

Temperature modulated dynamic mechanical analysis

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Abstract

Temperature modulated dynamic mechanical analysis (TMDMA) was performed in the same way as temperature modulated DSC (TMDSC) measurements. Temperature modulation with amplitude 0.5 K and period 20 min was realised by a series of linear heating and cooling cycles (saw-tooth modulation). As in TMDSC TMDMA allows for the investigation of reversible and non-reversible phenomena in the melting and crystallisation region of polymers. The advantage of TMDMA compared to TMDSC is the high sensitivity for small and slow changes in crystallinity, e.g. during re-crystallisation. The combination of TMDMA and TMDSC yields new information about local processes at the surface of polymer crystallites. It is shown that during and after isothermal crystallisation the surface of the individual crystallites is in equilibrium with the surrounding melt. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Temperature modulated DSC (TMDSC) as introduced by Reading [1] allows under certain conditions for the identification of reversing and non-reversing changes of sample properties. The temperature program normally used consists of an underlying heating or cooling rate superimposed with a periodical temperature perturbation. The concept of dividing the measured signal in an underlying signal and a periodic (reversing) component can not only be applied to calorimetric measurements but also to thermogravimetric [2], dilatometric [3,4], dielectric [5], and dynamic mechanical measurements [6]. The differ-

ence between the so-called underlying signal and the amplitude of the periodic component is considered to represent the non-reversing processes in the sample under investigation.

This concept was, e.g. applied successfully to distinguish between changes in (reversing) heat capacity and the (non-reversing) heat of reaction during isothermal and non-isothermal curing reactions [7]. On the contrary, for the investigation of relaxation processes, like glass transition, the concept of complex heat capacity [8,9] seems to be more convenient.

From the very beginning of TMDSC melting of polymers was considered to be one of the most important applications of this new technique. There was the hope to be able to measure baseline heat capacity in the broad melting region of semi-crystalline polymers. Unfortunately reversing or complex heat capacity obtained from temperature modulated

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scans in the melting region is not a measure of baseline heat capacity (fast degrees of freedom) rather than a complicated superposition of the heat capacity, latent heats, kinetics and last but not least effects related to heat transfer in the sample-calorimeter system [10]. To avoid latent heat effects Wunderlich and co-workers [11,12] performed quasi-isothermal measurements with stepwise increasing of mean temperature in the melting region of different polymers. Again it was not possible to obtain baseline heat capacity. They found a reversible melting of parts of the polymer crystals without super-cooling which contributes to the periodic part of the observed heat flow. With time the amount of material taking part in the reversible melting decreases but does not reach zero at infinite time. Combination of TMDSC and TMDMA seems to be a useful tool to study these effects in more detail. Especially the reason for the small changes in reversible melting with time should be detectable by TMDMA. The effect of reversible melting was also observed during quasi-isothermal crystallisation of poly(ethylene) [13,14].

In Fig. 1 the common crystallisation and melting behaviour during DSC and DMA scans is shown for the example of poly(caprolactone). The well known necessary super-cooling for polymer crystallisation in the order of 10 K can be seen. For reversible melting as observed during quasi-isothermal measurements with temperature amplitudes smaller than 0.005 K [15] no super-cooling 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 [16] and Strobl [17].

During quasi-isothermal measurements in the melting region of polymers often re-organisation and re-crystallisation is observed. These processes may be very slow and may influence reversible melting. Therefore, it seems to be necessary to study the changes in crystallinity not only by methods sensitive to the time derivative of crystallinity, like calorimetry. Because the changes in crystallinity during one period of a quasi-isothermal measurement as well as during re-organisation are often much smaller than 1% of a property must be studied which is very sensitive to changes in crystallinity. The shear modulus is such a quantity as shown in Fig. 1(C). It changes for more than four orders of magnitude during melting and crystallisation of PCL. Therefore, it seems to be

