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A METHOD FOR ANALYSIS OF THE MEASURED CURVES OF TMDSC INVESTIGATION IN THE MELTING REGION OF POLYMERS

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Abstract

The measured signal of the temperature-modulated differential scanning calorimetry (TMDSC) is discussed in the case of polymer melting. The common data evaluation procedure of TMDSC-signals is the Fourier analysis. The resulting information is the amplitude and the phase shift of the first harmonic of the periodic heat flow component. It is shown that this procedure is not sufficient for quantitative discussions if deviations from the symmetric curve shape occur in the measured heat flow curves. For polymer melting it is demonstrated that asymmetric curves will be measured if the experimental temperature amplitude is too large.

In this paper a data evaluation method is presented, which is based on the Fourier transform of the measured curves. The peaks of the first and second harmonics in the resulting spectra are used for the analysis of the asymmetry of the measured curves. In the case of polymer melting this analysis yields the maximum temperature amplitude which follows a correct linear data evaluation. This maximum temperature amplitude depends on the material.

Keywords: melting, polymers, signal analysis, TMDSC

Introduction

In the temperature modulated differential scanning calorimeter (TMDSC) the temperature program of a conventional DSC is superimposed with a periodic temperature perturbation $T_p(t)$. The temperature program can be described as a sum of a linear part and a periodic part T_p:

$$T(t) = T_0 + \beta_0 t + T_p(t) \quad (1)$$

where β_0 is the underlying heating rate and T_0 the initial temperature.

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In general the measured heat flow rate Φ can be described as a sum of two parts:

$$\Phi(t) = \Phi_u(t) + \Phi_p(t) \tag{2}$$

where $\Phi_u(t)$ is the underlying heat flow rate which corresponds to the conventional DSC curve, and $\Phi_p(t)$ is the periodic component. The characteristic parameters of the periodic component are the heat flow amplitude Φ_a and the phase shift φ between Φ_p and dT_p/dt. Those parameters are usually determined by the first harmonic of a Fourier analysis [1, 2]:

$$\Phi_a(t) = \sqrt{\Phi_s^2 + \Phi_c^2} \tag{3a}$$

$$\tan\varphi - \frac{\Phi_s(t)}{\Phi_c(t)} \tag{3b}$$

where Φ_s and Φ_c are the sine and the cosine component of the first harmonic of Φ_p, respectively. The equations

$$\Phi_s(t) = \frac{2}{kt_p}\int_{t-kt_p/2}^{t+kt_p/2}\Phi_p(t')\sin\omega_o t'\,dt' \tag{4a}$$

$$\Phi_c(t) = \frac{2}{kt_p}\int_{t-kt_p/2}^{t+kt_p/2}\Phi_p(t')\cos\omega_o t'\,dt' \tag{4b}$$

are used for the numerical determination of the heat flow amplitude and the phase. In Eq. (4) t_p is the period and $\omega_o(=2\pi/t_p=2\pi f_o)$ the angular frequency. The number k (=1,2,3,...) is a constant and different by different TMDSC instruments.

If Φ_p is a symmetric periodic function, the first harmonic describes the dynamic response of the sample. Otherwise information is lost when the Fourier analysis is applied. In other words the data evaluation using the first harmonic of the periodic heat flow component is only valid when the sample response is linear and Φ_p is a symmetric curve. In this case the frequency dependent complex heat capacity reads

$$c^*(\omega) = c'(\omega) - ic''(\omega) \tag{5}$$

The linear analysis is only valid for small temperature amplitudes T_a [3]. Furthermore, the underlying heating rate β_o must be taken into account. Immoderately high underlying heating rates lead to non-stationary effects [4]. From the mathematical point of view the Fourier analysis in Eq. (4) requires a constant

amplitude of $\Phi_p(t)$ during the time interval $[t-kt_p/2, t+kt_p/2]$ which is practically impossible and can be fulfilled only approximately. However, the error is often negligible if small underling scanning rates β_o are chosen.

