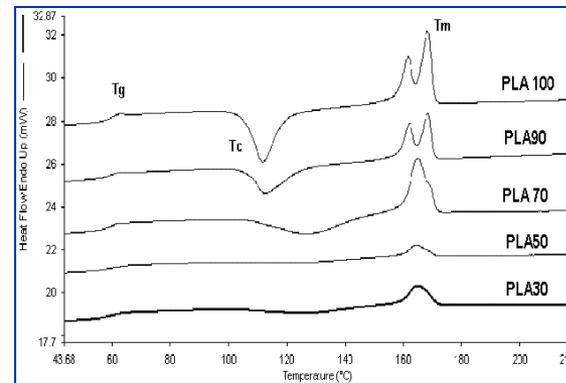


a.a. 2021-2022
Corso di

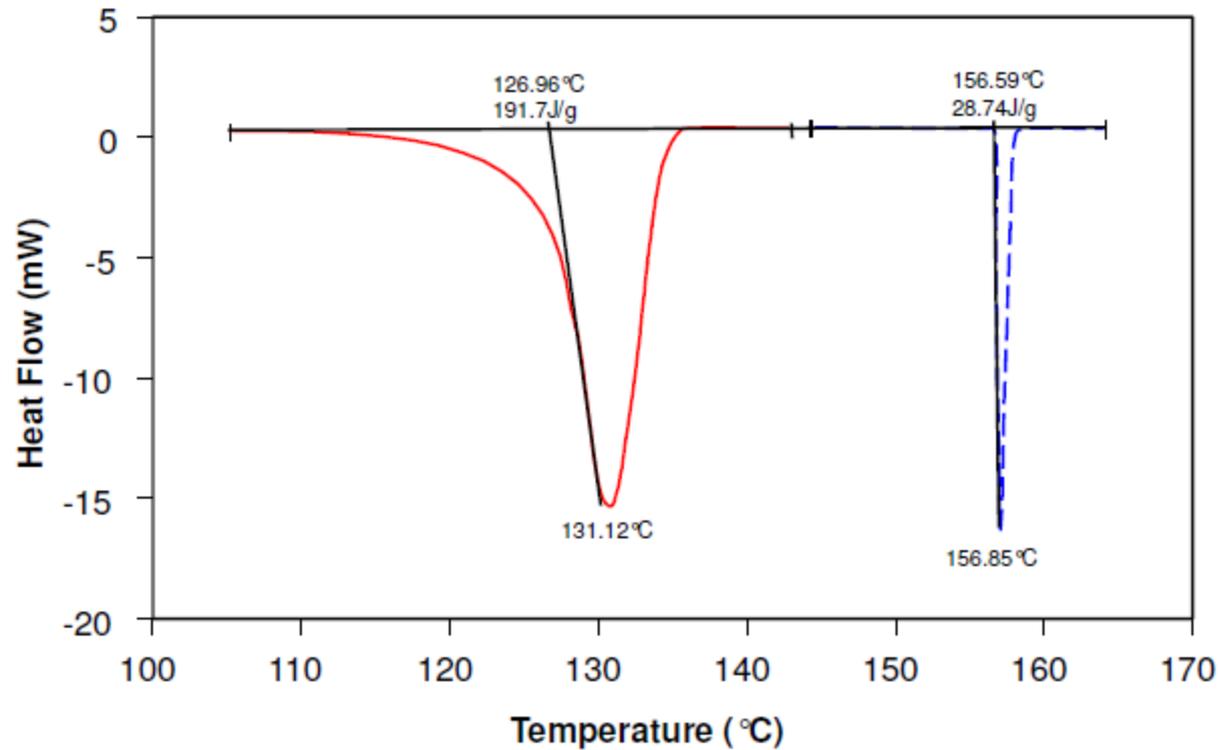
Chimica delle Macromolecole I

Prof. R. URBANI
Dipartimento di Scienze Chimiche e Farmaceutiche

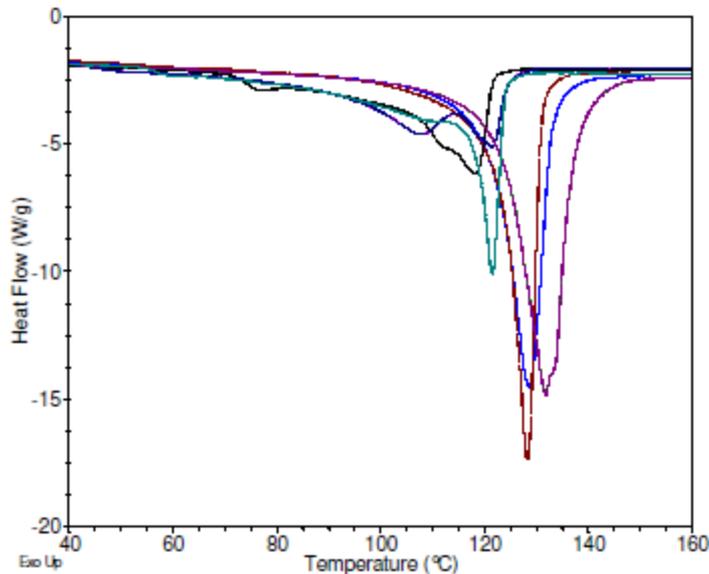
Applicazioni dell'Analisi Termica (DSC e TGA)



