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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

CRYSTALLIZATION OF POLYMERS STUDIED BY TEMPERATURE MODULATED CALORIMETRIC MEASUREMENTS AT DIFFERENT FREQUENCIES

C. Schick[1], *M. Merzlyakov*[1], *A. Minakov*[2*] *and A. Wurm*[1]

[1]University of Rostock, Department of Physics, Universitätsplatz 3, D-18051 Rostock, Germany
[2]General Physics Institute, Vavilov st. 38, 117942 Moscow, Russia

Abstract

Quasi-isothermal temperature modulated DSC (TMDSC) were performed during crystallization to determine heat capacity as function of time and frequency. Non-reversible and reversible phenomena in the crystallization region of polymers were distinguished. TMDSC yields new information about the dynamics of local processes at the surface of polymer crystals, like reversible melting. The fraction of material involved in reversible melting, which is established during main crystallization, keeps constant during secondary crystallization for polycaprolactone (PCL). This shows that also after long crystallization times the surfaces of the individual crystallites are in equilibrium with the surrounding melt. Simply speaking, polymer crystals are 'living crystals'. A strong frequency dependence of complex heat capacity can be observed during and after crystallization of polymers.

Keywords: AC calorimetry, crystallization, PCL, polymer, temperature modulation, TMDSC

Introduction

Calorimetry, mainly differential scanning calorimetry (DSC), is widely used to study crystallization and melting of polymers. The measured heat flow rate is determined by the large effects due to latent heat. Small changes in baseline heat capacity (fast degrees of freedom) can not be obtained from a DSC temperature scan, e.g. during crystallization. Nevertheless, for accurate determination of changes in degree of crystallinity the course of baseline heat capacity must be known. From extrapolation [1] or iterative [2] procedures under certain restrictions baseline heat capacity can be estimated. With introduction of temperature modulated DSC (TMDSC) by Gobrecht *et al.* [3] and further development of the technique by Reading, Wunderlich and Schawe [4–6] there was the hope to be able directly to measure baseline heat capacity. Unfortunately, modulus of complex heat capacity[**] obtained from TMDSC measurements with an underlying heating rate in the crystallization region of polymers is not a measure of baseline heat capacity. It is a complicated superposition of baseline

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[*] Author for correspondence: e-mail: minakov@ran.gpi.ru

[**] Because reversing heat capacity and modulus of complex heat capacity are two different terms for the same quantity we only use the term modulus of complex heat capacity $\left|c_p^*\right|$

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heat capacity, latent heat, kinetics and last but not least effects related to heat transfer in the sample-calorimeter system [7, 8].

In TMDSC a small periodic temperature (correctly speaking heating rate) perturbation in the order of some tenth of a Kelvin is superimposed to a temperature program as normally used in DSC.

$$T(t) = T_0 + q_0t + A_T\sin(\omega t)$$

$$q(t) = q_0 + \omega A_T\cos(\omega t) = q_0 + A_q\cos(\omega t) \tag{1}$$

where T_0 is starting temperature, q_0 is underlying heating or cooling rate, A_T is amplitude of temperature and A_q amplitude of heating rate perturbation, ω is angular frequency with $\omega=2\pi/t_p$, t_p is period. Quasi-isothermal measurements (q_0=0) allow for determination of heat capacity as a function of time [4, 5]. For example, isothermal (quasi-isothermal) crystallization experiments can be performed (Fig. 1 below). Like in DSC experiments the exothermic effect can be observed. Averaging the measured heat flow rate over one period of temperature perturbation yields the so-called total heat flow rate, <*HF*>. In response to the periodic temperature perturbation a periodic heat flow rate occurs. From the amplitudes of heating rate perturbation A_q and of measured heat flow rate A_{HF} the modulus of complex heat capacity can be obtained, for details e.g. [3, 8].

$$\left|C_p^*\right| = \frac{A_{HF}}{A_q} \tag{2}$$

Because of time dependent processes a phase angle between perturbation and response can be observed in TMDSC too. In the case of isothermal polymer crystallization information about growth rate is available from the measured phase angle as discussed by Toda *et al.* [9]. But again, the measured heat capacity during quasi-isothermal crystallization of polymers is not a measure of baseline heat capacity. Often an increase of measured complex heat capacity instead of the expected decrease is observed [10, 11]. Wunderlich [12] introduced the term 'reversible melting' to address the occurrence of some latent heat effects during quasi-isothermal TMDSC measurements. This reversible melting contributes to the periodic part of the observed heat flow rate. For reversible melting as observed during quasi-isothermal measurements no supercooling seems to be necessary. This was checked with temperature amplitudes down to 0.005 K [13]. It is still an open question what is the microscopic origin of this reversible melting. Possible explanations are given by Wunderlich [14] and Strobl [15].

