Analysis of the reorganization of poly(ethylene terephthalate) in the melting range by temperature-modulated calorimetry

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Summary

Although melting of flexible macromolecules is an irreversible process, it was demonstrated recently with temperature-modulated calorimetry (TMC) that some of the overall melting may be reversible within a fraction of a kelvin. This was taken as evidence for incompletely melted molecules with a remaining molecular nucleus. The reversing heat capacity that characterizes this effect was observed to decrease with time. It is shown by new TMC experiments that this time effect is not induced by the temperature modulation, but is due to an inherent annealing process. It is also proven that it is not dependent on the type of calorimeter.

Introduction

A small, locally reversible component of melting was first discovered by temperature-modulated differential scanning calorimetry (TMDSC) on the example of poly(ethylene terephthalate) (PET) (1,2). Later, the same effect has also been seen for poly(oxyethylene) (POE) of sufficiently high molecular mass (3), poly-*p*-dioxanone (4), poly(ether ether ketone) (PEEK) (5) and poly(trimethylene terephthalate) (6). Similarly, the full irreversibility of melting of well-crystallized, low molar-mass POE (3) and full reversibility of the melting of indium (7) and isotropization of liquid crystals (8) could be demonstrated with TMDSC.

The amount of locally reversible melting was noted to decrease with crystal perfection and with time. The latter was first observed when testing over a long period of time at constant underlying temperature with quasi-isothermal TMDSC (1). Based on these experiments and prior information on the melting of macromolecules (9), it was concluded that the reversible melting was a local process occurring on a molecular scale. If a part of a moleculae larger or equal to its molecular nucleus (10, 11) remained crystallized or restrained on the crystal when the modulation reversed the melting process, these partially melted molecules could then recrystallize reversibly within a fraction of a kelvin.

The kinetics of this process seems complex. A number of questions about the new observations are in need of answers. Two of these are addressed in this paper: 1. Is there any

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influence from the particular calorimeter used? 2. Is the modulation itself causing the time-dependence of the slow decrease of this process with time? In the research described in this paper four different calorimeters were used to address the locally reversible melting of PET, and the reversible heat capacity was measured after annealing in the melting range with and without modulation to check on the influence of modulation.

Experimental

For the study an easily available standard poly(ethylene terephthalate) (PET) was used, purchased from Scientific Polymer Products, Inc., (No.57 PET). Four different types of TMDSC equipment were employed: 1.) The Modulated Differential Scanning Calorimeter, MDSC[TM] of TA Instruments, Inc., Thermal Analyst 2910. This is a heat-flux calorimeter with modulation at the heater block, controlled at the sample thermocouple. Such arrangement leads to a constant modulation amplitude at the sample thermocouple and variable modulation amplitudes at the reference and the heater block. 2.) The Mettler-Toledo Alternating DSC, ADSC[TM] 820. Also a heat-flux type calorimeter, but the modulation of the heater is controlled in the heater block, so that thermal effects at the sample do not affect the modulation amplitude. 3. and 4.) Two power-compensation Dynamic DSCs, DDSC[TM] of Perkin Elmer of types DSC2 and DSC7. In this case the modulation is introduced at the average temperature. With the DSC 2 a sinusoidal oscillation was supplied from a lock-in amplifier to the temperature control. With the DSC 7, modulation was realized with a series of linear heating and cooling cycles (sawtooth modulation).

A detailed description of the TMDSC method can be found, for example, in (12). Quasi-isothermal measurements have been performed with sinusoidal modulation, amplitude $A_T = 0.5$ K and period $p = 60$ s, except for the Perkin Elmer DSC7 were a saw tooth modulation with the same parameters was used. In the quasi-isothermal method (13) the modulation occurs about a constant base temperature T_o:

$$T_s(t) = T_o + A_T \sin (\omega t - \varepsilon) \tag{1}$$

where T_s is the sample temperature; ω, the frequency $(2\pi/p)$; and ε, the phase lag from a reference oscillation. Data were taken after steady state had been attained. Larger temperature ranges can be covered by step-wise change of T_o, as illustrated in Fig. 1 (2). The TMDSC data were taken every 2 K as an average of 10 min, utilized after 10 min to assure steady state. The reversing heat flow in the melting region is small relative to the apparent heat capacity. The shift of fusion to higher temperature results from annealing due to the much slower heating in TMDSC. Only standard DSC can be used to measure the total heat of fusion, while the TMDSC permits to assess possible reversing effects during melting.

