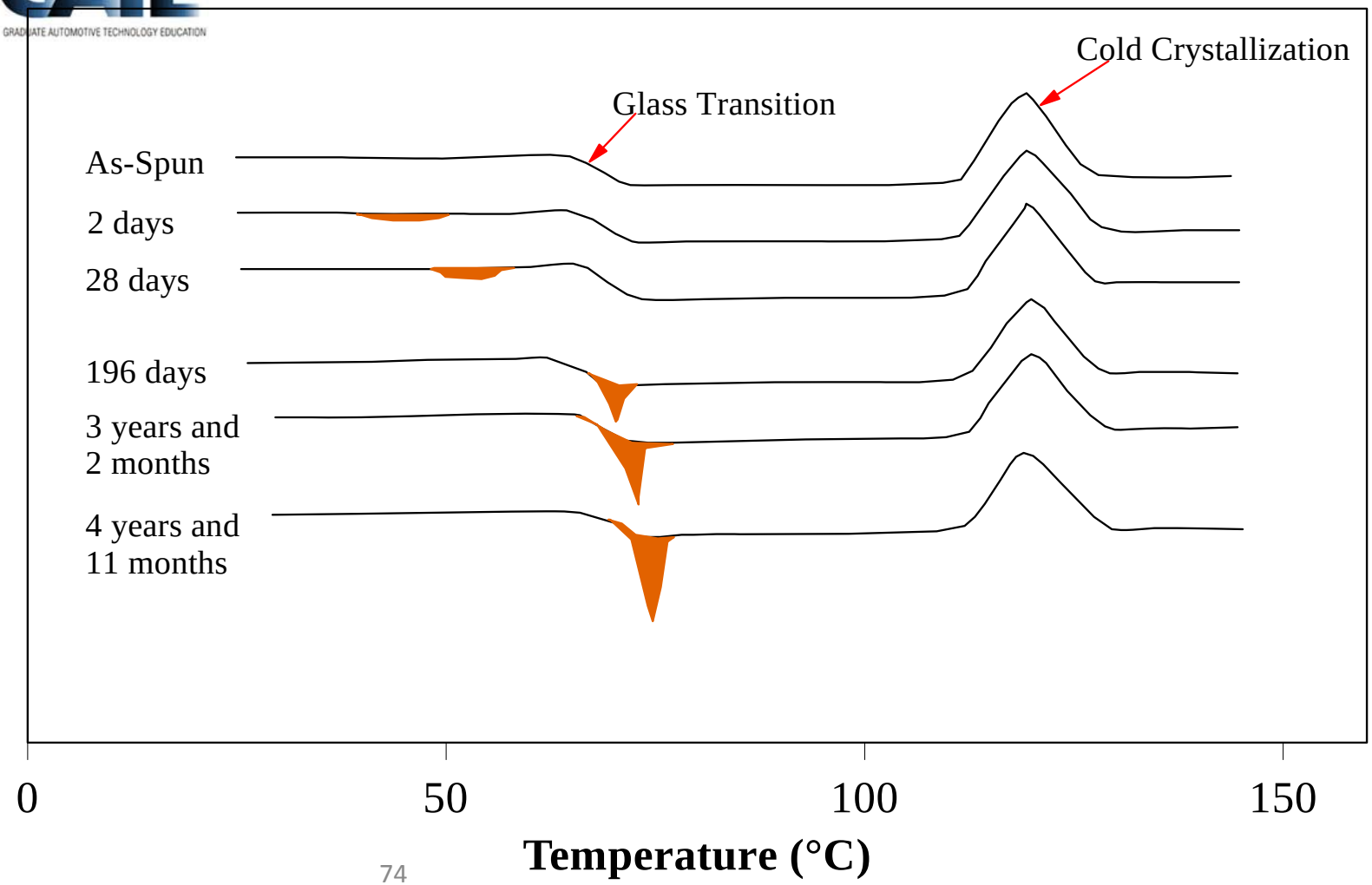
Water Content (%)	Tg (°C)
0.35	94
0.70	84
1.17	71
1.99	56
2.70	45
4.48	40
6.61	23
10.33	6

Physical Aging--Relaxation and Recovery

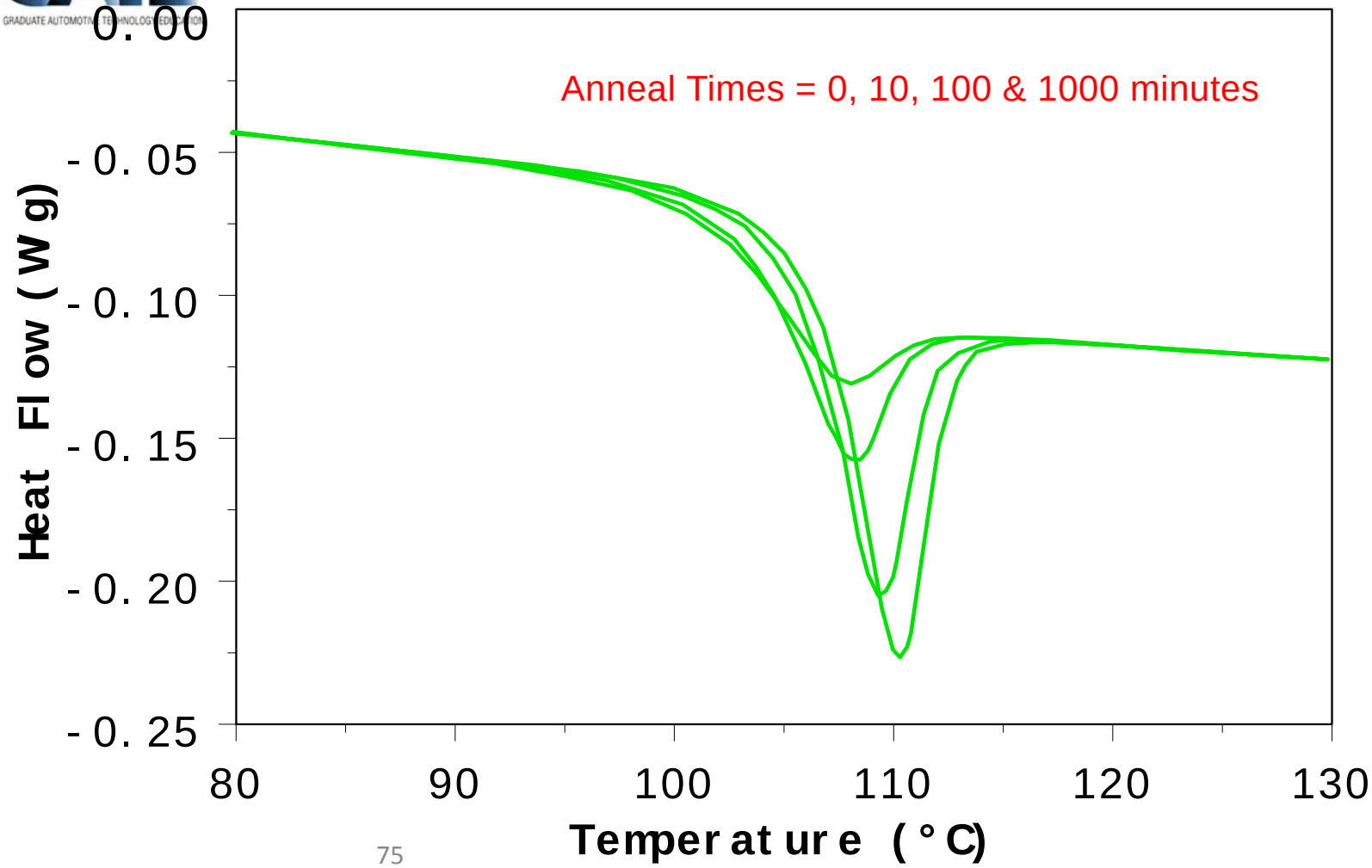


- Thermally reversible
- Involves changes below Tg
- Associated with non-equilibrium from melt state
- Affects the amorphous phase only
- Volume and enthalpy change with time
- The change in enthalpy with time is called relaxation or physical aging

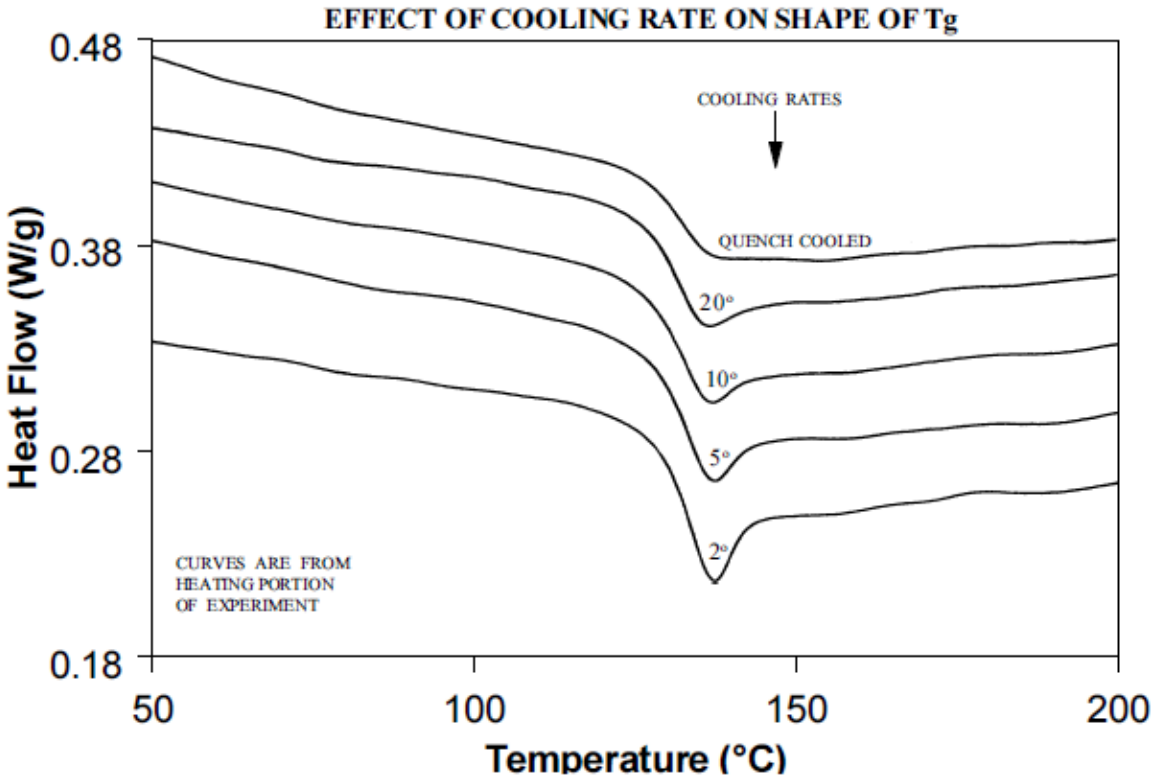
Effect of Aging on the Glass Transition [M. Todoki, Polymer Data Handbook]



DSC: Effect of Aging Time at 95°C on Shape of Polystyrene Tg



Physical Aging

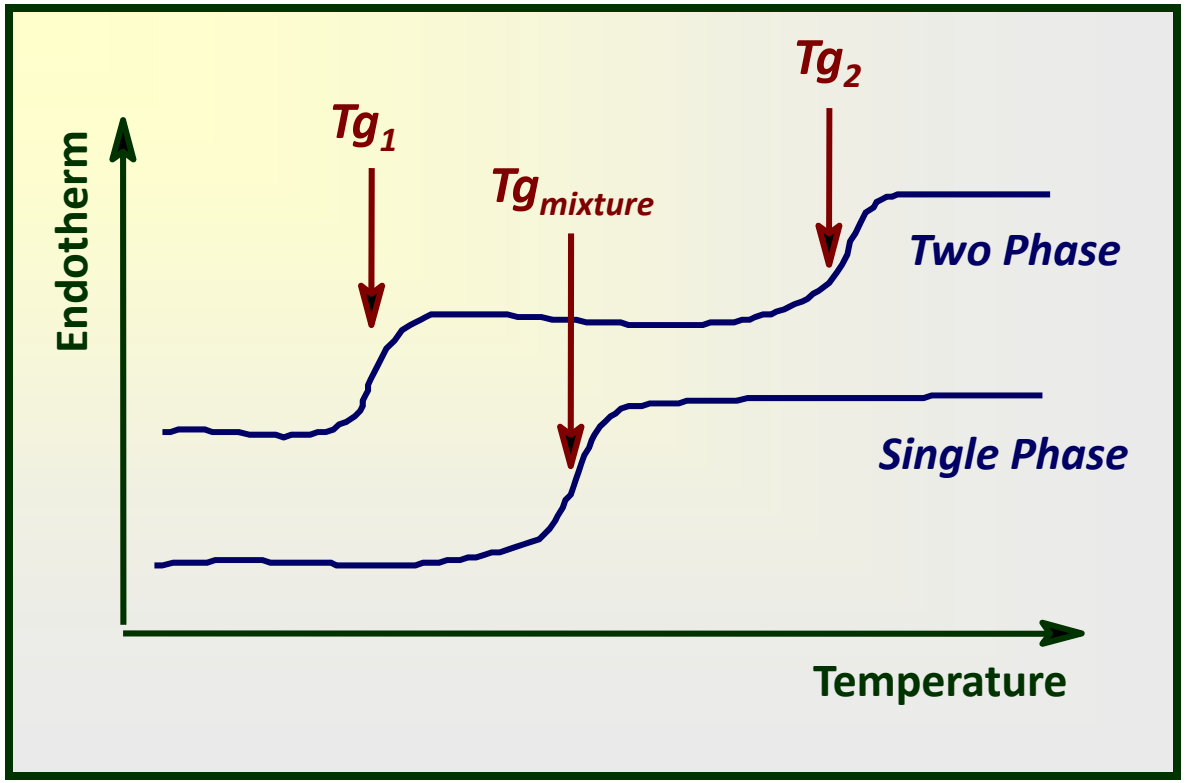


Heating the material above the Tg then cooling it through the Tg at a rate equal to or greater than the final heating rate reduces the relaxation effect.

Physical Aging Effect on Mechanical Properties

- General loss of ductility
- Modulus increases
- Yield strength increases
- Impact strength, elongation, fracture energy decrease

