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Temperature modulated differential scanning calorimetry (TMDSC) in the region of phase transitions. Part 2: some specific results from polymers

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Abstract

By means of four different examples (pressure crystallised, gel crystallised, nascent and highly stretched polyethylenes (PEs)) it is shown that temperature modulated DSC offers advantages against common DSC. It is possible to see dynamic processes inside the sample during melting. This way we found (i) that during melting of high pressure crystallised PE the so-called α_2-process (known from DMA) takes place, (ii) the lamellae doubling in gel crystallised UHMWPE can be seen in TMDSC signals, though no balance heat flow rate is visible in the common DSC, (iii) the same is true for the recrystallisation in nascent and highly stretched PE many degrees before the melting peak appears. To separate these results from the measured curves the knowledge of the heat transport into and within the sample is needed. A simple low pass filter model has proved its worth for this purpose. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polyethylene; Temperature modulated DSC; Melting; Time-dependent processes

1. Introduction

Temperature modulated differential scanning calorimetry (TMDSC) offers against normal DSC additional possibilities to get information about dynamic (i.e. time-dependent) processes inside the sample. This is especially of importance in polymer research, as macromolecules need time to rearrange at transitions of all kind. Fortunately the time constant of such processes falls often into the time window covered by common DSC equipment. On the other hand the transport of heat needs time as well and the timescale of these processes determines the time (or frequency) window of the TMDSC. In other words, if there are measurable dynamic processes in the sample there is always an influence of the transport processes too. We have to know that influence quantitatively to be able to separate it from the measured results before interpreting them in terms of, say, time-dependent excess heat capacity of the process in question. This is a trivial demand which of course was fulfilled before by what is called calibration of the TMDSC [1,2]. Nevertheless the influence of the heat transfer to and within the sample itself on the measured results has, as far as we know, not been considered in detail for the region of phase transitions before (today there are some more papers on this topic in this special issue [3]).

In phase transition region there are some complications, the most important one is the very change of enthalpy of the sample resulting in an extremely large change of the apparent heat capacity of the sample. For ideal first order phase transitions it becomes infinite and even during the non-ideal melting of

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polymers the excess heat capacity may be more than 50 times larger than outside this temperature region. In addition the thermal conductivity of polymers is three orders of magnitude smaller than that of inorganic materials leading to a very large damping of the temperature wave inside the sample. These two facts influence the results of TMDSC measurements in the melting region of polymers to a large extent. We have tried to evaluate this influence on the basis of a simple low pass filter model in the first part of this paper [4]. With this knowledge we want to show in this second part that it is easily possible in some cases to separate dynamic processes from these artefacts of the apparatus and get additional insight into the melting behaviour of polymers which cannot be found by normal DSC. This will show the advantages of TMDSC in polymer research, even though the frequency range (the time window) is very restricted compared to dynamic, mechanical and dielectric methods.

In what follows we present some distinct examples from our usual polymer research projects, namely the melting behaviour of (i) high pressure crystallised, (ii) gel crystallised, (iii) nascent and (iv) highly stretched polyethylene (PE). These are, of course, very different materials with different behaviour on melting which cannot be compared directly. The point in this paper is to clarify the possibilities and limits of the TMDSC method rather than to give detailed explanations of the measured behaviour from the polymer science point of view. Another paper containing those insights will be published elsewhere.

2. Experimental

We take the knowledge of the principle of the TMDSC method for granted [5–7]. The measurements were done on a Perkin-Elmer DSC7 with self-made sinusoidal temperature modulation possibility[1]. The DSC in question has a very symmetric measuring head leading to a flat (no periodic heat flow fluctuations visible) measuring curve with empty pans of equal mass. This way no empty pan correction was needed. Evaluation of the modulated measurement was done, unlike common Fourier analysis, using a method derived from lock-in techniques [8] which has proved its worth in separating small periodic signals from a very noisy background. The resulting quantities are, however the same, namely the underlying curve (essentially alike the common DSC curve) and the magnitude (amplitude, absolute value) and phase shift of the periodic part of the heat flow rate. The experimental parameters were chosen as small as possible – underlying heating rate: 0.1 K min^{-1}, temperature amplitude: 2–50 mK to avoid bad influences on the results from wrong parameters [9] as well as to be within the limits of linear response of the apparatus [6]. The temperature amplitude was chosen in relation to underlying heating rate and frequency to perform the measurement in only-heating or heating–cooling mode, respectively. Unfortunately, the maximum number of data points is limited in our version of the Unix software of the DSC7 which restricts the number of periods to 500. This way the maximum temperature region at the given underlying heating rate and frequency is even restricted and rather narrow for higher frequencies.