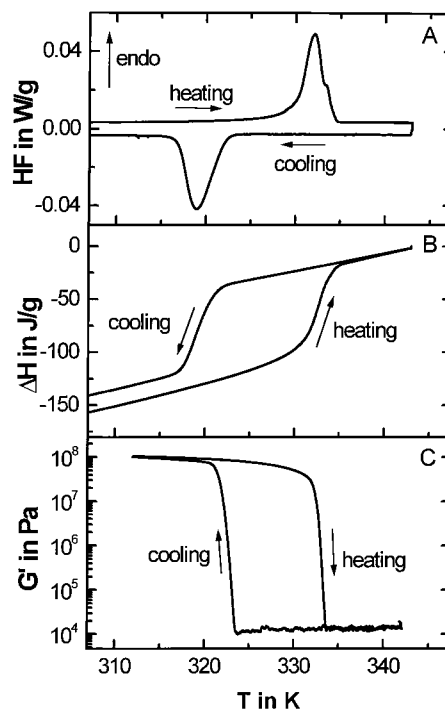


Fig. 1. Heat flow, HF, (part A) and enthalpy change, ΔH , (part B) from a conventional DSC scan and storage shear modulus, G' , (part C) from a DMA temperature scan for crystallisation and melting of PCL with cooling and heating rate of 0.1 K/min.

interesting to perform similar measurements as in TMDSC with a mechanic shear spectrometer. As shown in [6] it is possible to perform temperature modulated dynamic mechanical analysis (TMDMA) in a similar way as TMDSC. In this paper we want to describe TMDMA and to discuss some applications in comparison to TMDSC.

2. Experimental

As for TMDSC in TMDMA a linear temperature profile as normally used will be superimposed with a periodical temperature change. 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 crystallisation 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, it is easy to detect latent heat effects from the measured heat flow rate itself without any data treatment. Another advantage of saw-tooth modulation is to go from one quasi-isotherm to the next with the same heating (cooling) rate as used during temperature modulation. Because there is no additional break in the temperature program the processes during heating or cooling can be detected as in standard DSC or DMA, see e.g. Figs. 3 and 4 below.

For the TMDMA measurements an Advanced Rheometric Expansion System (ARESTM) from Rheometric ScientificTM was used. The RheotestTM software, includes a comfortable programming language. With that it is possible to synthesis any periodic temperature–time–program with or without underlying heating or cooling rate. For example saw-tooth modulation with angular frequency $\omega=2\pi/t_P$ (t_P -period) and temperature amplitude A_T can be realised by the Fourier series:

$$T_{\text{saw-tooth}}(t) = \frac{4A_T}{\pi} \sum_{i=0}^{\infty} (-1)^i \frac{\sin((2i+1)\omega t)}{(2i+1)^2}. \quad (1)$$

In practice for temperature generation it is enough to use the first three terms of the Fourier series in addition to the underlying linear temperature profile:

$$T(t) = T_0 + q_0 t + \frac{4A_T}{\pi} \times \left(\frac{\sin(\omega t)}{1} - \frac{\sin(3\omega t)}{9} + \frac{\sin(5\omega t)}{25} \right), \quad (2)$$

where T_0 is the starting temperature and q_0 is the constant underlying heating or cooling rate.

Fig. 2, part A shows an example for a TMDMA scan measurement in the melting region of an ethylene–octene copolymer (EOC) [18]. A period of 20 min and an underlying heating rate of 0.25 K/min was used. Typical for this material is the broad melting range (more than 100 K). Melting starts immediately above glass transition (T_g ca. 240 K) and ends at about 350 K. As in standard TMA the decrease of the storage modulus for more than two orders of magnitude during melting can be seen,

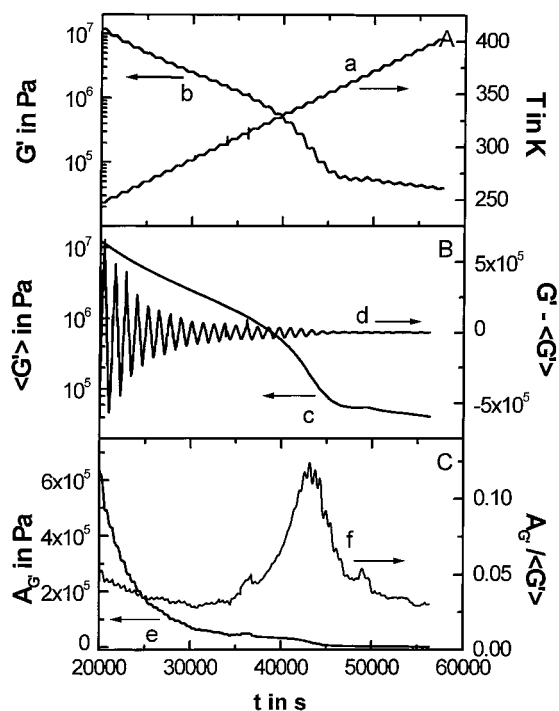


Fig. 2. Storage shear modulus, G' , (curve b) from a DMA measurement with a modulated temperature program (curve a). Curve c underlying (Eq. (3)) and curve d periodic part of G' , see text. Curve e is the amplitude of the periodic part (Eq. (6)) and curve f is the normalised amplitude, see text.

