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Dedicated to Professor Wunderlich on the occasion of his 65th birthday

MODULATED TEMPERATURE DSC MEASUREMENTS RELATING TO THE COLD CRYSTALLIZATION PROCESS OF POLY(ETHYLENE TEREPHTALATE)

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Abstract

The modulated temperature differential scanning calorimetric method (MT-DSC) yields three temperature dependent signals, an underlying heat capacity curve from the underlying heat flow rate (corresponding to the conventional DSC signal), and a complex heat capacity curve with a real part (storage heat capacity) and an imaginary part (loss heat capacity). These curves have been measured in the cold crystallization region for poly(ethylene terephtalate) with a modified Perkin-Elmer DSC-7. The underlying curve shows the well known large exothermic crystallization peak. The storage heat capacity shows a step change which reproduces the change in heat capacity during crystallization. This curve may be used as baseline, to separate the crystallization heat flow rate from the underlying heat flow rate curve. The loss heat capacity curve exhibits a small exothermic peak at the temperature of the step change of the storage curve. It could be caused by changes of the molecular mobility during crystallization.

Keywords: cold crystallization, DSC, heat capacity, modulated temperature DSC, poly(ethylene terephtalate)

Introduction

The modulated temperature mode of operation of differential scanning calorimeters increases the power of classical DSC and makes it possible to get additional information about the dynamic behavior of the sample. This is of importance in cases where time dependent events take place in the sample. In polymers most processes are time dependent and rather slow compared with other materials, because of the restricted mobility of the macromolecules. As a consequence equilibrium thermodynamics and thus the methods of classical calorimetry are often limited to rather trivial investigations resulting in wholesale quantities as overall heat of fusion, degree of crystallinity, heat of reaction, etc. On the other hand, the dynamical behavior of polymer materials is of special interest, for instance at the glass transition, when studying crystallization and fusion kinetics, superheating and supercooling effects, etc. For all cases

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with time dependent heat production or consumption, the method of temperature modulated DSC (MT-DSC) yield results that allow an insight into the dynamics of the process in question. Thus the MT-DSC is a very suitable completion of thermoanalytical methods, especially in polymer science.

In this paper we try to show the advantages and the power of this method by means of a process far from equilibrium, which is in addition time and temperature dependent, namely the cold crystallization of poly(ethylene terephtalate) (PET). Indeed this process is well known for many decades [1], nevertheless a new method can be judged better by means of understood results than on a new territory of polymer research.

Cold crystallization takes place in certain polymers that do not crystallize on fast cooling from the melt into the glassy state, but on following reheating above the glass transition. Obviously the vitrification favors the nucleation process and the crystallization can take place after devitrification. Nevertheless, the cold crystallization is a rather slow process because of the restricted mobility of the molecules in the highly viscous melt just above the glass transition and thus suitable for study in the frequency domain of MT-DSC.

Considerations about the method

In commercially available MT-DSC's the usual temperature program (heating, cooling, or isothermal) is superimposed with a periodical temperature change:

$$T(t) = T_0 + \beta_0 t + \sum_{k=1}^{\infty} T_{a,k} \cdot \sin(k\omega_0 t) \tag{1}$$

where T_0 is the starting temperature, β_0 the underlying scanning rate, $\omega_0=2\pi\nu$ (with ν the frequency used) and $T_{a,k}$ the temperature amplitude of the k^{th} harmonic. The sum in Eq. (1) describes any periodical temperature change. In the case of a sinusoidal temperature change the sum has only one term ($k=1$) [2].

From the measured signal the heat flow rate into the sample can be calculated [3]

$$\Phi(T(t)) = \Phi(T,t) + \sum_{k=1}^{\infty} \Phi_{a,k}(T,t) \cdot \cos(k\omega_0 t + \varphi_k) \tag{2}$$

where $\Phi_{a,k}$ is the amplitude of the k^{th} harmonic of the oscillating part of the heat flow rate and φ_k the corresponding phase shift. The underlying heat flow rate, is Φ and depends on the underlying scanning rate. It corresponds to the output signal of a conventional DSC. The sum describes the periodic part of the measured signal. By Fourier analysis we can get the first harmonic of it.