Effect of Miscible and Immiscible Blends on Tg

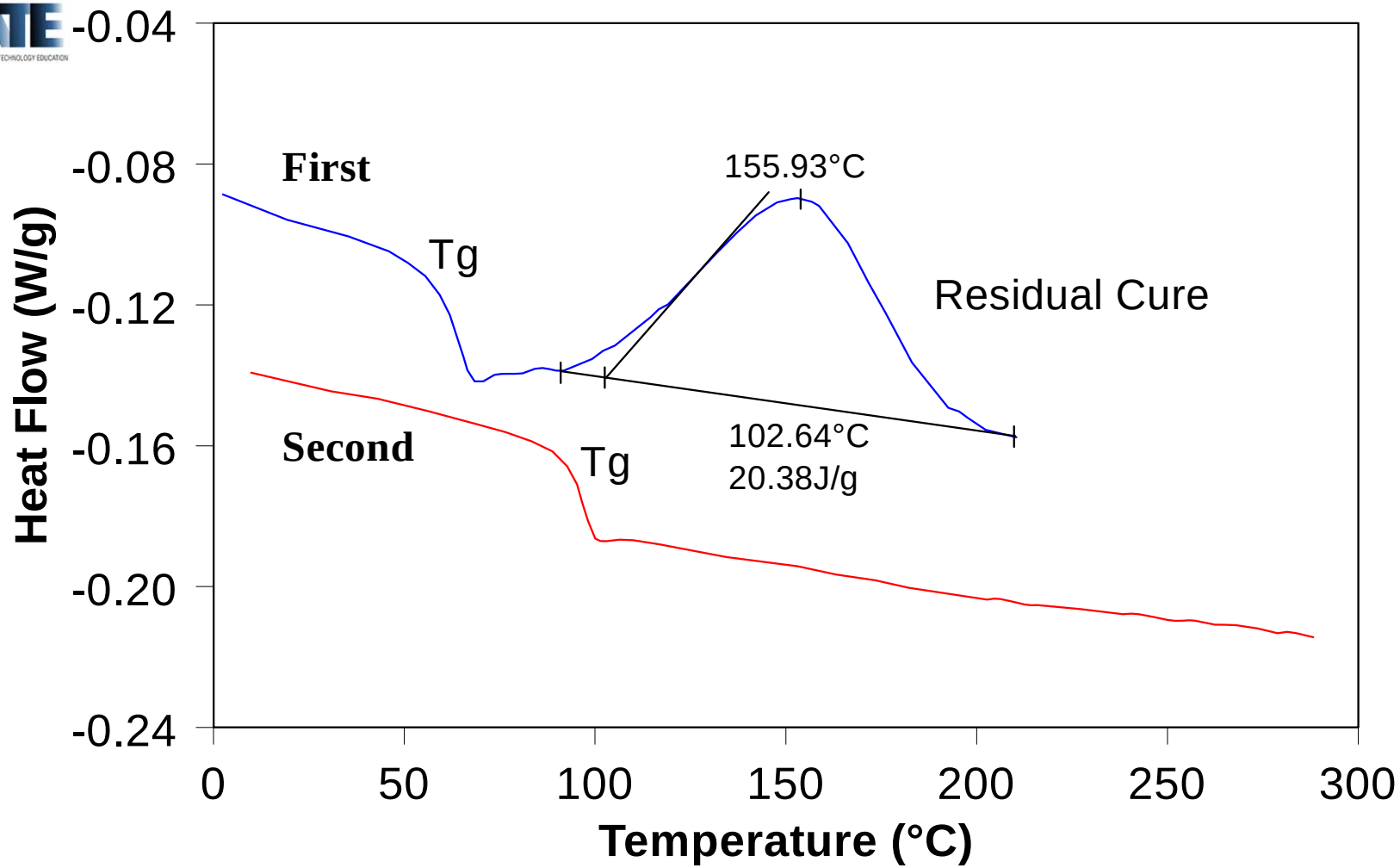


Curing of Thermosets
Crosslinking

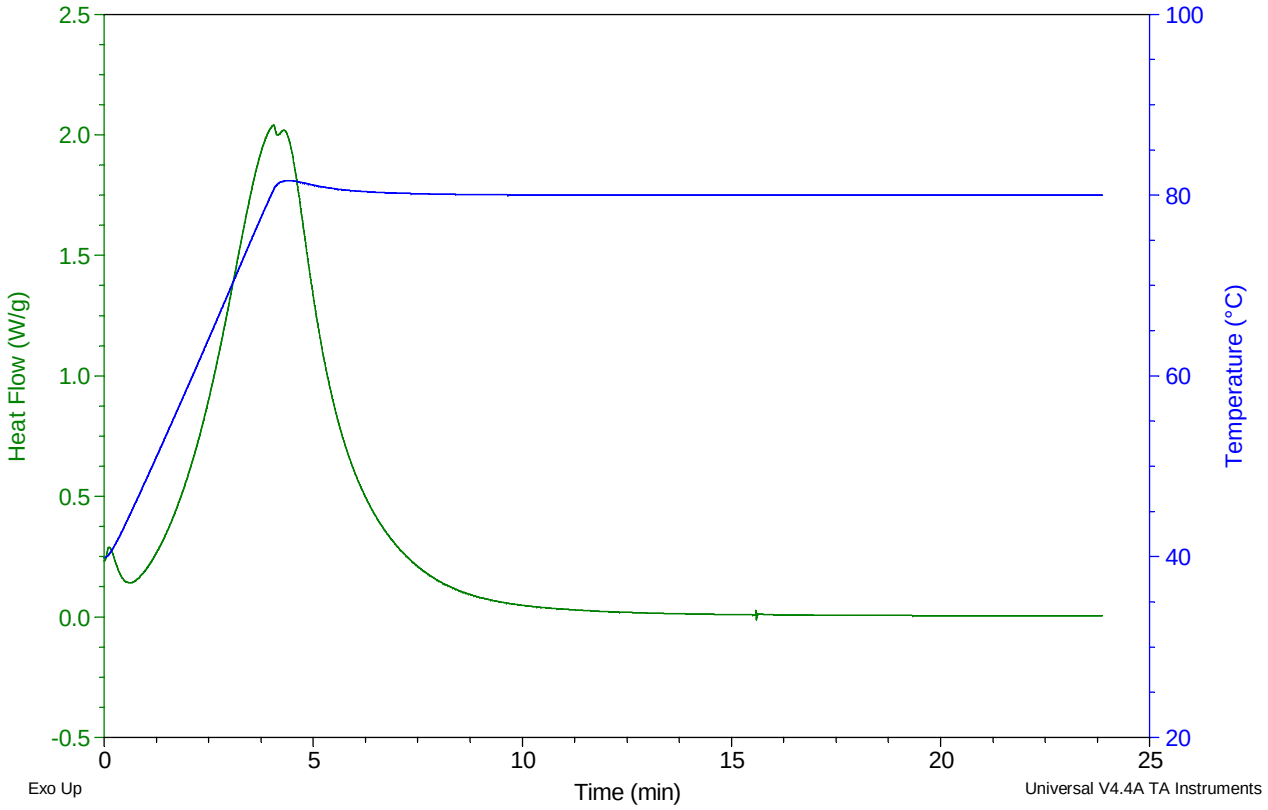
Thermosetting Polymers

- Curing reaction can be followed by monitoring a wide variety of physical properties including:
  - Heat of reaction
  - Heat capacity
  - Viscosity
  - Modulus
  - Others

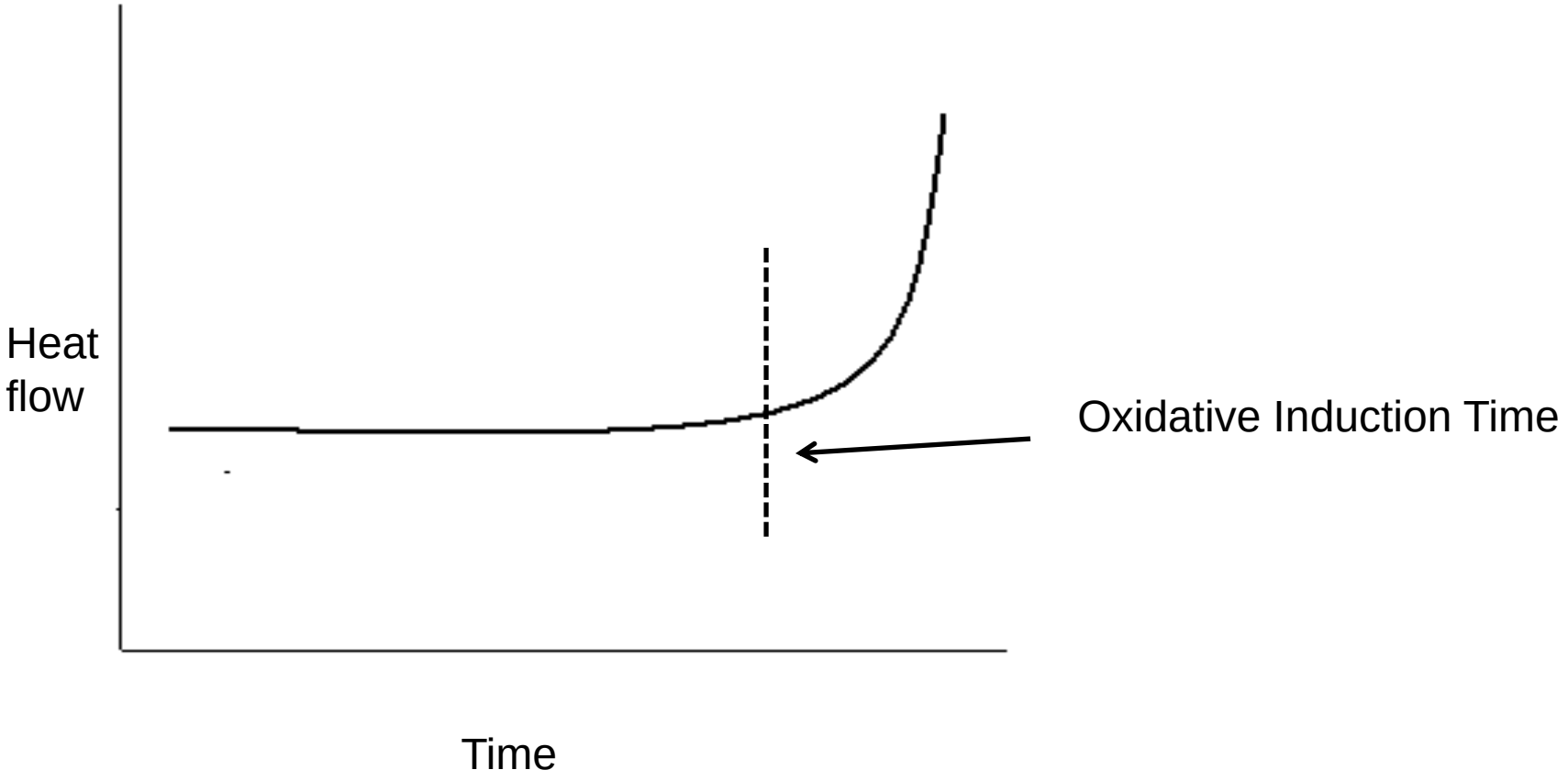
DSC Thermoset Cure: First and Second Heat



Isothermal Cure of Epoxy Resin



Oxidative Induction Time



MDSC Theory

Heat Flow Equation

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

$\frac{dH}{dt}$ = Total Heat Flow measured by the calorimeter

Cp = Specific Heat Capacity

$\frac{dT}{dt}$ = Underlying Heating Rate

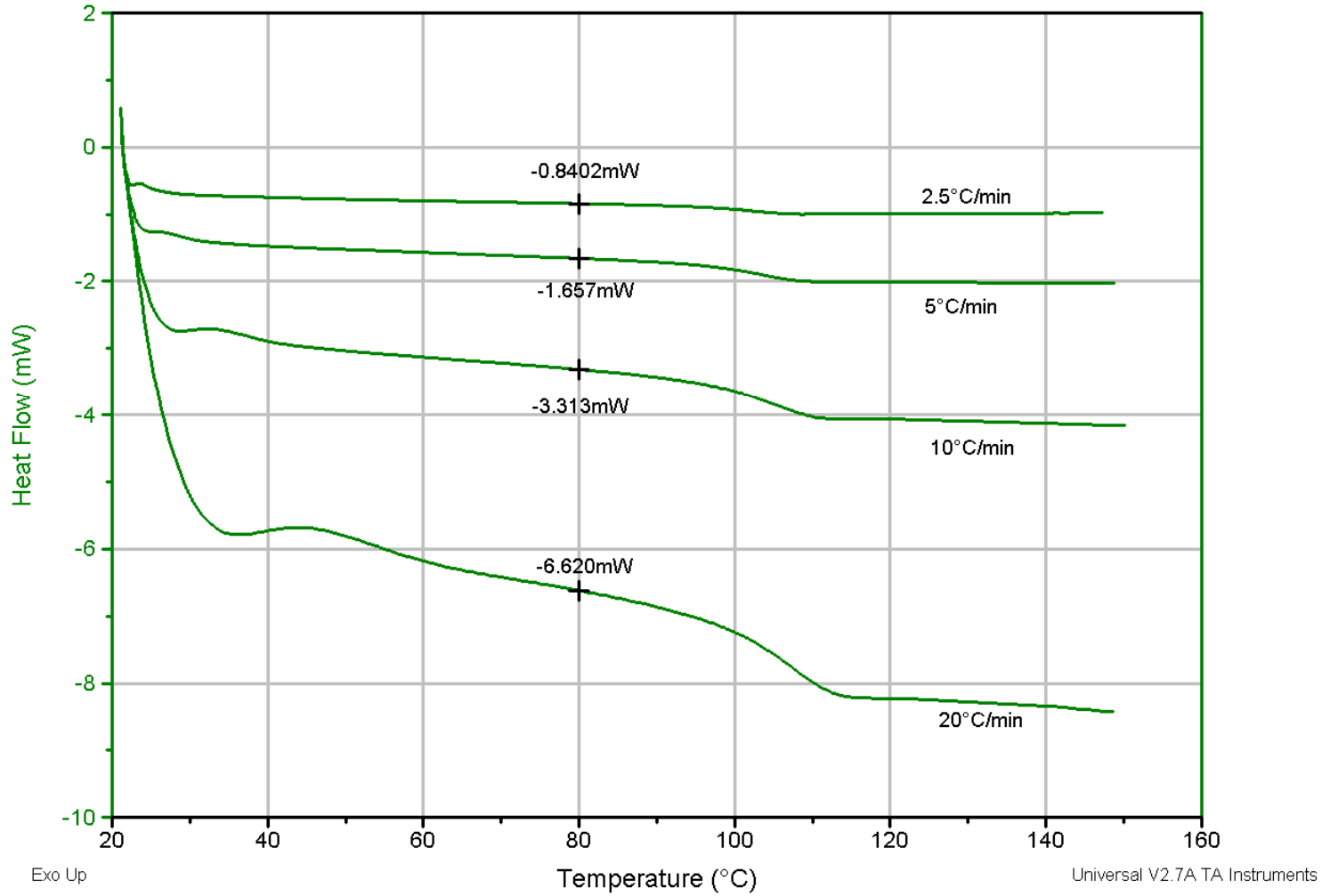
$f(T,t)$ = kinetic response of sample

Heat Flow Due to Heat Capacity

Sample: PMMA
Size: 10.0400 mg
Method: Heat@2.5,5,10,20
Comment: DSC@ 2.5,5,10&20°C/min

