

REVERSIBLE MELTING DURING CRYSTALLIZATION OF POLYMERS STUDIED BY TEMPERATURE MODULATED TECHNIQUES (TMDSC, TMDMA)

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Abstract

Quasi-isothermal temperature modulated DSC and DMA measurements (TMDSC and TMDMA, respectively) were performed to determine heat capacity and shear modulus as a function of time during crystallization. Non-reversible and reversible phenomena in the crystallization region of polymers can be observed. The combination of TMDSC and TMDMA yields new information about local processes at the surface of polymer crystals, like reversible melting. Reversible melting can be observed in complex heat capacity and in the amplitude of shear modulus in response to temperature perturbation. The fraction of material involved in reversible melting, which is established during main crystallization, keeps constant during secondary crystallization for PCL, PET and PEEK. This shows that also after long crystallization times the surfaces of the individual polymer crystallites are in equilibrium with the surrounding melt. Simply speaking, polymer crystals are 'living crystals'.

Keywords: calorimetry, crystallization, PCL, PEEK, PEN, PET, polymer, temperature modulation, TMDMA, TMDSC

Introduction

Calorimetry, mainly differential scanning calorimetry (DSC), is widely used to study isothermal crystallization 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 isothermal DSC measurements. With introduction of temperature modulated DSC (TMDSC) in 1993 by Reading *et al.* [1] and further development of the technique by Wunderlich [2, 3] there was the hope to be able to measure baseline heat capacity during quasi-isothermal crystallization. Unfortunately, reversing or complex heat capacity** obtained from TMDSC measurements during crystallization of polymers is not a measure of baseline heat capacity. It is a complicated superposition of baseline heat capacity, latent heat, kinetics and last but not least effects related to heat transfer in the sample-calorimeter system [4, 5].

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** 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 $|c_p^*|$

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.

$$\begin{aligned} T(t) &= T_0 + q_0 t + A_T \sin(\omega t) \\ q(t) &= q_0 + \omega A_T \cos(\omega t) = q_0 + A_q \cos(\omega t) \end{aligned} \quad (1)$$

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 [2, 3]. For example, isothermal (quasi-isothermal) crystallization experiments can be performed (Fig. 1 below). Like in isotherm 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, $\langle \text{HF} \rangle$. 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 or the reversing heat capacity can be obtained, for details see e.g. [1, 6].

$$|c_p^*| = \frac{A_{\text{HF}}}{A_q} \quad (2)$$

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.* [7]. But again, the measured heat capacity during quasi-isothermal crystallization of polymers is not a measure of baseline heat capacity. Often

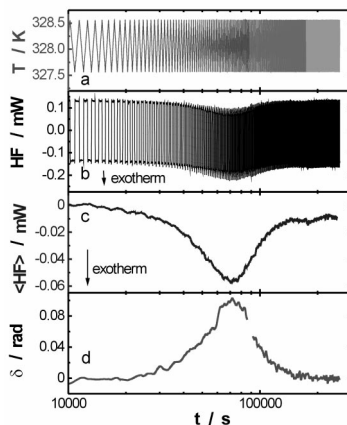


Fig. 1 Shows the heat flow rate during quasi-isothermal crystallization at average temperature 328 K. The sample was melted at 343 K and cooled at 1 K min^{-1} to the crystallization temperature. Temperature perturbation has an amplitude of 0.5 K and a period of 1200 s. The crystallization process has been followed for 3 days

an increase of measured complex heat capacity instead of the expected decrease is observed [8, 9], Fig. 6 below. Wunderlich [10] introduced the term 'reversible melting' to explain 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 with temperature amplitudes smaller than 0.005 K [11] no supercooling seems to be necessary. It is still an open question what is the microscopic origin of this reversible melting. Possible explanations are given by Wunderlich [12] and Strobl [13].

Experimental

Similar to TMDSC in temperature modulated dynamic mechanical analysis (TMDMA) the temperature profile as normally used is superimposed with a small periodical temperature perturbation. For the TMDMA measurements an advanced rheometric expansion system (ARES) from Rheometric Scientific was used. The Rheotest software includes a comfortable programming language. With that it is possible to synthesize any periodic temperature-time-program with or without underlying heating or cooling rate.