The sample masses in the new experiments were about 10 mg. Before each measured quasi-isotherm, the same sample preparation was carried out. From the melt at 573 K the sample was cooled to 373 K with a rate of 20 K min^{-1} and then crystallized for 10 min.
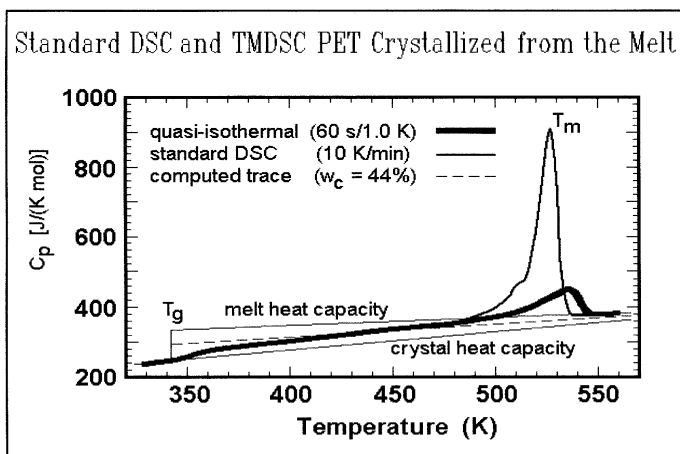
Standard DSC and TMDSC PET Crystallized from the Melt

Figure 1 Comparison of DSC and TMDSC, data of (2)

Subsequently the samples were heated with 20 K min^{-1} to about 10 K below T_o of Eq (1) which was then approached with 1 K min^{-1} to prevent an overshoot of temperature.

The value of the reversing heat capacity was calculated from the ratio of heat-flow amplitude to the heating-rate amplitude [dT_s/dt, see Eq. (1)]:

$$C_p(\text{rev}) = K \times \frac{HF}{A_T \omega} \tag{2}$$

where K is a calibration constant, and the heat flow HF is proportional to the temperature difference between reference and sample (ΔT). The data taken with the Perkin Elmer DSC2 of the melt at 573 K were calibrated with heat-capacity information from the ATHAS data bank (14). All other experimental data were fitted to this scale.

Results

Figure 2 shows the reversing heat capacity of PET as a function of time for a series of identical quasi-isothermal experiments at 513 K with the four calorimeters. This temperature is inside the melting range of PET, as can be seen from Fig. 1. The beginning of quasi-isotherm for the 2910 MDSC™ could not be considered since there was a small underlying heating for about 3 minutes before the system really reached steady state. The Perkin Elmer DSC7 system did not collect data until after the first three periods of the quasi-isotherm. In other respects the four curves coincide within the experimental uncertainty and no effort was made to separately identify the differently colored curves of the original data. The reversing heat capacity at 5 min, 2.6 J K^{-1} g^{-1}, corresponds to 500 J K^{-1} mol^{-1}, a higher value than seen in Fig. 1 for a better crystalline sample which was analyzed only after many quasi-isothermal measurements, and thus after rather long-time annealing. After 60 min of measurement $C_p(\text{rev})$ of Fig. 2 is about 400 J K^{-1} mol^{-1}, close to the data in Fig. 1. It is seen clearly that
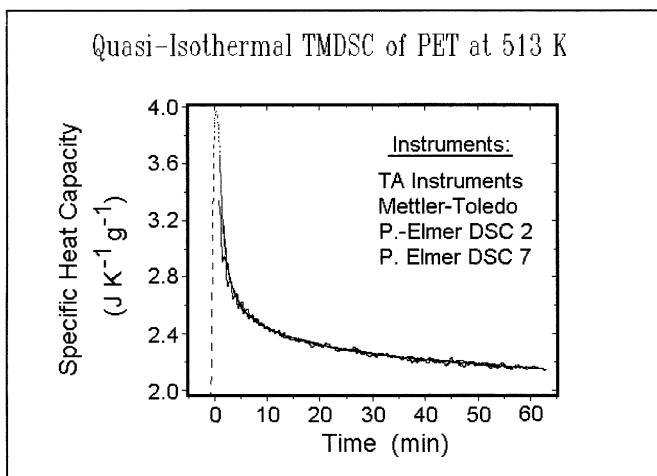
Quasi-Isothermal TMDSC of PET at 513 K