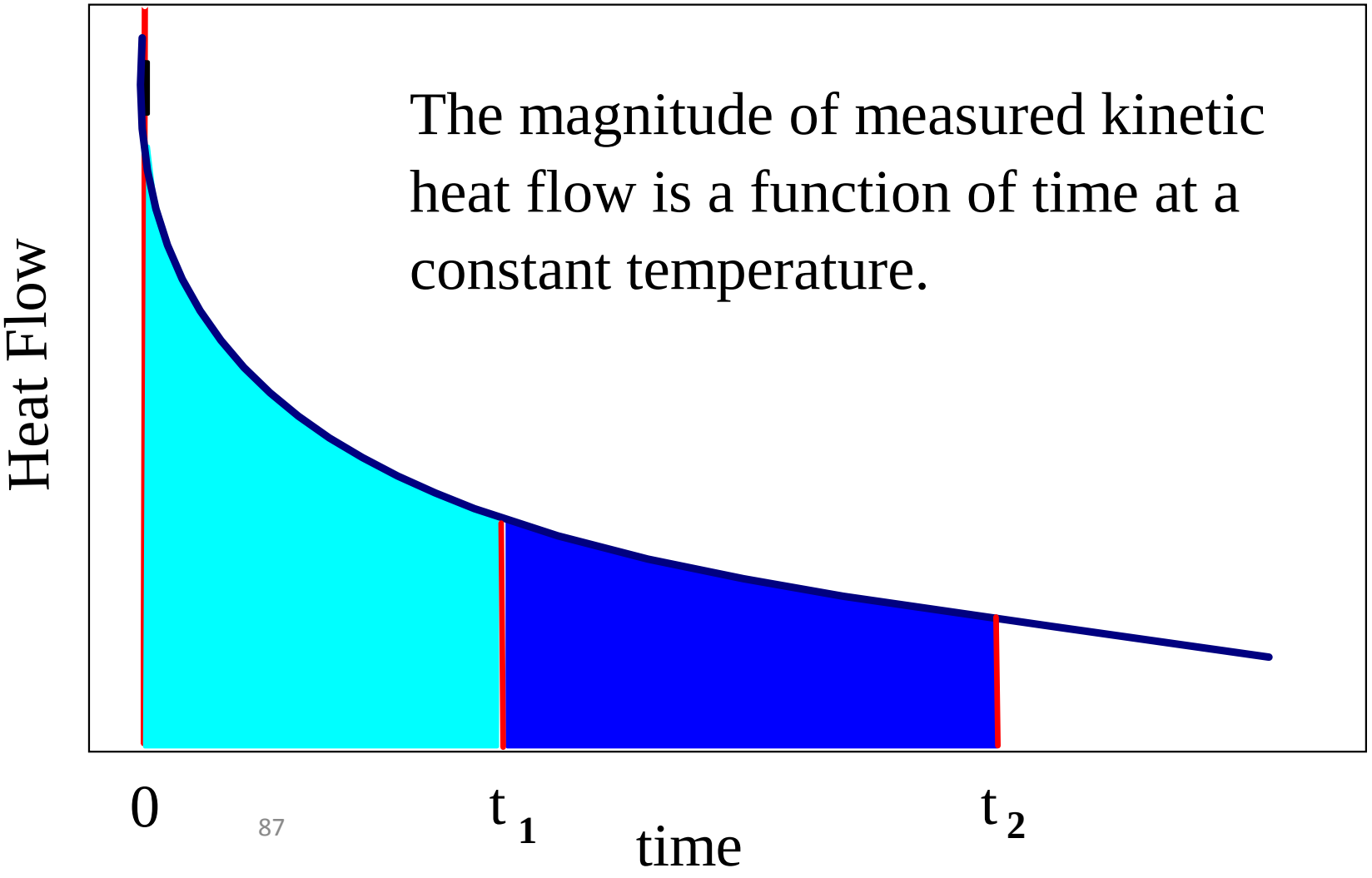
DSC

File: C:\TA\DATA\DSC\W-pmma.001
Operator: Thomas
Run Date: 20-Jan-00 09:58

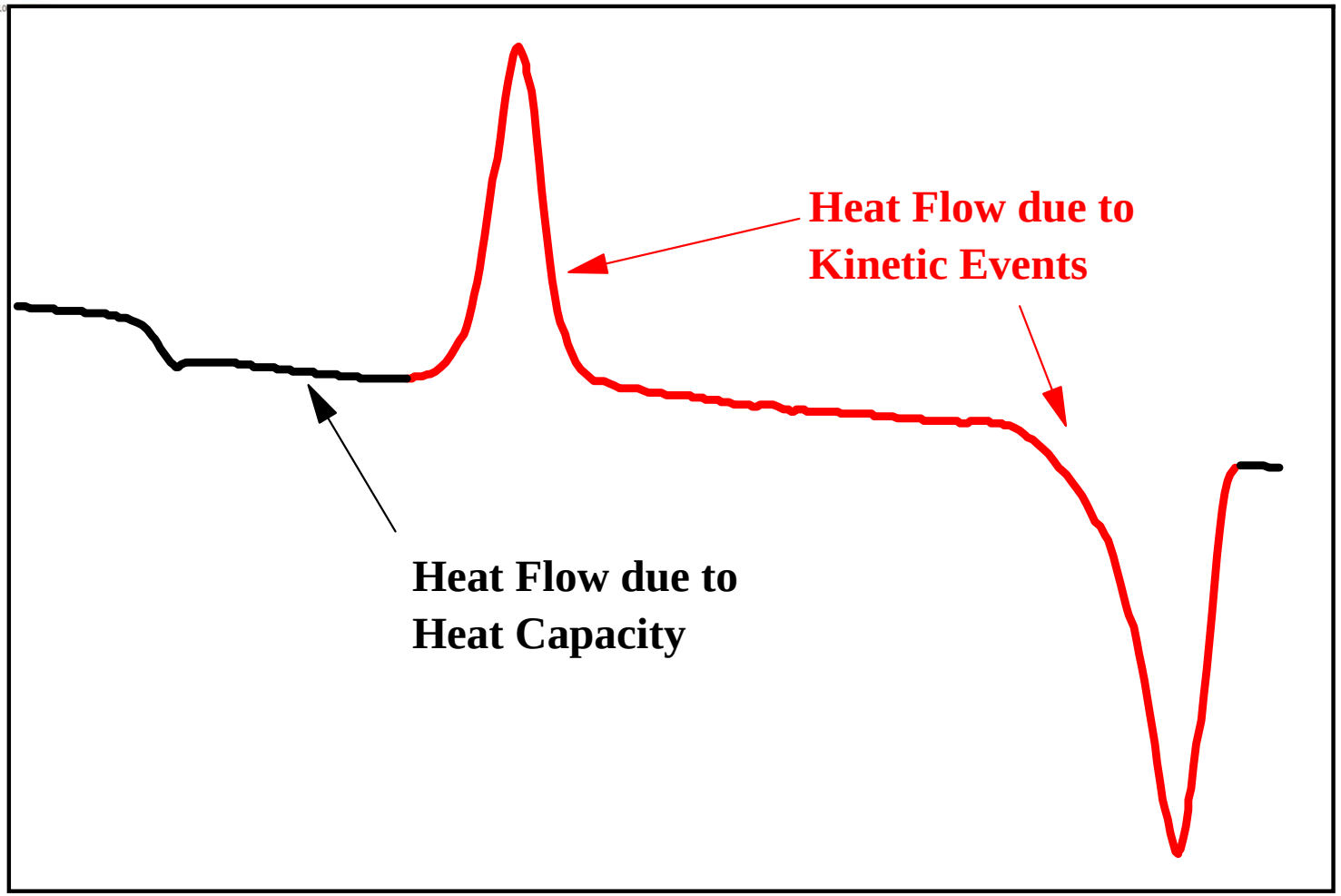


Kinetic Heat Flow

Isothermal Temperature



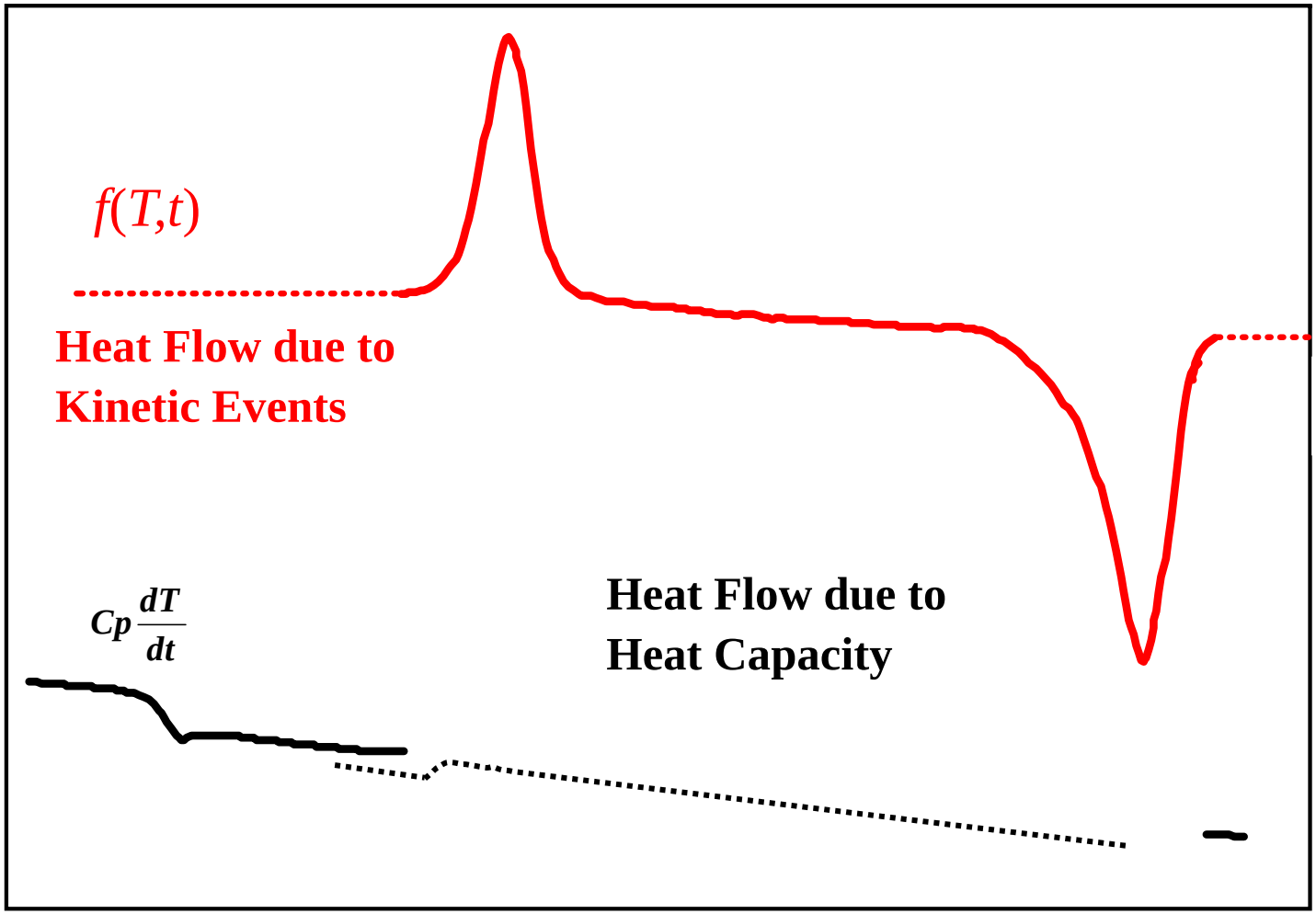
Standard DSC Measures the Sum of Heat Flow



Heat Flow

Temperature

Heat Flow Can Be Separated



General Theory of MDSC

Heat flow from DSC experiments is composed of two parts but DSC can only measure the sum of the two.

dH/dt	**=**	***Cp* (d*T*/d*t*)**	**+**	***f* (*T*,*t*)**
Total Heat Flow (DSC)	**=**	**Heat Capacity Component**	**+**	**Kinetic Component**
	=	**Heating Rate Dependent**	**+**	**Time Dependent**
	=	**MDSC Reversing**	**+**	**MDSC Nonreversing**

Distribution of Transitions in MDSC Experiments

Total = Heat Capacity Component + Kinetic Component

= Reversing Heat Flow + Nonreversing Heat Flow

- **glass transition**
- **melting (some)**

- **enthalpic relaxation**
- **evaporation**
- **crystallization**
- **decomposition**
- **cure**
- **melting (some)**

Physical Measurement Technique

Apply Stimulus → Measure Response

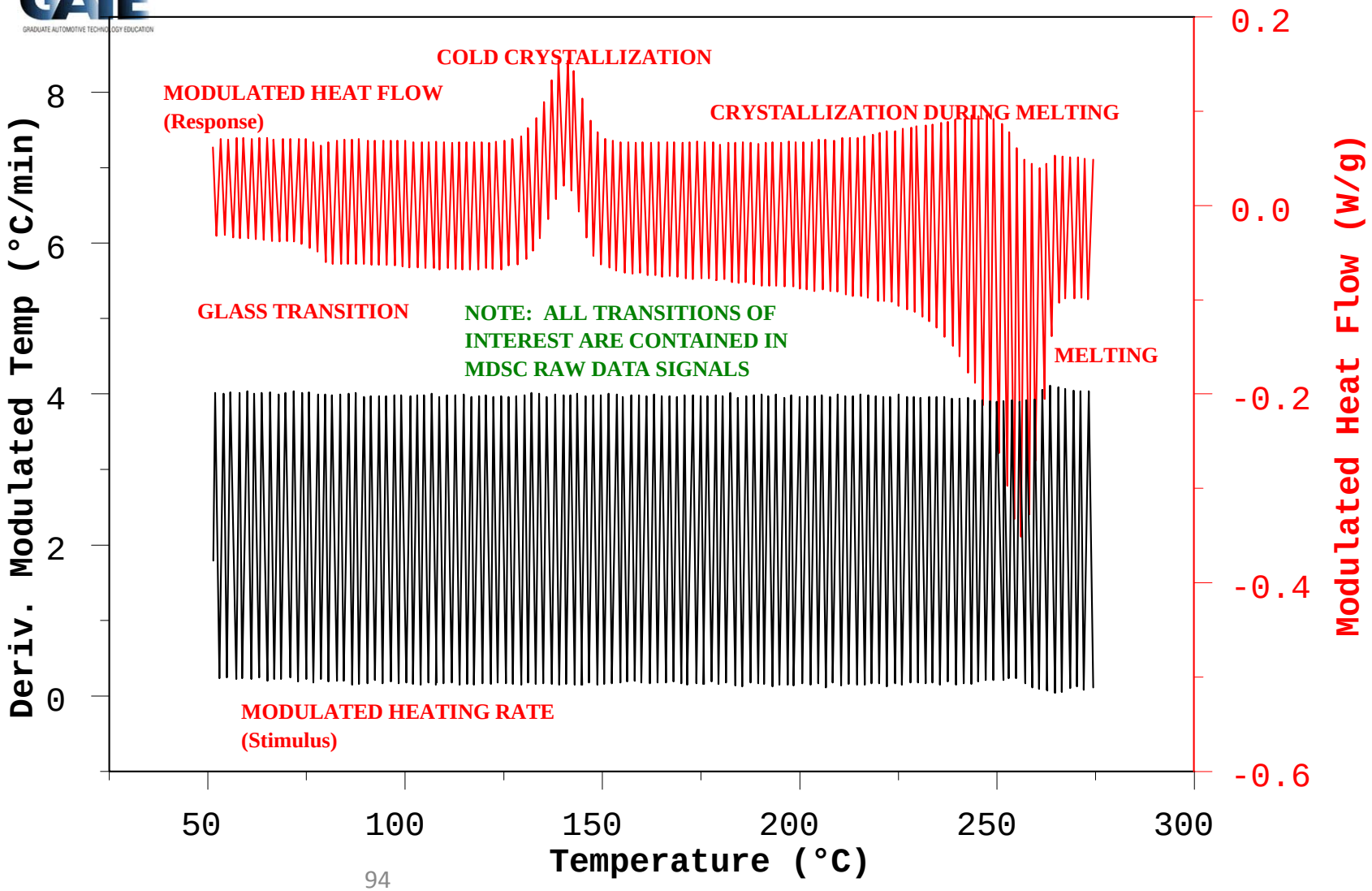
	Stimulus	Response
FTIR	IR Radiation	Absorbance Wavelength
NMR	Magnetic Field	Resonance Frequency
X-Ray Diffraction	X-Ray Radiation	Angle of Diffraction
MDSC	Sinusoidal Heating Rate	Amplitude of Heat Flow

Raw Signals in MDSC

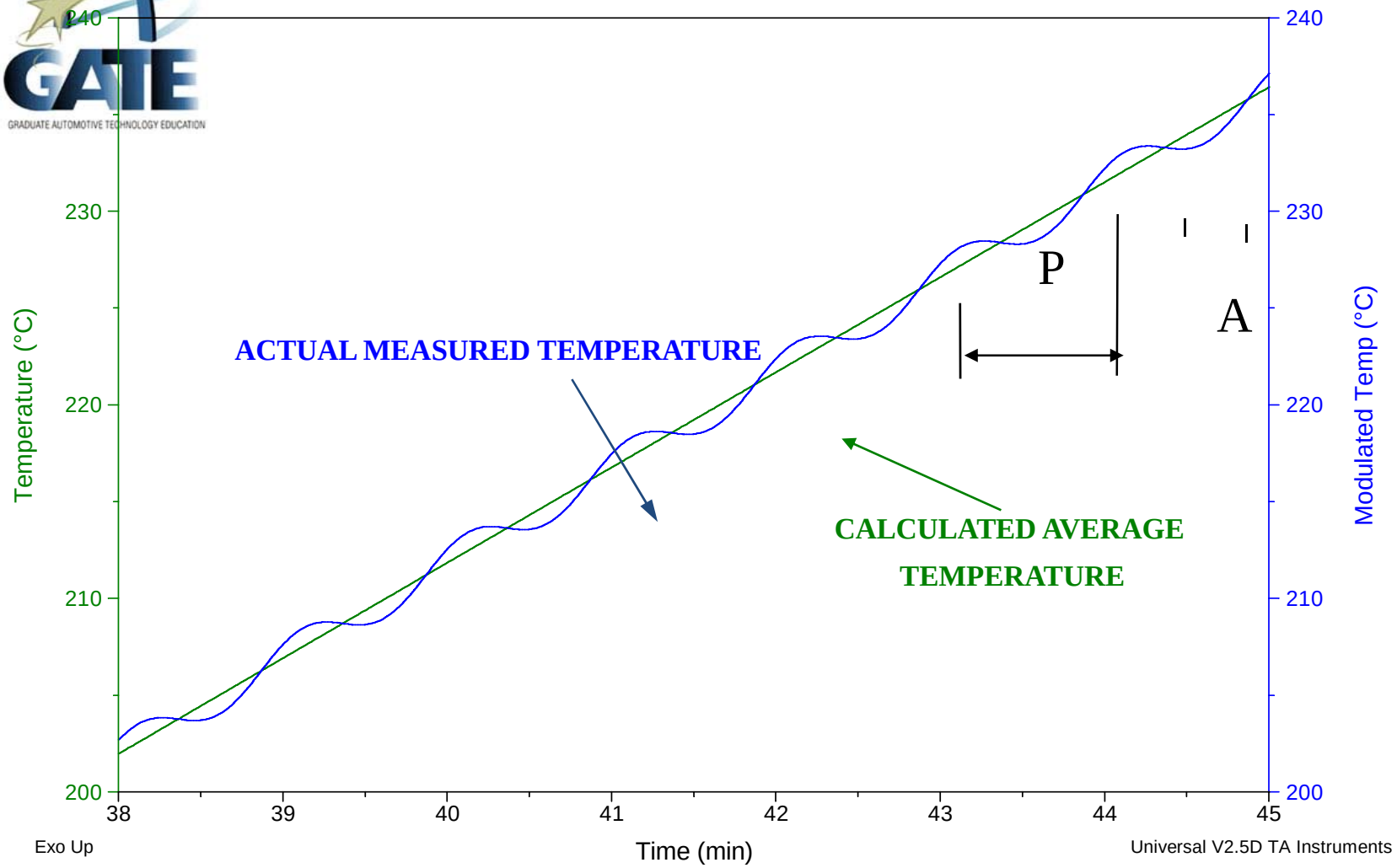
All Modulated DSC Signals are derived from three measured parameters.

- **Time**
- **Modulated Temperature (Stimulus)**
- **Modulated Heat Flow (Response)**

MDSC Raw Signal



Temperature Change (MDSC)



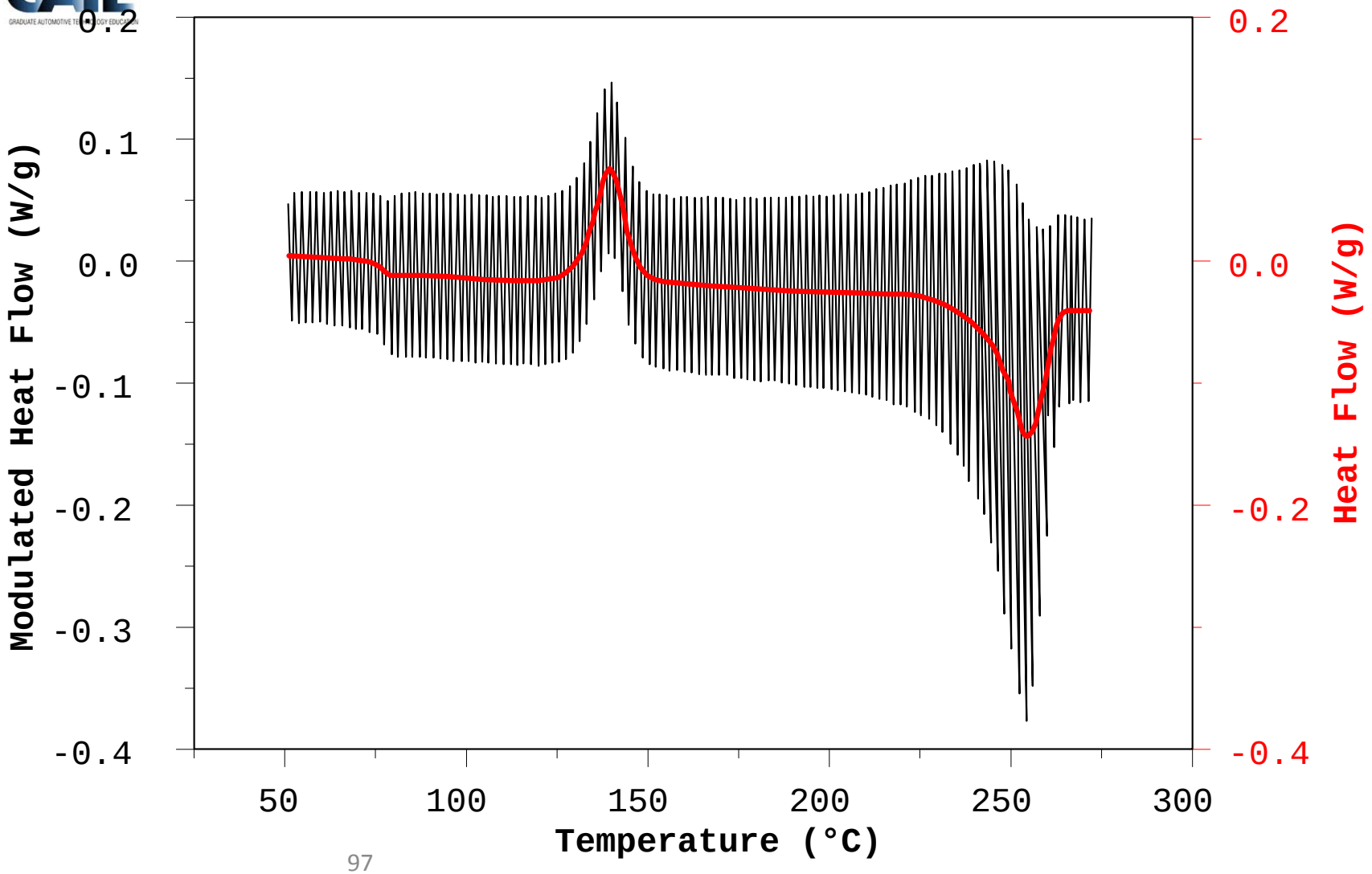
MDSC Signals: Total Heat Flow

The average value of the modulated heat flow signal. This signal is qualitatively and quantitatively equivalent to the heat flow signal from conventional DSC at the same average heating rate.

Definition: The sum of all thermal events in the sample

Calculation: Fourier Transformation analysis of the modulated heat flow signal is used to continuously calculate its average value

Total Heat Flow: Average of Modulated Heat Flow Signal



MDSC Signals: Heat Capacity

$$Cp = \frac{A_{MHF}}{A_{MHR}} \times K$$

Where:

A_{MHF} = Amplitude of Modulated Heat Flow

A_{MHR} = Amplitude of Modulated Heating Rate

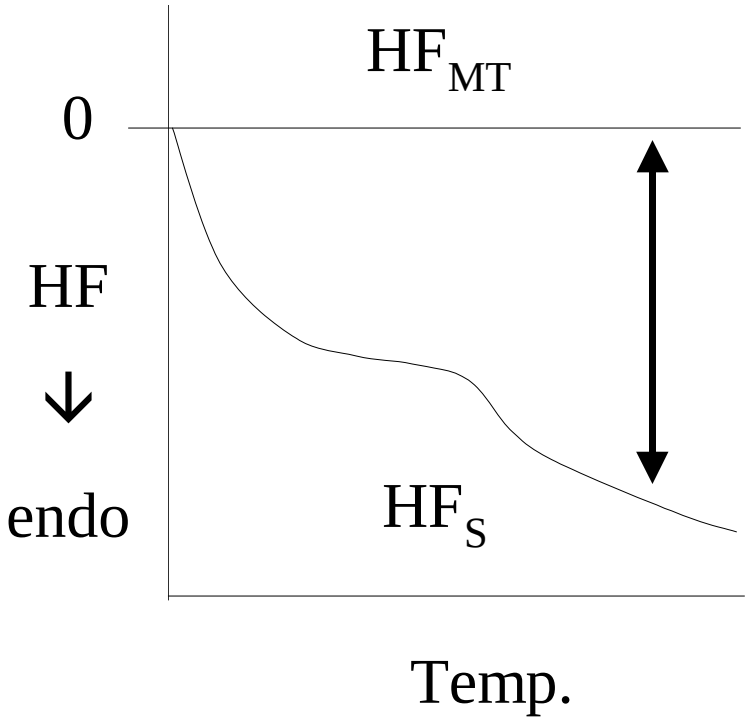
K = Heat Capacity Calibration Factor

Definition: The amount of heat required to raise the temperature of a material 1°C.