Fig. 2(A) curve b. The response to the periodic part of the temperature profile can be observed too. To evaluate the response to the temperature modulation it is necessary to divide the signal in the underlying change of G' due to irreversible crystal melting, curve c, and in the response to the temperature modulation, curve d. Curve c represents the gliding average of G' over one period ($\langle G' \rangle$).

$$\langle G' \rangle = \frac{1}{t_P} \int_{t-t_P/2}^{t+t_P/2} G'(t) dt \quad (3)$$

The periodic part (curve d) is the difference between the measured G' (curve b) and $\langle G' \rangle$ (curve c). From the periodic part (curve d) the amplitude $A_{G'}$ (curve e) of the response to the periodical temperature perturbation can be determined by Fourier analysis. The in- and out of phase components of the periodic

part are determined by gliding integration:

$$G'_{\text{in}}(t) = \frac{2}{t_p} \int_{t-t_p/2}^{t+t_p/2} [G'(t) - \langle G'(t) \rangle] \cos(\omega_0 t) dt, \quad (4)$$

$$G'_{\text{out}}(t) = \frac{2}{t_p} \int_{t-t_p/2}^{t+t_p/2} [G'(t) - \langle G'(t) \rangle] \sin(\omega_0 t) dt. \quad (5)$$

Amplitude $A_{G'}$ is given by

$$A_{G'} = \sqrt{G_{\text{in}}'^2 + G_{\text{out}}'^2}, \quad (6)$$

and phase angle φ between temperature perturbation and response in G' by

$$\varphi = \arctan \frac{G'_{\text{in}}}{G'_{\text{out}}}. \quad (7)$$

Because of big noise in the signals the phase angle was not considered.

The amplitude $A_{G'}$ decreases drastically with increasing temperature. This is not really surprising, because the value of G' itself changes during melting for several orders of magnitude. It seems to be better to discuss the amplitude $A_{G'}$ not in absolute but in relative numbers compared to the value of G' . A normalisation, like suggested in [6] is necessary. For this normalisation $A_{G'}$ is divided by the underlying storage modulus $\langle G' \rangle$ to get a fractional amplitude that represents the relative changes in the storage shear modulus due to temperature modulation, Fig. 2, curve f. On this way the measured shear modulus can be divided into the averaged underlying component representing non-reversing changes in sample properties and the normalised amplitude of module oscillations in response to the periodic temperature perturbation. The later contains information about reversing changes in sample properties with temperature.

As shown above a data treatment algorithm as in TMDSC can be used for TMDMA measurements. Nevertheless there is at least one fundamental difference. In TMDSC the measured response, underlying and periodic part, depends on heating rate perturbation and not on temperature perturbation. In TMDMA the situation is different. Shear modulus depends a little on temperature and mainly on structure which may

change with temperature. Therefore, we measure the response to temperature perturbation in TMDMA. From this point of view there is a big advantage of DMA compared to DSC measurements. While in DSC only the temperature or time derivative of changes in structure can be observed a quantity directly related to structure is measured in DMA. Unfortunately the relation between shear modulus, and e.g. crystallinity in heterogeneous materials is complicated and not well understood [19,20]. 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 the melting and crystallisation region of polymers as discussed below.

The presented DMA data have been measured with the Advanced Rheometric Expansion System (ARESTM) from Rheometric ScientificTM. 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 more faster than the temperature modulation.

The period length of the temperature modulation was limited to lower periods by the time constant of the equipment. This time constant has been checked with quasi-isothermal TMDMA measurements in the glass transition region of PET. In this region, for a given shear frequency, the shear modulus is temperature dependent. The time dependence is controlled by the shear frequency which is at least two orders of magnitude higher than frequency of temperature modulation. Therefore, no influence from the frequency of the temperature perturbation on the shear modulus is expected. The amplitude of G' was determined as a function of period of temperature modulation for constant programmed temperature amplitudes. The amplitude $A_{G'}$ stays nearly constant for periods longer than 600 s. The reason for this long time is that the temperature of the relatively small sample is controlled by the temperature of the large sample holders.