For sinusoidal temperature modulation Wunderlich showed how to separate the measured heat flow rate into the underlying and the periodic components [4]. In case of absence of any time dependent thermal event in the sample, the amplitude of the first harmonic reads

$$\Phi_a(T) = KT_a\,\omega_0 m c_p(T) \tag{3}$$

where m is the sample mass, c_p the specific heat capacity and K a calibration factor. This method allows to measure the heat capacity of the sample very precisely [5].

But if the thermal event is time dependent, it is more advantageous to interpret the measured curve with the aid of the tools of linear response theory. This method is discussed in detail in Ref. [3]. As one results we get the first harmonic of the (calibrated [6]) periodic component Φ_p of the heat flow rate:

$$\Phi_p = T_a\omega_0 m\,|c(T,\omega_0)|\cos(\omega_0 t + \varphi) \tag{4}$$

with $|c(T,\omega_0)|$ as the modulus of the complex heat capacity $c^*(T,\omega_0)$. This and the real part c' (the storage heat capacity) and the imaginary part c'' (the loss heat capacity) are connected *via* the following relations:

$$|c(T,\omega_0)| = \sqrt{(c'(T,\omega_0))^2 + (c''(T,\omega_0))^2} \tag{5}$$

$$c^*(T,\omega_0) = c'(T,\omega_0) - ic''(T,\omega_0) \tag{6}$$

$$c'(T,\omega_0) = |c(T,\omega_0)|\cos\varphi \tag{7}$$

$$c''(T,\omega_0) = |c(T,\omega_0)|\sin\varphi \tag{8}$$

Another method of evaluation of MT-DSC curves proceeds from the separation of the measured heat flow rate into a ‘reversing’ and a ‘nonreversing’ component [7]. From the ‘reversing’ component of the heat flow rate a heat capacity can be calculated which is identical with the modulus of the complex heat capacity. Differences of both evaluation methods are discussed in Ref. [8].

The approach of the complex heat capacity has proven its worth in the case of the glass transition process [3, 9]. Whereas results of MT-DSC investigations of the cold crystallization process have been published up to now only using Readings evaluation methods [10, 12].

These two results differ from one another and do not correspond to our results (presented in this paper) which are evaluated in terms of complex heat capacity.

Experimental

The measurements were done on a modified Perkin-Elmer DSC-7 power compensated scanning calorimeter. In this special case the program temperature was modulated with a sinusoidal temperature change. The frequency range was 2 to 200 mHz. The amplitude could be chosen between 0.1 and 10 K. In addition to the usual quantities, the average temperature between sample and reference furnace was measured in this special DSC. From this temperature and the oscillating component of the heat flow rate signal the storage $c'(T,\omega_0)$ and loss $c''(T,\omega_0)$ heat capacities have been calculated by Fourier analysis. The separation of the measured curve into an oscillating and an underlying component was carried out by averaging. From the underlying component the heat capacity c_β was determined as in conventional DSC.

The samples (mass: ca 4 mg) were prepared from commercial poly(ethylene therephthalate). We chose the following conditions for our measurements: frequency of sinusoidal temperature modulation from 28 to 42 mHz; amplitude T_a generally 0.2 K (smallest possible, to avoid influences on the sample behavior); underlying heating rate β_0: 1 K min^{-1} (slow, to avoid errors in separation into underlying and oscillating components [3] resulting in a temperature change (at the lowest frequency) of 0.4 K per period.

Before every measurement the sample was heated above the melting point and cooled fast (>80 K min^{-1}) to room temperature.

Results

The result of a MT-DSC measurement from room temperature to 300°C is shown in Fig. 1. Three different regions may be distinguished in this measurement: the glass transition, the cold crystallization and the melting region. In this paper we shall focus on the cold crystallization process, which is enlarged in Fig. 2 together with the glass transition. For the latter the already known behavior [3] is found again, in other words, a step change both in c' and c_β (which differ somewhat in temperature) and a peak in c'' which has its maximum at the temperature of the inflection point of the c' step.