Calculation: The basis for making the heat capacity measurement in MDSC can be explained from a series of conventional DSC experiments at different heating rates.

Conventional DSC Cp Measurement

$$Cp = K \times \frac{HF_S - HF_{MT}}{\text{Heat Rate x wt}}$$



Where:

K = Calibration constant

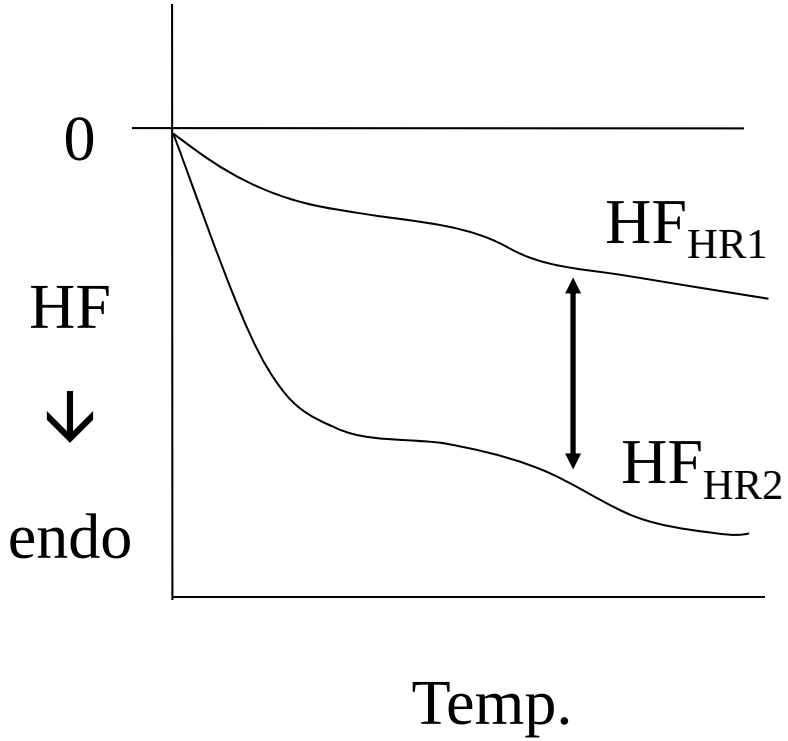
HF_S = Differential heat flow with sample

HF_{MT} = Differential heat flow with empty pans

wt = weight of sample

Alternative DSC Cp Measurement

$$Cp = K \times \frac{HF_{HR2} - HF_{HR1}}{(HR_2 - HR_1)\, wt}$$



Where:

K = Calibration constant

HF_{HR1} = Differential heat flow of sample at HR_1

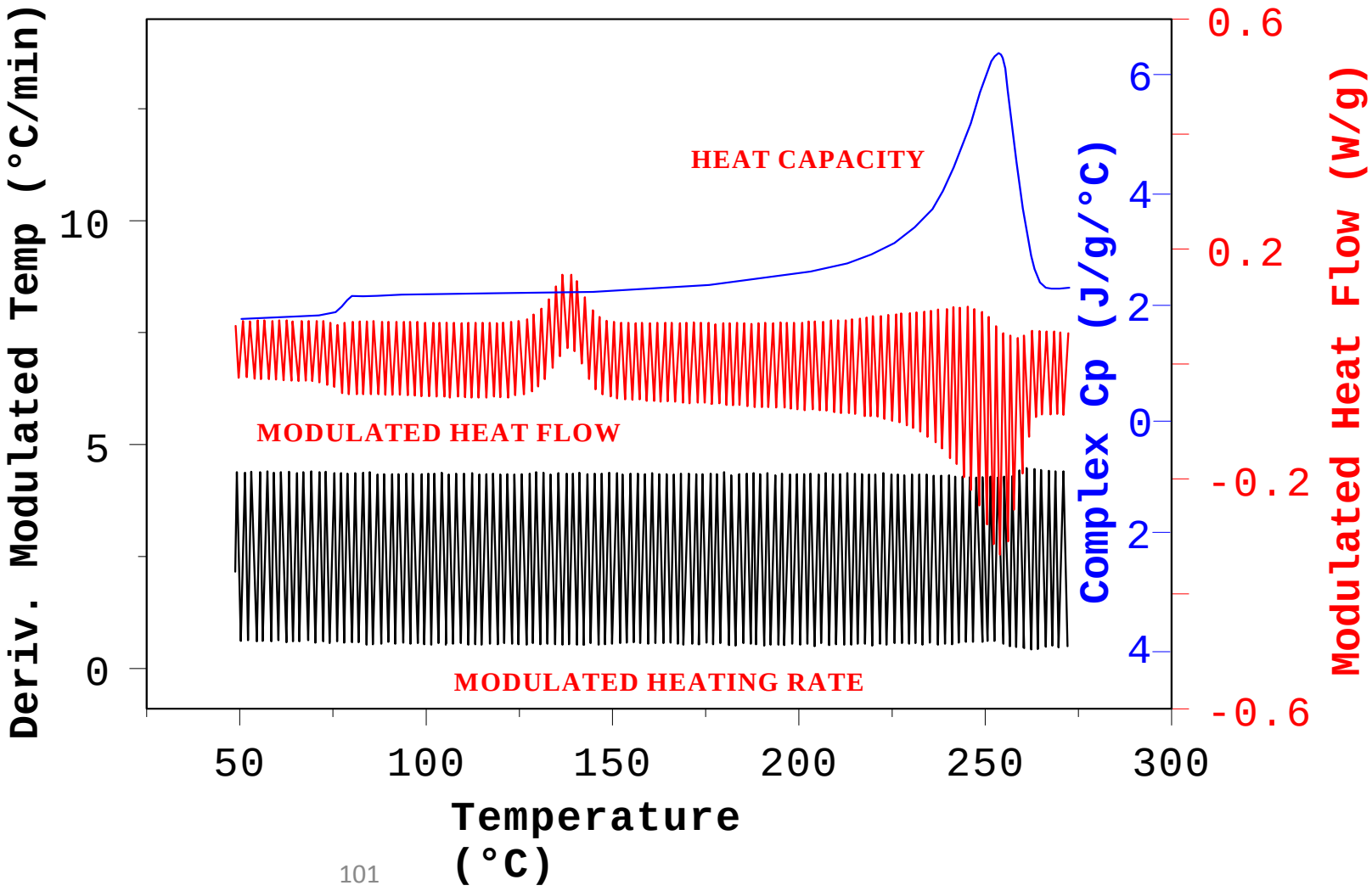
HF_{HR2} = Differential heat flow of sample at HR_2

HR_2 = Heating rate 2

HR_1 = Heating rate 1

wt = weight of sample

Heat Capacity from MDSC Raw Signals



MDSC Signals - Reversing Heat Flow (Heat Capacity Component)

Reversing Heat Flow is the heat capacity component of the total heat flow. It is calculated by converting the measured heat capacity into a heat flow signal using the classical heat flow equation as a theoretical basis.

Reversing Heat Flow = Cp x Avg. Heat Rate

Basis for Calculation

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

Where :

$\frac{dH}{dt}$ = total heat flow

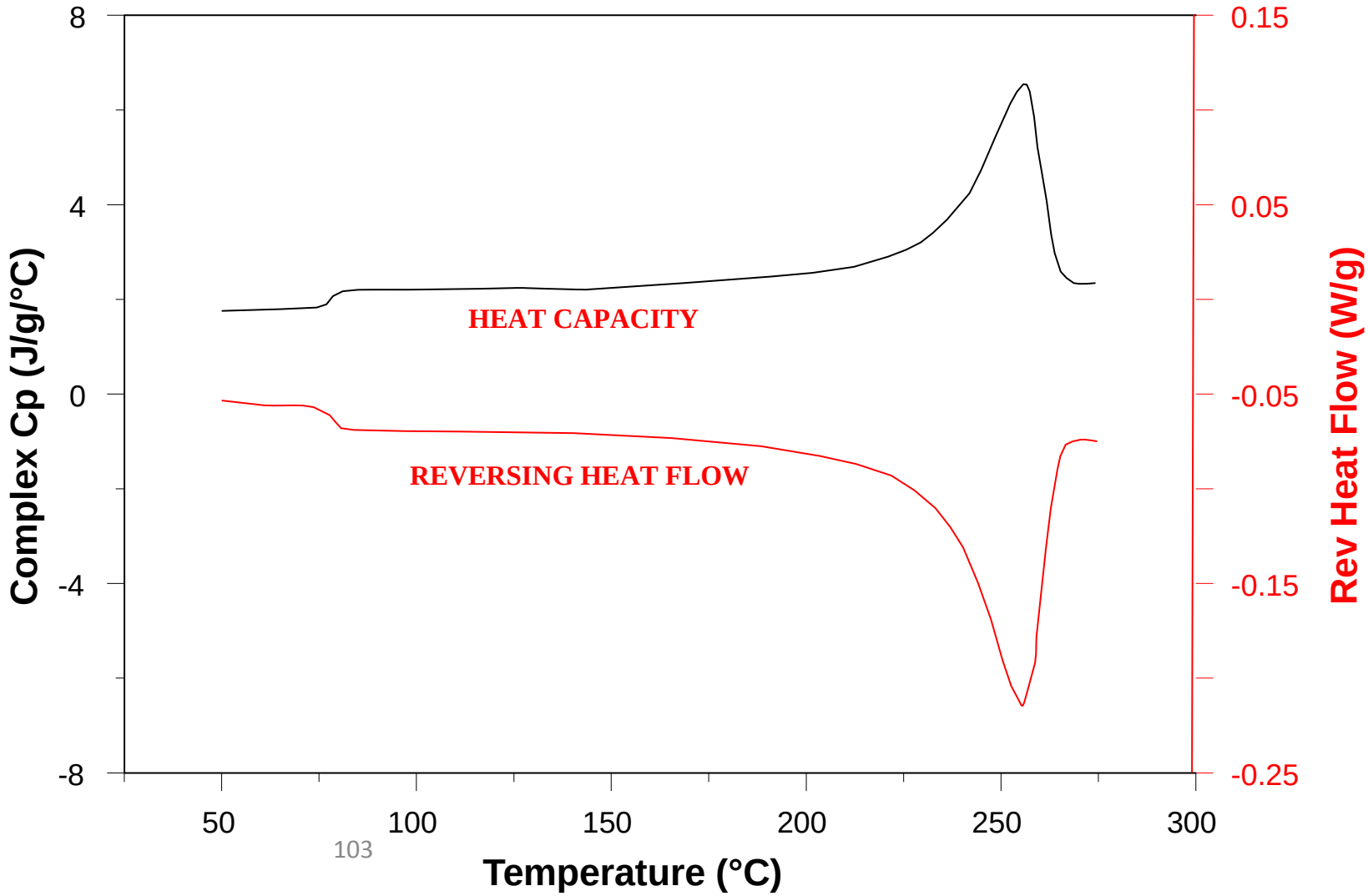
Cp = measured heat capacity

$\frac{dT}{dt}$ = average heating rate

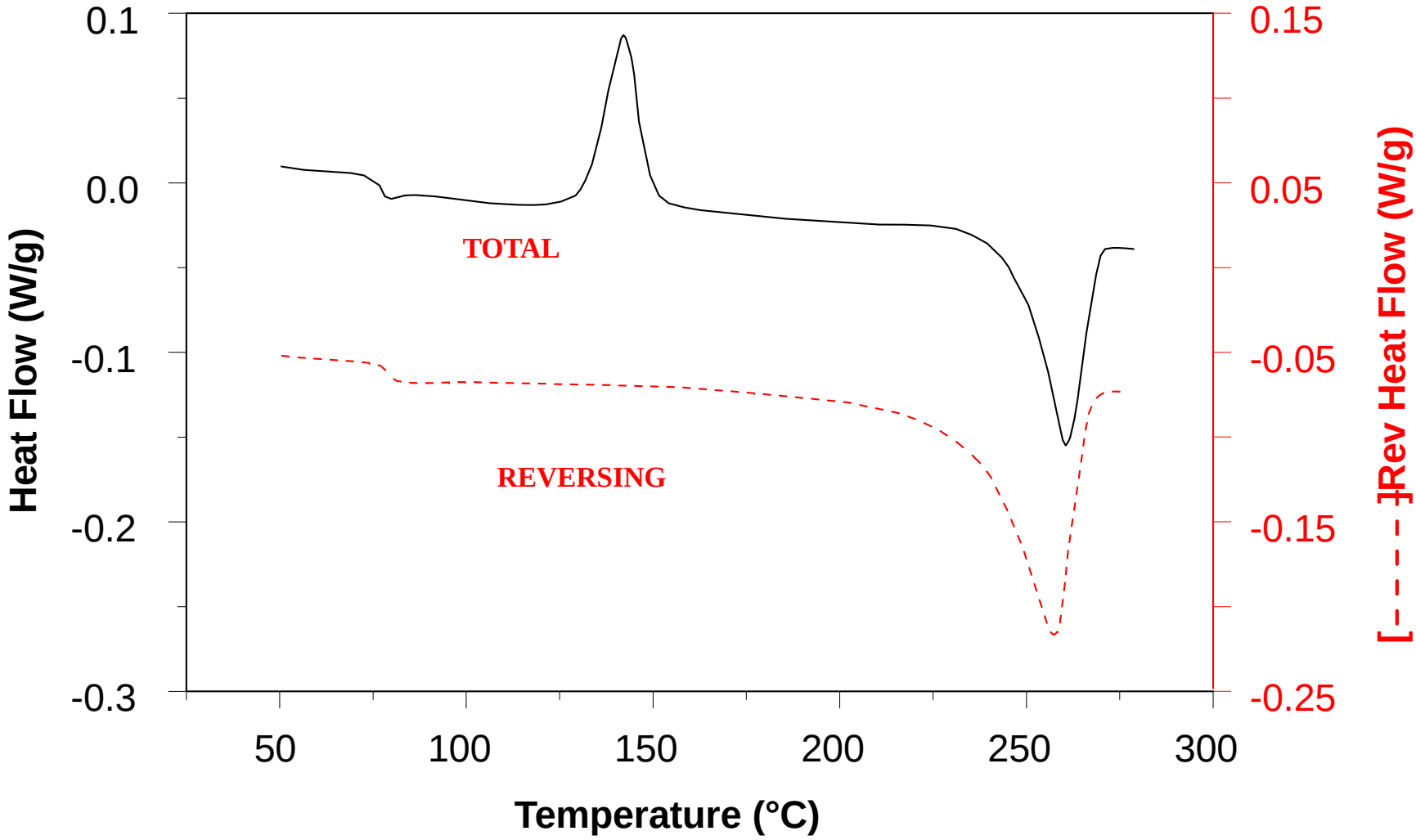
$Cp\frac{dT}{dt}$ = heat capacity component (Reversing)

$f(T,t)$ = heat flow from kinetic process (Nonreversing)

Reversing Heat Flow from MDSC Raw Signals



Quench Cooled PET: Total vs. Reversing Heat Flow



MDSC Signals - Nonreversing Heat Flow (Kinetic Component)

Nonreversing Heat Flow is the kinetic component of the total heat flow. It is calculated by subtracting the heat capacity component from the total heat flow using the classical heat flow equation as a theoretical basis.