The temperature control of the oven is realised with pressurised air by two heaters.

Periods of 1200 s for the temperature modulation and periods of 1–10 s for the mechanical perturbation have been used for the TMDMA measurements. For the TMDMA measurements these long periods are easy to realise 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 apparatuses like Perkin-Elmer Pyris 1 DSC or Setaram DSC 121 or 141 must be used. For the comparison a carefully temperature calibration is necessary. The DSC's are calibrated according to the GEFTA recommendation [21]. The calibration was checked in TMDSC mode with the smectic A to nematic transition of 8OCB [22]. 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.

A second problem for the DMA measurements must be taken into account. Due to the drastically change of the mechanical properties of the sample during melting or crystallisation a torque in the measurement range of the transducer must be realised over the whole measurement. This was only possible by changing the shear strain amplitude during the measurement by using the auto-strain function of the equipment.

The linear aliphatic poly lactone poly(caprolactone) (PCL), with structure $[(\text{CH}_2)_5\text{COO}]_n$ used in the experiments is a commercial sample synthesised by Aldrich Chemie with a molecular weight average of 55 700 g/mol. More details about the sample are reported in [23]. In contrary to the EOC the PCL shows a very narrow melting range. So it is not so time consuming to perform quasi-isothermal measurements with long periods and small differences in the mean temperatures of the quasi-isotherms in the whole melting range.

3. Results

3.1. Quasi-isothermal measurements in the melting region of PCL

The temperature modulation for TMDMA and TMDSC measurements has been realised by a series

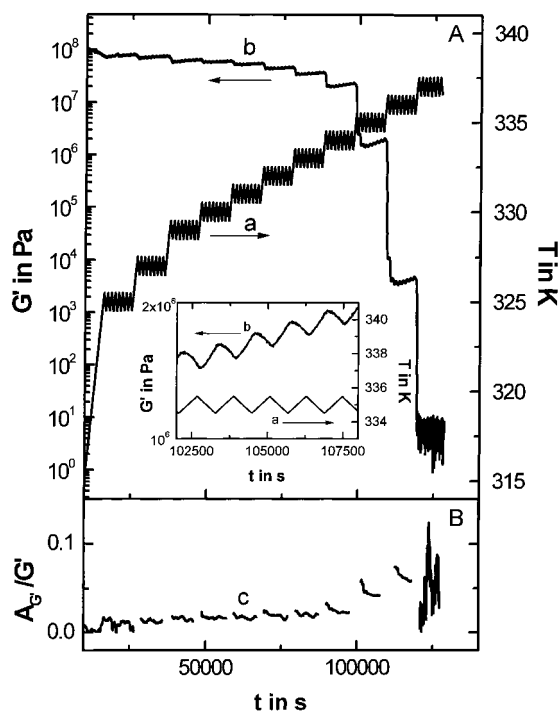


Fig. 3. Storage shear modulus, G' , (curve b) from a quasi-isothermal TMDMA measurement ($t_p=1200$ s, $A_T=0.5$ K) at different temperatures (curve a). The insert shows a part of curves a and b. From the periodic part of G' the amplitude $A_{G'}$ was determined (Eq. (6)). Curve c is the normalised amplitude of G' , see text.

of linear heating and cooling cycles (saw-tooth modulation). For both methods temperature modulation period was $t_p=1200$ s, temperature amplitude $A_T=0.5$ K and underlying heating rate was set to zero, $q_0=0$ K/min.

Curve b in Fig. 3 shows the measured G' data for the given quasi-isothermal temperature–time profile (curve a). During the first quasi-isotherms at low temperatures the G' curve follows the temperature modulation because of the temperature dependence of shear modulus. Also the decrease of the modulus between two quasi-isotherms is based on this temperature dependence and small premelting, see also Fig. 4.

