
**APPLICATIONS
OF CALORIMETRY IN A
WIDE CONTEXT –
DIFFERENTIAL SCANNING
CALORIMETRY,
ISOTHERMAL TITRATION
CALORIMETRY AND
MICROCALORIMETRY**

Edited by Amal Ali Elkordy

Applications of Calorimetry in a Wide Context – Differential Scanning Calorimetry, Isothermal Titration Calorimetry and Microcalorimetry

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Preface

This book (carrying at the beginning the name of “Calorimetry”) started when I received an invitation from the InTech Open Access Publisher to be the editor of the book for my experience and publications in the field of applications of calorimetry and biocalorimetry in the analysis of small and large drug molecules. I welcomed the invitation and I was enthusiastic to handle chapters submitted from colleagues all over the world with the aim of disseminating the high quality research in application of calorimetry for the benefits of scientists, students, academics and industry (pharmaceutical, biopharmaceutical and food industries).

Calorimetry is an analytical method which can thermodynamically characterise the phase transition by determining heat capacities, enthalpies and melting temperatures of substances including oils, lipids, biological macromolecules, small drug molecules and polymers. It was an honour to read submitted chapters, to write a chapter and to divide the book into sections. Accordingly, the name of the book was changed into “Applications of Calorimetry in a Wide Context - Differential Scanning Calorimetry, Isothermal Titration Calorimetry and Microcalorimetry” to reflect the content of the book.

Finally, without the support of many other expert colleagues, who helped in the review process, completion of this book would have been difficult. The editor would like to thank the following scientists who have helped in the peer-review process: Prof. Brian Barry, Bradford School of Pharmacy, University of Bradford, UK; Dr. Paul Carter, Department of Pharmacy, Health and Well-being, University of Sunderland, UK; Dr. Shu Cheng Chaw, Department of Pharmacy, Health and Well-being, University of Sunderland, UK; Dr. Eman Ali Elkordy, Faculty of Medicine, University of Tanta, Egypt; Prof. Gamal El Maghraby, Faculty of Pharmacy, University of Tanta, Egypt; Dr. Ebtessam Ahmed Essa, Faculty of Pharmacy, University of Umm Al Qura, Saudi Arabia; Prof. Robert Forbes, Bradford School of Pharmacy, University of Bradford, UK; Dr. Wendy Hulse, Formulation technical specialist 2, Ipsen, UK.

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Application of Differential Scanning Calorimetry into Pharmaceuticals

Application of Differential Scanning Calorimetry to the Characterization of Biopolymers

Adriana Gregorova

Additional information is available at the end of the chapter

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1. Introduction

Generally, polymers can be classified according to their thermal and mechanical properties into thermoplastics, thermosets and elastomers. Thermoplastics are amorphous or semi-crystalline polymers that soft or melt during heating and solidify during cooling. The heating/cooling/heating process can be repeated without perceptible changes in thermal and mechanical properties of thermoplastics. Thermosets during heating undergo chemical changes and this process is irreversible. Elastomers can be vulcanized (cross-linked under assistance of heat, light, or special chemicals like sulfur, peroxides) that makes them reversibly stretchable for small deformations but vulcanization is the irreversible process.

The resulted properties of polymer materials and mixtures depend on the chemical and physical properties of neat polymers, additives as well as the used processing methodology. Differential scanning calorimetry (DSC) is a physical characterization method used to study thermal behavior of neat polymers, copolymers, polymer blends and composites. Generally, the non-isothermal DSC is used for the identification of neat basic polymers as well as the determination of their purity and stability. Amorphous polymers exhibit a glass transition temperature and semi-crystalline polymers may possess the glass transition temperature, a crystallization temperature, a melting temperature with various crystallization and melting enthalpies. However, these properties alter by both a presence of additives and applied polymer processing methodologies. Basically, a small quantity of sample (up to 10 mg) in pan from various materials (e.g. aluminum pan) and empty pan (reference) are treated under a defined temperature program (various combinations of thermal scans-heating/cooling, and isothermal cycles), a pressure (stable) and an atmosphere (inert or reactive). Principally, sample and reference are maintained at the same temperature, while any transition occurred in the sample needs an energy supply, which is recorded by the DSC as a rate dQ/dt against a temperature or a time. The DSC is the thermal analysis mainly used

to determine a first-order transition (melting) and a second order endothermic transition (glass transition). The sudden change in the specific heat value, C_p corresponds with the glass transition temperature as follows (Bower, 2002):

$$\frac{dQ}{dt} = mC_p \tag{1}$$

where m is the mass of the sample.