In this paper we want to discuss the frequency dependence of the time course of complex heat capacity during quasi-isothermal crystallization experiments. For comparison we study the behavior of a polymer (polycaprolactone PCL) and a low molecular mass compound. To observe reversible and irreversible changes in crystallinity one can not only use TMDSC but also temperature modulated dynamic mechanical analysis (TMDMA) [16, 17].

Experimental

Often sinusoidal or saw-tooth modulation is applied during temperature modulated scan or quasi-isothermal measurements. Both types of modulation have advantages and disadvantages, depending on the application. In case of polymer melting and crystallization saw-tooth modulation seems to be more profitable if steady state is reached during each heating, cooling or isothermal part of the temperature program. In this case, contrary to sinusoidal modulation, latent heat effects can be easily detected from the measured heat flow rate without any data treatment.

If one wants to perform TMDSC measurements in a broad frequency range high sensitive DSC apparatuses with different time constants like Perkin Elmer Pyris 1 DSC and Setaram DSC 121 must be used [13]. For the comparison a carefully temperature calibration of both instruments is necessary. The DSC's are calibrated according to the GEFTA recommendation [18]. The calibration was checked in TMDSC mode with the smectic A to nematic transition of 8OCB [19].

Samples

The linear aliphatic polylactone PCL, with structure $[(CH_2)_5COO]$– used in the experiments is a commercial sample synthesized by Aldrich Chemie with a molecular mass average M_W=55700 g mol^{-1}. More details about the sample are reported in [20]. The low molecular mass compound 2,5-bis-(2-propyloxycarbonyl-phenylsulfonyl) terephthalic acid dipropyl ester [21] can be easily supercooled from the melt and isothermally crystallized at different temperatures ($\chi\approx0.98$). For this compound heat capacity of the crystalline and the liquid state is directly available from the measurements while for the polymers the data were taken from ATHAS data bank [22]. The expected baseline heat capacity c_{pb} for a semi-crystalline sample can be calculated using a simple two phase model according to

$$c_{pb}(T,\,t)=\chi(t)c_{p\,crystal}(T)+(1-\chi(t))c_{p\,melt}(T) \tag{3}$$

with $c_{p\,crystal}$ specific heat capacity for the crystal, $c_{p\,melt}$ that for the melt and χ degree of crystallinity.

Results

Low molecular mass compound

TMDSC allows for quasi-isothermal determination of heat capacity during crystallization. Figure 1 shows the results of a quasi-isothermal crystallization experiment for the low molecular mass compound. Logarithmic time scale was chosen to show modulation in temperature and heat flow rate for shorter times.

In curves b and c, after induction time, an exothermic effect in the heat flow rate due to crystallization can be seen. Because heat capacity of the crystals is smaller than that of the melt one expects a decreasing heat flow rate amplitude with increasing crystallinity.

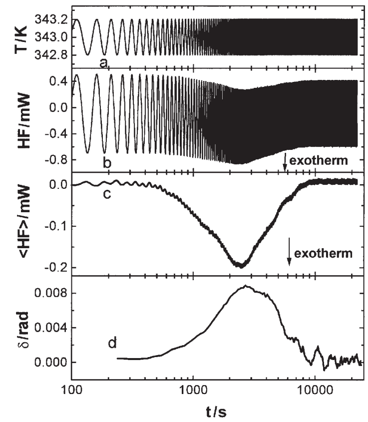

Fig. 1 Quasi-isothermal crystallization of 2,5-bis-(2-propyloxycarbonylphenylsulfonyl) terephthalic acid dipropyl ester at T_0=343 K, t_P=50 s, A_T=0.2 K. Curve a – quasi-isothermal temperature profile, b – measured heat flow rate, c – total heat flow rate <*HF*>, d – phase angle between heat flow rate and heating rate

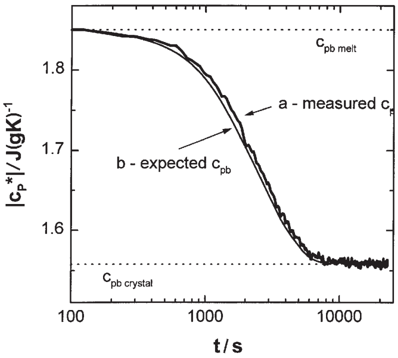

Fig 2 Modulus of complex specific heat capacity of the low molecular mass compound as a function of time from the data shown in Fig. 1. Curve a – c_p-value from the measured heat flow rate (Eq. (2) and curve b in Fig. 1), b – expected baseline heat capacity (Eq. (3))