Nonreversing = Total – Reversing

Basis for Calculation

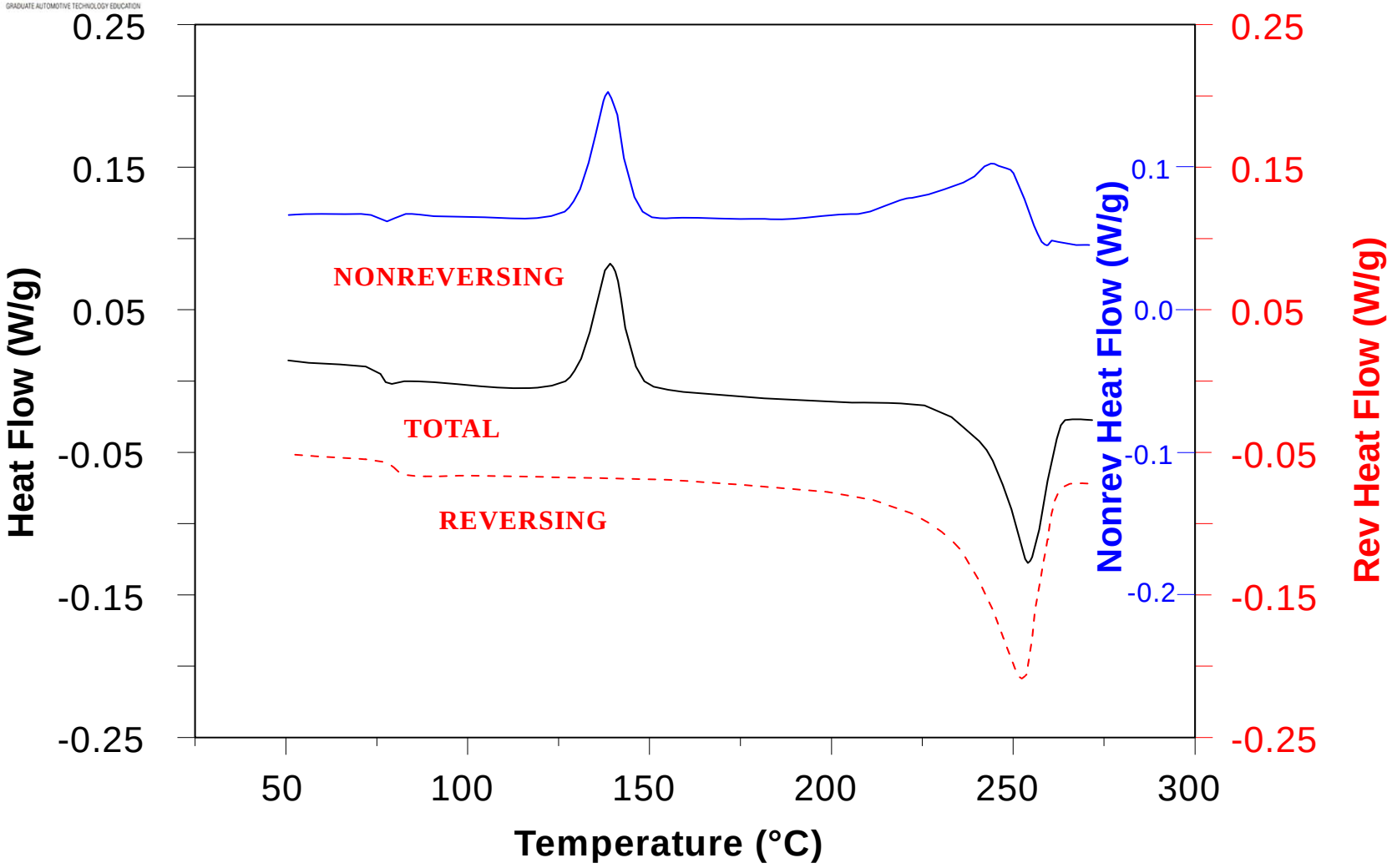
$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T,t)$$

$$\frac{dH}{dt} = \text{total heat flow}$$

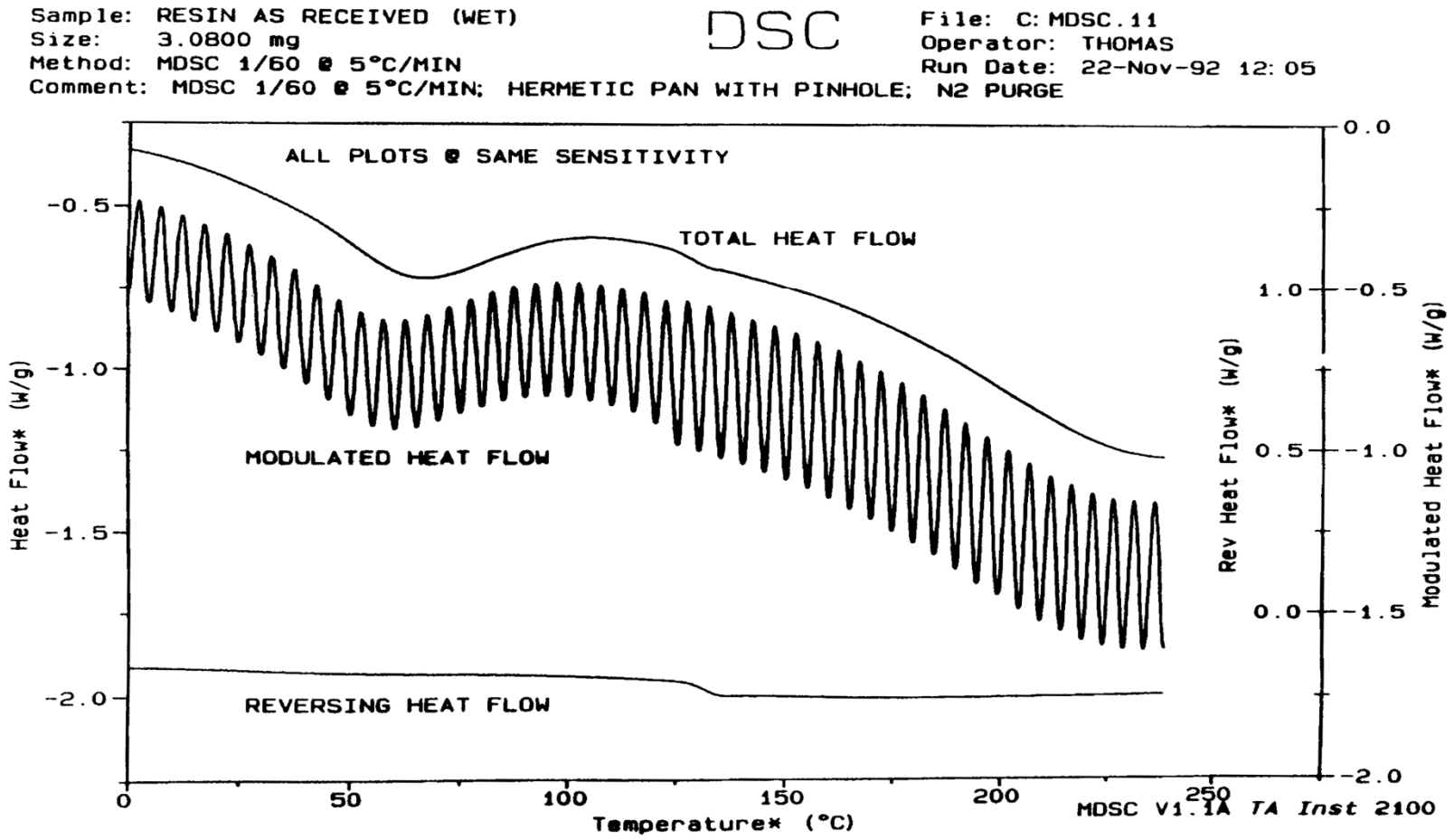
$$Cp\frac{dT}{dt} = \text{heat capacity component (reversing)}$$