As shown in [14, 15] a data treatment algorithm like in TMDSC can be used for TMDMA measurements. Nevertheless there is at least one fundamental difference. While heat flow is related to changes in sample properties, e.g. changes in crystallinity, shear modulus depends on structure itself. From this point of view there is a big advantage of DMA compared to DSC measurements. Whereas in DSC only temperature or time derivatives of changes in structure can be observed in DMA a quantity is measured which is directly related to structure. Unfortunately, the relation between shear modulus and e.g. crystallinity in heterogeneous materials is complicated and not well understood [16, 17]. Nevertheless shear modulus measurements allow for the investigation of small changes in crystallinity also if they occur over very long times. This gives the opportunity to study very slow processes during quasi-isothermal measurements in crystallization region of polymers as discussed below.

Samples of different diameters and thickness have been placed between two parallel plates. The resultant torque (τ) by the sample in response to a harmonic shear strain ($\gamma = \gamma_0 \sin(\omega t)$) has been measured. So there are two different harmonic perturbations of the sample, the first is the periodic shear strain and the second is the periodic temperature profile. In order to get enough (>50) data points for data evaluation during one period of the temperature modulation the mechanical perturbation has to be much faster than the temperature modulation.

The period length of the temperature modulation was limited to lower periods by the time constant of the equipment, for details see [15]. Periods of 1200 s for the temperature modulation, periods of 1–10 s for the mechanical perturbation and shear strain between 0.1 and 0.5% have been used for the TMDMA measurements. For the TMDMA measurements these long periods are easy to realize and reasonable results can be obtained. If one wants to compare the results from TMDMA measurements with that from TMDSC using the same temperature profile high sensitive DSC appa-

ratues like Perkin Elmer Pyris 1 DSC or Setaram DSC 121 or 141 must be used. For the comparison a carefully temperature calibration of both instruments is necessary. The DSCs 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]. The DMA apparatus was temperature calibrated with melting of water, indium, tin, and lead. A small solid sample of the calibrant was placed between the two parallel plates and the rapid change of its thickness during melting caused by a small compression was measured.

Samples

The linear aliphatic polylactone polycaprolactone (PCL), with structure $[(\text{CH}_2)_5\text{COO}]_n-$ used in the experiments is a commercial sample synthesized by Aldrich Chemie with a molecular mass average $M_w=55700 \text{ g mol}^{-1}$. More details about the sample are reported in [20]. The poly(ether ether ketone) (PEEK), with structure $[\text{O}-(\text{C}_6\text{H}_4)-\text{CO}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4]_n-$ is available from ICI, trade name Victrex 381G. The poly(ethylene terephthalate) (PET), with structure $[\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{COO}-\text{CH}_2-\text{CH}_2]_n-$ was received from ORWO (series K 36 $M_w=23000 \text{ g mol}^{-1}$) and the poly(ethylene-2,6-naphtalene dicarboxylate) (PEN) from Eastman Kodak. In contrary to PEEK, PET and PEN PCL shows a very narrow melting range.

For these compounds heat capacity of the crystalline and the liquid-state is available from the ATHAS data bank [21]. The expected baseline heat capacity c_{pb} for a semi-crystalline sample can be estimated using a simple two phase model according to

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

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

Results

Polycaprolactone (PCL)

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 $\Delta H=82 \text{ J g}^{-1}$. The ratio between the measured and the heat of fusion for an infinite crystal ($\Delta H^0=156.8 \text{ J g}^{-1}$ [21]) yields crystallinity $\chi=0.5$.

In Fig. 2 the measured complex heat capacity is shown together with the values for baseline heat capacity for the melt [21], the crystal [21] and the semicrystalline sample (Eq. (3)) at the end of the experiment ($\chi=0.5$). Complex heat capacity calculated from the heat flow rate amplitude does not reach this value. From the difference an excess heat capacity of about $0.17 \text{ J (g K)}^{-1}$ can be obtained.