DSC Melting of Polyethylene vs Indium



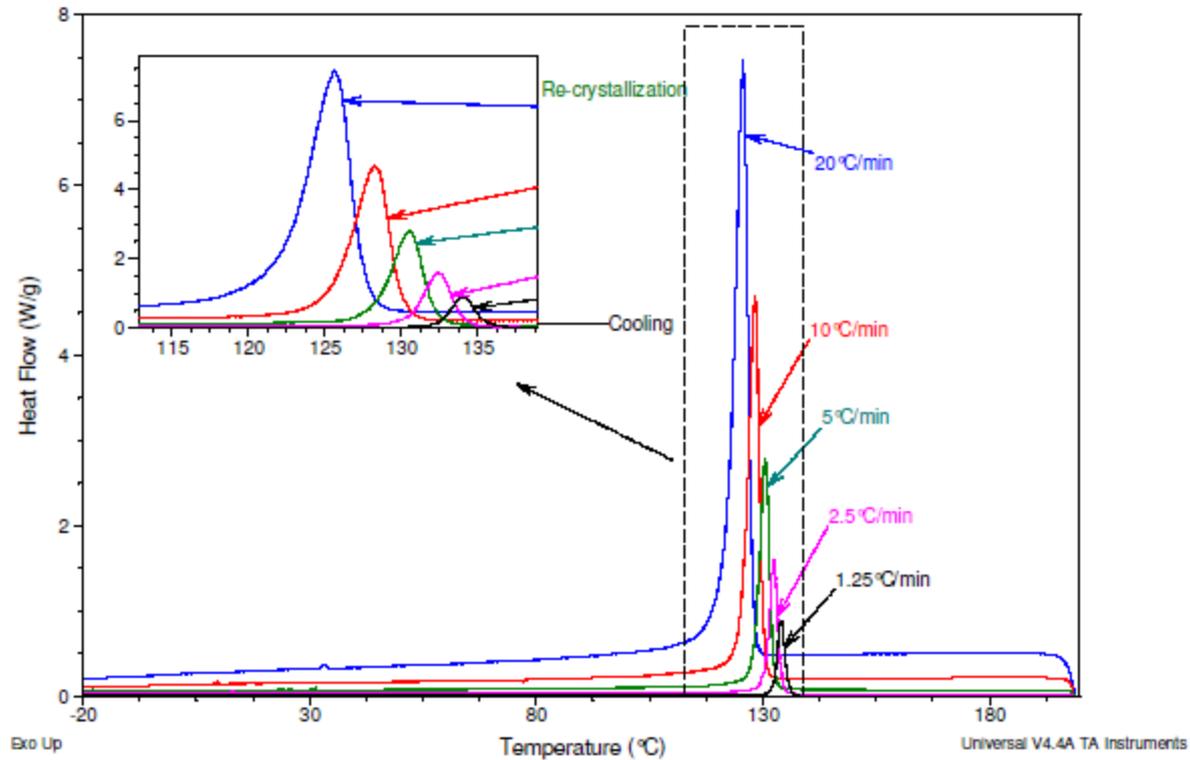
Different Types of Polyethylene



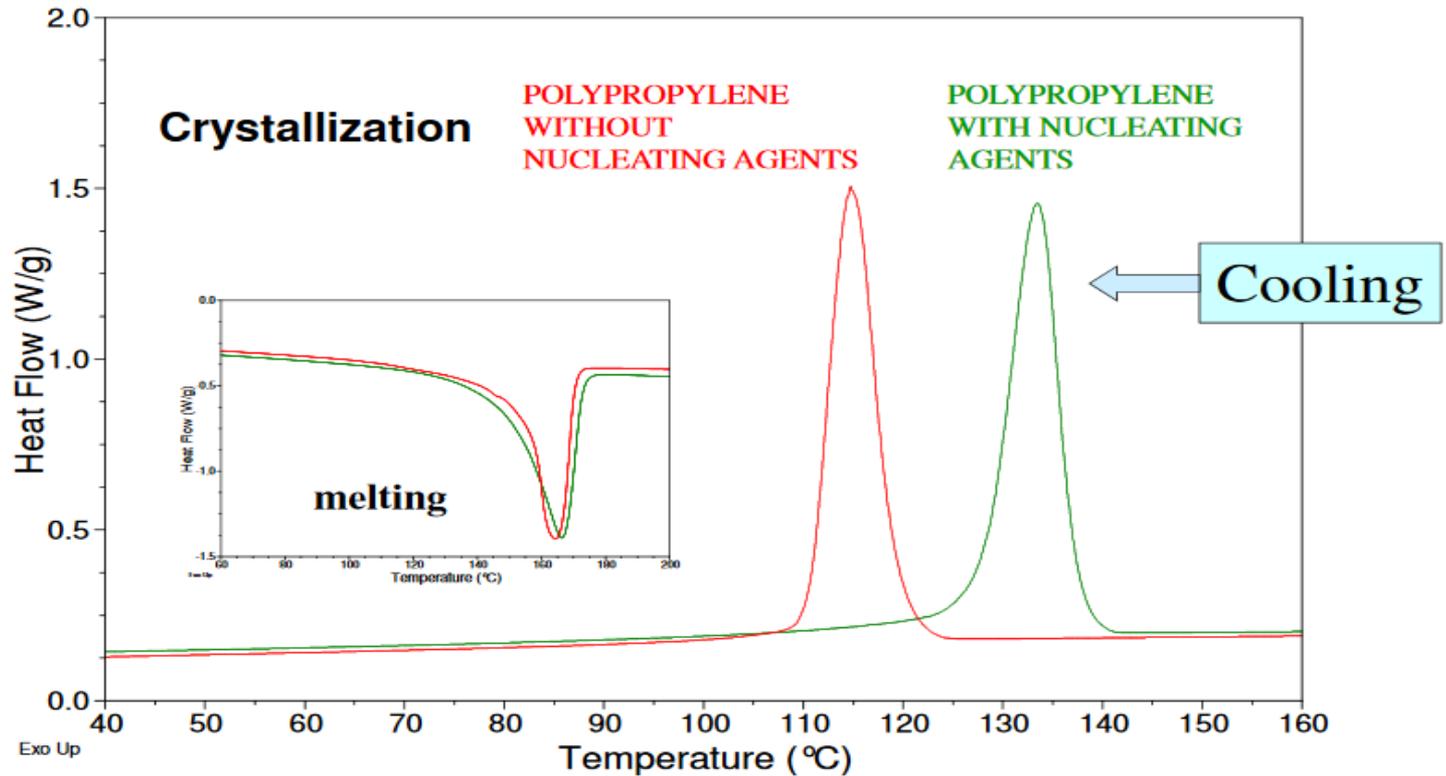
Peak shape depends on:

