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Thermochimica Acta 330 (1999) 85–92

thermochimica acta

Description of the irreversible melting of polymers measured by temperature modulated calorimetry[1]

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Received 28 July 1998; accepted 20 January 1999

Abstract

The melting behaviour of polymers is investigated by temperature modulated differential scanning calorimetry (TMDSC). The measurements are performed in both the quasi isothermal and the scanning mode. For the scanning mode measurements the specific complex heat capacity (given by real c' and imaginary part c'') was determined. The assumption that the crystals melt from their lateral surface only and that the melting rate is caused by superheating yields to a prediction of the frequency and underlying heating rate dependence of c''. These results are verified experimentally. By adaptation of this model a model function for description of $|c|$ (the modulus of the complex specific heat capacity) in quasi isothermal experiments is obtained. The comparison of this function with experimental data from poly(ethylene terephthalate) and syndiotactic polypropylene shows a good correspondence. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polymer melting; Temperature modulated calorimetry

1. Introduction

The conventional differential scanning calorimetry (DSC) is well introduced for the investigation of phase behaviour of polymers. By this method the heat flow rate into the sample is measured as a response on a given temperature program with a constant scanning rate β_0 or at isothermal conditions (β_0=0). In case of temperature modulated differential scanning calorimetry (TMDSC) the conventional temperature program is superimposed by a small periodic temperature perturbation $T_p(\omega_0)$. In the simplest case $T_p(\omega_0)$ is a sinusoidal function:

$$T(t) = T_i + \beta_0 t + T_p(\omega_0) \\ = T_i + \beta_0 t + T_a \sin \omega_0 t, \tag{1}$$

where T_i is the initial temperature, T_a the temperature amplitude and ω_0 (=$2\pi \cdot f_0$=$2\pi/t_p$) the angular frequency. f_0 and t_p are the frequency and the period, respectively. The introduction of the periodical temperature perturbation into the temperature programme provides additional information about the kinetics of the processes of interest.

A partial-crystalline polymer has a non-equilibrium structure. During heating in conventional DSC melting and recrystallisation effects can be observed simultaneously for many polymers. Both the structure of the crystals and of the melt depend on temperature.

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[1] Presented at the Fifth Lähnwitz Seminar of Calorimeter, 6/98.

PII: S0040-6031(99)00022-2

In additional to imperfect crystals and a reordered melt a partial crystalline polymer includes a rigid amorphous phase on the surface of the crystallites. This complicated molecular situation yields to time dependent processes during melting. This is reflected in the experimental results of TMDSC measurements. For quasi isothermal experiments (β_0=0), Wunderlich and co-workers [1–3] and Schick and co-workers [4] have shown that the sample response to the modulation decreases as a function of the measuring time. For non-quasi isothermal measurements it was shown that the measured signal depends on frequency [5–8] and underlying heating rate [9,10]. For understanding the experimental results additional to the irreversible melting of crystals a reversible melting process on the surface of the crystals was discussed [1,8]. Mathematical models for description of the frequency dependence of the measured signals are discussed in the literature [8–11].

In this paper we discuss TMDSC measurements in the melting range of polymers on basis of the models presented in [9–12]. For scanning experiments the dependence of the measured data on the underlying heating rate is discussed. On base of that results a fit function for quasi isothermal measurements is obtained. The theoretical results are compared to measured data of poly(ethylene terephthalate) (PET) and syndiotactic polypropylene (s-PP).

2. Experimental

2.1. The method

For TMDSC the measured heat flow rate Φ can be described as a sum of two parts, the underlying component of the heat flow rate $\Phi_u(t)$ and the periodic component $\Phi_p(t)$:

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

The characteristic parameters of the periodic component are the heat flow amplitude Φ_a and the phase shift φ between dT_p/dt and Φ_p. These parameters are usually determined by calculating the first harmonic of a Fourier analysis [13,14]:

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

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

where Φ_s and Φ_c are the sine and the cosine component of the first harmonic of Φ_p, respectively. This evaluation method is applicable in case of a symmetric periodic component of the heat flow rate. To guarantee the validity of this data evaluation procedure the temperature amplitude must be sufficiently slow. A procedure to determine the maximum temperature amplitude is published in [15]. The experimental conditions applied in this paper are analysed in such a way. If $\Phi_p(t)$ is not a constant in the time limits of one period an additional error is expected [16]. This error increases with smaller β_0.