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

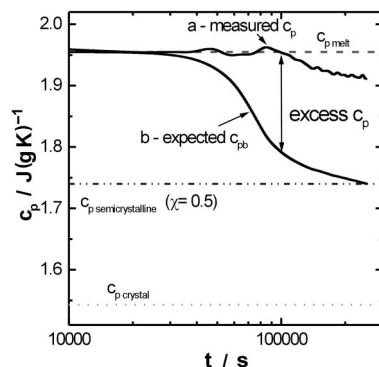


Fig. 2 Specific heat capacity of PCL as a function of time from the data shown in Fig. 1. Curve a – c_p -value from the measured heat flow rate (Eq. (2) and curve b in Fig. 1), b – expected baseline heat capacity (Eq. (3))

with the time dependence of crystallinity and Eq. (3). Crystallinity was estimated from the enthalpy change during crystallization. The normally used integration of the measured heat flow rate is not appropriate here. The maximum of the exothermic effect, 0.05 mW, is in the same order of magnitude as apparatus drift during total measuring time of three days. Therefore the change in crystallinity was estimated from measured phase angle which is proportional to the exothermal heat flow rate. The result for crystallinity is shown in Fig. 3, curve a, and that for expected baseline heat capacity in Fig. 2, curve b.

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 [11, 22]. The time course of excess heat capacity and degree of crystallinity is shown in Fig. 3.

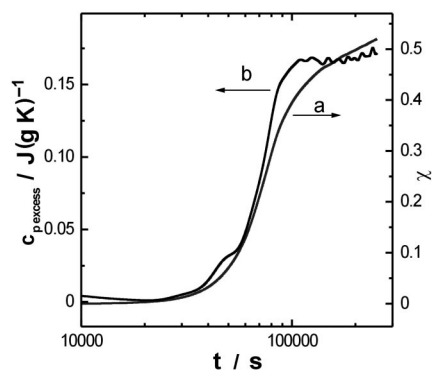


Fig. 3 Time evolution of crystallinity (curve a) and excess heat capacity (curve b), see text, during quasi-isothermal crystallization of PCL (Fig. 1)

As can be seen from Fig. 3 excess heat capacity and degree of crystallinity behave different. 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 [11].

Next, we checked if reversible melting can be probed with other techniques than calorimetry. Because shear modulus is very sensitive to changes in crystallinity TMDMA measurements were performed [14, 15].

First the influence of shear stress, applied during shear modulus measurements, on crystallization kinetics was checked. An isothermal crystallization experiment with continuous shearing was compared to one with only partly shearing of the sample [15]. No difference between both curves could be seen for shear stress frequency 0.5 Hz and amplitude 1% which is larger than that used for the other measurements. Therefore it seems to be possible to use DMA under this measuring conditions to study crystallization of PCL.

First the sample was melted at 343 K and then cooled with 1 K min^{-1} to the crystallization temperature. Figure 4, curve a shows the data of the storage modulus for a quasi-isothermal TMDMA crystallization experiment at 331 K with temperature amplitude 0.5 K and period 1200 s. The relatively high crystallization temperature was chosen to be able to follow the whole crystallization process in one measurement. The total time for this experiment was more than 6 days.

Crystallization starts after an induction time due to nucleation. With increasing crystallinity the storage modulus increases for 2.5 orders of magnitude, curve a. The relation between the storage modulus and crystallinity is very complicated. A lot of (for the most polymers unknown) sample properties are needed to describe this relation with theories taking into account combinations of amorphous and crystalline parts in the sample. So it is difficult to estimate changes in crystallinity from shear modulus measurements quantitatively. But the shape of the modulus curve allows to distinguish between two different crystallization regimes – until about 200.000 s main and up to the end secondary crystallization.

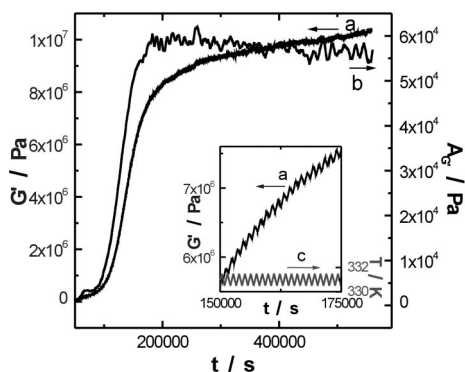


Fig. 4 Time evolution of storage shear modulus (curve a) and amplitude of storage modulus oscillations (curve b) during quasi-isothermal crystallization of PCL at $T_0=331 \text{ K}$, $t_P=1200 \text{ s}$, $A_T=0.5 \text{ K}$ (curve c)

The insert in Fig. 4 shows a magnified part of the modulus curve at the end of main crystallization. It is remarkable and unexpected that at the heating segments of temperature modulation there is always a decrease of storage modulus. This indicates that parts of the sample melt or undergo a glass transition, probably the rigid amorphous fraction. The decrease of modulus during heating can not be explained by the temperature dependence of shear modulus of the amorphous fraction because this is measured at the very beginning of the quasi-isothermal experiment (melt) and results in a very small amplitude A_G .