- Molecular weight distribution and branching
- Crystallinity
- Crystallite morphology as determined by thermal history

Effect of Cooling Rate



Effect of Nucleating Agents



Gli **agenti nucleanti** sono materiali inorganici o organici aggiunti ai polimeri per aumentare la cristallinità e accorciare i tempi del ciclo. Accelerano la transizione da materiale fuso a solido. Cambiare la cristallinità della plastica cambia proprietà come la densità e la trasparenza. I derivati chimici dell'**acido benzoico** sono noti per essere gli agenti nucleanti più efficaci. Alcuni agenti nucleanti comuni sono cariche minerali inerti come caolino, gesso, argilla ecc.

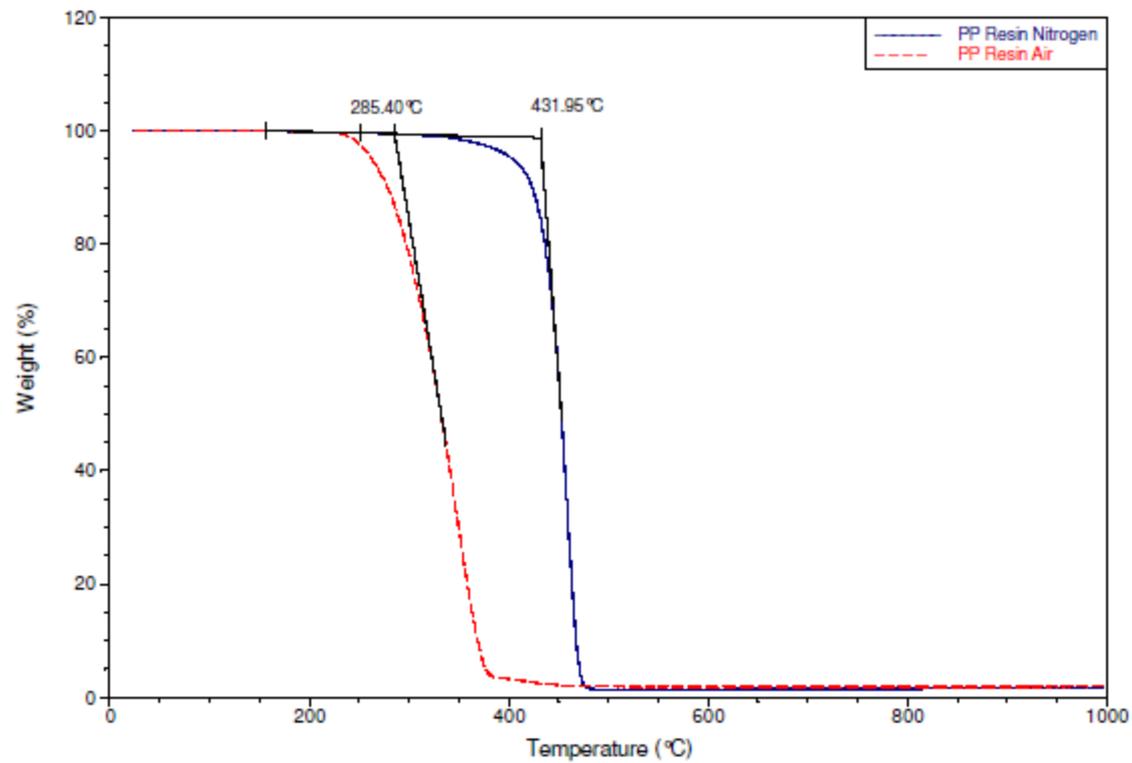
Thermal and Oxidative Stability

- Thermal and Oxidative Stability
 - Can be studied by multiple techniques
 - Studied in inert or oxidizing atmospheres
 - TGA – Best starting point
 - ◆ Weight loss or gain
 - DSC
 - ◆ Change in heat flow (typically exothermic)
 - Can also see the effect in other techniques like DMA & TMA

Starting Point for Material Characterization

- First Step – Thermogravimetric Analysis
- Look for:
 - Thermal and Oxidative Stability
 - Volatiles
 - Decomposition Temperature
 - Weight Loss Profile
 - ◆ Number of Steps
 - Residue
 - ◆ Char/Ash/Filler Presence

