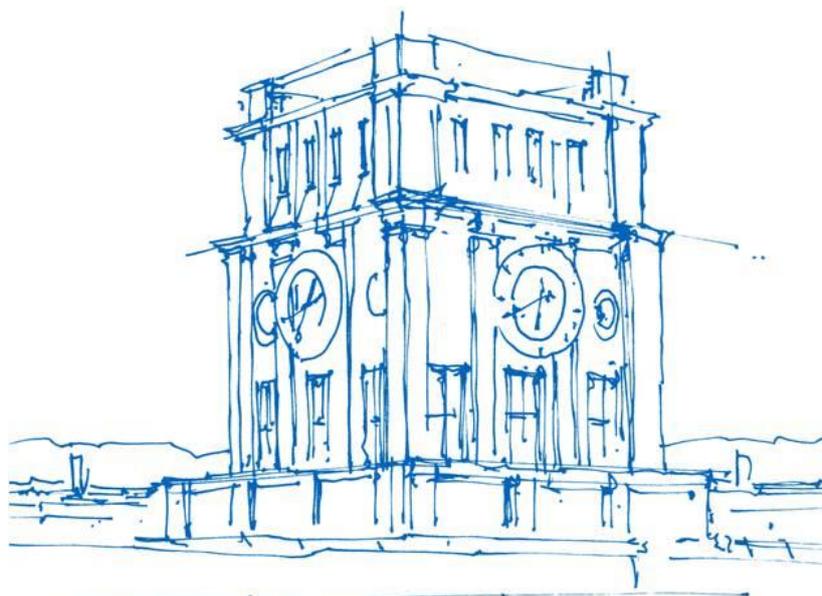


Characterization of Polymers with Differential Scanning Calorimetry

Technische Universität München
Physik-Department
Fachgebiet Physik weicher Materie

FoPra, SS 2019



Uhrenturm der TUM

Contents

1. Introduction

1.1 Thermoplastic polymers

1.2 Thermal analysis by differential scanning calorimetry

1.3 Glass transition

1.4 Melting

1.5 Crystallization

2. Differential Scanning Calorimetry

2.1 Working principle

2.2 Experimental procedure

3. Experiment

3.1 Thermal analysis of PP, PMMA and PVC

3.2 Data treatment

4. Questions

5. References

1. Introduction

Polymers are large molecules composed of tens or hundreds of repeating chemical units—the monomers—bound together, forming a long chain (Fig. 1). The physical properties of polymers may be as diverse as very soft, rubbery, or brittle to very robust, depending on the choice of monomers. Because polymers afford a wide range of mechanical and thermal properties that fit the needs in different aspects of human activities, they are very useful materials and play an important role in our daily life. The most common polymeric products include all kinds of plastic bottles, plastic bags, toys as well as rubbery shoe soles. Moreover, polymers can also act as functional additives in organic solar cells and bullet-proof jackets.

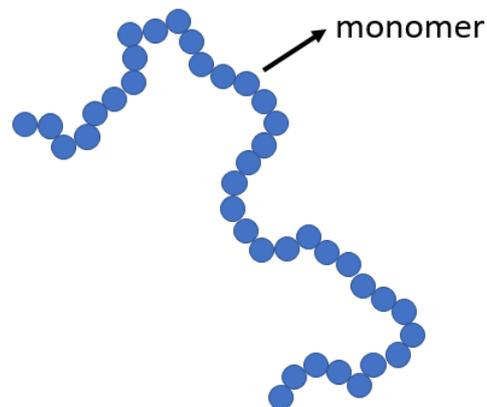


Figure 1. Schematic representation of a polymer. The repeating chemical units are called monomers.

1.1 Thermoplastic polymers

The term “thermoplastic polymer” refers to those polymers that are not chemically crosslinked. They will soften and melt upon heating and can thereby easily be molded into any desired shape, e.g. by injection molding.

These polymers are often semi-crystalline, i.e. they consist of crystalline and amorphous regions, as depicted in Fig. 2a. In the crystalline regions, the polymer chains arrange themselves in an ordered way, which is mainly possible at low temperatures. In the amorphous region, in contrast, the chains are randomly arranged.

Upon heating the semi-crystalline polymer, the chains become more flexible, which favors the amorphous state. Thus, as the melting temperature is reached, the crystallites start to melt, and the polymer becomes totally amorphous (Fig. 2b). Thus, the physical properties of thermoplastics strongly depend on the temperature.