Especially in the melting region of polymers distortions of the signal shape can be observed [5]. We assume that they are caused by differences in the kinetics of melting and recrystallisation. In this case deviations of the linear behaviour can be measured. One common method of discussing those non-linear effects is the visual analysis of the Lissajous figures [6].

First investigations of the periodic response in the melting region of Polyoxyethylene (POE) [5] and Poly(ε-caprolactone) (PCL) [7] seemingly indicate that local reversible melting processes occur without any nucleation process. It should be possible to describe this behaviour analogously relaxation processes [7, 8]. In that case the sample response should be linear (symmetrical) for small temperature amplitudes and the complex heat capacity is then a useful tool for the interpretation of the experimental results. Consequently, the objective is to find the limits for the temperature amplitude.

In this paper we propose a method for the analysis of measured curves using Fourier transform. This method yields a simple algorithm to determine of optimal experimental conditions.

Experimental

For TMDSC measurements a Perkin-Elmer DSC-7 was used in the DDSC-mode. The temperature modulation performed with a saw-tooth waveform. From its input parameters an underlying heating rate, a temperature amplitude and a frequency can be calculated [9]. The first harmonic of the base-line subtracted curves was calibrated [10, 11] and used for the calculation of the complex heat capacity. The integration interval of the Fourier analysis was one period (i.e. k=1 in Eq. (4)).

To compare the results obtained with our algorithm with the commonly used Lissajous figures measurements were performed using a sinusoidal temperature modulation. For these measurements the instrument was a Perkin-Elmer DSC-4 with a measuring and control system of IFA GmbH [12]. The original conventional DSC-software of the IFA system was modified.

The samples were Polystyrene (PS), Poly(ε-caprolactone) (PCL) and syndiotactic Polypropylene (*s*-PP). The PS-sample was commercial Polystyrene (PS-168N; BASF) with a molecular weight M_w=2.7·10^5 g mol^{-1} (M_w/M_n=2.8). The sample weight was 4.230 mg. The PCL sample was provided from van Ekenstein (University of Groningen). This sample had a weight of 4.380 mg. The *s*-PP sample (sample weight: 4.94 mg) under study was synthesised by S. Jüngling in Prof. Mühlhaupt's group in the Institute of Macromolecular Chemistry of the Univer-

sity of Freiburg. The number average molecular weight M_n was $1.04 \cdot 10^5$ g mol^{-1} (M_w/M_n=2.3) [13].

All samples were prepared from thin foils and placed in flat DSC pans. Before each measurement samples were melted and recooled.

Results and discussion

PS was investigated in the glass transition region at 372 K using a sinusoidal temperature perturbation (measured with DSC-4) in the quasi isothermal mode (β_o=0 K min^{-1}). The temperature amplitude was 3 K and the frequency 16.7 mHz. With those experimental conditions non-linear effects in the sample response are expected causing small deviations from a sinusoidal heat flow signal. This means that higher harmonics appear [3]. The visual analysis in the time domain of the baseline subtracted heat flow curve does not show visible deviations from the sinusoidal shape. The related Lissajous-diagram ($\Phi(T)$) is shown in Fig. 1. After a relatively short time (ca. 15 s) the system was in the steady state and the Lissajous figure looks like an elliptic curve. No deviations could be observed. For a better resolution of the signal deformation the measured curve in the steady state range was Fourier transformed. The resulting spectrum is plotted in Fig. 1. The spectrum has two peaks, a large one at the experimental frequency f_o and a smaller one at the frequency of the second harmonic ($2f_o$). The second peak includes the information of the non-linear response of the sample in the glass transition region. The analysis of the Fourier spectra should be a more quantitative method sensitive to the non-linear effects.