In the cold crystallization region from 110 to 150°C, the large exothermic peak characterizing the heat of crystallization is only visible in the underlying (conventional) heat capacity curve, whereas the storage heat capacity shows a small step change and the loss heat capacity shows a very small exothermic peak in this temperature region. As the loss heat capacity is very small, the modulus $|c|$ (corresponding to the reversing component) equals almost the storage heat capacity. Reading has found this step change as well [10], however, his curve of the reversing component shows an 'overshot' which probably is an artifact caused by by the choice of period time, underlying heating rate and sample mass [13].

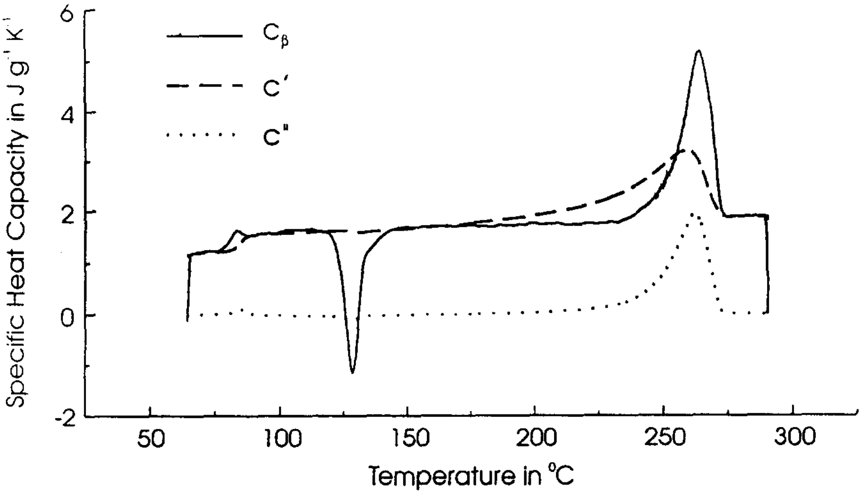

Fig. 1 Complex specific heat capacity and underlying (total) heat capacity c_β of PET (ν=28 mHz, T_a=1 K, β_0=2 K min^{-1})

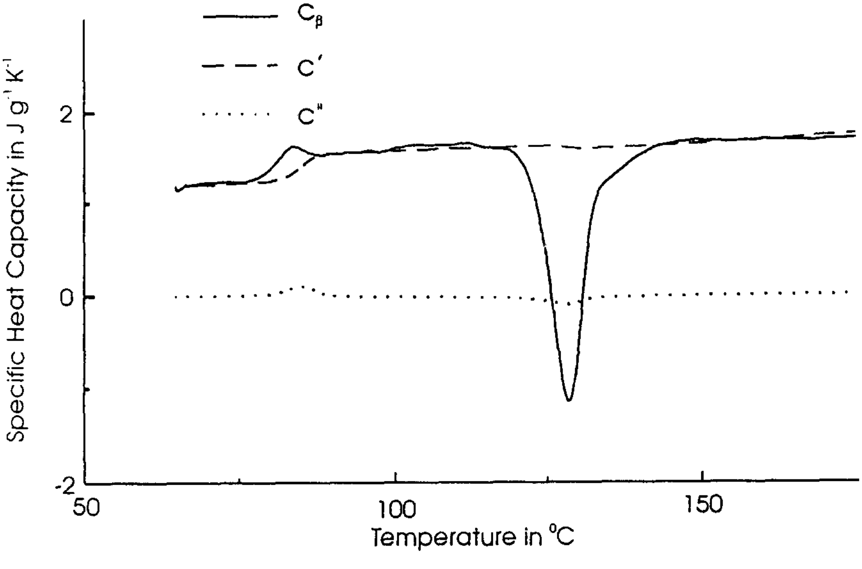

Fig. 2 Complex specific heat capacity and underlying (total) heat capacity c_β of PET in the glass transition and cold crystallization regions (parameters as in Fig. 1)

In order to test the influence of the cold crystallization process on the complex heat capacity, underlying heating rate and frequency were changed. The results are shown in Figs 3 to 6. From Figs 3 and 4 we find that the step in c' and the peak in c'' shift in the same manner with the underlying heating rate as the crystallization peak in c_β (which corresponds to the conventional DSC signal). Furthermore, the minimum temperatures of c'' and Φ are identical (Fig. 4).