Thin samples (2–4 mg), cut from larger pieces, were encapsulated in normal aluminium sample pans using a reference pan of exactly the same weight because of symmetry reasons. The sample thickness was always as thin as possible (ca. 0.2 mm) to avoid larger temperature gradients.

The polyethylenes under investigation are characterised as follows: UHMWPE: Mw: 3000 kg mol^{-1}, PEl30, Mw: 4.6 kg mol^{-1}, Mw/Mn: 3.6. PEl30 was slowly (10 K h^{-1}) crystallised in a high pressure dilatometer at 500 MPa. UHMWPE was used as nascent material directly from the manufactory or solution crystallised making a gel by cooling the hot solution and drying this gel afterwards [10].

3. Results

3.1. High pressure crystallised PE130

This is a PE wax with low molecular mass and broad mass distribution. The melting behaviour of the high pressure crystallised material is unusual [11], there are two distinct melting peaks one large broad between 110°C and 130°C and a smaller and narrow one at 134°C (Ref. [11] and Fig. 1). Obviously some

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[1] By adding the voltage from a precision function generator to the program voltage in the control circuit

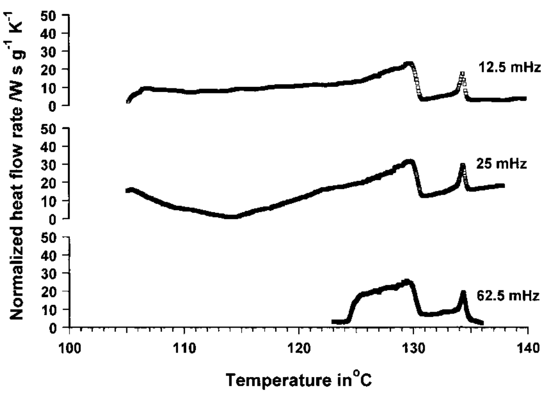

Fig. 1. Normalised underlying curves from TMDSC runs in heating-only mode high pressure crystallised PE130 in the melting region at three frequencies (m=3 mg, ω=0.078, 0.157, 0.393 rad s^{-1}, period=80, 40, 16 s, T_A=11.5, 5.8, 2.3 mK, respectively, underlying heating rate 0.1 K min^{-1}).

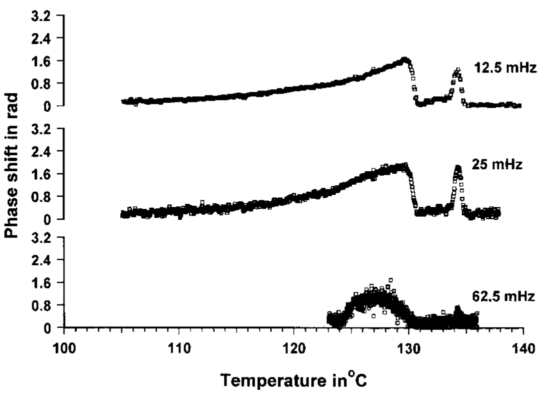

Fig. 3. Phase shift curves from TMDSC runs in heating-only mode of high pressure crystallised PE130 in the melting region at three frequencies (m=3 mg, ω=0.078, 0.157, 0.393 rad s^{-1}, period= 80, 40, 16 s, T_A=11.5, 5.8, 2.3 mK, respectively, underlying heating rate 0.1 K min^{-1}).

phase separation takes place if we crystallise the sample at 500 MPa. The DSC curve of the material crystallised at ambient pressure shows, as usual, only one broad melting peak at significantly lower temperatures [11] (compare even Fig. 5). This interesting behaviour get us to investigate it with TMDSC. The uncorrected results from the measurements at three different frequencies are given in Figs. 1–3. As expected the (normalised) underlying heat flow rate curves (Fig. 1) do not depend on frequency for a given underlying heating rate, the melting peaks look equal. Because of the very low heating rate (0.1 K min^{-1}) and small sample masses (3 mg) the curves are fluctuating (up to 70 µW) and noisy (<10 µW). The last curve, where the measurement starts within the melting peak (because of the limited number of data points), looks different in the beginning because of the effect of annealing at start temperature.