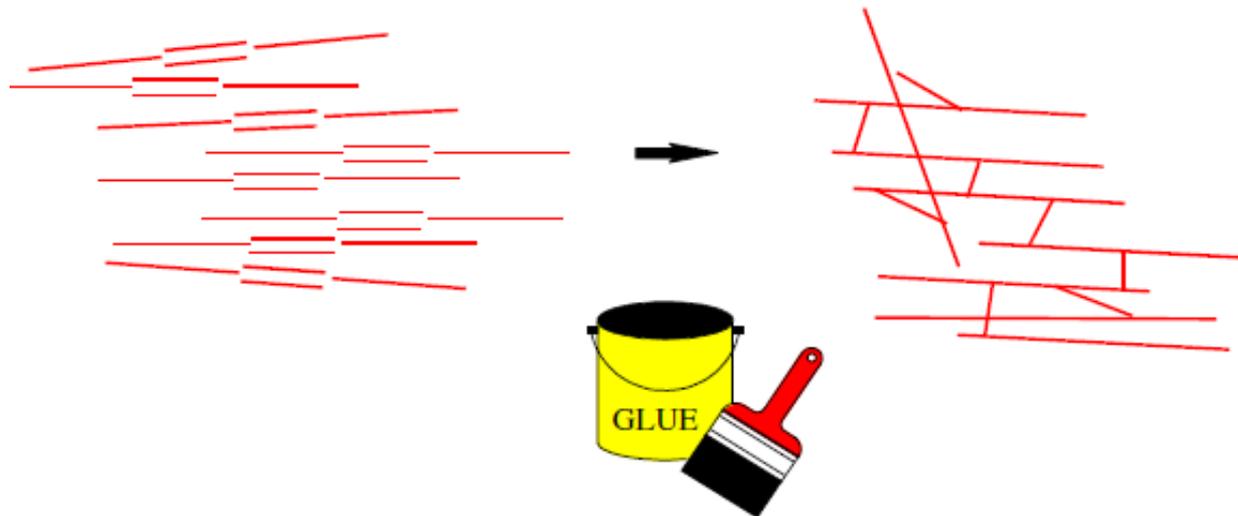
Oxidative Stability - Polypropylene



Polimeri termoindurenti

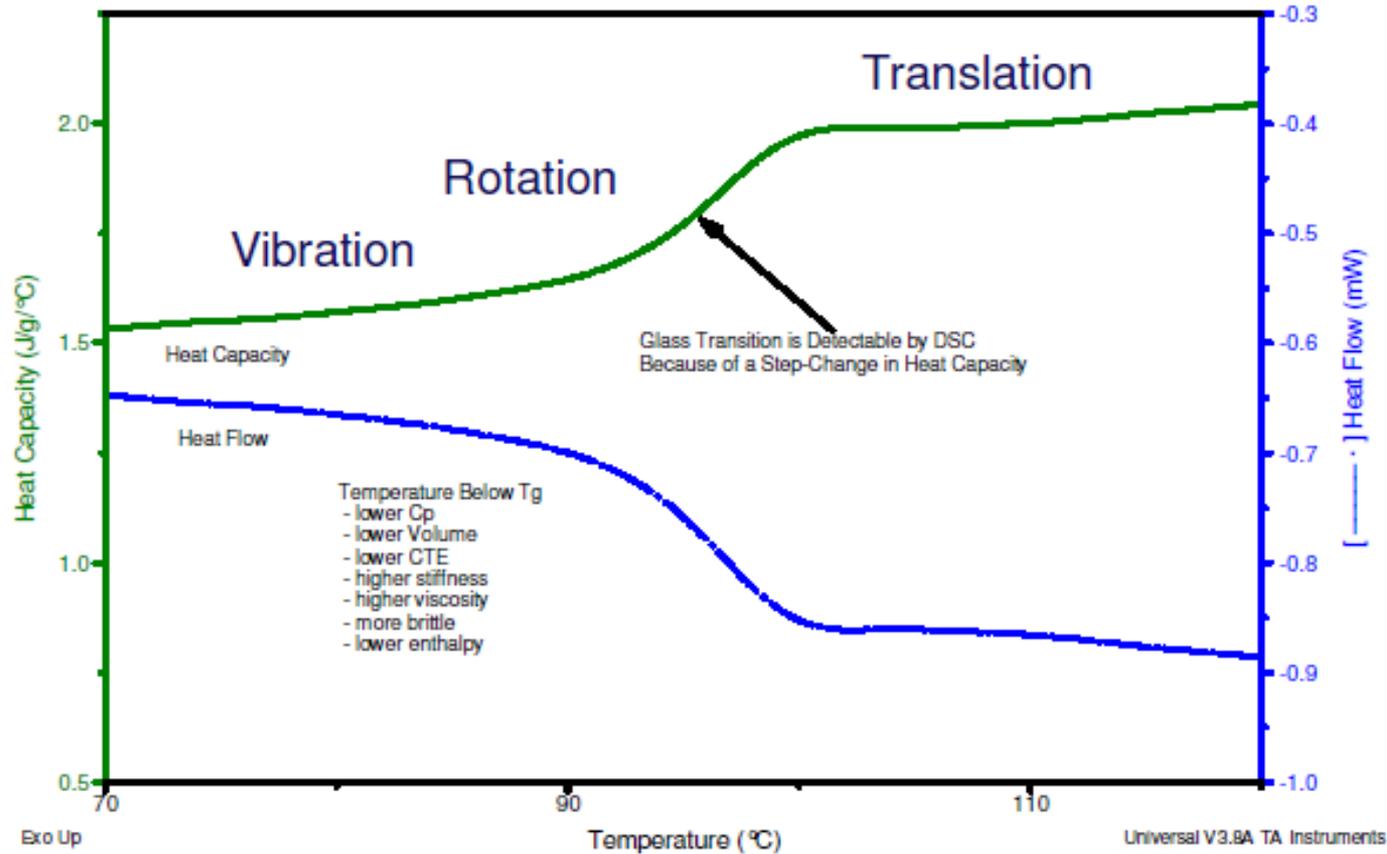


Thermosetting polymers react (cross-link) irreversibly. A+B will give out heat (exothermic) when they cross-link (cure). After cooling and reheating C will have only a glass transition T_g .