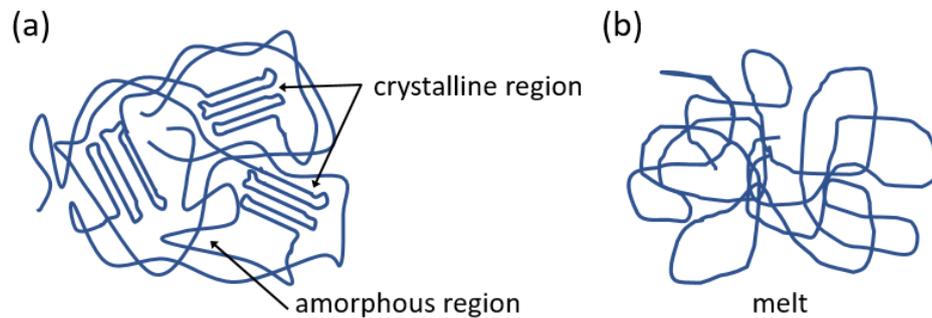


Figure 2. (a) Typical morphology of a semi-crystalline polymer, consisting of crystalline and amorphous regions. (b) Polymer melt in the amorphous state.

Besides the temperature, also the molecular structure of the polymer determines whether the polymer can form crystals and how high the degree of crystallinity is. For example, in poly(vinyl chloride) (Fig. 3a), the polymer chains cannot form crystallites and stay amorphous even at low temperatures. Polypropylene, in contrast (Fig. 3b), has the ability to form crystallites, as the temperature is decreased.

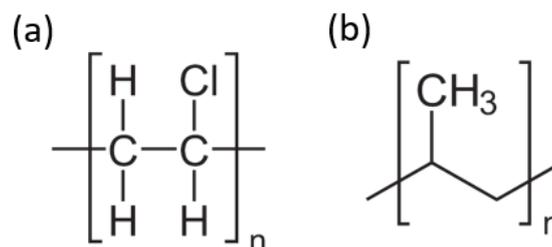


Figure 3. Chemical structure of (a) poly(vinyl chloride) and (b) polypropylene, where the former is an amorphous polymer, while the latter is a semi-crystalline polymer.

1.2 Thermal analysis by differential scanning calorimetry

In thermal analysis of thermoplastic polymers by differential scanning calorimetry (DSC), the heat flow rate upon a temperature change is measured. Heating up/cooling down the thermoplastic polymer sample, there will be endothermic or exothermic phase transitions. For example, heating the polymer, it will undergo the glass transition and then melt; when subsequently cooling down the polymer, it crystallizes. The corresponding endothermic/exothermic peaks in the plot of heat flow rate versus temperature are shown in Figure 4. Several important characteristic transitions are observed, such as the glass transition temperature (T_g), the melting point (T_m) and the crystallization temperature (T_c) along with the degree of crystallinity (χ_c). These transitions and the corresponding terms are described in detail in the following sections.