$$f(T,t) = \text{kinetic component (nonreversing)}$$

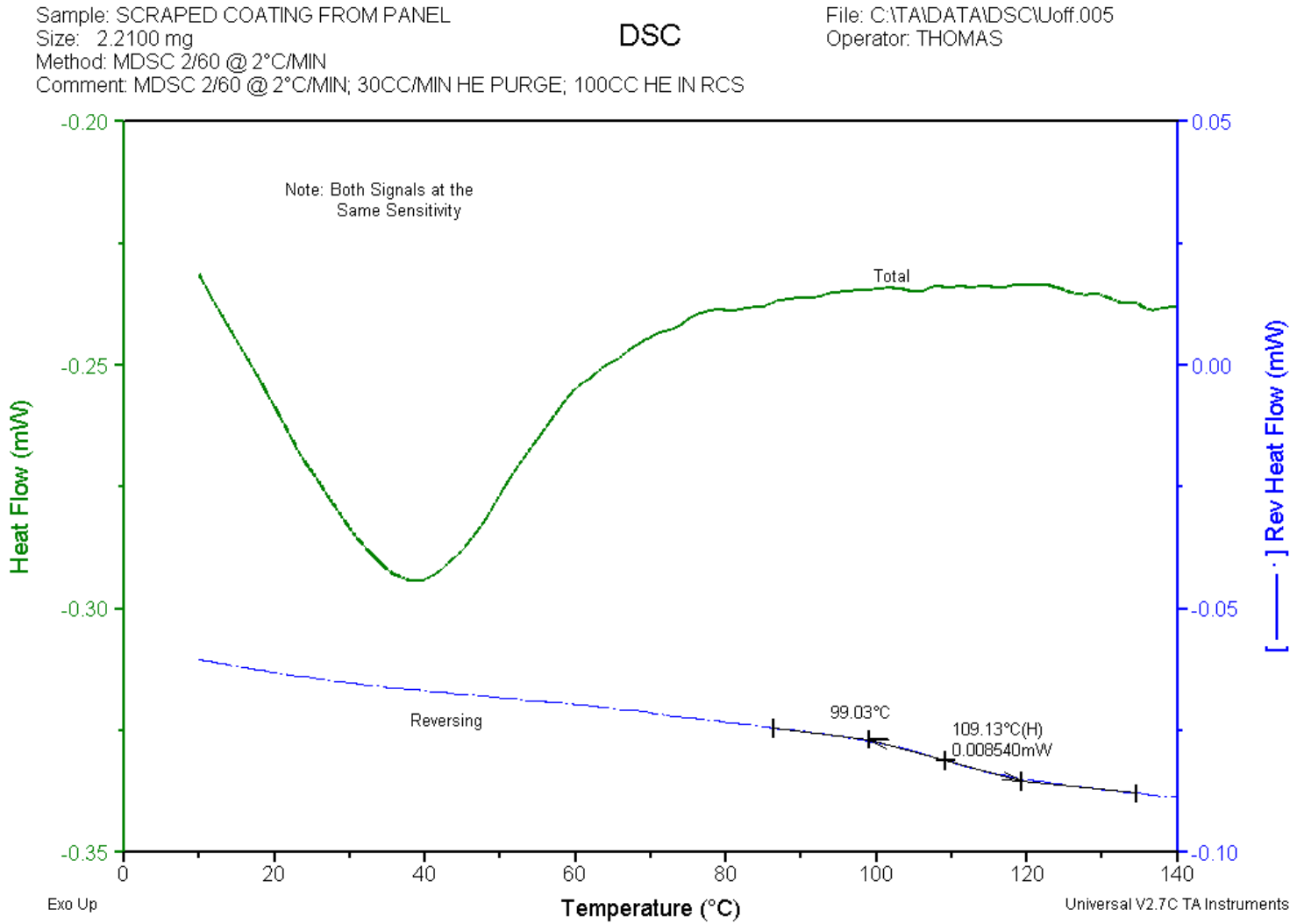
Quench-Cooled PET: Deconvoluted Signals



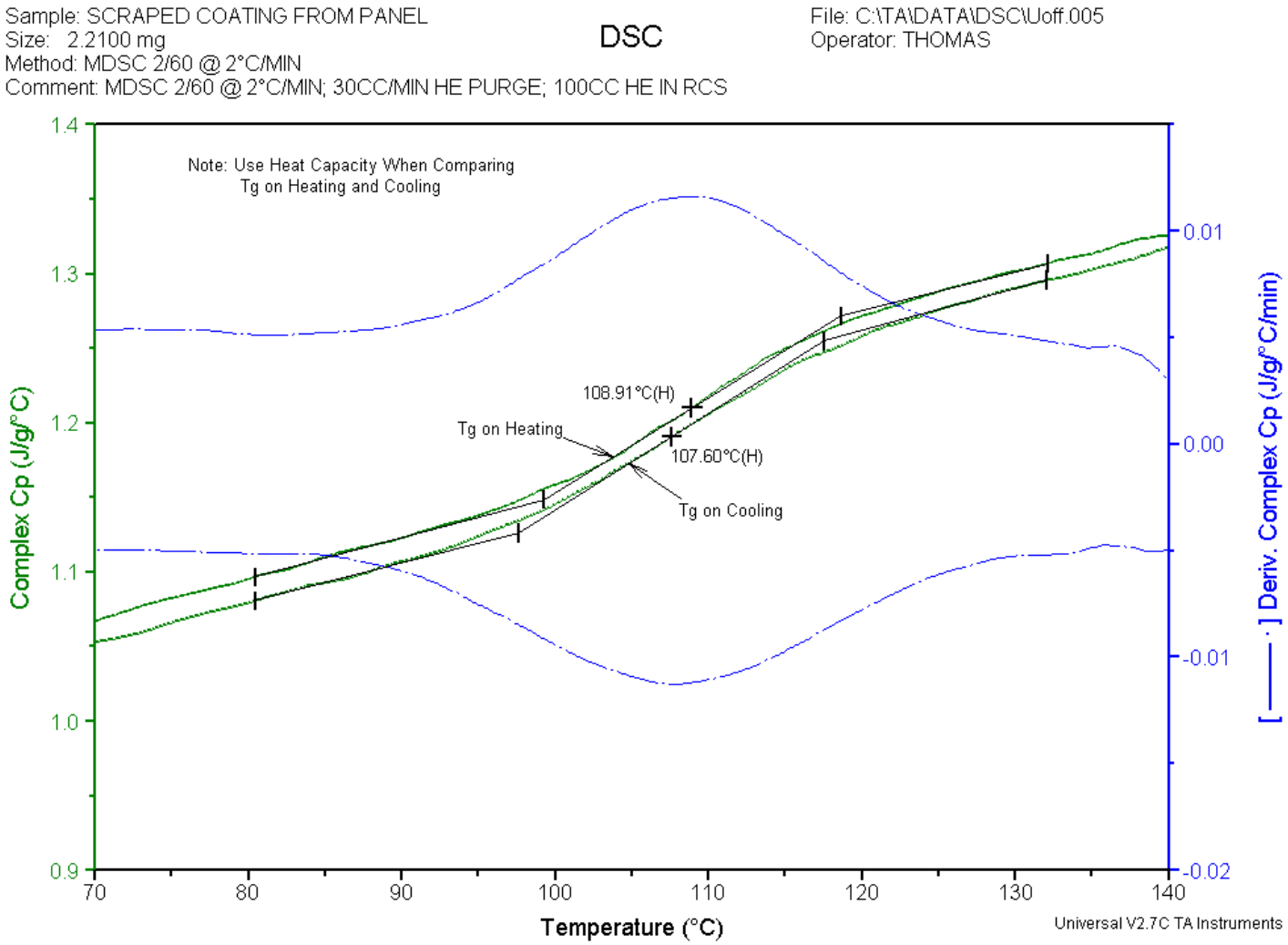
Glass Transition of Polymer Resin



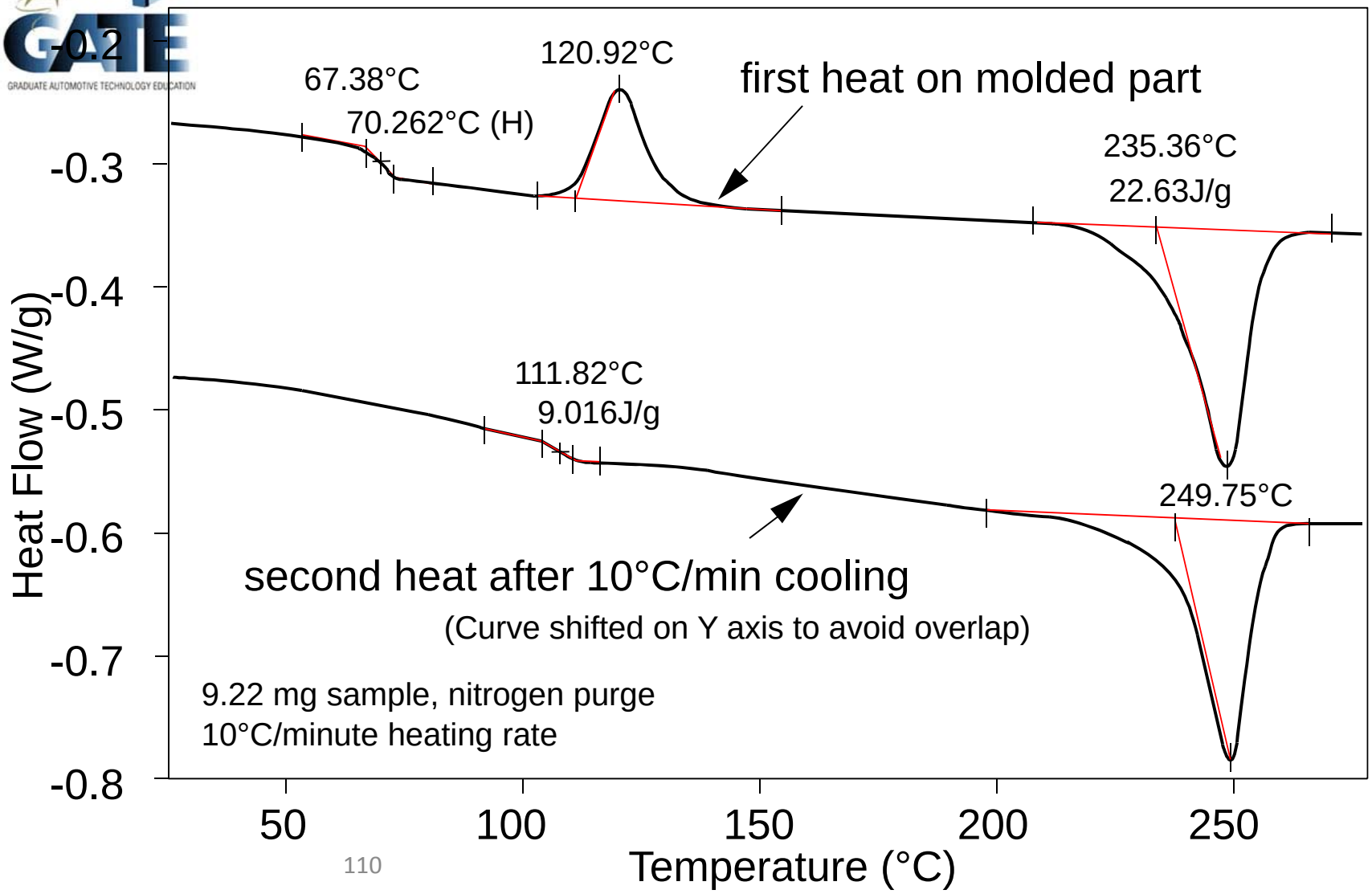
MDSC: Glass Transition of Epoxy Coating



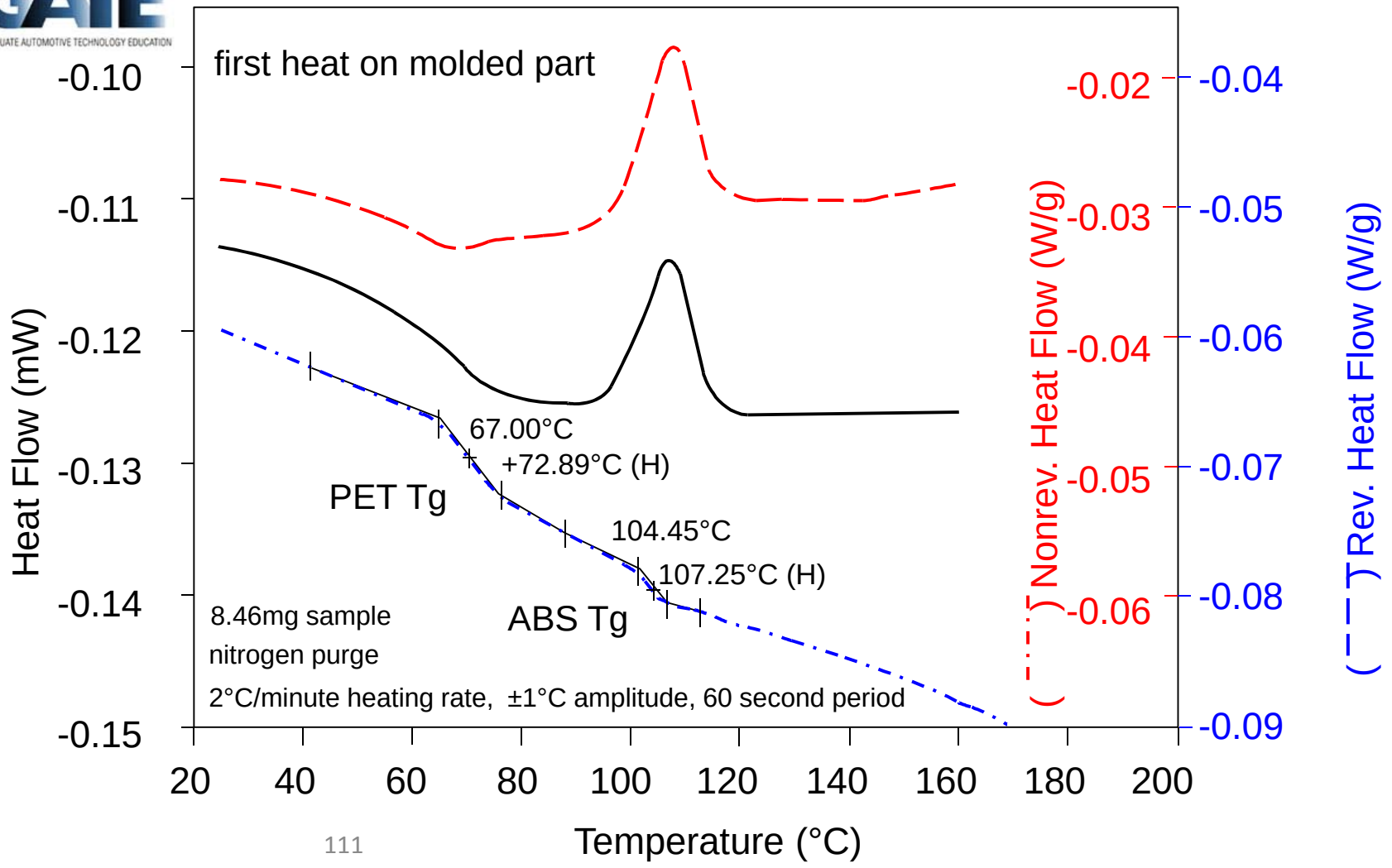
MDSC: Glass Transition of Epoxy Coating



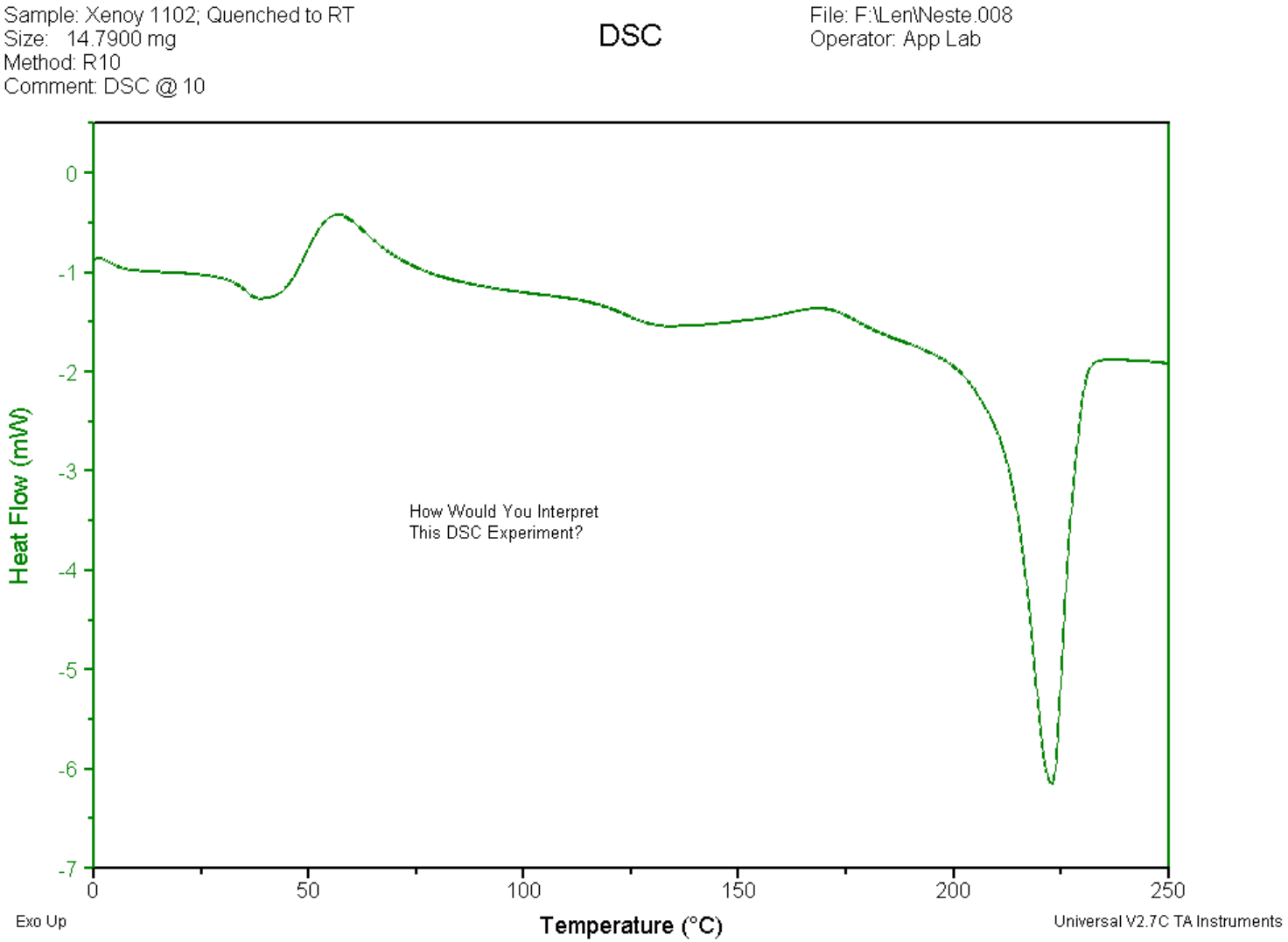
PET/ABS Blend – Conventional DSC



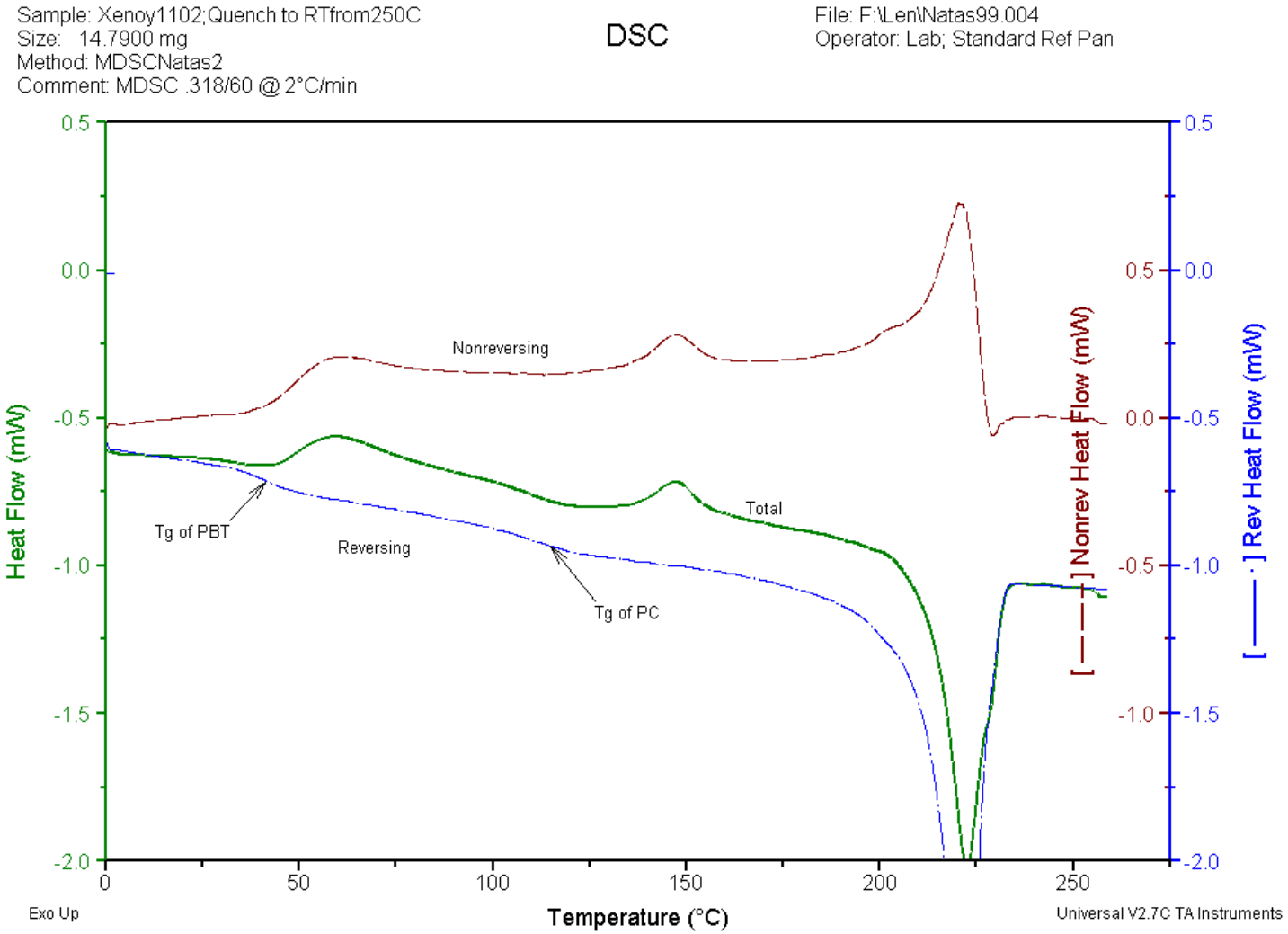
PET/ABS - MDSC


first heat on molded part
-0.10
-0.11
-0.12
-0.13
-0.14
-0.15
Heat Flow (mW)
-0.02
-0.03
-0.04
-0.05
-0.06
( ) Nonrev. Heat Flow (W/g)
-0.04
-0.05
-0.06
-0.07
-0.08
-0.09
( ) Rev. Heat Flow (W/g)
67.00°C
+72.89°C (H)
PET Tg
104.45°C
107.25°C (H)
ABS Tg
8.46mg sample
nitrogen purge
2°C/minute heating rate, ±1°C amplitude, 60 second period
20
40
60
80
100
120
140
160
180
200
Temperature (°C)