But in the main melting region starting at 333 K there is a drastically decrease of the storage modulus caused by melting at each temperature step from one to the next quasi-isotherm. During the first cooling

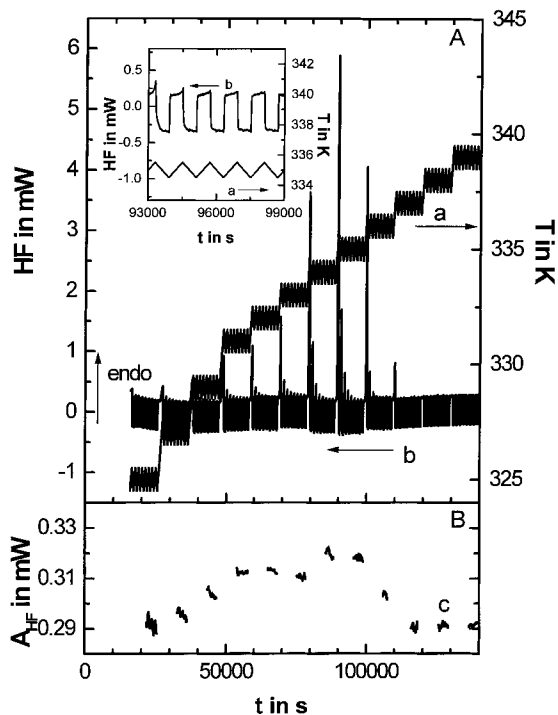


Fig. 4. Heat Flow, HF, (curve b) from a quasi-isothermal TMDSC measurement ($t_p=1200$ s, $A_T=0.5$ K) at different temperatures (curve a). The insert shows a part of curves a and b. Curve c is the amplitude of the heat flow.

cycle at the new quasi-isotherm a nearly constant value of G' can be observed but with next heating the storage modulus decreases further. This is shown in more detail in Fig. 5 part A. After the second period the G' curve follows the temperature modulation profile that means there is a decrease during heating and an increase during cooling. But this effect is too big to be described only by the temperature dependence of the storage modulus. So there is another reversible contribution to G' .

Considering the data from the TMDSC measurements in Figs. 4 and 5(b) one can see, that the decrease of the modulus corresponds to an endothermic and the increase of G' to an exothermic excess heat flow, see [15] for details. This means, with TMDMA and TMDSC melting during heating and crystallisation during cooling can be observed. In addition to this a relatively small increase of the mean value of the storage modulus with time caused by re-crystallisation effects was found with TMDMA. It is impossible to detect this effect with TMDSC because the exothermic

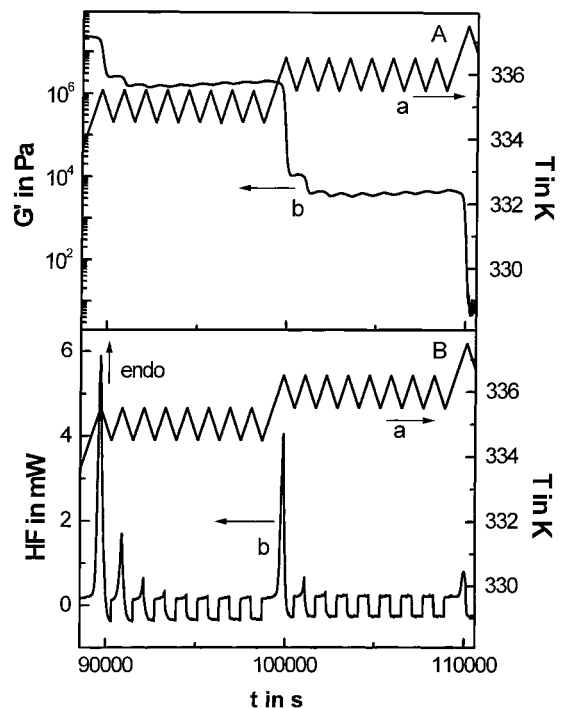


Fig. 5. Details of Fig. 3, part A, and Fig. 4, part B, showing irreversible melting of PCL during quasi-isothermal measurements ($t_p=1200$ s, $A_T=0.5$ K).

heat flow due to re-crystallisation is below the detection limit of DSC.

Curve c in Fig. 3 shows the normalised amplitude of the storage modulus and in Fig. 4 the heat flow amplitude. Both show the typical behaviour in the melting region – a decay with time for each quasi-isotherm and a peak over temperature for the excess part at infinite time. The excess parts are related to reversible melting as introduced by Wunderlich [24] and discussed for PCL in more detail in [15].

