Introduction

According to Wunderlich et al. [1] six basic thermal effects govern the thermal analysis of polymers: vibrational heat capacity, heat capacities arising from large amplitude molecular motion, reversible transitions, annealing, secondary crystallization, and primary crystallization and melting. The first three of them are reversible, whereas the last three are irreversible. All these effects may occur during melting. The measured heat capacity is then always the superposition of all effects appearing. While the vibrational heat capacity and primary crystallization and melting are always present for semicrystalline polymers, the other effects may appear or not. It is therefore an interesting task to distinguish the different reversible and irreversible processes during polymer melting. It was claimed [2, 3] that temperature-modulated differential scanning calorimetry (TMDSC) allows the deconvolution of the measured signals into reversing and nonreversing contributions to heat capacity. Then an assignment to the reversible or irreversible effects given earlier should be possible. Nevertheless, the meaning of the complex (reversing) heat capacity in the melting region of polymers is not well understood. Here we compare the heat capacity of semicrystalline polymers with the heat capacities obtained from simple model calculations to highlight some of the inherent problems of heat capacity determination by TMDSC.

TMDSC [4] is one tool to determine the complex heat capacity in the melting region of polymers. The modulus of the complex heat capacity, often called the reversing scan measurement. A time dependence of the melting process is observed for poly(ethylene terephthalate) and bisphenol A polycarbonate. For an ethylene–octene copolymer the temperature dependence of the fraction melting reversingly is obtained. The model, which does not take any time dependence into account, also predicts the contribution from the nonreversing melting to the phase angle. Limitations and possible extensions of the model are discussed.

Abstract Temperature-modulated differential scanning calorimetry allows the measurement of the total heat capacity, the so-called reversing heat capacity, and their difference, the so-called nonreversing heat capacity. There is an ongoing controversy about the meaning of these quantities in the melting region of polymers. To better understand the contributions to the reversing heat capacity, the results from model calculations are compared with experimental results for different semicrystalline polymers under different experimental conditions. This allows a more precise distinction between reversing and nonreversing contributions to the total heat capacity in a temperature-modulated differential scanning calorimetry scan measurement.
heat capacity, is shown for several semicrystalline polymers in the temperature range between the glass-transition, $T_g$, and final melting, $T_m$, in Fig. 1. By subtracting baseline heat capacity \[5\], the excess heat capacity was obtained, and this is presented versus normalized temperature.

Obviously the polymers behave extremely differently. While polyethylene shows a large excess heat capacity over the whole temperature range between the glass transition and melting, syndiotactic polystyrene and bisphenol A polycarbonate (PC) give a basically flat curve, which indicates the absence of excess heat capacity over a relatively wide temperature range. Other polymers fill in the space between these two limiting cases. Because the excess heat capacity must be related to molecular processes at the crystal surfaces \[6, 7, 8\] a close inspection should yield information about the dynamics of the molecular processes \[9, 10, 11, 12, 13\]. Under certain conditions, complex heat capacity measurements allow us to distinguish between reversing and nonreversing contributions to polymer melting. Unfortunately, just in the melting range nonreversing processes such as melting itself contribute significantly to the complex heat capacity. Under these conditions a deconvolution into a reversing and a nonreversing component according to Reading and coworkers \[2, 3\] is meaningless unless the contribution from the nonreversing processes to the complex heat capacity is known.

A full description of the different contributions to the apparent heat capacity seems to be difficult because of serious calibration problems in the melting range of low thermal conducting materials such as polymers \[14\]. If melting is not an instantaneous process but, for example, nucleated and therefore not only temperature-dependent but also time-dependent, the problem becomes even more complex \[15, 16, 17, 18, 19, 20\].

Here we address the question of how nonreversing melting contributes to the amplitude of the periodic part of the heat flow rate in TMDSC and consequently to the complex (reversing) heat capacity. Possible falsification of the measured heat capacity and the phase angle is discussed with the example of extremely simplified (partly unrealistic) model calculations. To do so, the total heat capacity is assumed to be the superposition of a reversing baseline heat capacity and an excess heat capacity with a known contribution from reversing melting. Applying a typical temperature time profile as in TMDSC to this model sample yields a modulated heat flow rate. Here it is assumed that all processes occur instantaneously. No time-dependent processes, such as relaxation, super heating, or heat transfer, are taken into account. Total, complex, reversing, and nonreversing heat capacities are computed as common in TMDSC \[2, 21, 22\]. The results of model calculations for different temperature time profiles for different semicrystalline polymers are compared with the measurements.

### The model

#### Analytical function for baseline and excess heat capacity

For the calculations it is assumed that the heat capacity in the melting region consists of two contributions. The first is the always the reversible baseline heat capacity, $c_{p\, b}$, which changes during the melting in a sigmoidal manner. The second contribution is the excess heat capacity, $c_{p\, excess}$ due to the heat of fusion, which can be nonreversing, reversing, or partly reversing.

$$c_p(T, t) = c_{p\, b}(T, t) + c_{p\, excess}(T, t)$$

(1)

The baseline heat capacity results from the heat necessary to change the temperature of the sample without changes in the phase distribution \[5\]. By assuming the baseline heat capacity to be the superposition of the heat capacities of the liquid and the solid (crystalline and rigid amorphous) material, one can calculate the baseline heat capacity according to Eq. (2) from the temperature dependence and the time dependence of the crystallinity, $\chi_c$, and the temperature dependence of the liquid and crystalline heat capacities, $c_{p\, liquid}$ and $c_{p\, crystalline}$ respectively.

$$c_{p\, b}(T, t) = \chi_c(T, t)c_{p\, crystalline}(T) + [1 - \chi_c(T, t)]c_{p\, liquid}(T)$$

(2)