However, the determination of the glass transition of polymers with a high crystallinity content is limited. The first-order transitions such as the crystallization of a polymer during a heating (cold crystallization) or a cooling cycle (crystallization) and a melting of polymer crystals can be described by the following formula (Bower, 2002):

$$\frac{dQ}{dt} = \kappa \Delta T = \kappa \dot{T}(t - t_0) + \left. \frac{dQ}{dt} \right|_{t_0} \tag{2}$$

where κ is a thermal conductance between a sample holder and a sample, \dot{T} is a temperature increase rate, and t_0 is the start of transition.

Figure 1 shows the example of thermal transitions occurring in the injection molded sample of poly(lactic acid) (PLA) such as the glass transition, the cold crystallization and the melting. PLA is a thermoplastic aliphatic semi-crystalline biodegradable polyester. The presented molded sample had been cooled very rapidly during the processing (injection molding), so as the consequence during the second heating cycle appeared the cold crystallization peak.

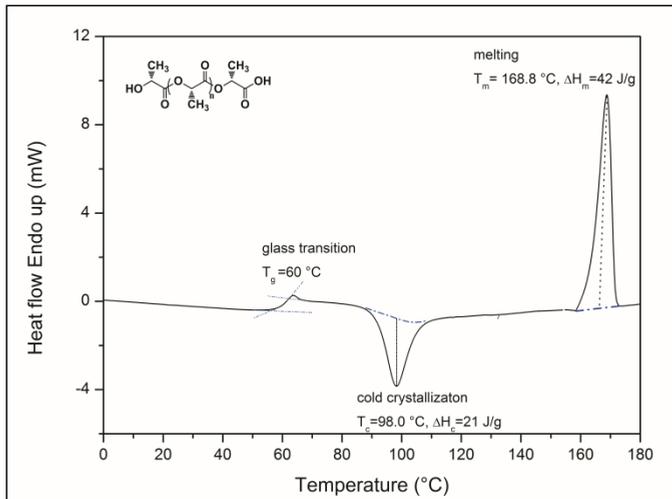


Figure 1. DSC thermogram of commercial poly(lactic acid) with $\overline{M}_w = 70\ 400$ and PDI = 1.8 detected during 2nd heating cycle (0-180°C, 10°C/min, N₂ atmosphere)

There are two types of DSC systems: 1) heat-flux (sample and reference pans are in an identical furnace block) and 2) power compensation (sample and reference pans are in two separate furnace blocks). From the practical point of view, it is important to pay attention to issues influencing an accuracy of results as follows:

- an instrument calibration, baseline subtractions,
- a selection of working gas (N₂, He, O₂),
- a selection of pans (e.g. Al-, Pt-, Ni-, Cu-, Quartz-pans, hermetic or non-hermetic pans),
- a proper thermal contact between sample and pans,
- a temperature program (heating cycle usually should start about 50°C under and finish about 10-20°C above the expected measured transition temperature),
- a sufficient slow scanning rate (to avoid the neglecting of the requested thermal transition),
- a sufficient purity and source of sample (neat polymer, polymer blend, composite, before or after processing, kind of the processing).

The aim of this chapter is to show some examples of the practical use of the DSC within the investigation of an amorphous biopolymer – lignin and semi-crystalline biodegradable polymer – poly(lactic acid) as well as to discuss the dependence of the thermal properties on the value of the molecular weight of polymer, the polymer processing methodology and the presence of additives in the polymer mixtures.

2. Effect of molecular weight on glass transition temperature

Amorphous and semicrystalline polymers undergo a phase change from a glassy to rubbery stage at a glass transition temperature (T_g).