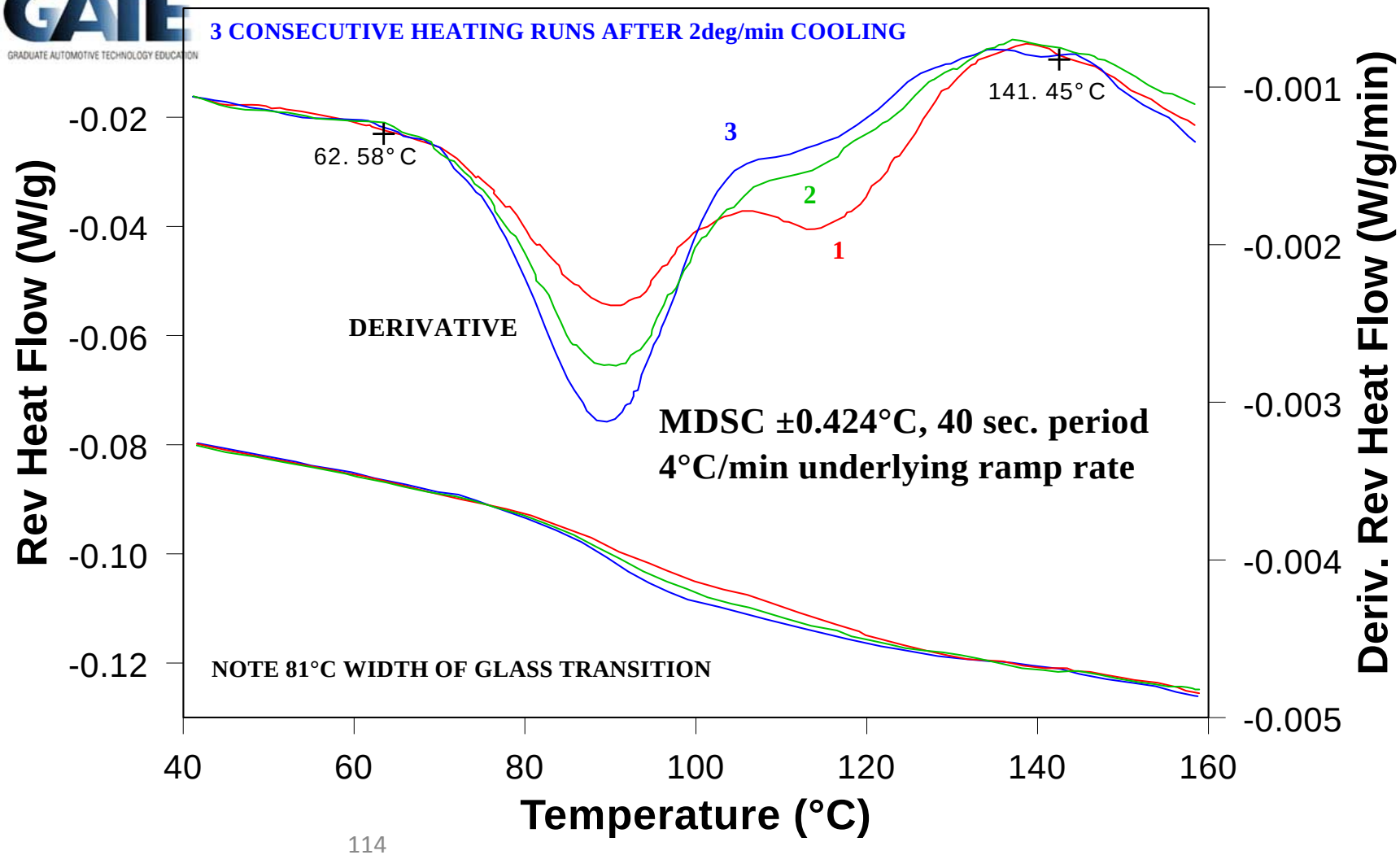
DSC of Polymer Blend



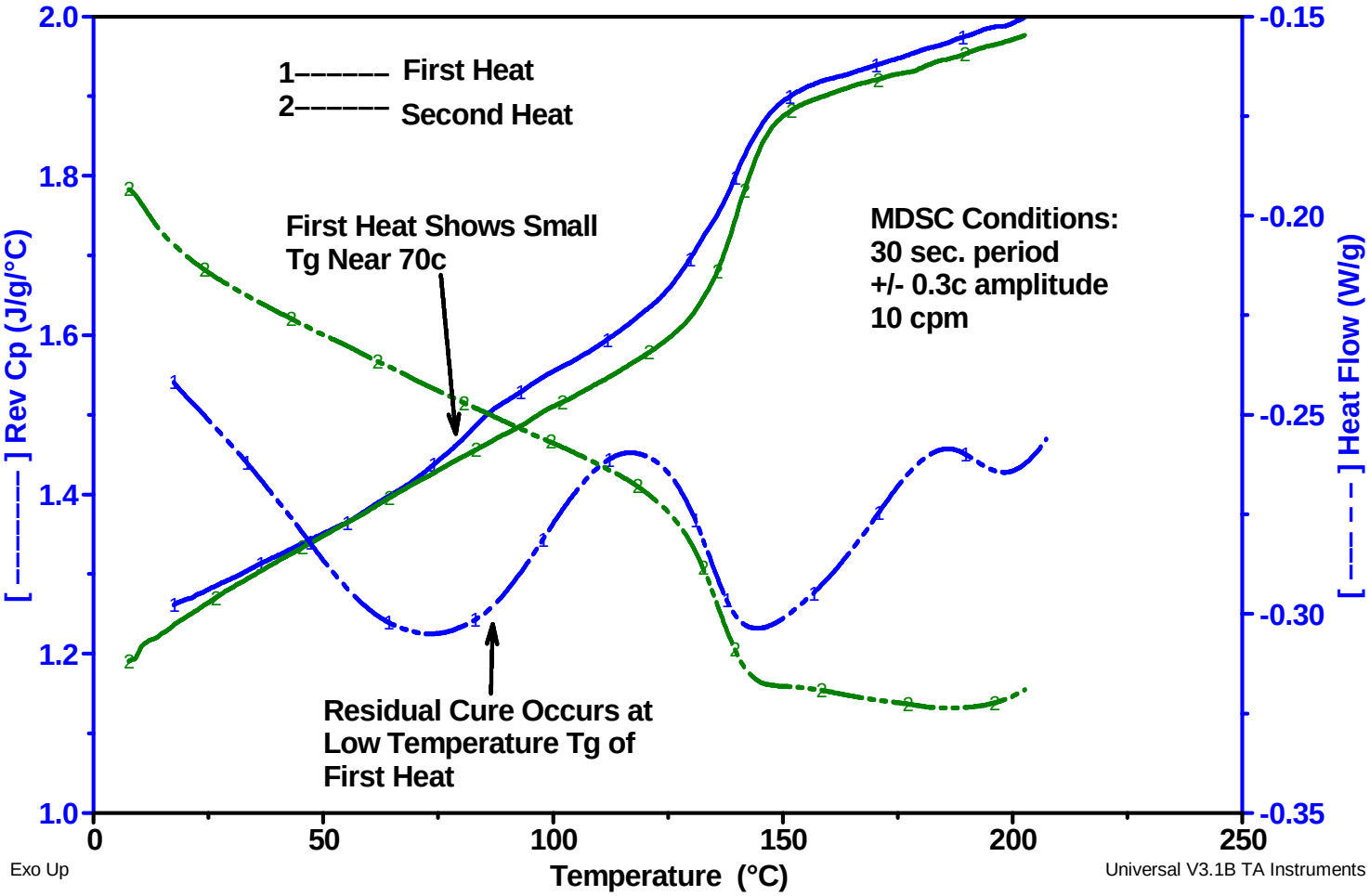
MDSC of Polymer Blend



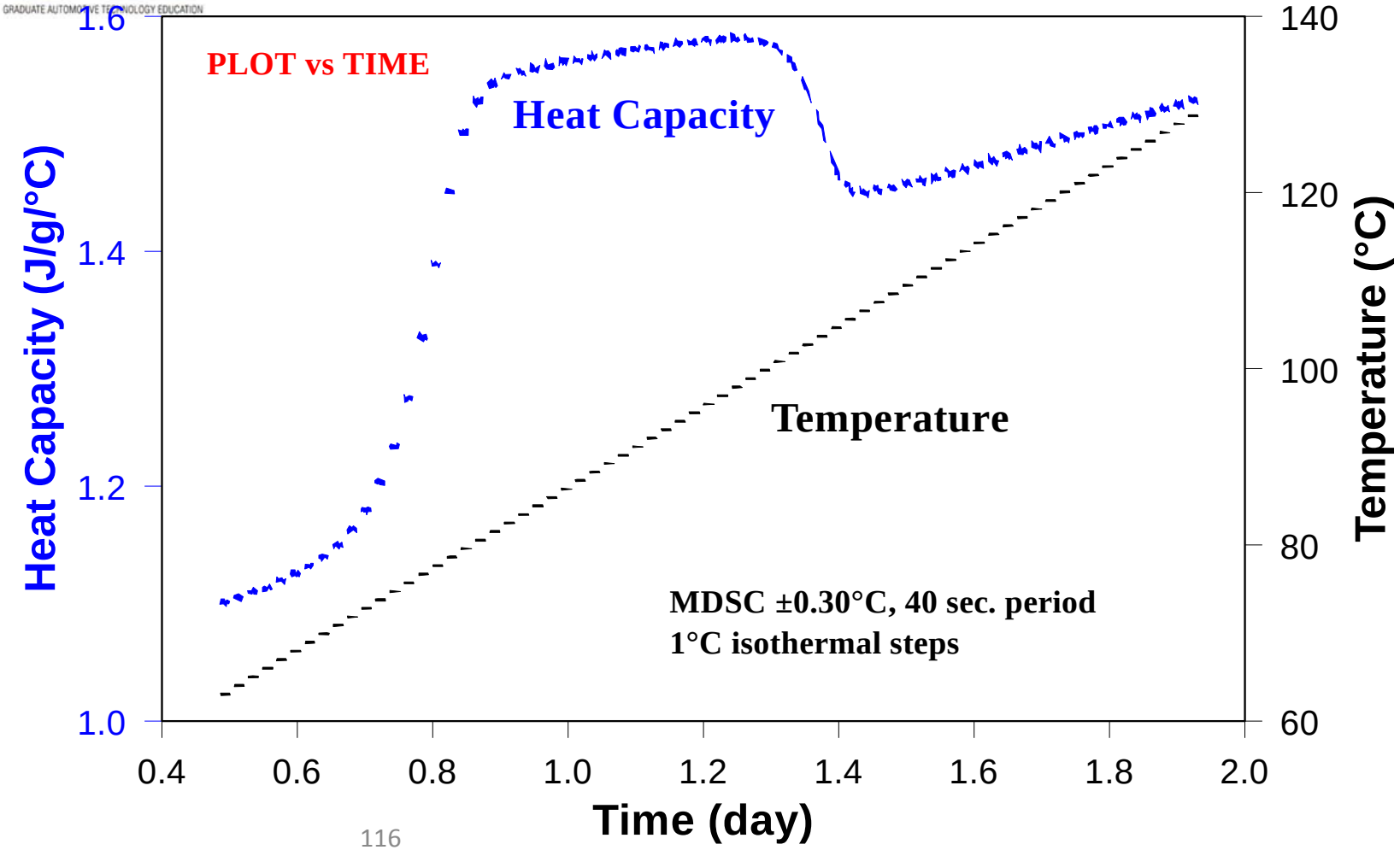
MDSC: Detection of Two Glass Transitions in PC/PEE Blend



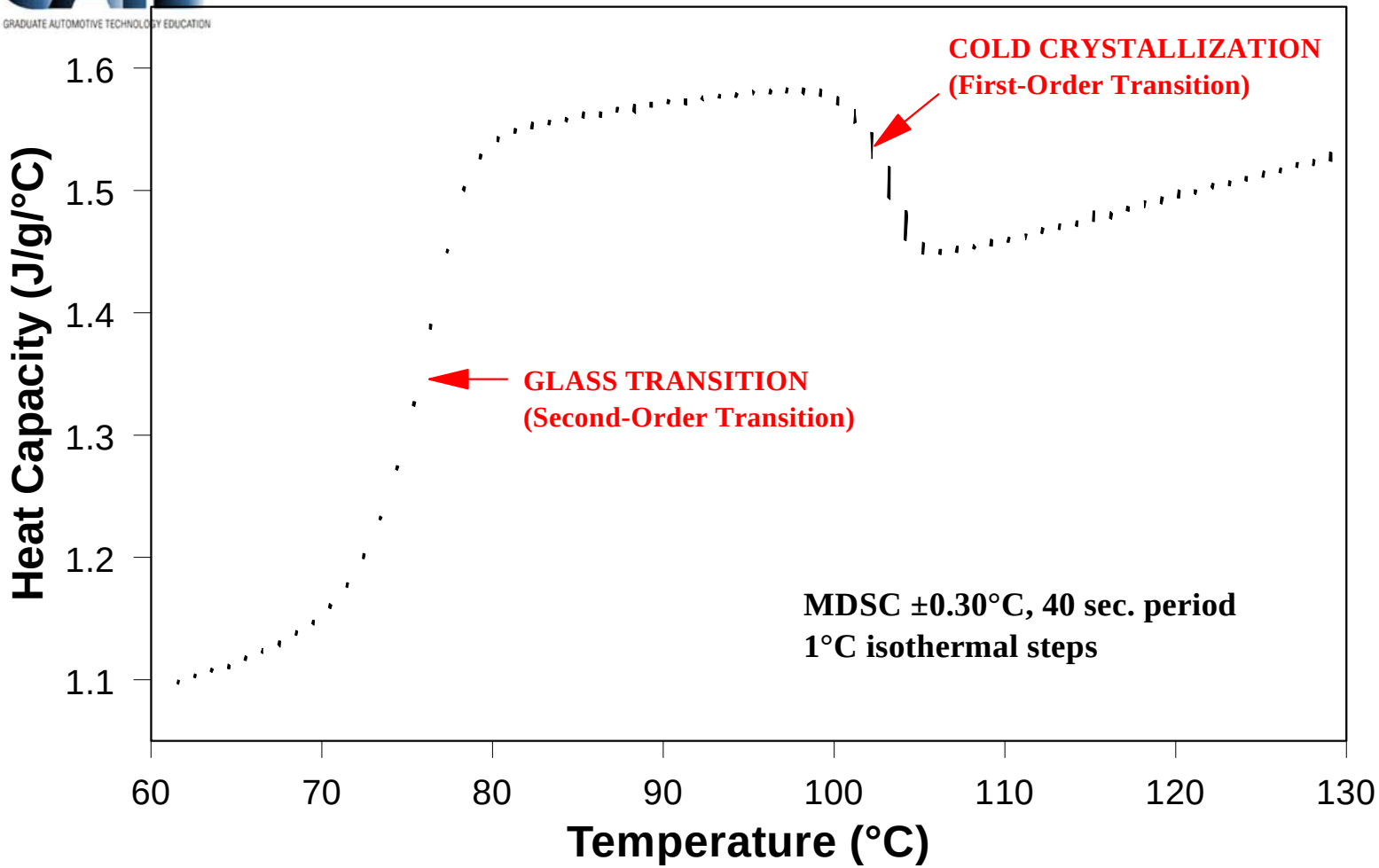
FAST MDSC® ON THE Q1000



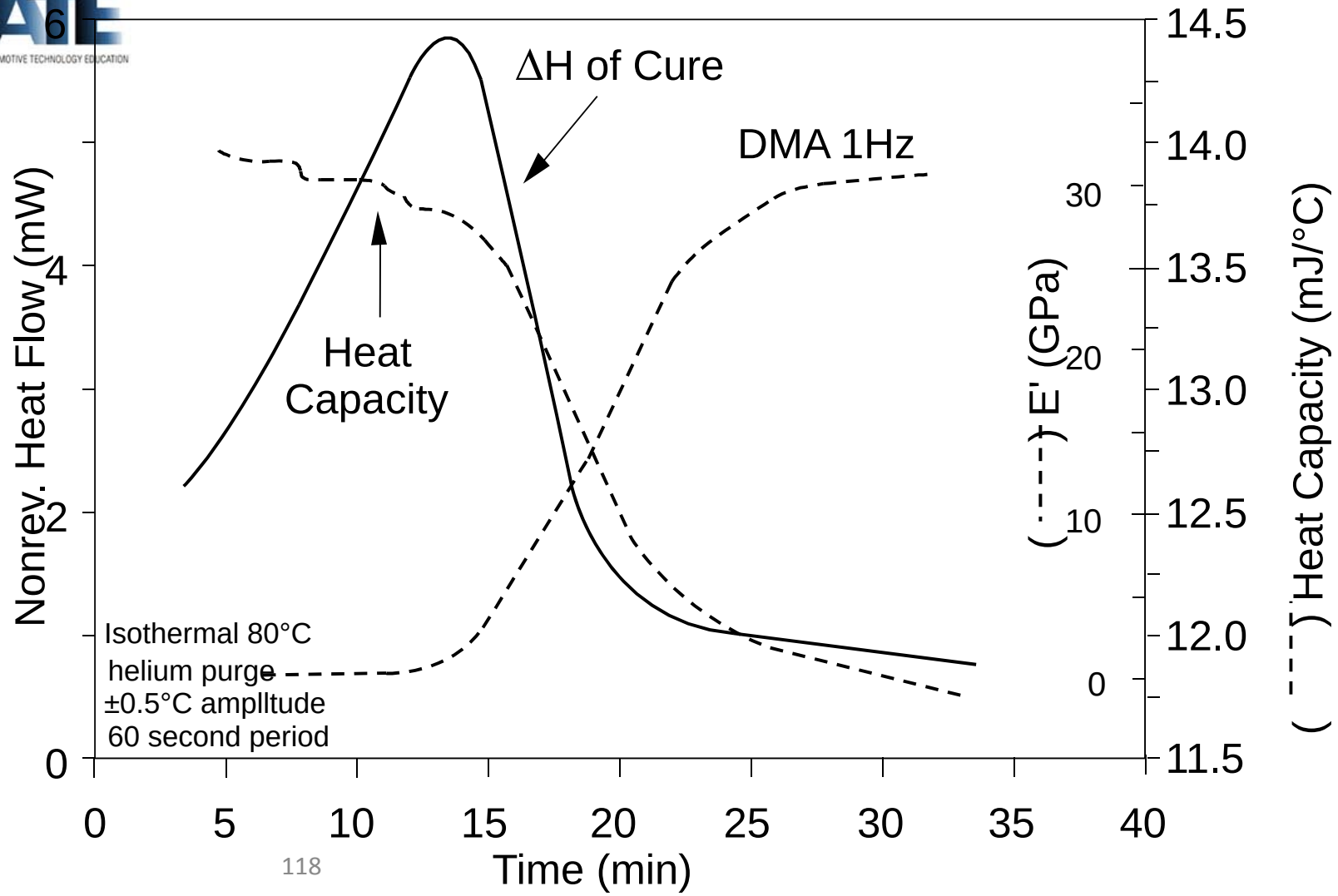
MDSC: Heat Capacity for PET During Isothermal Steps



MDSC: PET Heat Capacity During GlassTransition & Cold Crystallization

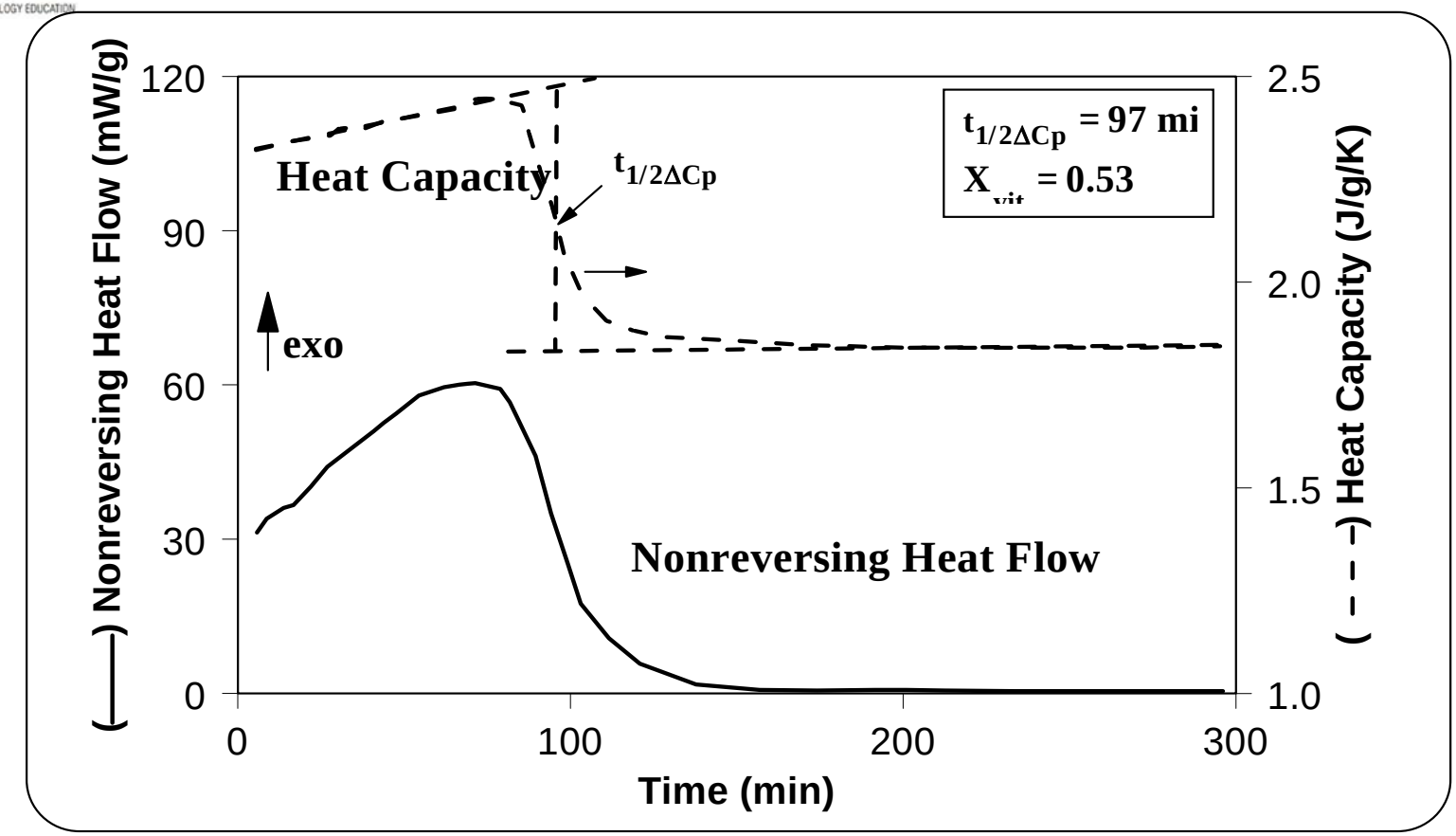


Isothermal Epoxy Cure



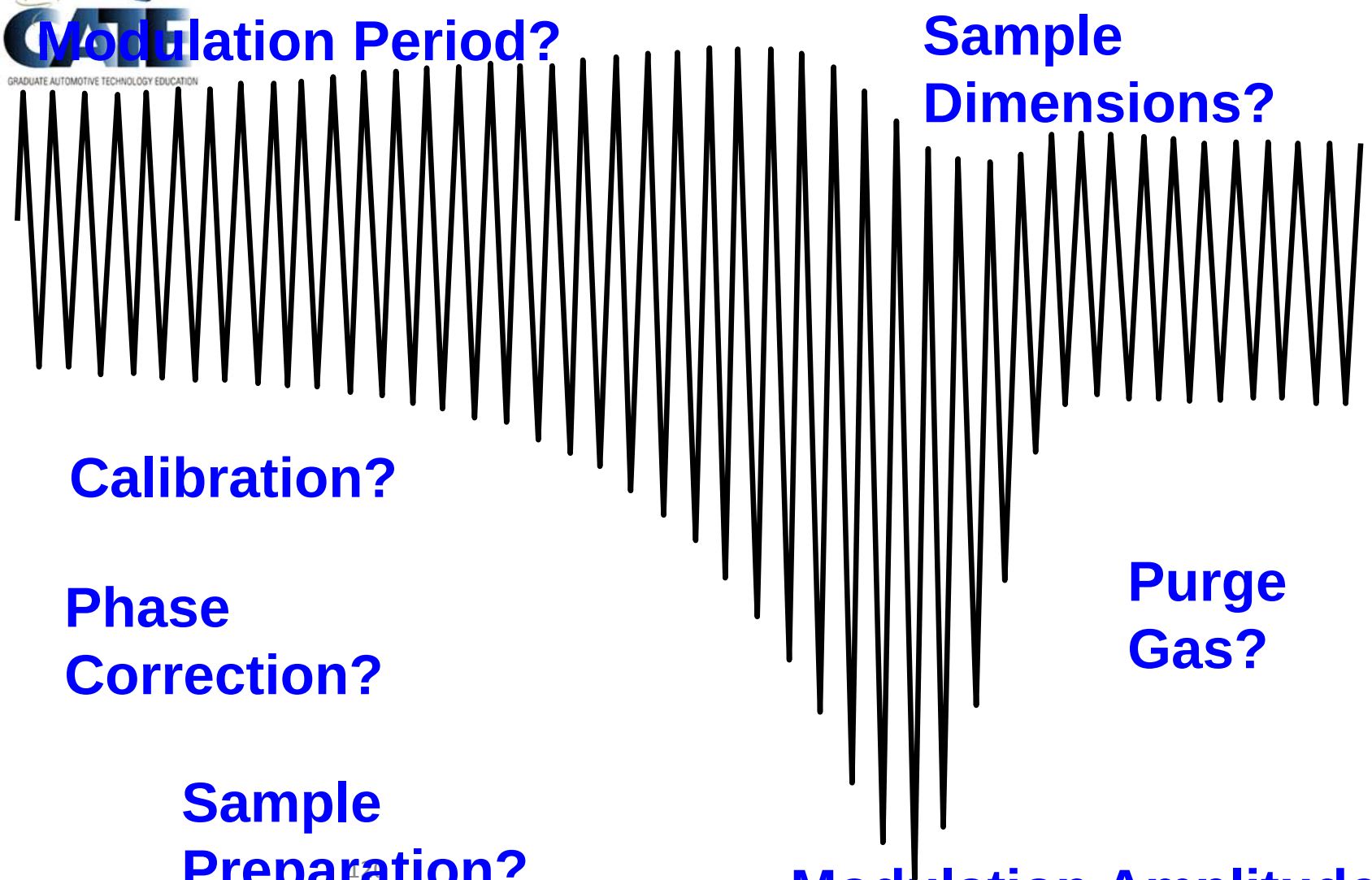
MDSC: Heat Capacity vs. Cure Time

Epoxy-Amine System MDSC™ Result at 70°C Cure[=]