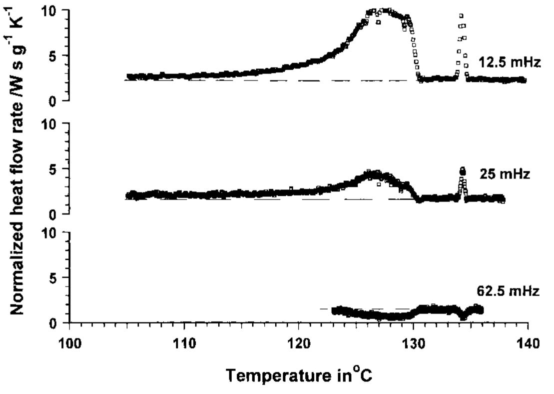

Fig. 2. Normalised magnitude curves from TMDSC runs in heating-only mode of high pressure crystallised PE130 in the melting region at three frequencies (m=3 mg, ω=0.078, 0.157, 0.393 rad s^{-1}, period=80, 40, 16 s, T_A=11.5, 5.8, 2.3 mK, respectively, underlying heating rate 0.1 K min^{-1}).

For the magnitude and phase curves (Figs. 2 and 3) the situation is different, there is a clear dependence on frequency, both the peak shape and the peak height change distinctly. To weigh this result correctly we have to assess the influence of the heat transfer to the sample and its correction. From the considerations in the first part of this paper [4] we have to start from the following equation:

$$c_p = \frac{\phi_{\mathrm{A,\,corr}}}{m \cdot T_{\mathrm{A}} \cdot \omega} = \frac{\phi_{\mathrm{A,\,meas}}}{m \cdot T_{\mathrm{A}} \cdot \omega}\sqrt{1 + \omega^2 R_{\mathrm{th}}^2 C_p^2} \tag{1}$$

where c_p is the (excess) specific heat capacity function, the fraction of the normalised heat flow rate magnitude (or amplitude) (as in Fig. 2) with $\phi_{\mathrm{A,\,corr}}$ and $\phi_{\mathrm{A,\,meas}}$ the sample-corrected and measured heat flow rate magnitude, respectively, m the mass, T_{A} the temperature amplitude, $\omega = 2\pi f$ the angular frequency and the square root the correction factor in question with R_{th} the apparent thermal resistance and C_p the apparent heat capacity of the sample. The correction factor (the square root) is the same for the heat capacity as for the heat flow rate amplitude, so we can restrict ourself to discuss only the latter. The product $R_{\mathrm{th}}C_p=\tau$, the time constant, can be estimated for this sample $\tau=1.1$ s outside the transition region and the correction factors (the square root in Eq. (1)) would there become 1.00, 1.01, 1.09, respectively, for the three frequencies used. In other words the heat capacity determined from the measured heat flow rate magnitude would be below 1%, 1% and 9% too low, respectively. In the melting region the apparent heat capacity of the sample changes by a factor of about 8 (from separate measurements at higher heating rates in C_p-mode, and even from the underlying curve) which would yield correction factors of 1.2, 1.7, 3.6, respectively, at peak maximum. Taking these correction factors into account would change the peak height considerably but not the quality of the peak shape. From Fig. 2 it is clear that obviously the measurements at different frequencies show a distinct change in the quality of the heat flow rate magnitude which cannot be explained by heat transfer influence only. In particular at 62.5 mHz the measured magnitude within the melting region drops below the value outside of it, which never can be explained via. Eq. (1). Consequently there is no excess heat capacity influencing the modulated signal and thus no correction factor needed for that frequency.

The results of the phase shift measurements (Fig. 3) support these arguments. From the first part of this paper [4] the influence of sample heat transfer on the phase angle reads

$$\phi = \tan^{-1}(-\omega R_{\mathrm{th}} C_p), \qquad (2)$$

which gives rise to an increase of the phase shift[2] with frequency (and heat capacity of the sample). The measured phase shift decreases, however (Fig. 3). This means (i) that the apparent heat capacity of the sample decreases (Eq. (2)) and/or (ii) as the periodic heat flow into the sample drops almost to zero, that the phase shift between the temperature modulation and the heat flow rate signals (normally $\pi/2$) drops too.