From the amplitude of the heat flow rate Φ_a and the phase shift φ the complex specific heat capacity $c^*(\omega) = c'(\omega) - ic''(\omega)$ can be determined by its real and imaginary part ($i = \sqrt{-1}$):

$$c' = |c|\cos\varphi, \tag{4a}$$

and

$$c'' = |c|\sin\varphi, \tag{4b}$$

where $|c|$ is the modulus of the complex specific heat capacity:

$$|c| = \sqrt{c'^2 + c''2} = \frac{\Phi_a}{K_a m T_a}, \tag{5}$$

where m is the sample mass. The calibration factor for the amplitude K_a depends on the heat transfer conditions. In this paper K_a is determined for each sample by comparing the specific heat capacity of the melt with the results of conventional DSC measurements. For scanning experiments an additional calibration procedure is used [17,18].

A Perkin-Elmer DSC-7 was used in the DDSC-mode. The temperature modulation was performed using a saw-tooth waveform. From the DDSC input parameters an underlying heating rate, a temperature amplitude and a frequency can be calculated [9].

2.2. Samples

The samples were PET and s-PP. The PET sample was commercial (Du Pont). The PET samples with different morphology were prepared in two regimes:

1. The sample was cooled from the melt (270°C) to 170°C with a cooling rate of ca. 100 K/min. At 170°C it was crystallised for 10 min and than fast cooled to room temperature.

2. A sample with a more stable structure was obtained by stepwise cooling from the melt. Starting from 270°C the sample was cooled for 10 K with -1 K/min. At this temperature it was annealed for 2 h. Afterwards it was cooled to the next annealing temperature 10 K less with -1 K/min. The final annealing temperature was 170°C. At the end the sample was cooled with -100 K/min to room temperature.

The s-PP sample under study was synthesised by the Institute of Macromolecular Chemistry of the University of Freiburg. The number average molecular weight M_n was 1.04×10^5 g/mol (M_w/M_n=2.3) [19]. The sample was cooled from the melt to 130°C and annealed for 3 h.

For preparation the samples (typical mass was approximately 5 mg) were putted into aluminium DSC pans. The crystallisation was performed in a Perkin-Elmer DSC 4. The temperature amplitudes for the TMDSC experiments are 0.1 K (for s-PP) and 0.05 K (for PET).

3. Complex heat capacity and order function

Using TMDSC a time and frequency dependent heat capacity is observed in the melting region of polymers. Time dependent non-equilibrium processes in the sample are the reason for that behaviour. In the framework of irreversible thermodynamics a set of time dependent order functions ζ_i can be introduced to describe such processes. For simplification we discuss the case with only one function $\zeta(t)$. The generalised isobaric specific heat capacity can be written as

$$c(t) = c_{st} + c_{dyn}(t), \tag{6}$$

where c_{st} is the static specific heat capacity of the meta stable equilibrium while the function $\zeta(T,t)$ is considered in $c_{dyn}(t)$. By Fourier transformation of $c(t)$ the complex specific heat capacity $c^*(\omega)$ is determined as

$$c^*(\omega)=c_{st}+c^*_{dyn}(\omega) = c_{st} + c'_{dyn}(\omega) - ic'_{dyn}(\omega), \tag{7}$$

where $c_{st}+c'_{dyn}$ is the real part c' and c''_{dyn} the imaginary part c'' of the complex specific heat capacity. Predicting that $d\zeta \propto dS$ (the system is rather close to equilibrium), the correspondence between $\zeta(t)$ and the complex specific heat capacity is given by Fourier transformation [20]:

$$c^*_{dyn}(\omega) \propto -\int_0^\infty \dot{\zeta}(t)\exp(-i\omega t)\,dt. \tag{8}$$

For a given time dependence of the order parameter ζ the complex specific heat capacity can be calculated by Eq. (8). In case of melting the time derivative of ζ is the melting rate. For polymer melting different models for ζ as a function of time are discussed in [8]. A simple model is that the polymer lamella melt in one dimension from the lateral surface (growth face) with a constant melting rate $-\dot{\zeta}_0$. In such a case the kinetics are described by a step function for $\dot{\zeta}$:

$$\dot{\zeta}(t) = -\dot{\zeta}_0\Theta(t-t_0), \tag{9}$$

where $\dot{\zeta}_0$ is a positive constant. From Eq. (9) we obtain for the complex specific heat capacity:

$$c'_{dyn}(\omega) = 0, \tag{10a}$$

and

$$c''_{dyn}(\omega) \propto \frac{1}{\omega}. \tag{10b}$$

This means that the real part is a constant in the melting region and the signals from the imaginary part are always positive. c'' increases with decreasing frequency.