Using Fourier analysis, as for the periodic part of the heat flow rate, an amplitude of the shear modulus oscillations can be obtained, curve b. One can see an increase during main crystallization with a relatively abrupt change to a constant or slowly decreasing value during secondary crystallization. This is contrary to the behavior of the storage modulus itself which is related to crystallinity, increasing up to the end of the measurement.

Poly(ether ether ketone) (PEEK)

Similar experiments as for PCL were performed for PEEK. The sample was melted at 643 K and cooled to the crystallization temperature with 1 K min^{-1} . In Fig. 5, curve b shows the measured heat flow rate for a quasi-isothermal crystallization at 606.5 K.

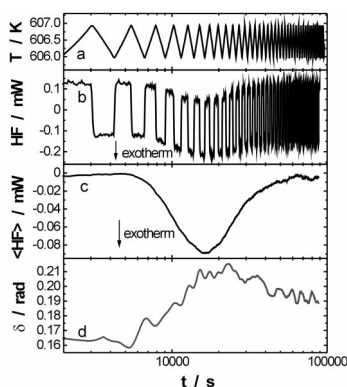


Fig. 5 Quasi-isothermal crystallization of PEEK at $T_0=306.5 \text{ K}$, $t_p=2400 \text{ s}$, $A_T=0.5 \text{ K}$. Curve a – quasi-isothermal temperature profile, b – measured heat flow rate, c – total heat flow rate $\langle HF \rangle$, d – phase angle between heat flow rate and heating rate

Again an exothermic effect can be seen. From the heating scan to the melt at 643 K, just after quasi-isothermal crystallization, a heat of fusion of 27 J g^{-1} was obtained. With $\Delta H^0=130 \text{ J g}^{-1}$ [21] the degree of crystallinity was estimated to 0.21. According to Eq. (4) the changes in degree of crystallinity with time and from Eq. (3) the expected baseline heat capacity was calculated.

$$X(t) = \frac{\int_0^t \langle HF \rangle dt}{\Delta H^0} \quad (4)$$

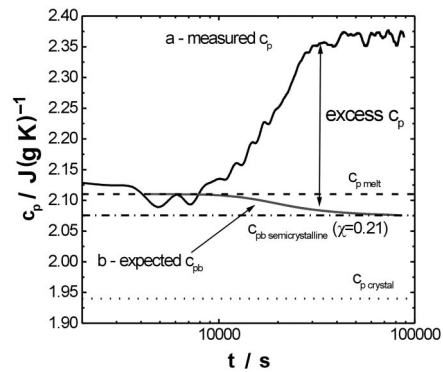


Fig. 6 Specific heat capacity of PEEK as a function of time from the data shown in Fig. 5. Curve a – c_p - value from the measured heat flow rate (Eq. (2) and curve b in Fig. 5), b – expected baseline heat capacity (Eq. (3))

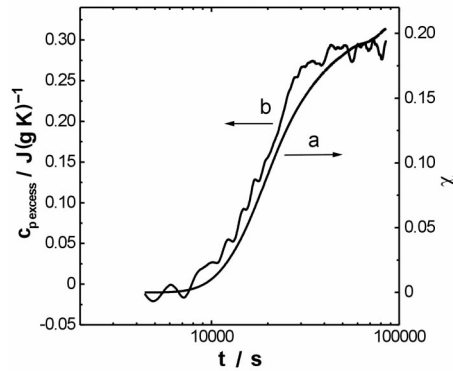


Fig. 7 Time evolution of crystallinity (curve a) and excess heat capacity (curve b), see text, during quasi-isothermal crystallization of PEEK (Fig. 5)

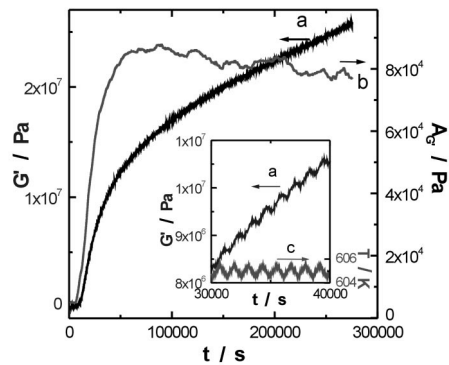


Fig. 8 Time evolution of storage shear modulus (curve a) and amplitude of storage modulus oscillations (curve b) during quasi-isothermal crystallization of PEEK at $T_0=605$ K, $t_p=1200$ s, $A_T=0.5$ K (curve c)