Figure 2 Comparison of data from the four calorimeters used.

at longer times the reversing heat capacity would decrease even further, as was proven in a 360 min long-time annealing experiment at 522 K, described in (1).

Figure 3 represents Perkin Elmer DSC2 traces, illustrating the time dependence of the reversing heat capacity of PET at 513 K after different durations of isothermal annealing, indicated by the arrows in the figure. Each annealing is then followed by quasi-isotherms for
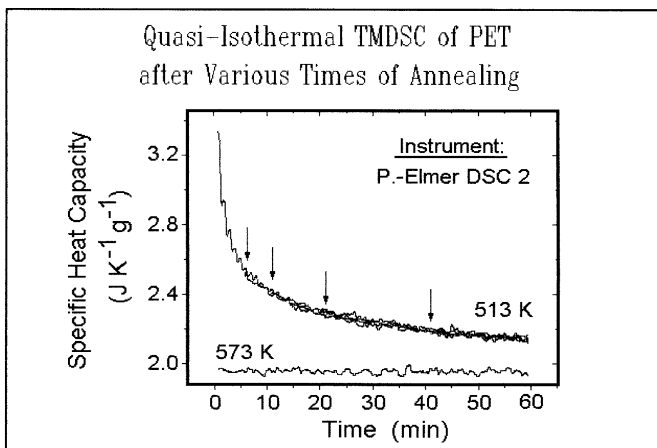
Quasi-Isothermal TMDSC of PET
after Various Times of Annealing

Figure 3 Data by TMDSC after isothermal annealing times without modulation indicated by the arrows. For comparison a TMDSC trace is given for the melt at 573 K.

measurement with temperature modulation. Irrespective of the length of annealing, all curves repeat the curve that was taken with modulation from the beginning. Analogous results were obtained from all other calorimeters.
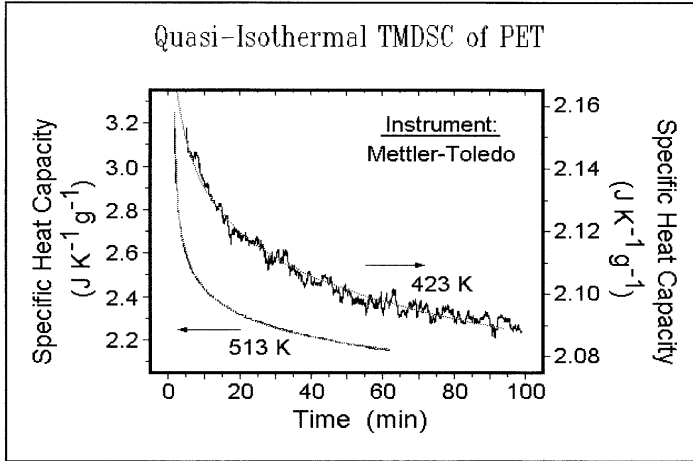
Figure 4 Data by TMDSC at 423 and 513 K fitted to Eq. (3).

Figure 4 shows the reversing heat capacity of PET as a function of time for quasi-isothermal experiments at 423 K, at the temperature where in Fig. 1 the heat capacity reaches the approximate value calculated for the measured crystallinity, and at 513 K, as before. As is commonly in dielectric and mechanical spectroscopy, the relaxation of the heat capacity was fitted to a Kohlrausch-Williams-Watts (KWW) equation (15), also called a stretched exponential function:

$$c_p(t) = c_{p\infty} + A\exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \tag{3}$$

Figure 4 shows such fitting (dotted curves) which yields the parameters $c_{p\infty}$ = 1.9 J K^{-1} g^{-1}, A = 3.2 J K^{-1} g^{-1}, τ = 22 s, β = 0.18 and $c_{p\infty}$ = 1.9 J K^{-1} g^{-1}, A = 0.6 J K^{-1} g^{-1}, τ = 60 s, β = 0.10 at 513 and 423 K, respectively.