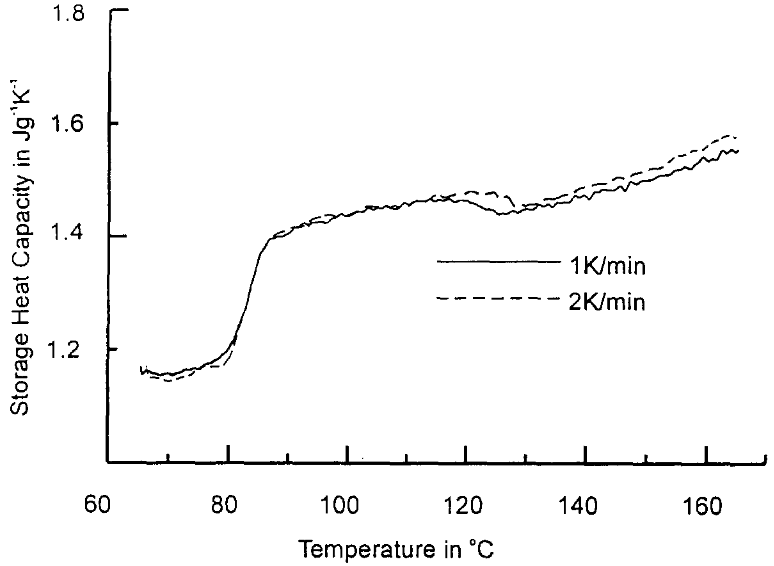

Fig. 3 Storage heat capacity of PET at different underlying heating rates (T_a=0.2 K, ν=42 mHz)

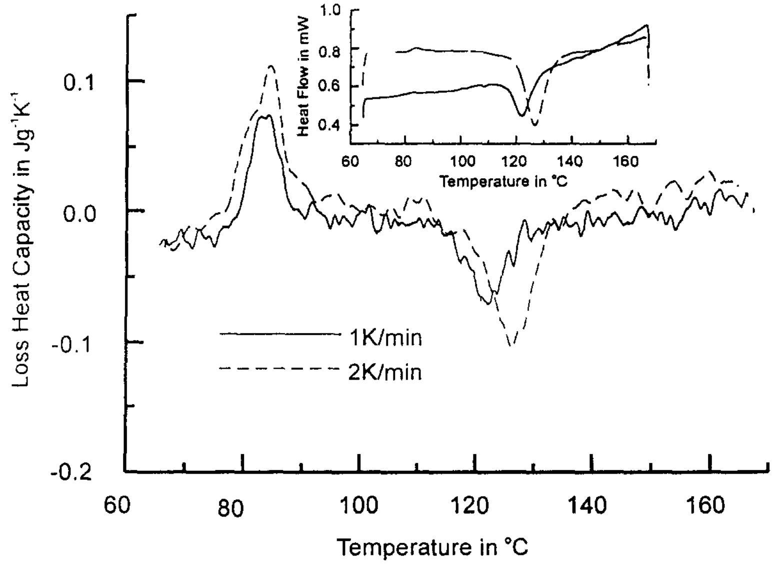

Fig. 4 Loss heat capacity of PET at different underlying heating rates (T_a=0.2 K, ν=42 mHz)