In Fig. 6 the measured complex heat capacity and expected baseline heat capacity are shown. In case of PEEK complex heat capacity increases during crystallization while baseline heat capacity decreases. This increase in heat capacity also explains the step-like change in the measured phase angle [23].

Excess heat capacity is shown together with changes in degree of crystallinity in Fig. 7.

Analogous to PCL the occurrence of reversible melting was checked by TMDMA measurements. The results are shown in Fig. 8.

Poly(ethylene terephthalate) (PET) and the poly(ethylene-2,6-naphthalene dicarboxylate) (PEN)

With TMDMA we also performed crystallization experiments on PET and PEN. For these measurements the samples were melted and quenched below glass transition. The glassy sample was then heated with 1 K min^{-1} to the crystallization temperature.

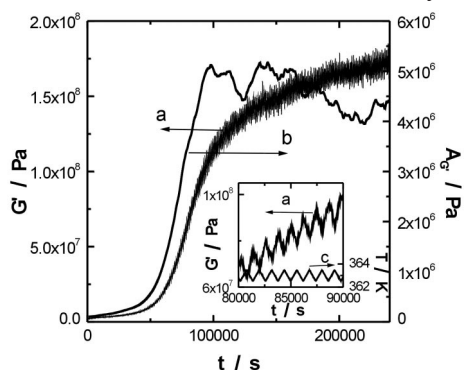


Fig. 9 Time evolution of storage shear modulus (curve a) and amplitude of storage modulus oscillations (curve b) during quasi-isothermal crystallization of PET at $T_0=363 \text{ K}$, $t_p=1200 \text{ s}$, $A_T=0.5 \text{ K}$ (curve c)

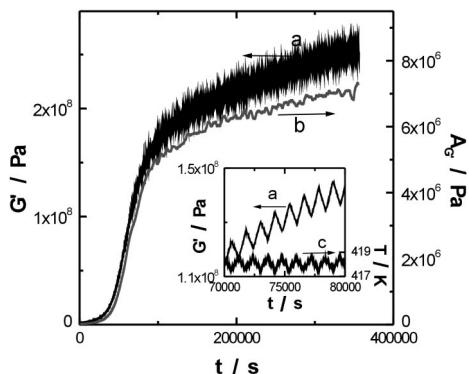


Fig. 10 Time evolution of storage shear modulus (curve a) and amplitude of storage modulus oscillations (curve b) during quasi-isothermal crystallization of PEN at $T_0=418 \text{ K}$, $t_p=1200 \text{ s}$, $A_T=0.5 \text{ K}$ (curve c)

In contrary to PEEK and PCL which were crystallized from the melt PET and PEN were crystallized from the glassy-state (cold crystallization). The results for storage modulus and its amplitude are shown in Figs 9 and 10 for PET and PEN, respectively.

For PET the amplitude of storage modulus behaves similar to that of PCL and PEEK. It increases fast during main crystallization up to about 100.000 s and stays constant during secondary crystallization. For PEN the amplitude of storage modulus behaves different. It increases also during secondary crystallization with nearly the same course as storage modulus itself.

Discussion

First it was checked if baseline heat capacity can be measured with TMDSC. Quasi-isothermal crystallization of the low molecular mass compound 2,5 bis (2-propyloxy-carbonyl-phenylsulfonyl) terephthalic acid dipropyl ester was investigated [24]. It was found that measured complex heat capacity coincides within experimental uncertainty with expected baseline heat capacity. This was 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 60 K below the melting temperature the crystalline-state is much more stable than the melt,) 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 direct measure of baseline heat capacity.

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. 11.

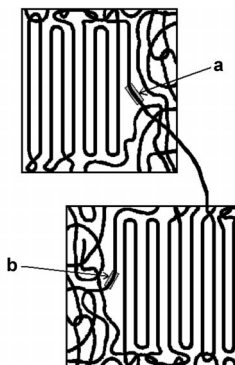


Fig. 11 Sketch of polymer molecules at the surface of the crystals

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.