Discussion

The identity of the results from the different calorimeters in Fig. 2 shows that the apparatus does not have any influence on the measured parameters. All available TMDSC calorimeters were able to produce the same quantitative reversing heat capacities. Thus, the observed relaxation of the reversing heat capacity must be due to processes within the sample. The second and main conclusion can be drawn from Fig. 3. It is that the temperature modulation by itself does not induce the relaxation. Any melting and crystallization that may occur during heating and cooling due to modulation does not measurably change the relaxation condition, as can be seen from Fig. 3. Temperature modulation probes thus only those parts of the molecules which can be attached and detached from the crystallites.

It is impossible to fit the relaxation curves with a simple exponential decay function. In reference (1) it was necessary to use the sum of two exponentials to extrapolate to an ultimate steady-state value, which still was higher than expected for the partially melted sample, indicated by the dashed line in Fig. 1. Usage of the KWW fit seems to be more advantageous, but brings considerable errors if the measuring time is relatively short and the extrapolation to infinite time is not reasonable in the present case. Rather high heat capacities result for both temperatures (365 J K^{-1} mol^{-1}, close to the values expected for the melt, see Fig. 1). Nevertheless, one notices that at higher temperature the time constant τ of the relaxation is smaller, in contrast to crystallization rates, but in accord with annealing rates (16). Analogous results were obtained in the study of PEEK (5), where a gradual decrease of the relaxation time with an approach to the melting-peak temperature was observed.

Some insight about the nature of the change in heat capacity can be gathered from the development of the Lissajous figures with time, illustrated in Fig. 5 on data of (2). The first
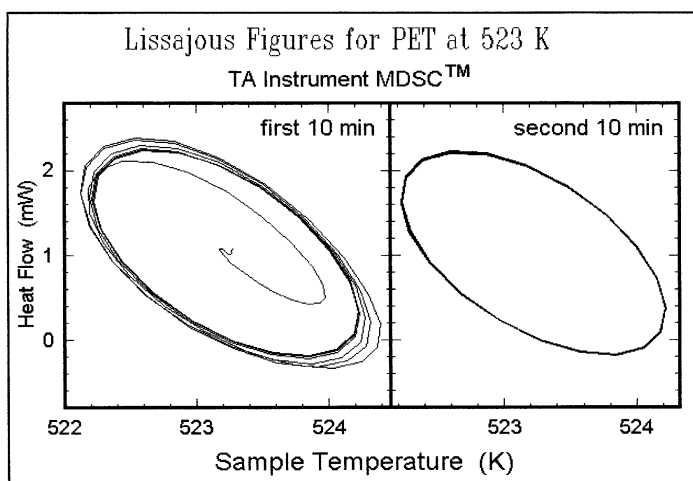

Figure 5 Development of Lissajous figures with time (2).

four oscillations of temperature are needed to reach steady state. Thereafter, the changes are very gradual and show on Fourier analysis no higher harmonics, in contrast to observations for PEEK (5). By eye one can also see no deviations from a true ellipse, *i.e.* there is no distinct melting and crystallization region that would differ from sinusoidal heat flow.

Conclusions

Instrumental effects can be excluded as reasons for the observed "reversible melting." The TMDSC measures quantitatively a process that continuously progresses, independent of the modulation. The reversing heat capacity remains higher than expected even at long times and exists over a wide temperature range. It is still not fully explained. More quantitative information is needed to separate the possible latent heat effects from local, submolecular

melting and crystallization from a conceivable glass transition of the rigid amorphous fraction, and the true reversible heat capacity which is well known from the ATHAS data bank (14). It is hoped that in the future it will be possible to gain sufficient details about possible molecular nucleation and the recently described new model of melting, crystallization, and perfection based on data on polypropylene (17,18) which seems also to agree with TMDSC of melting and crystallization of low molar mass PEO (19).

Acknowledgments

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