This decrease is easy to see by eye if one compares heat flow rate amplitudes before and after crystallization. According to Eq. (2) modulus of complex heat capacity decreases too, curve a in Fig. 2. From the measured total heat flow rate, <*HF*> curve c in Fig. 1, changes in degree of crystallinity, $\chi(t)$, can be obtained.

$$\chi(t)=\frac{\int_0^{r}<HF>\mathrm{d}t}{\Delta h^{\circ}(T)} \tag{4}$$

where $\Delta h^0$is heat of fusion of an infinite and perfect crystal. From Eqs (3) and (4) the expected baseline heat capacity can be estimated. The result is shown in curve b in

Fig. 2. Within experimental uncertainty measured and baseline heat capacity coincide. No frequency dependence of heat capacity can be observed for this compound.

PCL

Figure 3 shows the heat flow rate during quasi-isothermal crystallization at average temperature 328 K. The sample was melted at 343 K and cooled at 1 K min^{-1} to the crystallization temperature. Temperature perturbation has an amplitude of 0.5 K and periods in the range 20 s to 1200 s. The crystallization process has been followed for 3 days. A strong frequency dependence of modulus of complex heat capacity can be observed. To enlarge the frequency range a curve at 1 Hz obtained from AC calorimetric measurements [23, 24] is added.

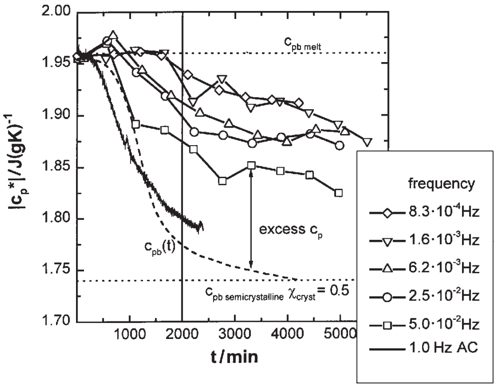

Fig. 3 Modulus of complex heat capacity during crystallization of PCL at 328 K (327.5 K for AC-calorimetric measurement) as a function of crystallization time. Parameter is frequency of temperature modulation. Temperature amplitude 0.5 K for TMDSC and 0.02 K for AC-calorimeter. c_{pb} denotes baseline heat capacity according to Eq. (3)

After crystallization the sample was heated with 10 K min^{-1} to the melt at 343 K. From this DSC scan the heat of fusion was determined to Δh=82 J g^{-1}. The ratio between the measured and the heat of fusion for an infinite crystal (Δh^0=156.8 J g^{-1} [22]) yields crystallinity $\chi\approx0.5$.

In Fig. 3 modulus of complex heat capacity is shown together with the values for baseline heat capacity for the melt [22] and the semicrystalline sample (Eq. (3)) at the end of the experiment (χ=0.5). Complex heat capacity calculated from the heat flow rate amplitude does not reach this value. From the difference an excess heat capacity of about 0.1 J $(g\ K)^{-1}$ at $5\cdot10^{-2}$ Hz (t_p=20 s) and 0.17 J $(g\ K)^{-1}$ at $8.3\cdot10^{-4}$ Hz (t_p=1200 s) after 3000 min crystallization can be obtained. The excess heat capacity of 0.17 J $(g\ K)^{-1}$ at $8.3\cdot10^{-4}$ Hz corresponds to the small variation of crystallinity during one period of temperature perturbation of about 0.1%

$$\Delta\chi=2c_{p\ \text{excess}}\,A_T/\Delta h^0 \tag{5}$$

with A_T=0.5 K and (Δh^0=156.8 J g^{-1} [22])). Taking into account the degree of crystallinity of 50% the change of 0.1% corresponds to a change of 0.2% of the crystalline material.

To determine the excess heat capacity during crystallization as a function of time it is necessary to estimate the curve for the baseline heat capacity. This was done with the time dependence of crystallinity and Eq. (3). Crystallinity was estimated from the enthalpy change during crystallization. The result for crystallinity is shown in Fig. 4, curve a, and that for expected baseline heat capacity in Fig. 3, dashed line.