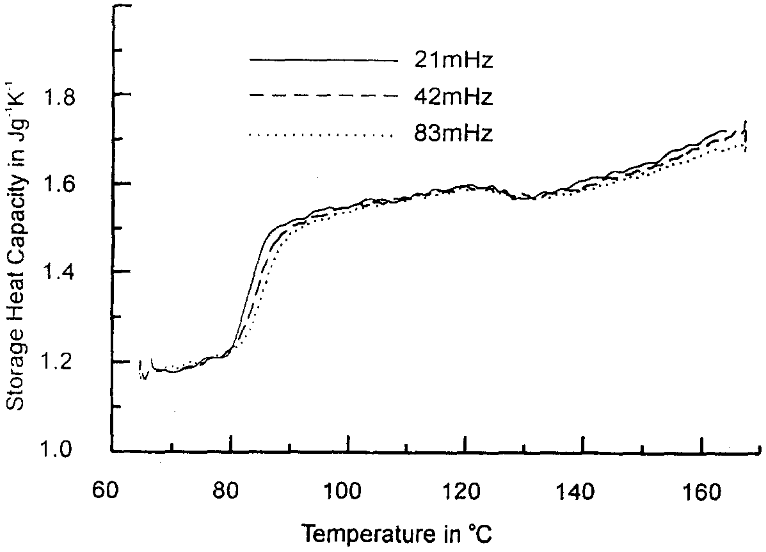

Fig. 5 Storage heat capacity of PET at different frequencies (T_a=0.2 K, β_0=1 K min^{-1})

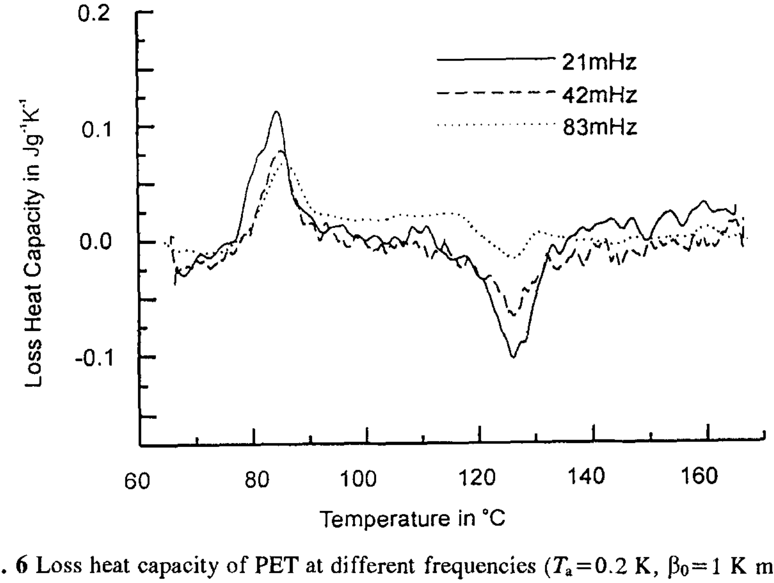

Fig. 6 Loss heat capacity of PET at different frequencies (T_a=0.2 K, β_0=1 K min^{-1})

In Figs 5 and 6 the influence of changed frequencies is shown. Again, the behavior of the complex heat capacity in the glass transition region is as already known [3, 9], whereas there is no change of c' and c'' in the cold crystallization region, except that the peak area of c'' decreases with frequency. This is in accordance with the dielectric behavior in the cold crystallization region, which shows a frequency independent decreasing step in the real part of the dielectric constant and a frequency independent maximum in its imaginary part [14]. In Fig. 7 the storage heat capacity curves of a heating run with cold crystallization and the following cooling run without any crystallization are compared. The latter curve shows only the broad and flatter step of the glass transition, nevertheless it does not coincide with the heating curve in that part above the crystallization region where the material should be in an identical state. Here *c'* of the heating run is higher than in the cooling run. We assume that in this region the crystallization was not completed during the heating run and that the real part (strictly speaking the modulus) of the heat capacity reflects the different degrees of crystallinity during both runs.