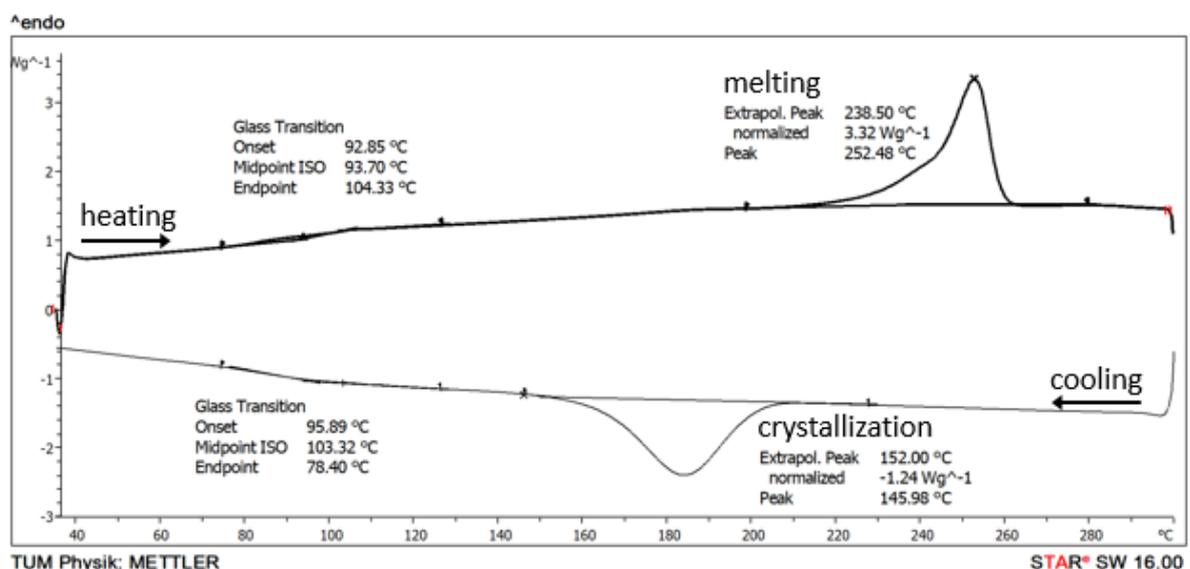


Figure 4. Heat flow rate in dependence on temperature, showing the glass transition temperature and the melting point during heating (upper line), and the crystallization and the glass transition during cooling (lower line).

1.3 Glass transition

The glass transition temperature, T_g , is a characteristic temperature for each polymer. Heating up a polymer from its solid state, the mobility of polymer chains undergoes a stepwise increase at T_g , where it turns from a glassy, brittle state to a rubbery, elastic state. In the plot of the heat flow rate versus temperature, the heat flow rate significantly increases at T_g , as shown in Figure 4. This glass transition proceeds over a certain temperature range, going from a low heat absorption

rate to a higher heat absorption rate, and T_g is determined as the temperature in the middle of this range. The increase in the heat absorption rate indicates the increase in the heat capacity, C_p (energy needed per unit temperature change), of the polymer.

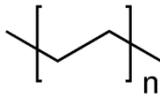
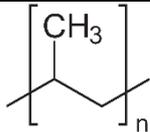
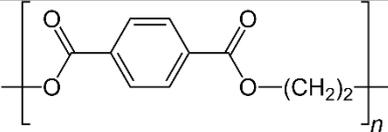
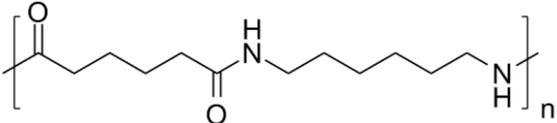
1.4 Melting

Upon further heating the thermoplastics, the crystallites in the semi-crystalline polymer will melt at the so-called melting point, T_m . At T_m , the well-defined structure of the crystallites is destroyed, and the polymer becomes totally amorphous. In DSC, this is reflected in a significant peak of heat absorption (Fig. 4), where the absorbed heat is used for melting of the crystalline fraction of the polymer. Thus, the total amount of absorbed heat can be used to calculate the crystallinity (χ_c) of the polymer before the measurement, by the following equation:

$$\chi_c = \frac{\Delta H}{\Delta H_{crystal}}$$

Here, ΔH is the heat adsorbed during the melting of the actual sample, which is determined by the area under the melting peak. $\Delta H_{crystal}$ is the enthalpy of melting of the crystal, i.e. the heat needed to melt the crystal per unit mass. The enthalpies of melting of some common polymers are provided in Table 1.

Table 1. Enthalpies of melting for commonly-used polymers [1]

Polymer name /abbreviation		Chemical structure of monomer	$\Delta H_{crystal}$ (J/g)
Polyethylene	PE		293
Polypropylene	PP		207
Poly(ethylene terephthalate)	PET		145
Polyamide 66	PA 66		176

1.5 Crystallization

Upon cooling down the polymer from its amorphous state, some of the polymer chains rearrange into an ordered structure, i.e. the polymer crystallizes. However, melts from long and therefore entangled polymers cannot crystallize completely. Thus, the polymer melt will become partially crystalline, but partially still be amorphous, with crystallinities typically in the range 10-80 %. The crystallinity, χ_c , is used to quantify the volume fraction of the polymer sample that is crystalline. The crystallization process is exothermic, resulting in a heat-releasing peak in DSC scan (Fig. 4).

2. Differential Scanning Calorimetry

2.1 Working principle

Differential scanning calorimeters (DSC) are widely used to characterize the thermal properties of materials.

The DSC chamber contains two sample positions, one of which is used for the sample and the other one as a reference (Fig. 5). The reference is usually an inert material, which has no thermal transitions in the temperature range under investigation. During the measurement, both, the sample and the reference are heated with a defined rate in the chamber within the pre-set temperature range, where the sample is expected to undergo thermal transitions. The temperature difference between the sample and the reference is measured by thermopile sensors giving the differential thermocouple voltage, which is converted into energy per unit time by the instrument using a calibration constant. The result is expressed as the heat flow rate versus temperature for the sample, as compared to that of the reference.