[=] Thermochimica Acta, 268, 121-142 (1995), Dr. B. Van Mele, et al at Vrije Universiteit Brussels (Belgium)

MDSC: Experimental Considerations



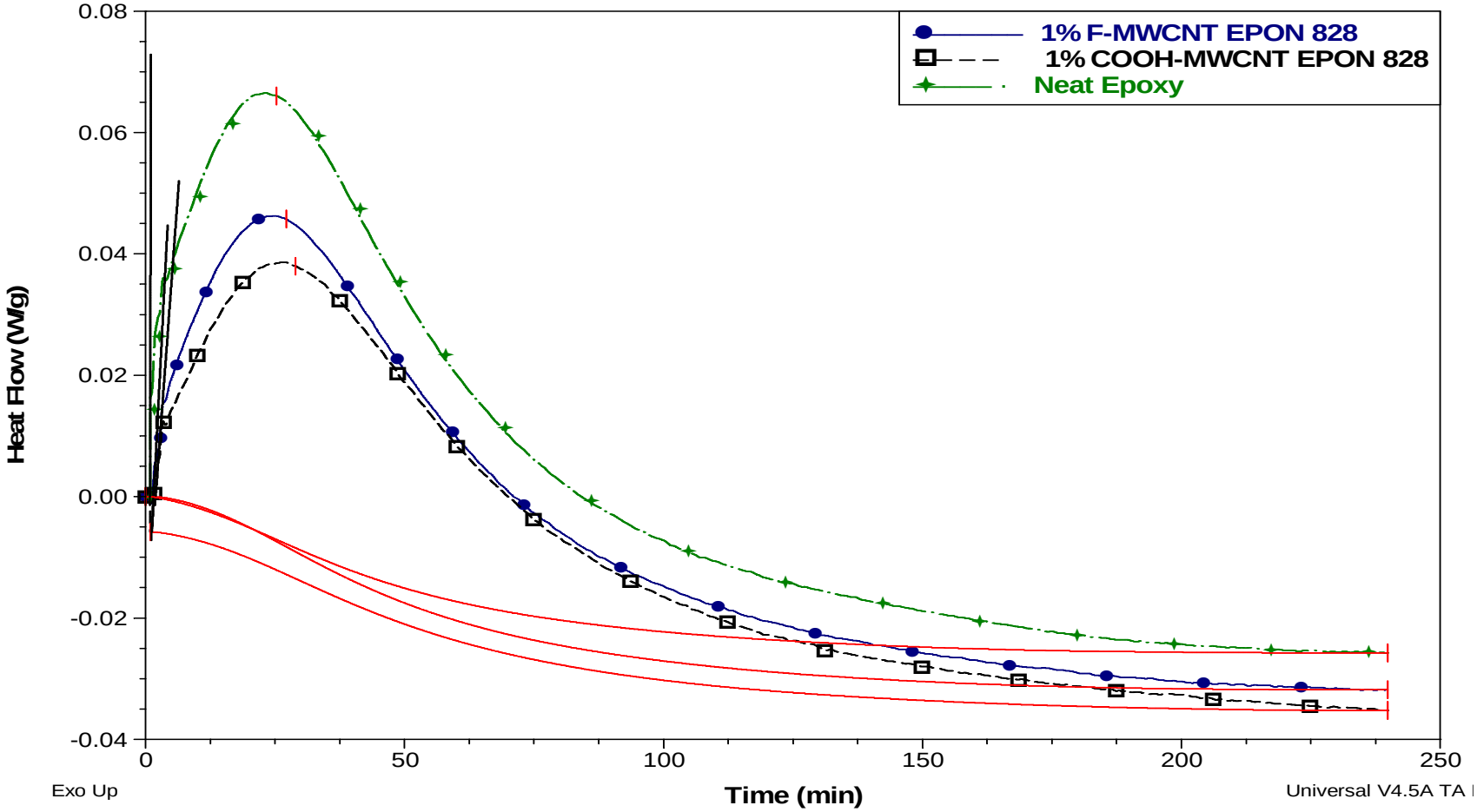
Modulated DSC
Isothermal approach

- The approach assumes that the reaction follows autocatalyzed exothermic systems and obeys the general rate equation:

$$\frac{d\alpha}{dt} = k(T)\ \alpha^{m}(1-\alpha)^{n}$$

- where $d\alpha/dt$ = reaction rate (1/sec)
  α = fractional conversion k(T) = specific rate constant at temperature T
- This approach requires three or more isothermal experiments to generate the kinetic parameters :
  - Activation energy (Ea), Pre-exponential factor Z Heat of reaction (ΔH), Reaction order (n, m) Rate constant (k)

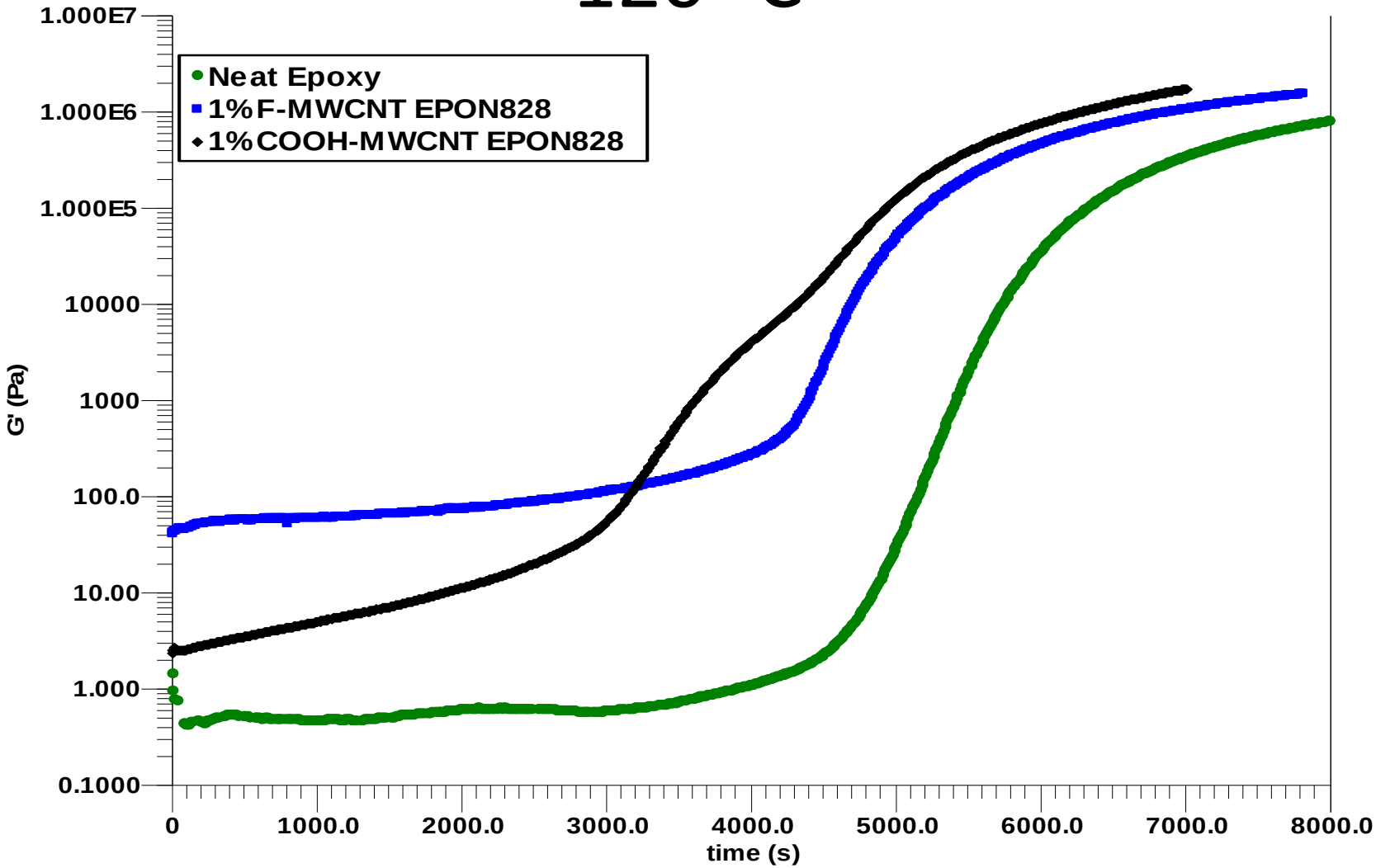
Isothermal DSC Thermograms at 120 °C for Neat resin and Nanocomposites



Activation Energies and Rate Constant for the Neat Resin and Nanocomposites

Sample	Average (ΔH) J/g	E_a kJ/mol	Rate constant min^{-1} $T_{Iso120\ °C}$
Neat Epoxy	**319.6**	**47.5**	**0.0428**
1.0 % COOH-MWCNT/EPON 828	**239.8**	**61.7**	**0.0390**
1.0 % F-MWCNT/EPON 828	**263.4**	**47.7**	**0.0428**

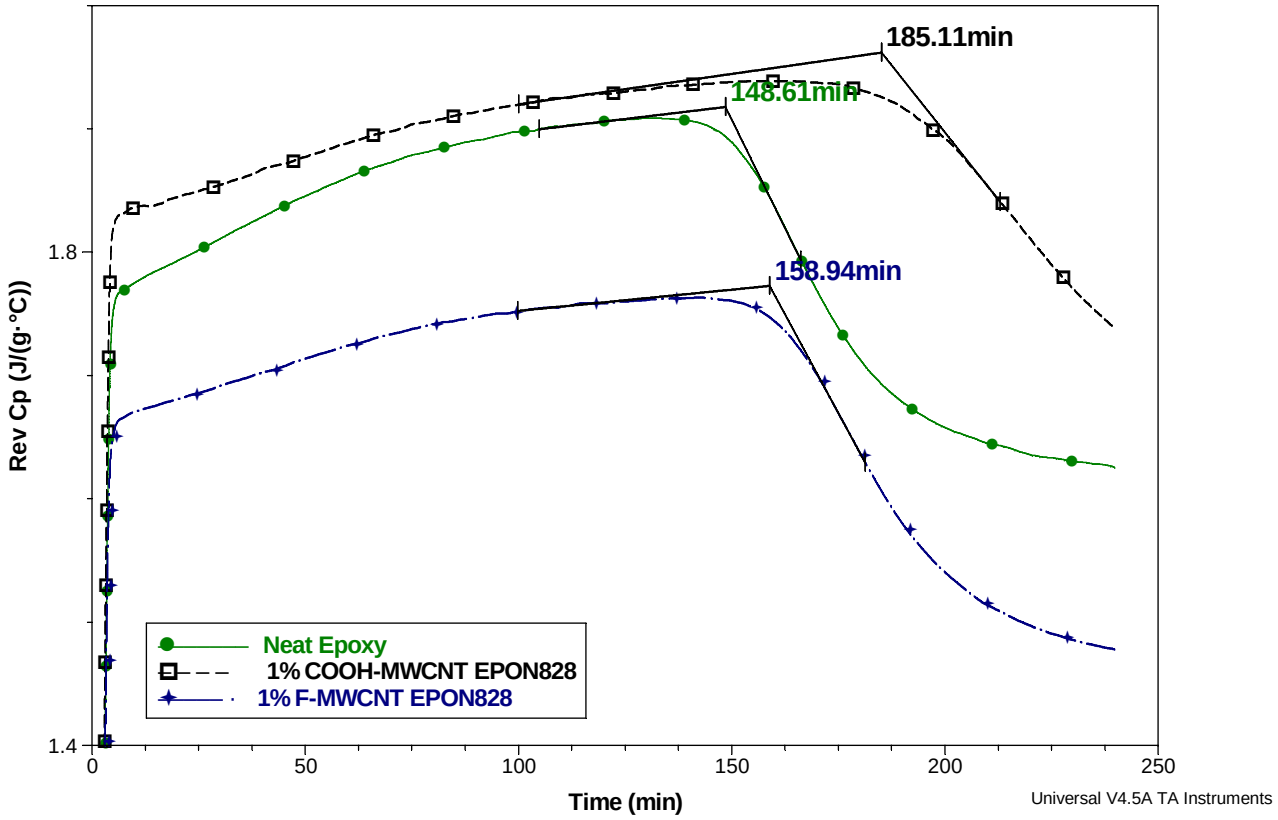
Isothermal Cure Behavior of Neat Epoxy Resin and Nanocomposites at 120 °C



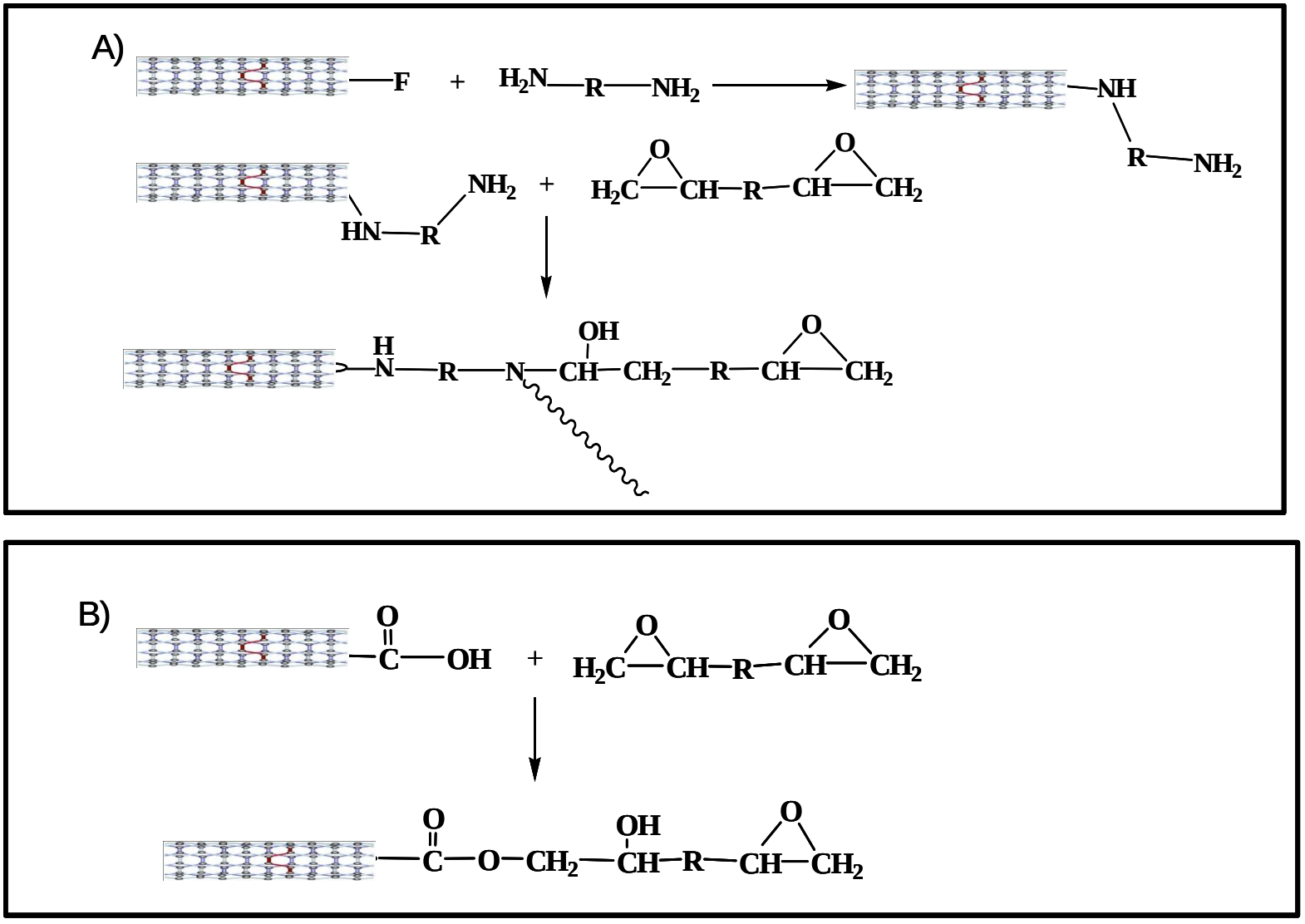
Gelation, Vitrification and Degree of Conversion and of the Neat Resin and Nanocomposites

Sample	Gel point time (min) °C	t_{vitr}(min)	Tg (°C)	Degree of Conversion (%)
Neat Epoxy	**81.4**	**149**	**119**	**95**
1.0 % COOH-MWCNT/EPON 828	**58**	**185**	**120**	**96**
1.0 % F-MWCNT/EPON 828	**78.5**	**160**	**119**	**96**

Heat Capacity



Carbon Nanotube Reaction Schemes



MDSC: Sample Preparation

- Thin, Low Mass Samples
  - Minimize Thermal Gradients
  - Allow for Faster Periods, Larger
  - Modulation Amplitudes

- Thicker, Heavier Samples
  - Minimize Baseline Curvature
  - Improve Sensitivity

MDSC: Sample Pans Standard Crimped

- Low, Consistent Mass
- Best Choice for MDSC Measurements
- Solids, Powders, Films
- Volatility may be an issue

MDSC: Sample Pans Standard Hermetic

- Use for liquid/volatile samples
- Higher Mass, Less Sensitivity
- Use Heat Sink Compound

MDSC: Purge Gas

- Nitrogen
  - Economical
  - Wide Operating Range
  - Provides Good Sensitivity

- Helium
  - Higher Thermal Conductivity
  - Facilitates Wider Range of Modulation Conditions
  - Reduces Baseline Curvature

MDSC: Purge Gas Flow Rates

- Use Purge Gas Flow Rate of 50 mL/min. (N2) & 25 ml/min (He)
  - ↗ Faster rates increase noise
  - ↗ Slower rates decrease sensitivity, increase baseline curvature

- Flow Purge Gas through Vacuum Port at 50 mL/min.
  - ↗ Improves response of furnace
  - ↗ Facilitates wider range of modulation parameters

MDSC: Heat Capacity Calibration

- Provides for Accurate Heat Capacity Measurements
- Use Either Sapphire Disc (wide temperature range) or HDPE (polymer melt)
- Choose one-point or average values
- Effects of Experimental Conditions

Variations in DSC

- Pressure DSC
- Photo DSC