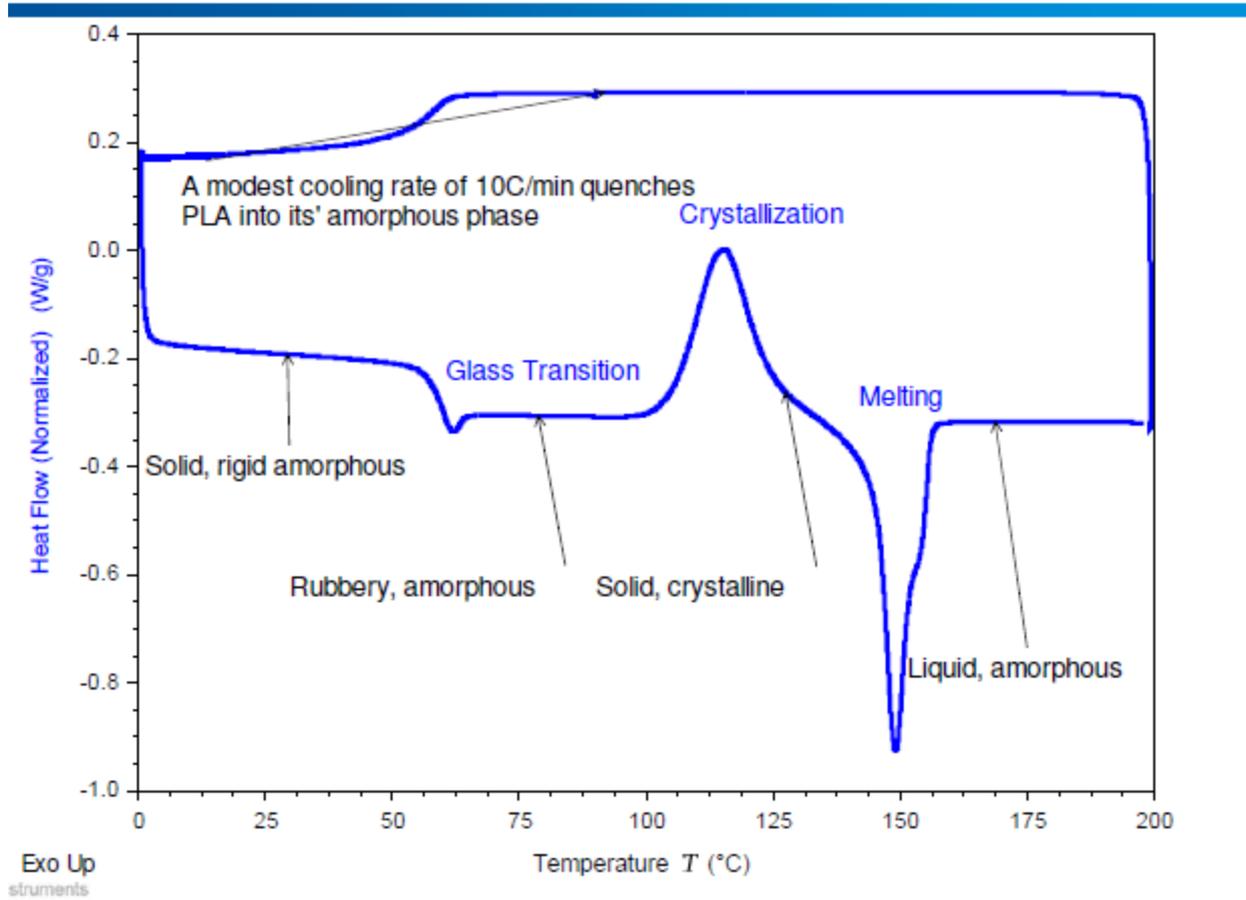


Changes at the Tg

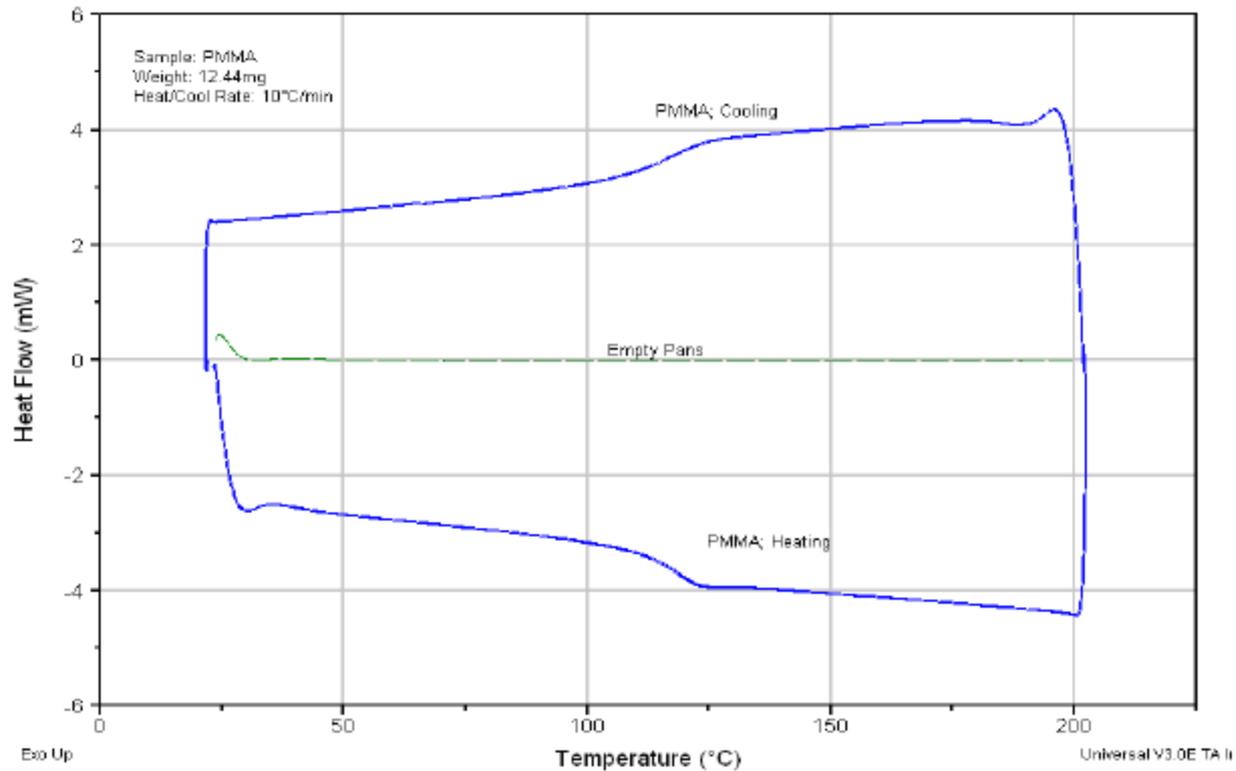
Polystyrene - Modes of Molecular Motion/Mobility