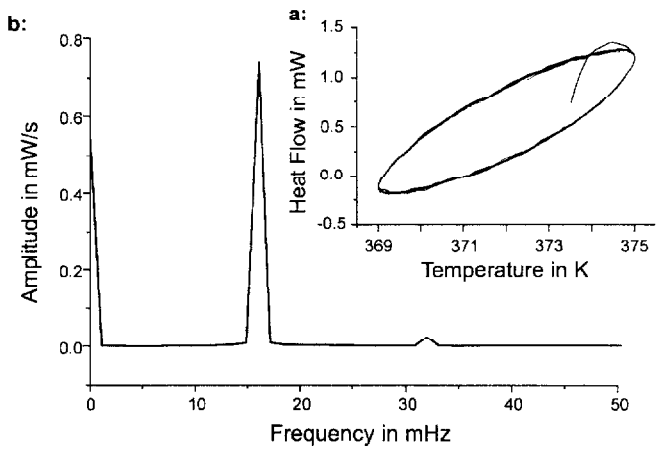

Fig. 1 Baseline subtracted heat flow of PS measured at sinusoidal temperature perturbation at 372 K (T_a=3 K, f_o=16.7 mHz); a: Lissajous figure; b: Fourier spectrum

In the DDSC the temperature program can be described as a saw-tooth modulated curve. Its Fourier series reads:

$$T(t) = T_o + \beta_o t + T_a \sum_{j=0}^{\infty} \frac{\sin((2j+1)\omega_o t)}{(2j+1)^2} \quad (6)$$

In case of linear response the periodic component of the heat flow signal Φ_p reads:

$$\Phi_p(t) = \Phi_a \sum_{j=0}^{\infty} \frac{\cos((2j+1)\omega_o t - \varphi_{2j+1})}{(2j+1)^2} \quad (7)$$

where the amplitude is $\Phi_a = mlc|\omega_o T_a$ and φ_n is the phase shift of the n^{th} harmonic. Equation (7) shows that the peaks in the spectrum of the heat flow rate occur only at the odd harmonics. The peak intensity decreases with increasing frequency. In real measured curves peaks can be found at the predicted frequencies but their intensity is smaller than calculated by Eq. (7). This is caused by heat transfer in the sample holder [10]. In case of linear sample response the theoretical as well as the measured periodic component of the heat flow is shown symmetric half periods. Asymmetric curve shapes result in contributions of even harmonics.

To study the real shape of an experimental curve, *s*-PP was investigated at a temperature amplitude of 0.1 K and a frequency of 13.5 mHz. The underlying heating rate was 0.5 K min^{-1}. Prior to the measurements the quenched sample was crystallised at 130°C for 3 h. After this pretreatment no recrystallisation effects can be observed during the melting in the main peak region [14]. If the run is started at 130°C, first small melting effects occur directly after T_o. The main melting peak is located in the temperature range between 145 and 154°C. The spectrum of the complete curve is shown in Fig. 2. In agreement with Eq. (7) the spectrum only shows peaks at odd harmonics. This result indicates that non-linear effects are negligible at those experimental conditions. The number of detectable peaks at the higher harmonics contains information about the frequency range of the instrument. In our case the largest frequency is higher than 175 mHz. The spectrum shows that the periodic component of the heat flow curve must be symmetric in the complete measured range. Since non-linearities are expected to occur in the melting peak region first, this curve interval was transformed separately. The resulting spectrum (Fig. 2b) does not show even harmonics as well.