A more sophisticated model is presented in [12]. There the time dependent order parameter reads:

$$\dot{\zeta}(t) = \dot{\zeta}_0\left(\exp\left(-\frac{t}{\tau_1}\right) - \exp\left(-\frac{t}{\tau_2}\right)\right), \tag{11}$$

where τ_1 is a characteristic time which describes the molecular processes close to the lateral surface (growth face) of the crystals. The characteristic time τ_2 depends on the average length of the crystals. From Eq. (11) follows the dynamic part of the complex specific heat capacity:

$$c'_{dyn}(\omega) \propto \left(\frac{\tau_2}{1+\omega^2\tau_2^2} - \frac{\tau_1}{1+\omega^2\tau_1^2}\right), \tag{12a}$$

and

$$c''_{dyn}(\omega) \propto \left(\frac{\tau_2^2}{1+\omega^2\tau_2^2} - \frac{\tau_1^2}{1+\omega^2\tau_1^2}\right). \tag{12b}$$

In this model both the real and imaginary part of the complex specific heat capacity are frequency dependent. This is in agreement with the experimental behaviour of polymers [8,9,12]. Eq. (9) represents a special case of Eq. (11) for the conditions $\tau_1 \rightarrow 0$ and $\tau_2 \rightarrow \infty$.

4. Results and discussion

4.1. TMDSC scanning experiments in the melting region

For s-PP the specific complex heat capacity was measured for different underlying heating rates. The curves are shown in Fig. 1. The imaginary part c'' shows positive peaks. The peak intensity increases with increasing underlying heating rate. In contrast to c'' the real part c$'$ shows peaks which can be positive and negative. The changes in c$'$ are smaller than that in c$''$. If the melting process is measured with different frequencies the peak intensities decreases with increasing frequency.

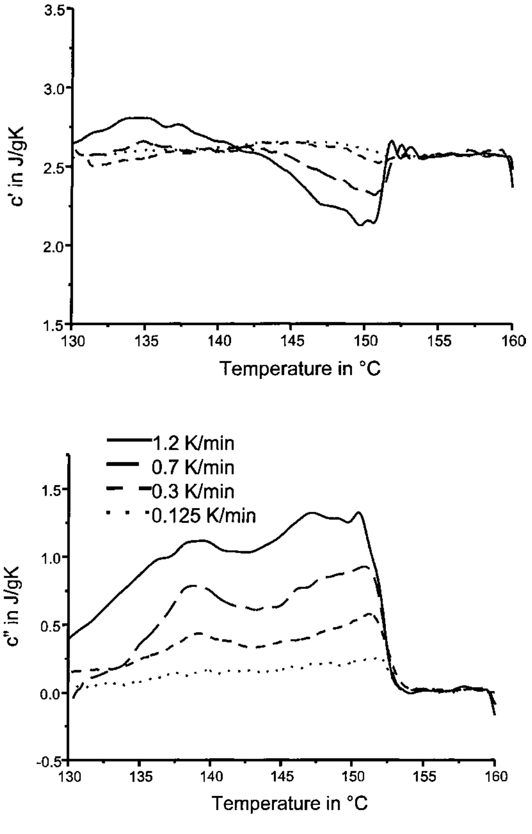

Fig. 1. Real and imaginary part of the complex specific heat capacity of s-PP measured by different underlying heating rates (t_p=48 s, T_a=0.1 K).

We assume: (i) the polymer crystals melt in one dimension with a constant melting rate; (ii) the melting rate is temperature dependent.