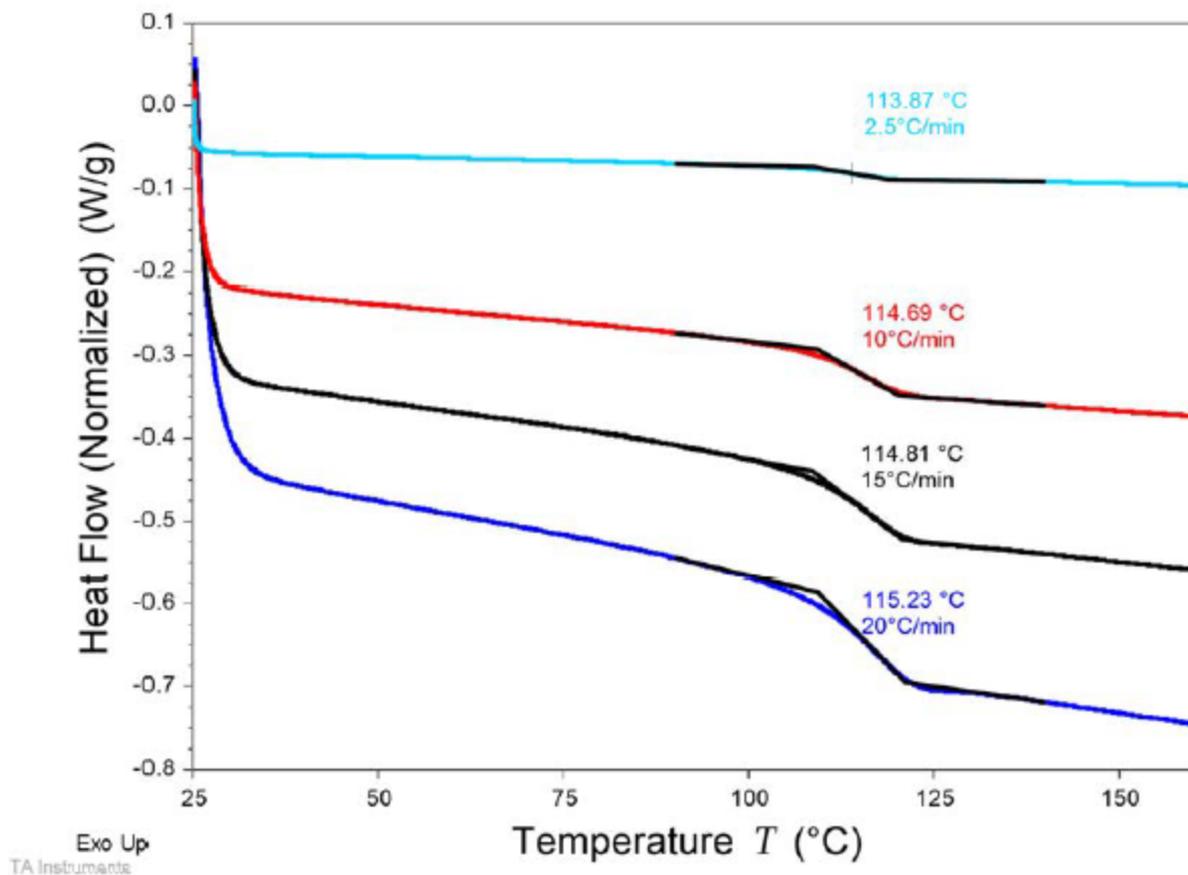
DSC Analysis of Polylactic Acid (PLA)