A comparison of different parts of the periodic component of the measured curve is shown in Fig. 3. The upper curve in Fig. 3 was measured in the melt, the other one is a section from the main melting range. In the melt the measured Φ_p-signal has the expected curve shape. In the melting peak region the curve shape

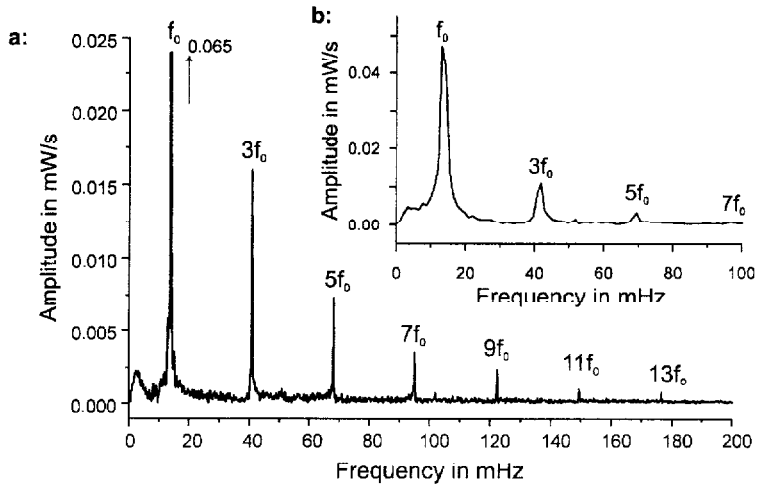

Fig. 2 Fourier spectrum of the heat flow curve of *s*-PP (β_0=0.5 K min^{-1}, f_0=13.5 mHz, T_a=0.1 K); a: Spectrum from the complete curve from 130 to 160°C; b: Spectrum determined from the heat flow curve in the melting region (145.1 to 152.6°C)

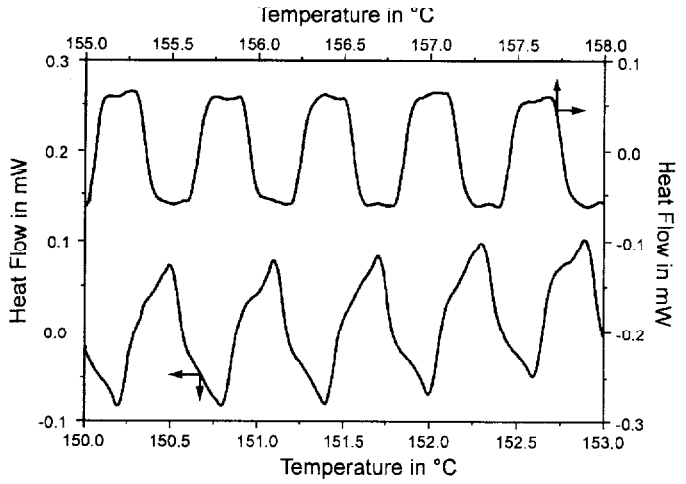

Fig. 3 Periodic component of the heat flow rate of *s*-PP in the melting range and in the melt

is changed. During melting, time dependent processes cause an additional phase shift. This phase shift is frequency dependent and causes, for instance, the frequency dependence of c'' [7]. From the results in Ref. [7] follows, that the phase shift in the melting region decreases with increasing frequency. Figure 4 is calculated from Eq. (7) assuming that the phase shift occurs only in the first harmonic. The calculated curves are similar to the measured curves. If φ_1=0 is inserted in Eq. (7) the resulting curve is approximately identical to the curve of the

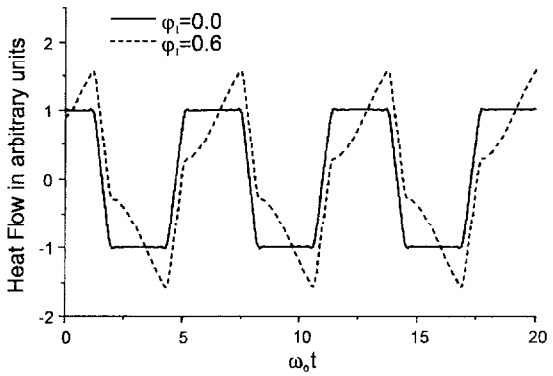

Fig. 4 Simulated curves of the periodic component of the heat flow rate at a saw-tooth modulation for different phase shifts of the first harmonic

melt. The differing curve shape in the melting range is caused by the phase shift. In the melting range the phase shift of the harmonics decreases with increasing frequency.