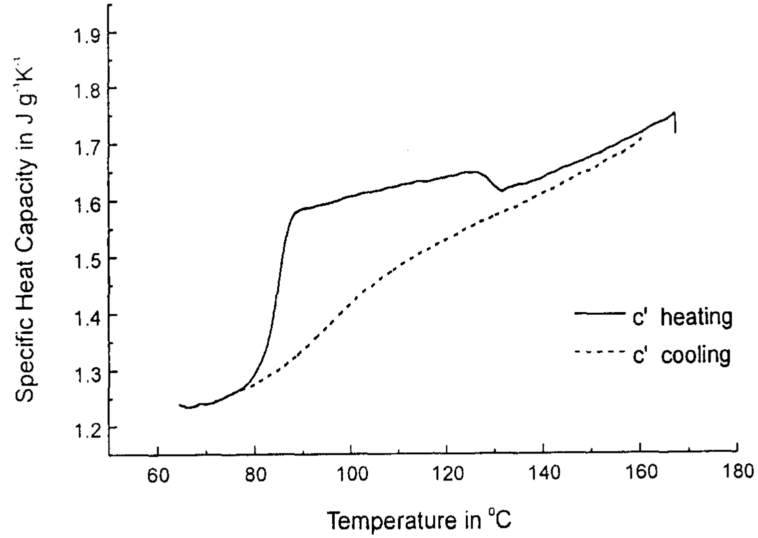

Fig. 7 Storage heat capacity of PET in the region of glass transition and cold crystallization (T_a=1 K, β_0=2 K min^{-1}, ν=36 mHz)

Discussion

The question arises, whether the small (exothermic) peak in the loss heat capacity during the cold crystallization process is real or an artifact. Indeed, the measured curve is a superposition of the underlying heat capacity c_β with a large peak from the heat of crystallization and a small oscillating part, and it is not easy to determine *c''* exactly, especially since the result reacts very sensitively to phase errors. In practice the separation of the measured curve is carried out by averaging procedures. In order to check whether this evaluation

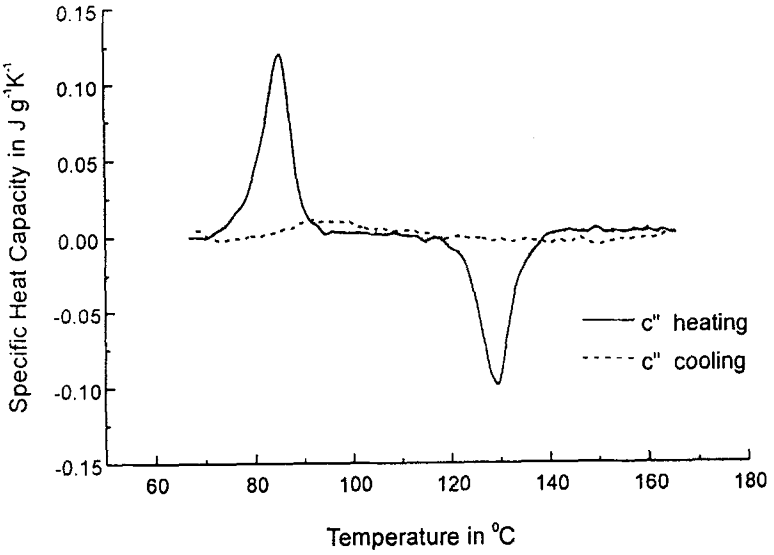

Fig. 8 Loss heat capacity of PET in the region of glass transition and cold crystallization (T_a=1 K, β_0=2 K min^{-1}, ν=36 mHz)

method can cause a peak in c'' we did some simulation calculations. Therefore, we synthesized a measured curve by multiplying a real empty pan curve with a fictive heat capacity of 0.005 Jg^{-1}K^{-1} and added a negative Lorentz curve (to simulate the cold crystallization heat flow). Such a synthetic curve (Fig. 8), which contains no phase shift due to sample processes, as used as input curve for the original evaluation software. The results of the evaluation is shown in Fig. 9. In the region of the Lorentz peak both c' and c'' show very small oscillations (which are lower in magnitude than the apparatus noise), but there is no peak in the imaginary part. Thus, we have to draw the conclusion that the measured peak in the loss heat capacity of PET is, indeed, caused by a real physical process in the sample.

What sort of process is it? The cold crystallization takes place more than 100 K below the melting region, this is truely far from equilibrium and thus we have a strongly irreversible process, that should not be influenced by small temperature fluctuations. Such processes are not sensitive to linear response and their heat flow rate will not be part of the oscillating signal and, consequently, they don't become visible in the loss heat capacity.