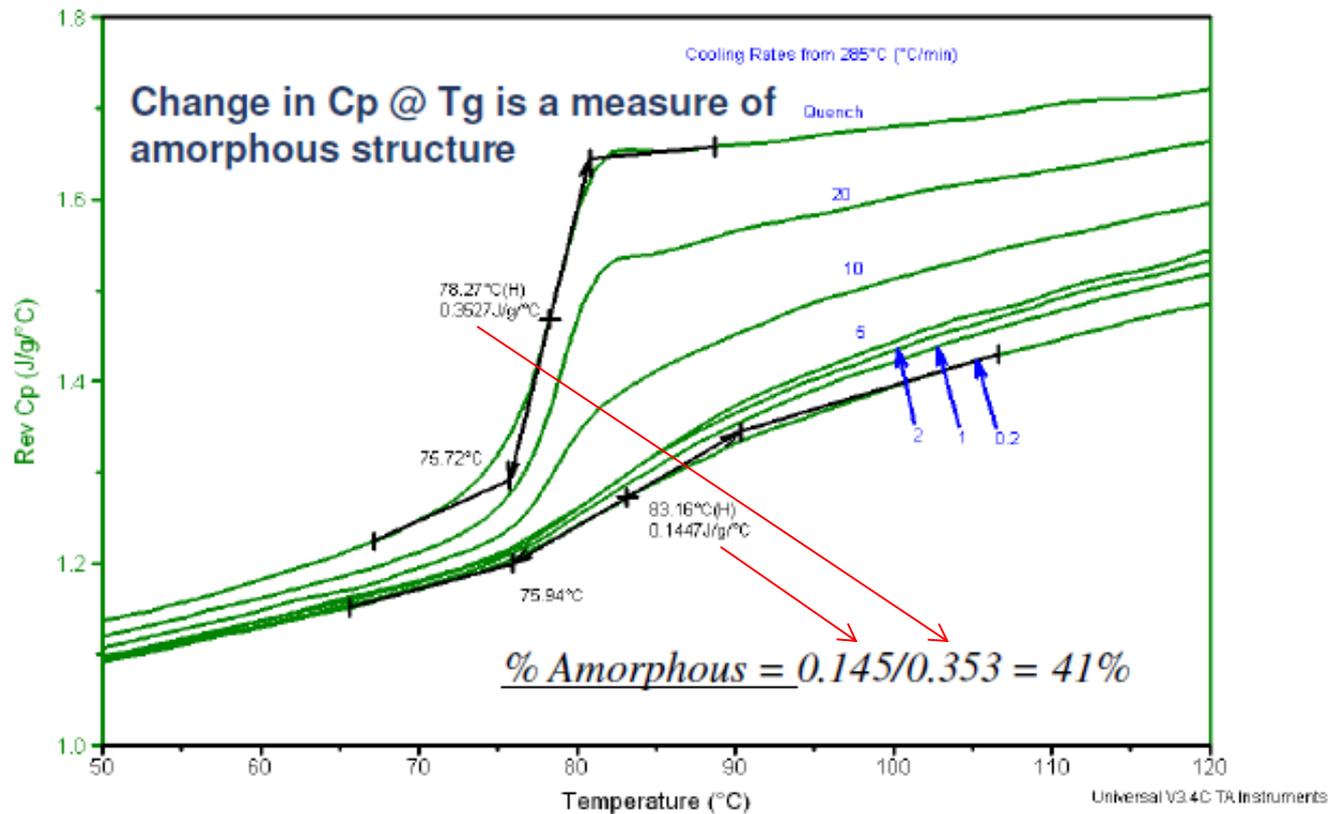
A Glass Transition is Reversible



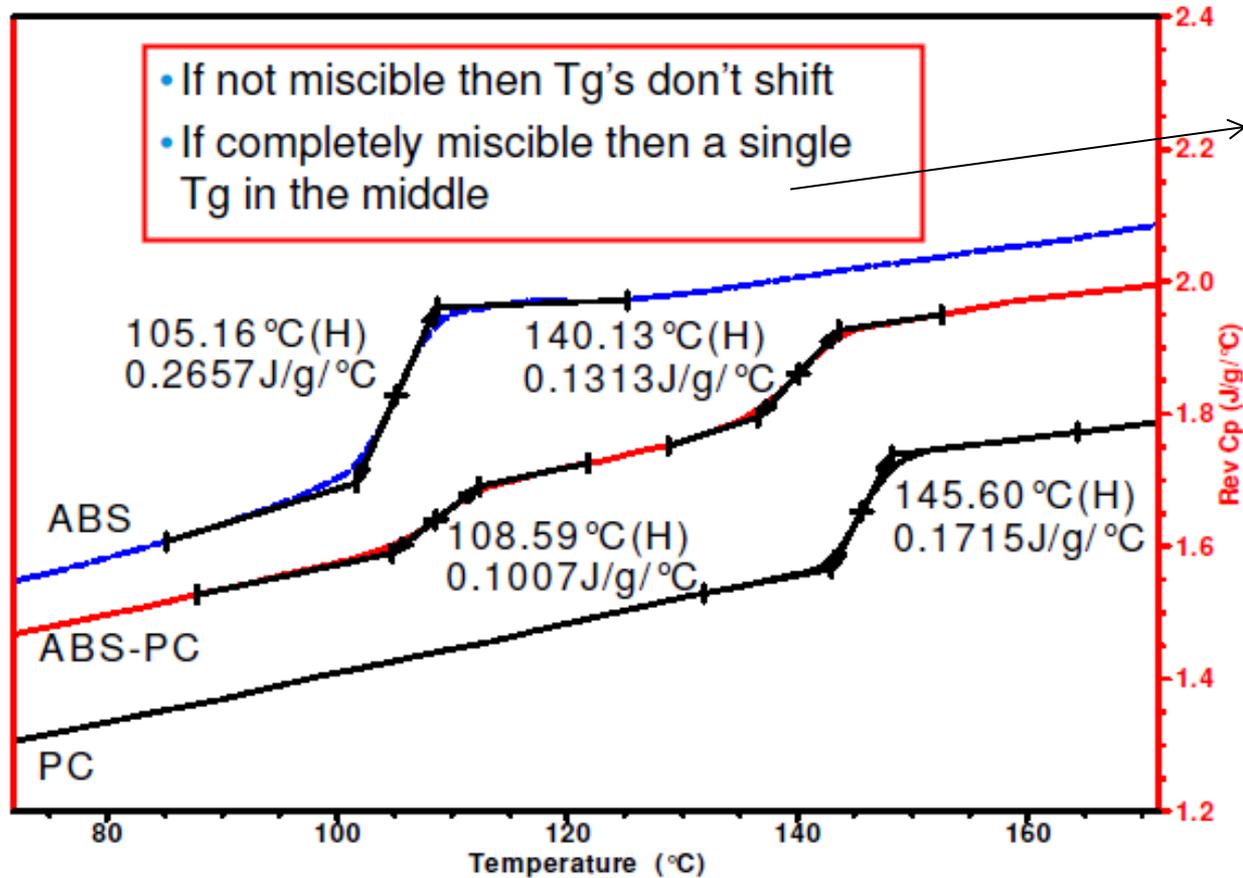
10mg PMMA Sample at Different Heating Rates