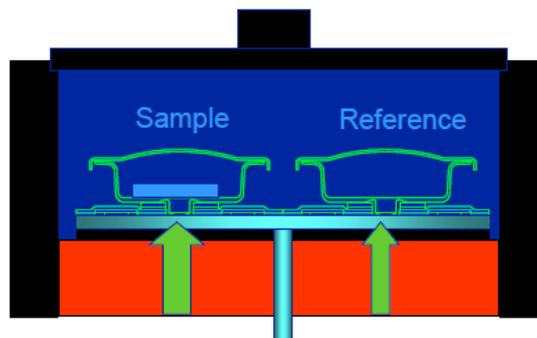


Figure 5. Components and setting in a DSC chamber, including two positions respectively for the sample and the reference pans. The sample and the reference are heated by the same furnace, and their temperature will be measured respectively [2].

2.2 Experimental procedure

First, an overview on the handling of the DSC instrument will be given by the tutor. After that, switch on the DSC device, open the N₂ gas valve and start the software in the computer. Lastly, turn on the cooling agent.

The next steps to perform the measurements on the three samples are as follows:

1. In the software, define the temperature scan procedure by combining isothermal and dynamic segments. Run the measurement with the sequence heating, cooling and then heating*. Thus, the scan will be programmed as followed, at the example of polypropylene:
 - (1) stay isothermal at -40 °C for 10 min
 - (2) dynamic temperature scan from -40 °C to 200 °C with 20 °C/min
 - (3) stay isothermal at 200 °C for 10 min
 - (4) dynamic temperature scan from 200 °C to -40 °C with 20 °C/min
 - (5) stay isothermal at -40 °C for 10 min
 - (6) dynamic temperature scan from -40 °C to 200 °C with 20 °C/minChoose the following parameters:
 - nitrogen gas (N₂) flow rate: 50 ml/min
 - pan: Aluminum 40 µl standard
2. Save as...(date_polymer_group#)
3. Key-in the sample name and sample mass
4. Send measurement
5. As soon as “waiting for sample insertion” shows up in the bottom column, carefully place the sample into the chamber and click OK.
6. While the measurement is running, watch on the gas flow to be 50 ml/min.
7. As soon as “waiting for sample removal” shows up in the bottom column, carefully take out the sample.
8. Display and analyze the last measurement using the software.

*The purpose for the first heating run is to eliminate the thermal history during the processing of the polymer, which can possibly lead to changes of the glass transition temperature and the crystallinity of the polymer.

3. Experiment

3.1 Thermal analysis of PP, PMMA and PVC

Do DSC experiments on the following polymer samples within the temperature ranges given (all at rates of 20 °C/min):

- (a) polypropylene, scan from -40 °C to 200 °C
- (b) poly(methyl methacrylate), scan from 70 °C to 170 °C
- (c) poly(vinyl chloride), scan from 40 °C to 130 °C

Program the temperature scan as described in section 2.2, with the corresponding temperature range given for each polymer sample.

3.2 Data treatment

- Classify the polymers into amorphous polymers and semi-crystalline polymers.
- Using the first cooling run, determine T_c . (if there is a crystallization peak)
- Using the second heating run, determine T_g , T_m and the crystallinities, using the values provided for $\Delta H_{crystal}$ in Table 1.

4. Questions

- In the plots of the DSC results, what does “exo” and “endo” mean? Is it relative to the polymer sample or relative to the DSC instrument?
- Compare the DSC plots from the first heating run with the second heating run of the three polymer samples. Do they provide the same glass transition temperature and melting temperature? Try to give some possible reasons for the difference.
- Why does the melting peak (for crystalline polymers) span over a certain temperature range rather than being a sharp peak?
- Provide the definition of heat capacity.
- Looking at the heat flow rate curves of the second heating run, does the heat capacity increase or decrease, after the temperature is increased from below to above T_g ? What is the reason for this decrease/increase?
- Try to find the heat capacity of polymers, wood, glass and metals, and sort the values. Which one is the largest and which one the smallest? How can the difference of heat capacity be felt, when we hold the materials in our hands?
- Based on the experimental results, which polymers among the three are glassy, and which ones are more fluid-like at room temperature? Try to explain how T_g affects the applications of these polymers.

5. References

[1] Bernhard Wunderlich, "Thermal Analysis of Polymeric Materials", Springer, Berlin (2005) pp. 777-800

[2] Sutariya, P. G. (2014). What is Thermal Analysis ? [PowerPoint slides]. Retrieved from [http://bhavanscollegedakor.org/images/pdf/sci/what%20 thermal_analysis.pdf](http://bhavanscollegedakor.org/images/pdf/sci/what%20thermal_analysis.pdf)