However, the appearance of crystallites in the polymer melt influences the mobility of the molecules, which in turn, is sensitive to linear response and should be visible in the loss heat capacity [3]. During crystallization, chain segments will be fit into the crystals and the mobility of the remaining molecule will be reduced. In addition a 'rigid amorphous' [15] layer (with reduced mo-

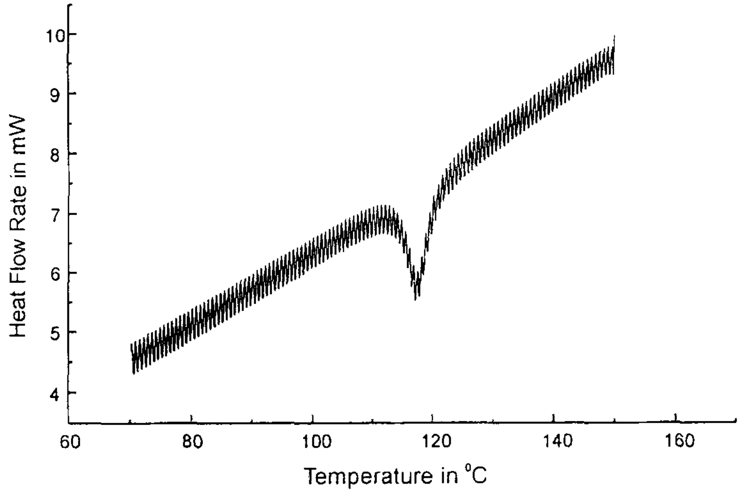

Fig. 9 Synthetic measuring to simulate the evaluation error

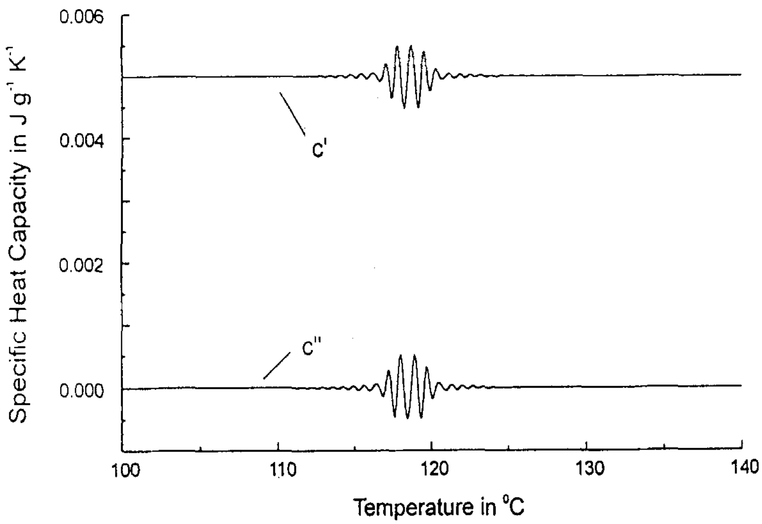

Fig. 10 Results from simulation evaluation of the synthetic curve of Fig. 9

bility) is formed on the surface of the crystals. As a result, we find a vitrification effect of the liquid movements which influences the relaxation behavior of the sample [16]. Such an effect is directly coupled to the crystallization and should be proportional to the crystallization rate. The position of the signal in question should be independent of the frequency of the disturbance. Both of these assumptions are in accordance with our experiments (Fig. 8).

The measured difference of the peak areas in c'' of the glass process in the heating and cooling run could eventually be found again in the peak area of the loss heat capacity on cold crystallization. In every case this would be in accordance with the energy conservation principle.

Conclusions

The results of our MT-DSC measurements of PET yield three different heat capacity curves which contain information on different aspects of the cold crystallization. The underlying heat capacity c_β (which corresponds to the conventional DSC-curve) contains the crystallization heat flow rate, from which the total heat of crystallization and the crystallization kinetics may be determined. The storage heat capacity c' determines to a great extent the decrease of the heat capacity during crystallization that is coupled to a decrease of molecular mobility. Degrees of freedom of cooperative movements in the liquid are lost at that time. This curve contains no information about the irreversible heat flow and may be used as baseline to separate the crystallization peak from the underlying curve (the difference of c_β and c' yields the 'nonreversing' component due to Reading's evaluation method). Finally, a small peak in the loss heat capacity c'' could be connected with the change in molecular mobility and thus with the change of the relaxation answer to temperature distortions during the crystallization, however, it is not completely understood yet.

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