3.2. Quasi-isothermal measurements during crystallisation of PCL

Because heat capacity of polymer crystals is smaller than that of the melt one expects during crystallisation a decrease of heat capacity with increasing crystallinity. TMDSC allows for the quasi-isothermal determination of heat capacity during crystallisation. But as for melting an excess heat capacity occurs which can be related to reversible melting during and after quasi-

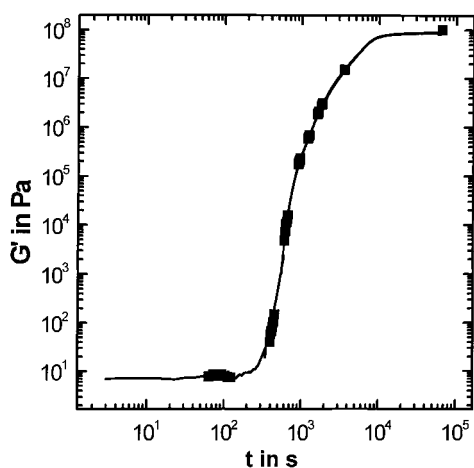


Fig. 6. Time evolution of the storage shear modulus during isothermal crystallisation of PCL at 326.5 K with continuous sinusoidal deformation (—) and partial sinusoidal deformation (■), see text.

isothermal crystallisation [25,13]. Because crystallisation of polymers is far from being well understood [17] additional information about these processes are needed. To check applicability of TMDMA in this field TMDMA and TMDSC measurements during quasi-isothermal crystallisation of PCL were carried out.

First the influence of shear stress, applied during shear module measurements, on crystallisation kinetics was checked. An isothermal crystallisation experiment with continuous shearing was compared with one with only partly shearing of the sample. The result is shown in Fig. 6. No difference between both curves can be seen for the shear stress frequency 0.5 Hz and amplitude 1% which is larger than that used for the measurements. Therefore, it seems to be possible to use DMA under this measuring conditions to study crystallisation of PCL.

Fig. 7, curve a shows the data of the storage modulus for a quasi-isothermal TMDMA crystallisation experiment at 331 K with temperature amplitude of 0.5 K and period of 1200 s. The low crystallisation temperature was chosen to be able to follow the whole crystallisation process in one measurement. The total time for this experiment was more than six days.

Crystallisation starts after an induction time due to nucleation. With increasing crystallinity the storage modulus increases, curve a. The relation between the

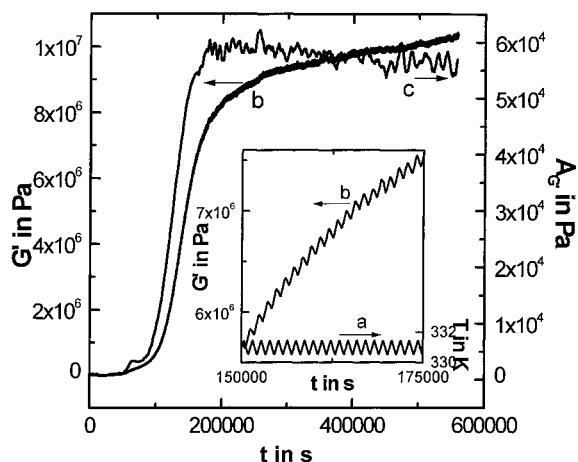


Fig. 7. Time evolution of the storage shear modulus (curve b) during quasi-isothermal crystallisation of PCL at $T_0=331$ K, $t_P=1200$ s, $A_T=0.5$ K (curve a). Curve c shows the amplitude of the storage modulus.

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 quantitatively from shear modulus measurements. The shape of the modulus curve allows to distinguish between two different crystallisation regimes – until 200 000 s main and up to the end secondary crystallisation.

The insert in Fig. 7 shows a magnified part of the modulus curve at the end of main crystallisation. It is remarkable and unexpected that at the heating segments of the temperature modulation there is always a decrease of the storage modulus. This indicates that parts of the sample melt or undergo a glass transition, probably the rigid amorphous fraction. Consider the amplitude of the storage modulus (curve c in Fig. 7) one can see an increase during the main crystallisation with a relatively abrupt change to a constant or slowly decreasing value. This is contrary to the behaviour of the storage modulus itself which is related to crystallinity, increasing up to the end of the measurement.