In our opinion there is only one possible explanation for these results, the melting process needs time and thus the melting rate cannot follow the temperature changes at higher frequencies anymore. (In common DSC this would result in an overheating effect, which Wunderlich found for chain extended PE [12]). Consequently there is only a periodic temperature fluctuation of the sample in this region without any periodic flow of latent heat for melting and crystallisation. From the huge decrease of the normalised magnitude we have to draw the conclusion that the temperature amplitude of the sample must be much lower than it would be outside the melting region, because the apparent heat capacity drops down below the (static) heat capacity of the liquid and solid state. From the unchanged underlying heat flow rate curve follows, on the other hand, that the average temperature increases to the same extent as for lower frequencies (and with it the melting rate) corresponding to the underlying heating rate.

It is possible, by plotting the measured magnitude in the melting region against ω, to determine the frequency yielding a zero magnitude of the periodic heat flow rate as f=35 mHz and ω=0.22 rad s^{-1} , which may serve as a zeroth approximation of the characteristic frequency of the process in question. The reciprocal value (4.5 s) can be interpreted as the time constant of a relaxation process. Entering this value together with the temperature of the melting peak into the activation diagram of polyethylene [13,14] (see the cross in Fig. 4) we end up precisely at the α_2-process a crystal process which characterises the diffusion of the

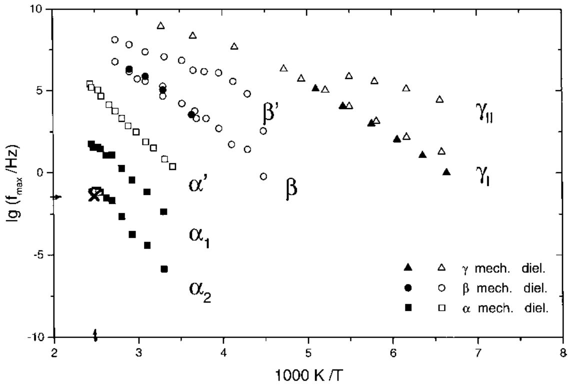

Fig. 4. Activation diagram of relaxation processes in polyethylene [13,14]. The α-processes takes place in the crystal, the β-processes characterizes the glass process in the amorphous and the γ-process means the local process. The cross marks the result from TMDSC.

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[2] We neglect the sign in Eq. (2) and define the *phase shift* of the heat flow rate signal as always positive (i.e. behind the temperature signal in time).

polymer in chain direction [15]. Polyethylene forms under high pressure chain-extended crystals. During melting numerous gauche conformations have to enter the all-*trans* chain. This is only possible, if the end-to-end distance shortens correspondingly, a process which occurs by chain diffusion after freeing of the chain from the neighbours in the crystal lamellae. This process is of special importance for high pressure crystallised material with very long all-*trans* sequences, but is, of course, even found with normal pressure crystallised material forming much thinner lamellae, where the time constant is lower (higher characteristic frequency). The results from the second run of the same samples (crystallised at ambient pressure) support this idea (Fig. 5). There is again a tendency of magnitude decrease with frequency, but the characteristic frequency (i.e. zero magnitude change) is outside the window of our apparatus at too high frequencies.

These measurements show clearly that it is in principle possible to get information from time-dependent processes in the sample by means of TMDSC if the process in question falls into the time window of the apparatus. Unfortunately the frequency range of TMDSC is maximum two decades, so only a fraction of the magnitude (or phase angle) versus frequency curve can be measured this way. Nevertheless, there is additional knowledge about melting behaviour available from TMDSC measurements compared with information got from common DSC runs.

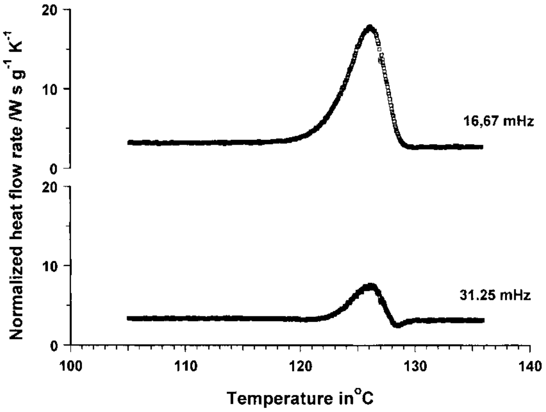

Fig. 5. Normalised magnitude curves from TMDSC runs in heating–cooling mode of at ambient pressure crystallised PE130 (second run) in the melting region at two frequencies (m=3 mg, ω=0.105, 0.196 rad s^{-1}, period=60, 32 s, T_A=23 mK, respectively, underlying heating rate 0.1 K min^{-1}).