At T_g the segmental mobility of molecular chains increases and a polymer is more elastic and flexible. The value of T_g is dependent on the various factors such as a molecular weight of polymer, a presence of moisture, a presence of the crystalline phase (in the case of semicrystalline polymers). The dependence of T_g on a number-average molecular weight is described by Flory-Fox equation:

$$T_g = T_g^\infty + \frac{K}{M_n} \quad (3)$$

where T_g^∞ is a glass transition for polymer with the infinite number-average molecular weight, K is an empirical parameter related to the free volume in polymer and M_n is a number-average molecular weight of polymer.

2.1. Thermal properties of Kraft lignin extracted with organic solvents

In this sub-chapter, an example of the effect of various extraction solvents on molecular weight properties and thermal properties of Kraft lignin is shown.

Lignin is polydisperse amorphous natural polymer consisting of branched network phenylpropane units with phenolic, hydroxyl, methoxyl and carbonyl groups. Its molecular weight properties as well as functional groups depend on its genetic origin and used isolation method. Differential scanning calorimetry is the useful method to determine its glass transition temperature. The value of T_g depends on the molecular weight, the thermal treatment, the humidity content and the presence of various contaminants in lignin sample.

Generally, phenyl groups together with the cross-linking restrict the molecular motion of lignin as an amorphous polymer in contrast to propane chains. Moreover, the intermolecular hydrogen bonding decrease T_g in the contrast to the methoxyl groups (Hatakeyama & Hatakeyama, 2010). Lignin might be defined as a natural polymeric product produced by the enzymatic dehydrogenation polymerization of the primary methoxylated precursors such as *p*-coumaryl-, coniferyl- and sinapyl- alcohols (Figure 2).

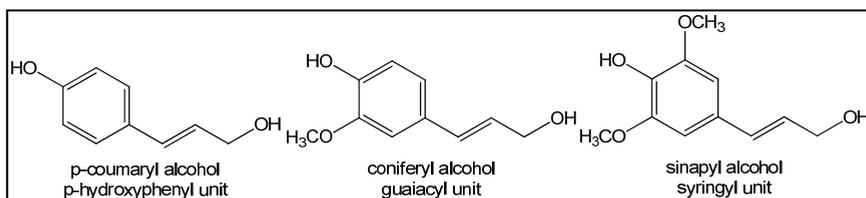


Figure 2. Lignin monomer building units

The structure of lignins depends on their natural origin and also on the external and internal conditions existing during lignin macromolecule synthesis and isolations. The large heterogeneity of lignin’s structures makes it difficult to determine the overall structure of lignin. High variability of substituents on phenyl propane unit together with auto-coupling reaction gives rise to different lignin’s structures depending on its origin and isolation method (Figure 3).

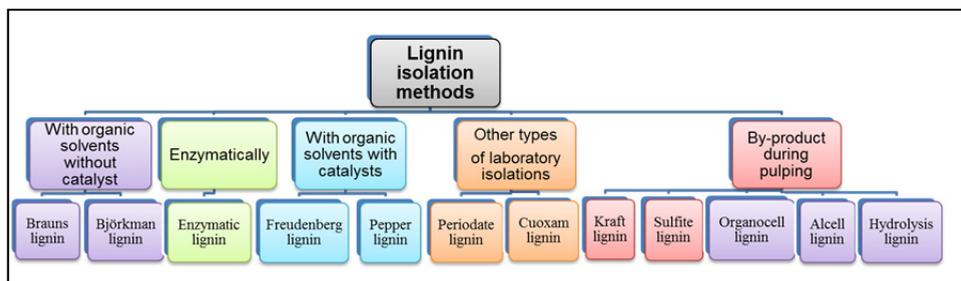


Figure 3. Lignin isolation methods

Kraft lignin used in this study was isolated from commercial spent pulping black liquor through the acidification with 98% sulphuric acid to pH=2 (Zellstoff Pöls AG, Austria). Precipitated, filtered, washed and dried Kraft lignin was extracted at the room temperature with organic solvents with Hildebrand solubility parameters in the range of 18.5-29.7 MPa^{1/2} (see Table 1) and then again filtered and dried.