Quantification of Amorphous Structure



Partially Miscible Amorphous Phases

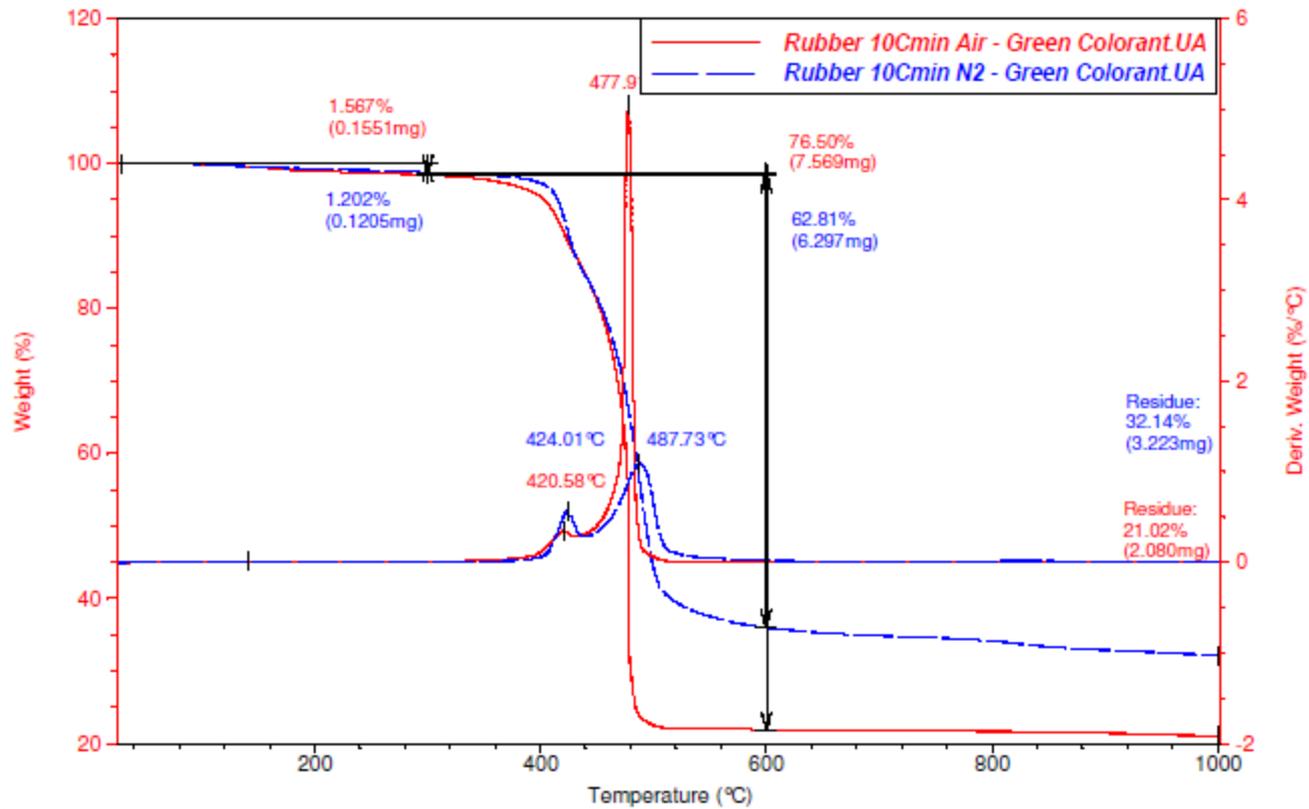


$$T_g = \frac{T_{g1}w_1 + T_{g2}w_2}{w_1 + w_2}$$

ernts

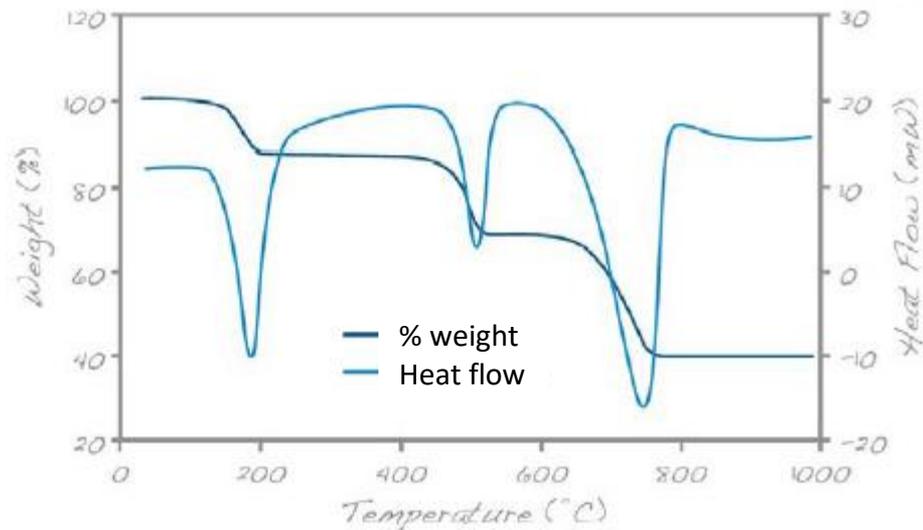
ABS: copolimero acrilonitrile-butadiene-stirene

TGA Rubber in Air vs Nitrogen

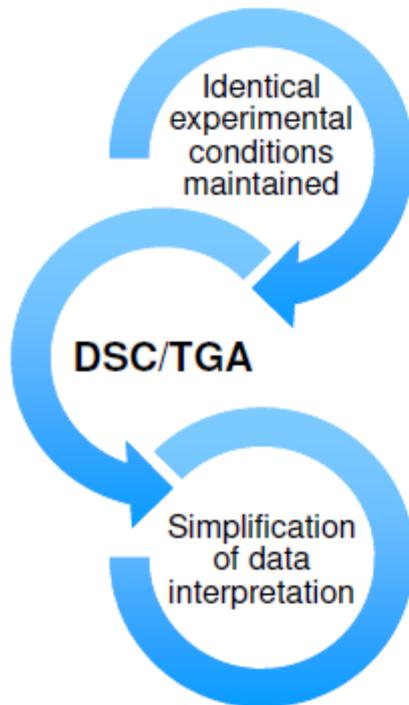


Simultaneous DSC-TGA (SDT)

Simultaneous application of *Differential Scanning Calorimetry (DSC)* and *Thermogravimetry (TGA)* of a material will measure both *heat flow* and *weight change* as a function of time, temperature and atmosphere in a single experiment.



Simultaneous DSC-TGA (SDT)



- Identical experimental DSC and TGA conditions:
 - Sample Mass
 - Heating Rate
 - Atmosphere (purge gas and flow rate)
 - Sample Crucible
- Simplification of data interpretation
 - Is the sample weight stable during an endothermic or exothermic thermal event?
 - The complimentary information allows differentiation between endothermic and exothermic events which have no associated weight loss (melting and crystallization) and those which involve a weight change (volatilization, oxidation, degradation).