Also with TMDSC it is possible to investigate quasi-isothermal crystallisation if the sensitivity of the instrument is high enough to detect the heat flow due to crystallisation and modulation. For TMDMA

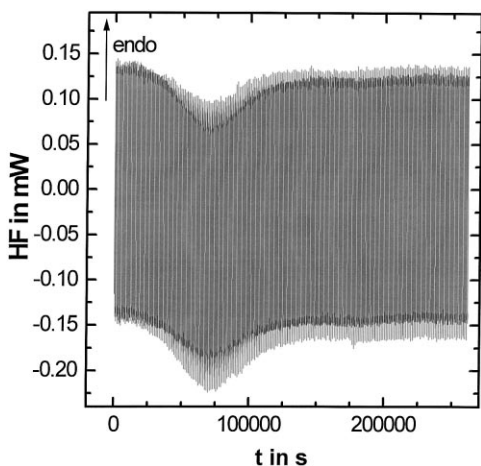


Fig. 8. Time dependence of the heat flow during quasi-isothermal crystallisation of PCL at $T_0=328$ K, $t_p=1200$ s, $A_T=0.5$ K.

there are no limitations caused by the rate of changes in crystallinity because shear modulus itself depends on crystallinity. On the contrary, the heat flow measured in TMDSC depends on the rate of changes and is therefore limited for very slow processes.

Fig. 8 shows the heat flow during quasi-isothermal crystallisation at main temperature of 328 K with a period of 20 min and an amplitude of 0.5 K with the Perkin-Elmer Pyris 1 DSC. The exothermic crystallisation process has been followed for three days. The specific heat capacity was calculated as the ratio of the amplitudes of heat flow and heating rate (Fig. 9, curve a). A small decrease with time can be observed but the value is much higher than expected from ATHAS data bank for the semi-crystalline PCL [26].

The degree of crystallinity of the sample was estimated from heat of fusion ($\Delta h=82$ J/g) obtained from a DSC scan from 328 K to the melt at 343 K just after quasi-isothermal crystallisation. The ratio between the measured and the heat of fusion for an infinite crystal [26] ($\Delta h^0=156.8$ J/g) yields a crystallinity $X\approx 0.5$. The expected phonon heat capacity $c_{p\text{ phonon}}$ for a semi-crystalline sample can be calculated according to

$$c_{p\text{ phonon}}(T, t) = X(t)c_{p\text{ crystal}}(T) + (1 - X(t))c_{p\text{ melt}}(T), \quad (8)$$

with $c_{p\text{ crystal}}$ specific heat capacity for the crystal and

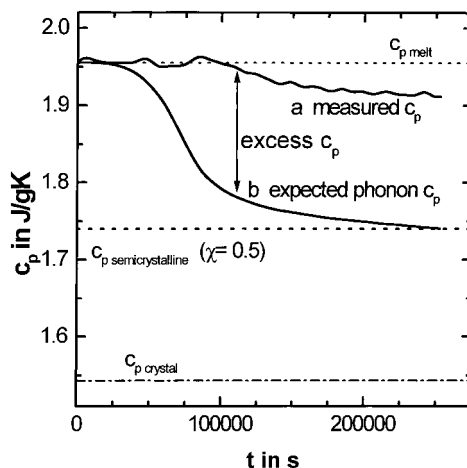


Fig. 9. Comparison of the c_p value from the measured heat flow (curve a) during quasi-isothermal crystallisation at $T_0=328$ K (see Fig. 8) with expected phonon heat capacity (curve b), see text.

$c_{p\text{ melt}}$ that for the melt, both available from ATHAS data bank [26]. With this data it is possible to calculate the expected phonon heat capacity for the sample with $X=0.5$ at 328 K ($c_{p\text{ semicrystalline}}$). The heat capacity calculated from the heat flow amplitude does not reach this value at the end of the experiment where crystallinity reaches 0.5. From the difference an excess heat capacity of about 0.17 J/g K can be obtained. To determine the excess heat capacity during crystallisation as a function of time it is necessary to estimate the curve for the expected phonon heat capacity. This was done with the time dependence of crystallinity and Eq. (8). Crystallinity was estimated from the enthalpy change during crystallisation. The normally used integration of the measured heat flow is not appropriate here because the maximum of the exothermic effect is only 0.05 mW and the total measuring time was three days. Therefore, a sophisticated method to estimate the change in crystallinity from the measured phase angle [27] was used. The result for crystallinity is shown in Fig. 10, curve a and that for expected phonon heat capacity in Fig. 9, curve b.

The difference between curves a and b in Fig. 9 yields the excess heat capacity related to a reversible process, present also at the end of crystallisation. The excess heat capacity is shown in curve b in Fig. 10. As for the amplitude of the shear modulus in Fig. 7 it reaches a constant value much faster than crystallinity.