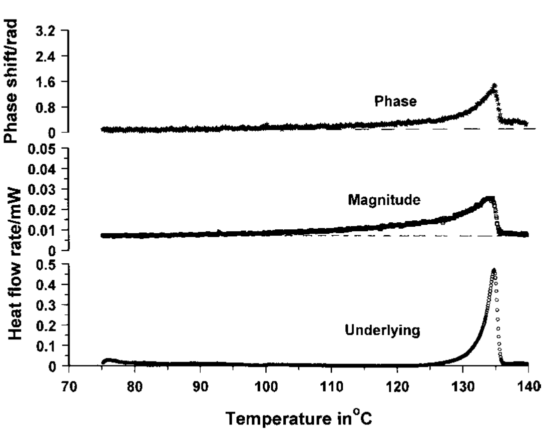

Fig. 6. TMDSC curves from a run in heating-only mode of gel crystallised UHMWPE in the melting region (m=3.6 mg, ω=0.078 rad s^{-1}, period=80 s, T_A=11.5 mK, underlying heating rate 0.1 K min^{-1}).

3.2. Solution (gel) crystallised UHMWPE

From X-ray measurements this material has a very narrow lamellae thickness distribution around 130 Å. On heating, the lamellae thickness doubles from 125 to 250 Å in the temperature region between 110°C and 120°C [10]. Normal DSC measurements (not included here) did not show any effect in this region, the curve was almost horizontal there (see the underlying curve in Fig. 6). Here the question arose, whether there would be some visible effect in the TMDSC. The result of the respective measurement is presented in Fig. 6, both magnitude and phase of the modulated heat flow rate deviate from horizontal line already at 100°C in contrast to the underlying curve[3]. Obviously there is a process going on which reacts on the modulated temperature change in such a way that the magnitude of the modulated part of the heat flow rate into the sample increases, whereas the average of the positive and negative amplitudes is zero even though the average temperature has changed a little during one period. As there is no residual change of latent heat (enthalpy) in the region 100–125°C during

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[3] Of course this curve is rather noisy because of the very low underlying heating rate, but it reflects, however, the results got at higher heating rates in c_p-mode

one period, the degree of crystallinity must be considered constant. However, in this region the thickness of the lamellae doubles, which is only possible if there is some melting and recrystallisation (without change of the degree of crystallinity). From the increase of the magnitude of periodic heat flow rate in that region follows that the melting and recrystallisation cannot take place simultaneously, because the latent heats would neutralise each other and the balance would be zero. There must be some difference in the timescales of these processes which falls into the time window of the modulation. One explanation may be as follows: during the upper (half) period (where the sample is heated faster than with underlying rate) the process of melting of the small lamellae is faster than the crystallisation of the thicker ones because we are going away from steady state (increasing overheating). During the lower (half) period the situation is reverse, the crystallisation becomes faster against melting because now we are going away from steady state for this process (increasing undercooling). In common DSC measurements (at constant heating rate) both processes are in steady state, the rates of melting and crystallisation are equal and there is no balance heat flow rate.

What about the heat transfer to the sample in this case, does its correction influence our interpretation? Eq. (1) states (i) that the measured magnitude of the modulated heat flow rate is systematically too small, which implies that the real magnitude would be even larger, and (ii) that we cannot proceed from the underlying heat flow rate curve to estimate the changes in the sample properly if time-dependent processes are involved. The latter is supported by the measured phase shift (see Fig. 6) which follows the magnitude curve rather than the underlying one. According to Eq. (2) tan ϕ should be proportional to the apparent heat capacity C_p. For small arguments tan ϕ can be approximated by ϕ itself and the proportionality of the phase shift and the magnitude curve is given. The apparent heat capacities from the common DSC run (underlying curve) and from the modulated heat flow rate are different and the difference allows insights into the processes involved.

Even for this examples we are successful with TMDSC measurements to get additional informations, because the timescale of the processes in question falls within the time window of the apparatus again.