In contrast to *s*-PP quenched PCL shows recrystallisation effects in the melting region. At β_0=0.5 K min^{-1} the DSC curve shows the main melting peak at 58°C and a smaller second peak at 60°C. In the temperature range of the second peak those crystals melt, which grew by recrystallisation in the temperature range of the first peak. To investigate the influence of the temperature amplitude on the melting behaviour, the PCL sample was measured at the underlying heating rate of 0.5 K min^{-1} and a frequency of 20.8 mHz. The temperature amplitude was varied between 0.04 and 1 K. Despite the small heat flow amplitude in the melting region (between 60 and 150 μW at T_a=0.04 K) the TMDSC results can be evaluated quantitatively. Experimental results show that the data evaluation is possible if heat flow amplitudes were in the order of magnitude of the noisy.

In the melt all $\Phi_p(t)$ curves show the typical symmetrical oscillations. In the melting region a deviation from the curve symmetry is visible. As Fig. 5 shows, the asymmetry depends on the temperature amplitude. This is caused by differences in the kinetic behaviour of melting and recrystallisation processes during the heating and the cooling segment, respectively. When reversible local melting processes without nucleation [7, 15] are assumed, the asymmetry should decrease with smaller T_a. The temperature amplitudes used for the measurements in Fig. 5 yields a noticeable disturbance of the equilibrium of the sample. Which is expected to change the polymer structure relatively strong during the modulation whereas the linear data evaluation (Eq. (4)) is only applicable in case of small temperature perturbation. Consequently the complex heat capacity depends on the temperature amplitude (Fig. 6). In this case the validity of a quantitative interpretation of signals resulting from Fourier analysis of the measured heat flow is rather questionable.

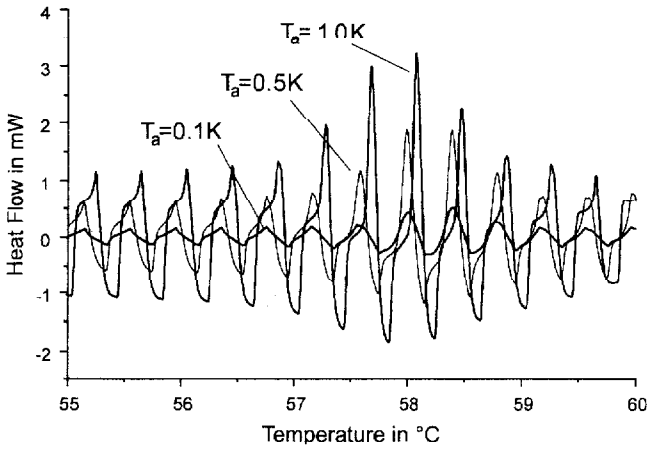

Fig. 5 Periodic component of the heat flow rate of PCL in the melting range measured with different temperature amplitudes (β_0=0.5 K min^{-1}, f_0=20.8 mHz)

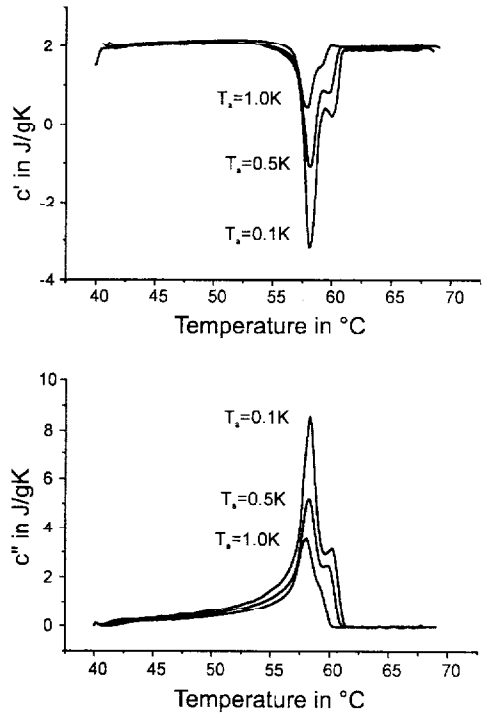

Fig. 6 Complex heat capacity of PCL evaluated from measurements with different temperature amplitudes (β_0=0.5 K min^{-1}, f_0=20.8 mHz)