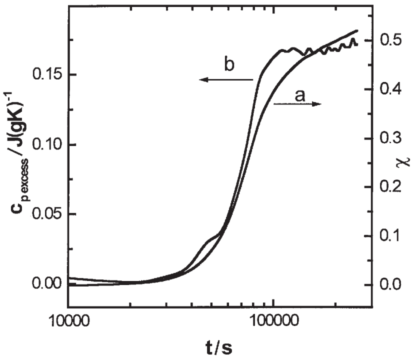

Fig 4 Time evolution of crystallinity (curve a) and excess heat capacity at period 1200 s (curve b) during quasi-isothermal crystallization of PCL at 328 K (Fig. 3)

Complex heat capacity is always larger than baseline heat capacity, except the very beginning when both equal heat capacity of the melt. The difference between complex and baseline heat capacity can be considered as excess heat capacity because of some latent heat occurring due to reversible melting. Reversible melting of PCL is studied in more detail in [13]. (Excess heat capacity at period 1200 s and degree of crystallinity as a function of time are shown in Fig. 4.)

As can be seen from Fig. 4 excess heat capacity and degree of crystallinity behave different way. While degree of crystallinity is still increasing during secondary crystallization excess heat capacity stays more or less constant. This indicates that some additional information is available from the excess heat capacity [25].

Discussion

First it was checked if it is at all possible to measure baseline heat capacity by TMDSC. Quasi-isothermal crystallization of the low molecular mass compound 2,5 bis (2-propyloxycarbonyl-phenylsulfonyl) terephthalic acid dipropyl ester was investigated. As shown in Fig. 2 the measured complex heat capacity coincides within experimental uncertainty with expected baseline heat capacity. This is not unexpected because for a low molecular compound the situation is relatively simple. During crystallization the molecules, as a whole, are added to the crystal. That means the molecules are either part of the melt or part of the crystal. Because crystalline state is the thermodynamic equilibrium state at crystallization temperature (supercooling 60 K) there is no chance to detach a molecule from the crystal by increasing temperature for some tenth of a Kelvin. In this particular case complex heat capacity is a measure of baseline heat capacity. No frequency dependence is expected.

For polymers the situation is more complicated. Due to the chain structure a molecule maybe, at the same time, part of the crystal and of the melt. A very simplified sketch of such a situation is shown in Fig. 5. Consider the surface of a polymer crystal after infinite long isothermal crystallization. A fraction of a polymer chain maybe part of the crystal another fraction part of the melt. In the present paper we do not want to discuss the influence of differences in mobility in the melt, like rigid or mobile amorphous fractions. Taking into account these differences will not considerably change the general picture discussed here.

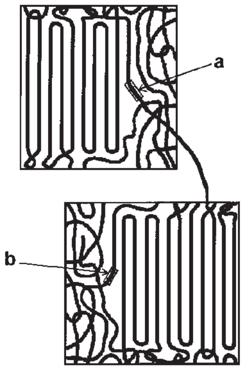

Fig. 5 Sketch of polymer molecules at the surface of crystals

In polymers with sufficiently high molecular mass some amorphous material always remains between the crystalline lamellae or other types of polymer crystals. Because of some restrictions for the molecules it is not possible to move them to the crystal surface in the right way. Therefore they can not be attached to the crystal. There maybe different reasons for these restrictions. One possibility is that the chain is also part of another crystal (e.g. molecule a in Fig. 5) and it is not possible to attach more segments to one or to the other crystal because of geometrical reasons. The same may happen if the chain is part of the same crystal (loops) or because of entanglements in the amorphous regions (e.g. molecule b in Fig. 5).

Consider a situation as schematically shown in Fig. 5. The segments under consideration (a, b) should be attached to the crystal because of thermodynamic reasons. This is not possible due to geometrical restrictions. The segment will remain in some kind of 'local' equilibrium because the magnitude of the force trying to move the segment to the crystal equals the 'elastic' force due to deformation of the chain.

From a classical point of view one can argue that small changes in temperature may change the 'local' equilibrium a little by increasing the force in direction to the crystal while decreasing temperature and by increasing the force in direction to the melt while increasing temperature. Because some segments maybe attached and detached during temperature modulation some latent heat occurs. This latent heat, involved in the measured heat flow rate, explains the observed excess heat capacity. For such a simple picture it is difficult to explain the observed linear response over a rather wide range of temperature amplitudes, 5 mK to 2.5 K for PCL [13].

Another way to explain excess heat capacity starts from some fluctuations around the 'local' equilibrium of the segments under consideration. Without external perturbations the segment under consideration is sometimes part of the crystal and to another time part of the melt. Or, in other words, we can describe the crystal as a 'living' crystal. Such attachment-detachment fluctuations yield large fluctuations in entropy. As in the case of glass transition [26] one can argue that these entropy fluctuations can be measured within linear response approach as the entropy compliance (heat capacity). For heat capacity the following relation can be given:

$$C_\mathrm{p}=\frac{\overline{\Delta S^2}}{k} \tag{6}$$

where $\overline{\Delta S^2}$ is mean entropy fluctuation and k Boltzmann constant.