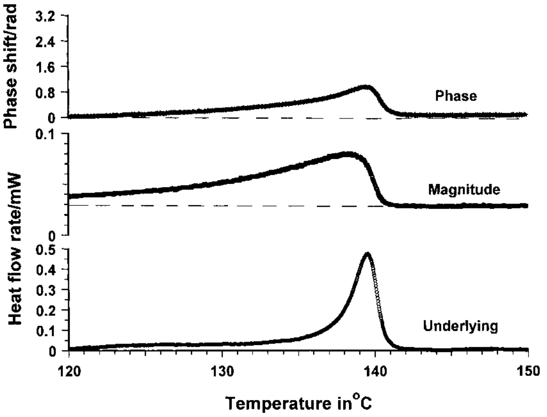

Fig. 7. TMDSC curves from a run in heating–cooling mode of nascent UHMWPE in the melting region (m=3.8 mg, ω=0.196 rad s^{-1}, period=32 s, T_A=23 mK, underlying heating rate 0.1 K min^{-1}).

3.3. Nascent UHMWPE

For this material, PE got directly from the manufacture process, the situation is similar to that of gel crystallised PE. Even this PE has originally a high degree of crystallinity with thin and very narrow distributed lamellae which increase in thickness (15–60 nm) on heating [16]. The result of TMDSC measurements is presented in Fig. 7. Again we find in principle the same behaviour: the underlying curve (and common DSC runs at higher heating rates as well) show a narrow melting peak at even higher temperature as for gel crystallised PE (Fig. 6) and both magnitude and phase of the modulated heat flow rate deviate much earlier from horizontal line. Again we may argue that there is a melting and recrystallisation going on which only can be seen in the modulated signal. The interpretation may be as in Section 3.2, even here the processes of melting and crystallisation have different time constants depending on the deviation from steady state heating and these time constants fit just to the time window of the TMDSC.

3.4. Highly stretched UHMWPE

It is very easy to stretch the gel crystallised UHMWPE in a temperature region well below the melting temperature, say, 20 times [16]. Such a sample was investigated in the TMDSC. The result is given in Fig. 8. Again there is a distinct difference between the

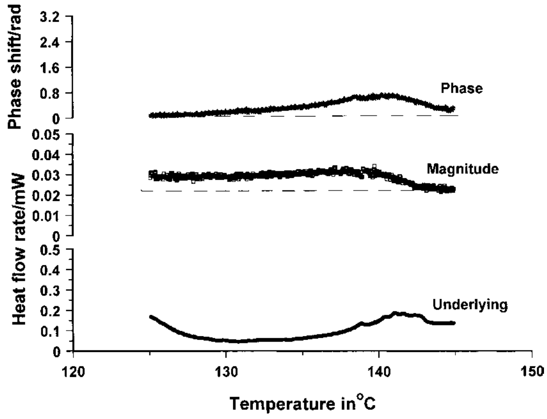

Fig. 8. TMDSC curves from a run in heating–cooling mode of highly (20×) stretched UHMWPE in the melting region (m=3.8 mg, ω=0.196 rad s^{-1}, period=32 s, T_A=23 mK, underlying heating rate 0.1 K min^{-1}).

underlying signal on the one hand and the magnitude and phase curves on the other hand. Unfortunately the underlying curve is very noisy because of the low sample mass and low underlying heating rate, but common DSC runs at higher heating rate give similar results. Nevertheless it is clear from the magnitude curve, that there are some processes already at 125°C but with zero balance enthalpy change. The underlying melting peak starts at about 135°C and proceeds until 143°C, whereas the magnitude peak starts below 125 and drops to zero earlier. In every case the shape is very different and again there are two different excess heat capacities, namely a static and a dynamic one. Of course the small "hills" on the underlying peak, which presumably are caused by shrinking of the sample in the melting region, are not reproduced in the other two curves. This process is independent of the temperature modulation.

4. Conclusions

The outlined different examples show that TMDSC offers the possibility to study time-dependent processes even in the melting region. A necessary condition is that the timescale must fit to the time window of the TMDSC. Unfortunately this means a strong restriction of the possible applications of this method, because the frequency range of common TMDSC is maximum two decades. Nevertheless it is possible to get new insights into, say, time-dependent melting behaviour of polymers. To separate these effects quantitatively from influences of the apparatus and, in particular, from heat transfer effects to and within the sample in the melting region, a detailed investigation of these influences is unavoidable. This is a laborious task which, together with the slow (of necessity) heating rate make TMDSC measurements very time consuming. This becomes even worse if the frequency must be varied. That is why this method will never be suitable as routine method to measure material properties. However, it is of importance in research, in particular in polymer research, as the knowledge of time consuming thermal processes often cannot be obtained with common DSC.

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