PCL shows a phase shift which is larger than $\pi/2$ during melting. Therefore c' is decreasing during melting. For the chosen experimental parameters this relatively large phase shift in this small temperature range can be only detected if the integration interval of the Fourier analysis is one period, e.g. in Eq. (4) k must be 1.

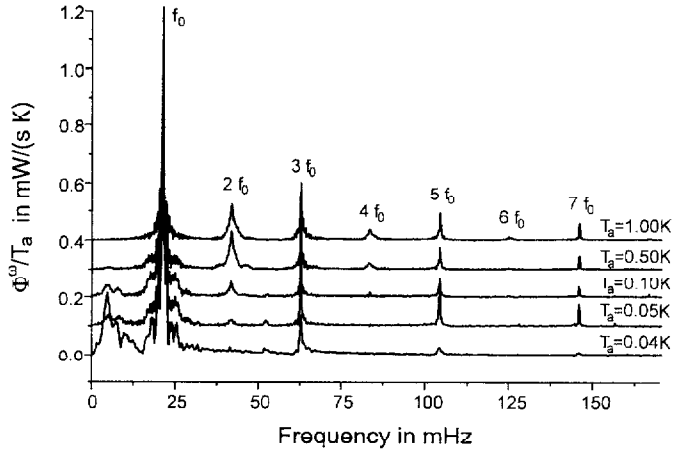

Fig. 7 Normalised spectra of heat flow curves of PCL determined for different temperature amplitudes (β_0=0.5 K min^{-1}, f_0=20.8 mHz)

Normalised spectra of measured curves at different amplitudes are shown in Fig. 7. At large T_a the spectra have peaks at odd as well as even harmonics. The reason for the peaks at even harmonics is the asymmetry of the dynamic component. The height of these peaks decrease with decreasing temperature amplitude. At T_a=0.04 K practically no even harmonics can be detected. In this case the periodic component of the heat flow rate is symmetric also in the melting region. In this case the influence of the temperature perturbation on the actual state of the sample is sufficiently small and the sample response can be described using linear evaluation procedures.

For an analysis of the spectra we discuss the ratio of the peak areas of the second and the first harmonic R_{21}:

$$R_{21} = \frac{\Phi_{a2}}{\Phi_{a1}} = \frac{\int_{\text{Peak at } 2f_0} \Phi^{\omega}(f)\mathrm{d}f}{\int_{\text{Peak at } f_0} \Phi^{\omega}(f)\mathrm{d}f} \tag{8}$$

where Φ^{ω} is the Fourier transformed measured heat flow rate.

R_{21} includes information on the differences in the sample behaviour between the heating and cooling half period of the temperature perturbation. This property is plotted as a function of the logarithm of the temperature amplitude in

Fig. 8. The dependence of R_{21} as a function of $\log T_a$ can be described in a good approximation by

$$R_{21} = \begin{cases} a\log\left(\dfrac{T_a}{T_a^{max}}\right) & \text{for } T_a \geq T_a^{max} \\ 0 & \text{for } T_a < T_a^{max} \end{cases} \quad (9)$$

where a is the slope and T_a^{max} the critical amplitude. For PCL we evaluate a=0.276 and T_a^{max}=0.04 K. If $T_a<T_a^{max}$ the sample response is linear and no nucleation effects should be necessary for local structure changes. In this case we can describe the sample response as a relaxation process in a partially crystalline non-equilibrated melt close to the growth-face of the crystals.