For fluctuations we assume some characteristic time scale and a frequency dependent heat capacity because of the corresponding relaxation process. In Fig. 3 a strong frequency dependence of heat capacity can be observed. Excess heat capacity as a function of frequency is shown in Fig. 6.

Especially the sigmoidal shaped curve in Fig. 6 strongly supports the occurrence of a relaxation process which can be related to internal entropy fluctuations. As can be seen from Fig. 6 the frequency range available as yet is not broad enough for a detailed discussion of the curve shape. From this curve one expects for frequencies higher than about 10 Hz to measure baseline heat capacity without contributions due to reversible melting.

Next consider main crystallization of a polymer. Because the force in direction to the crystal growth front is larger than that due to geometrical restrictions crystallization proceeds. If one wants to study crystallization by TMDSC measurement con-

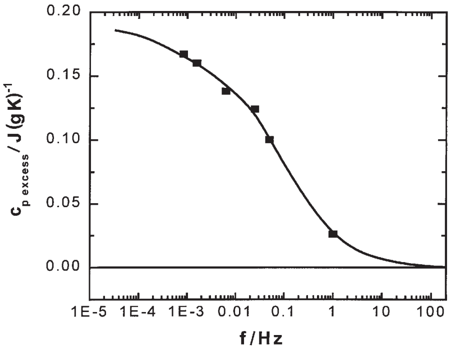

Fig. 6 Excess heat capacity after 2000 min crystallization at 328 K as a function of temperature modulation frequency. Data from Fig. 3

ditions must be chosen to fulfill requirements of linearity and stationarity as discussed in [6, 7]. Changes in sample properties (e.g. degree of crystallinity) must be negligible during one modulation period. Crystallization temperatures must be chosen such way that growth-rate is slow enough to met these conditions. Then within one modulation period the situation is similar to that at the end of crystallization. Finally, the same equilibrium situation occurs as discussed above and again a frequency dependent excess heat capacity is expected.

Our measurements support such a simple picture. Figure 3 shows that the measured heat capacity behaves different from the expected baseline heat capacity with increasing crystallinity. This difference results in an excess heat capacity which stays constant after the end of main crystallization. It can be related to reversible melting during crystallization.

As shown in Fig. 4 the time dependence of the quantity determined from the periodic part of heat flow rate $c_{\mathrm{p\,excess}}$ is different from that of crystallinity. Therefore the reason for the increase of the amplitude is not only the increase of the fraction of crystalline material. It seems that the response to the temperature modulation is sensitive to effects on the surface of the crystallites as discussed above.

In Strobl's four state scheme for polymer crystallization and melting [15] an equilibrium between the melt and the native crystals is assumed. Consider a polymer molecule of which a fraction is part of the crystal and another fraction is part of the surrounding melt as discussed above. For such a fluctuation process no nucleation, also no molecular nucleation [14], is necessary as long as a fraction of the molecule is part of the crystal. During main crystallization, the number of crystallites and their surface as well as the number of molecules in such a situation is increasing. At the end of main crystallization the whole sample is filled with crystallites and remaining amorphous parts in-between. From this time (about 100,000 s in Fig. 4) the number of crystallites and their surface remains practically constant. The observed behavior of $c_{\mathrm{p\,excess}}$ and crystallinity supports such a picture if one consider that reversible melting happens at the surface of all crystals not only at the actual growth front. Consequently all crystals stay at least for the time of our experiment in a state of something like a 'living' crystal. With the help of temperature modulated experiments it seems to be possible to study the dynamics of such small effects related to the surface of the crystals. At the moment we do not know which surfaces, growth or fold or both, are involved in the process of reversible melting but qualitatively such a simple picture explains the results obtained for PCL.

Conclusions

Temperature modulated DSC allows for the investigation of reversible and non-reversible phenomena in the crystallization region of polymers. Frequency dependent TMDSC measurements yield new information about the dynamics of local processes at the surface of polymer crystals, like reversible melting. The fraction of material involved in reversible melting, which is established during main crystallization, keeps constant during secondary crystallization. This shows that also after long crystallization times the surfaces of the individual crystallites are in equilibrium with the surrounding melt. Simply speaking, polymer crystals are ‘living crystals’. At sufficiently high frequency, above about 10 Hz for PCL at 328 K, it should be possible to measure baseline heat capacity during crystallization of polymers.

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