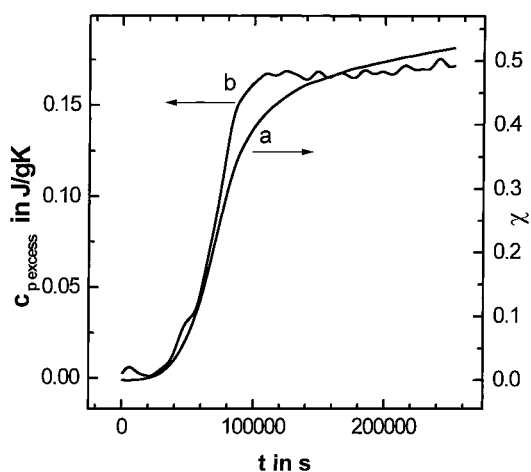


Fig. 10. Comparison of the time evolution of the crystallinity (curve a) and the excess heat capacity (curve b), see text, during quasi-isothermal crystallisation, $T_0=328$ K (Fig. 8).

4. Discussion

From the measurements shown in Figs. 3–5 the reason for the decay of the amplitude of reversing heat flow during quasi-isothermal melting can be seen. At short times melting of PCL continues for several periods of temperature modulation. The additional peaks in the heat flow, see Figs. 4 and 5, contribute to the amplitude of the first harmonic from Fourier analysis. This is an example showing that the amplitude of the periodic component of the heat flow contains not only reversing contributions. Here the non-reversing melting during the first periods contributes to the amplitude of the periodic component. The excess heat capacity is therefore not only a measure of reversible melting as discussed, e.g. in [28].

After finishing melting another non-reversing process may influence reversible melting. As shown in Figs. 3 and 5(a) the shear modulus decreases during melting for the first periods but then shear modulus increases slightly with time. This may be due to re-crystallisation or re-organisation. During re-crystallisation some of the molecules taking part in the reversible melting are influenced in such a way that they cannot further contribute to this process. It is possible that they become part of a more stable crystal or of the more equilibrated melt. This is still an open question but it seems to be very interesting to find an

answer to it better understand the processes of melting and crystallisation of polymers.

Fig. 9 shows that the measured heat capacity decrease less than the expected phonon heat capacity with increasing crystallinity. The difference results in an excess heat capacity which stays constant after the end of main crystallisation. It can be related to reversing melting during crystallisation. This excess heat capacity (curve b in Fig. 10) behaves similar to the amplitude of the storage modulus (curve b in Fig. 7). So the same reversible process will be tested with both independent methods. From the excess heat capacity the amount of material taking part in the reversible process was estimated to about 0.2% of the crystalline material.

As shown in Figs. 7 and 10 time dependence of the quantities determined from the periodic part of shear modulus and heat flow AG and $c_{p,excess}$, respectively, are different from that of crystallinity. Therefore, the reason for the increase of the amplitude is not 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.

In Strobl's four state scheme for polymer crystallisation and melting [17] 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 a part of the surrounding melt. A small temperature increase will allow to remove another fraction of the molecule from the growth front of the crystal and to attach it again if temperature is decreasing. For such a process no nucleation, also no molecular nucleation [16], is necessary as long as a fraction of the molecule is part of the crystal. During main crystallisation number of crystallites and their surface in growth direction as well as the number of molecules in such a situation is increasing faster than crystallinity. At the end of main crystallisation the whole sample is filled with crystallites and remaining amorphous parts in-between. From this time (about 200 000 s in Fig. 7 100 000 s in Fig. 10) the number of crystallites and their surface remains practically constant. The observed behaviour of amplitudes and crystallinity, Figs. 7 and 10, 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 crystallisation process for more than six days in a state of something like a “living” crystal. From temperature modulated experiments it seems to be possible to study such small changes in crystallinity of about 0.2% related to the surface of the crystals.

5. Conclusions

Temperature modulated dynamic mechanical analysis allows for the investigation of reversible and non-reversible phenomena in the melting and crystallisation region of polymers. The advantage of TMDMA compared to TMDSC is the high sensitivity for small and slow changes in crystallinity, e.g. during re-crystallisation. The combination of TMDMA and TMDSC yields new information about local processes at the surface of polymer crystals. Also after long crystallisation times the surfaces of the individual crystallites are in equilibrium with the surrounding melt as shown with temperature modulated measurements with amplitude 0.5 K.

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