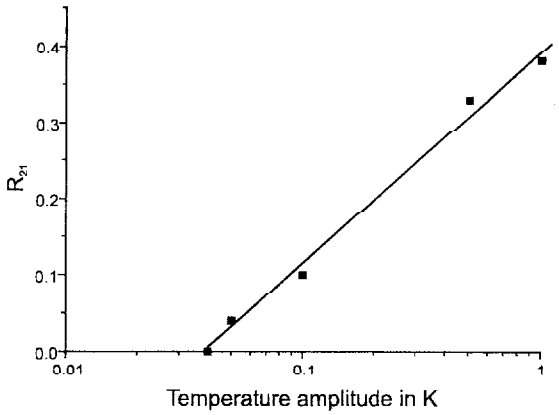

Fig. 8 Ratio of the areas of the second and first harmonic (determined on the curves in Fig. 7) as function of the temperature amplitude

Another indication for non-linearity is the dependence of the complex heat capacity on the temperature amplitude. In the linear case the c'- and c''-curves should be independent of T_a. This should be valid at amplitudes smaller than T_a^{max}. However, Fig. 9 shows, that the c'- and c''-curves are corresponding within the limits of measurement accuracy even at larger temperature amplitudes. For PCL the experimental limit is R_{21}<0.1. In practice it is recommended to use temperature amplitudes smaller than T_a^{max}.

Conclusions

For a quantitative description of the local processes during polymer melting a linear analysis of the measured curves can be useful. The prerequisite of this evaluation method is a linear sample response to a small temperature perturbation. It is shown that the critical temperature amplitude depends on the material. T_a^{max} should be dependent on the stability of the crystals. A determination method

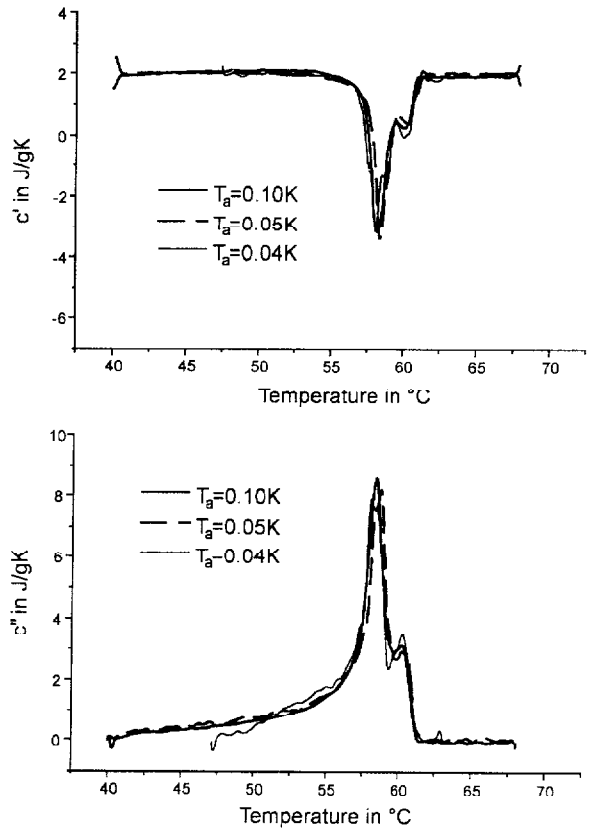

Fig. 9 Complex heat capacity of PCL evaluated from measurements with different temperature amplitudes (β_0=0.5 K min^{-1}, f_0=20.8 mHz)

for T_a^{max} is the analysis of the spectrum of the measured curve. The spectrum can be calculated by Fourier transform of the measured heat flow signal. The ratio between the second and the first harmonic R_{21} is a qualitative measure for the non-linearity of the measured curves. Furthermore R_{21} is useful to determine the limits of the linearity of the experimental results. The presented procedure is applicable for all symmetrical waveforms of temperature modulation.

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