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 be moved 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. 11) 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. 11).

Consider a situation as schematically shown in Fig. 11]. 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 segments 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 in direction to the crystal while decreasing temperature and a little 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 [11]. 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 [25] 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:

$$c_p = \frac{\overline{\Delta S^2}}{k} \quad (5)$$

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

For fluctuations we assume some characteristic time scale and a corresponding relaxation process. This is discussed in more detail in [11, 22].

Next consider main crystallization of a polymer. Because the force in direction to the crystal growth front is larger than geometrical restriction crystallization proceeds. If one wants to study crystallization by TMDSC measurement conditions must be chosen to fulfill requirements of linearity and stationarity as discussed in [4, 5]. 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. Then within one modulation period the situation is simi-

lar to that at the end of crystallization. Finally, the same equilibrium situation occurs as discussed above and again an excess heat capacity or excess part in shear modulus can be seen.

Our measurements support such a simple picture for all polymers under investigation. Figures 2 and 6 show that the measured heat capacities behaves different from the expected baseline heat capacities with increasing crystallinity. The difference can be described as an excess heat capacity which stays constant after the end of main crystallization. It can be related to reversing melting during crystallization. This excess heat capacity (curve b in Figs 3 and 7) behaves similar to the amplitude of the storage modulus ($A_{G'}$, curve b in Figs 4, 8 and 9). This indicates that the same reversible process is tested by both independent methods. From the excess heat capacity the amount of material taking part in the reversible process was estimated at 0.5 K amplitude and 1200 s period to be about 0.2 and 1% of the crystalline material for PCL at 328 K [22] and for PEEK at 606.5 K, respectively.

As shown in Figs 3, 4, 7, 8 and 9 time dependence of the quantities determined from the periodic part of heat flow rate and shear modulus $c_{p, \text{excess}}$ and $A_{G'}$, respectively, are 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. One possible explanation is that with the temperature modulation effects on the surface of the crystallites are tested. At the moment we do not know why PEN behaves different. Our first idea was that there may be a difference between melt- and cold-crystallization. But as can be seen from Fig. 9 the cold crystallized PET behaves in the same way as the melt crystallized samples. From our simple picture given above we do not expect a difference between cold- and melt-crystallization. Nevertheless, if one compares the absolute value of the shear modulus at the beginning of secondary crystallization with the amplitude of shear modulus oscillation due to temperature modulation with period 1200 s and amplitude 0.5 K one can observe some differences. For PCL and PEEK shear modulus equals about $1 \cdot 10^7$ Pa and the amplitude equals about $6 \cdot 10^4$ Pa while for PEN and PET the shear modulus equals about $2 \cdot 10^8$ Pa and the amplitude about $6 \cdot 10^6$ Pa. It seems that the amplitude for the cold crystallized samples is significantly larger compared to the melt crystallized samples. The reason for this difference is not known yet.

In Strobl's four-state scheme for polymer crystallization and melting [13] an equilibrium between the melt and the just developed 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. A small local temperature fluctuation will allow to remove another fraction of the molecule from the growth front of the crystal and to attach it again. For such a fluctuation process no nucleation, also no molecular nucleation [12], is necessary as long as a fraction of the molecule is part of the crystal. During main crystallization 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. 3, 200.000 s in Fig. 4, 40.000 s in Figs 7 and 8, 100.000 s in Figs 9 and 10) the number of crystallites and

their surface remains practically constant. The observed behavior of amplitudes and crystallinity, Figs 3, 4, 7, 8 and 9, 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 during the whole crystallization process, more than 6 days in Fig. 4, in a state of something like a 'living' crystal. From temperature modulated experiments it seems to be possible to study such small effects related to the surface of the crystals. Consider a given number of molecules per area surface in a situation as shown schematically in Fig. 11 then the excess phenomena should be proportional to the surface area. 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, PEEK, PET and PEN.

Conclusions

Temperature modulated DSC and dynamic mechanical analysis allows for the investigation of reversible and non-reversible phenomena in the crystallization region of polymers. The combination of TMDMA and TMDSC yields new information about local processes at the surface of polymer crystals, like reversible melting. Reversible melting can be observed in complex heat capacity and in the amplitude of shear modulus in response to temperature perturbation. 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'.

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