In the first approximation the temperature dependence of $\dot{\zeta}$ is a linear function of the superheating $T-T_f$:

$$\dot{\zeta}(T) = \left(\frac{\partial \dot{\zeta}}{\partial T}\right)_{T_f} (T - T_f). \tag{13}$$

In [9,11] it is shown that for this model the real part of the complex heat capacity is constant and the imaginary part is proportional to the reciprocal frequency:

$$c(\omega)' = c_p, \tag{14a}$$

and

$$c''(\omega) = \frac{\Delta h_f}{\omega} \left(\frac{\partial \dot{\zeta}}{\partial T}\right)_{T_f}. \tag{14b}$$

It is clear that this simple model cannot describe the experimental behaviour of c'. Therefore, we discuss in the first step only c''. For the model in discussion it is shown in [9] that the area of the c'' peak reads:

$$\int_{\text{Peak}} c'' \mathrm{d}T = \frac{\beta_0}{\omega} \frac{\Delta h_f}{\langle T - T_f \rangle}, \tag{15}$$

where $\langle T-T_f \rangle$ denotes an averaged superheating. $\langle T-T_f \rangle$ should be frequency independent for a given underlying heating rate β_0. From the peak area of the c'' data the average superheating is determined by Eq. (15) for s-PP. The results presented in Fig. 2 show an agreement with the expectation.

From the same model follows for the influence of the underlying heating rate [9]:

$$\langle T - T_f \rangle \propto \sqrt{\beta_0}, \tag{16a}$$

$$\int_{\text{Peak}} c'' \mathrm{d}T \propto \sqrt{\beta_0}. \tag{16b}$$

In Fig. 3 the validity of this relation is shown for s-PP.

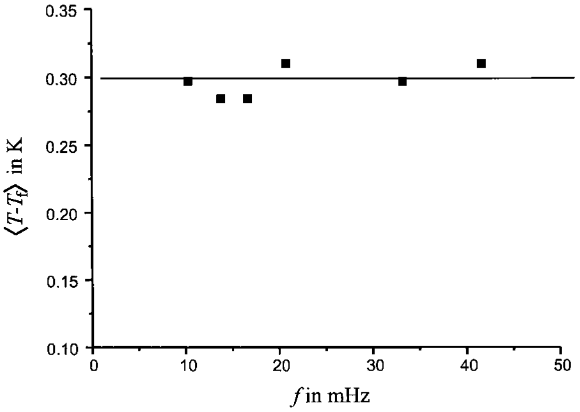

Fig. 2. Averaged superheating of s-PP as a function of frequency (T_a=0.1 K, β_0=0.5 K/min).

According to the assumption the experimental data shown in the Figs. 2 and 3 can be explained by the irreversible melting of the crystals during heating. The measured signals in the melting region basically depend on the underlying heating rate. The small periodic temperature perturbation is only the "aid" to measure this process. The general prediction for this discussion is a sufficient small temperature amplitude (as described above). Local irreversible and time dependent processes during polymer melting as described in [1,8,12] should be negligible (in the sense of this discussion).

An assumption for the temperature dependence of c'' can be found experimentally on the example of s-PP. The values (from Fig. 1) of c'' at 145°C and 150°C are plotted as a function of $\sqrt{\beta_0}$ in Fig. 4. We obtain a linear behaviour. An empirical function to fit the experimental results reads:

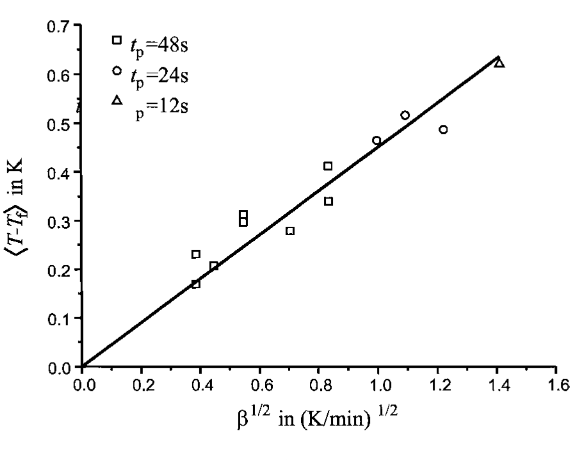

Fig. 3. Averaged superheating of s-PP as a function of the square root of the underlying heating rate (T_a=0.1 K).

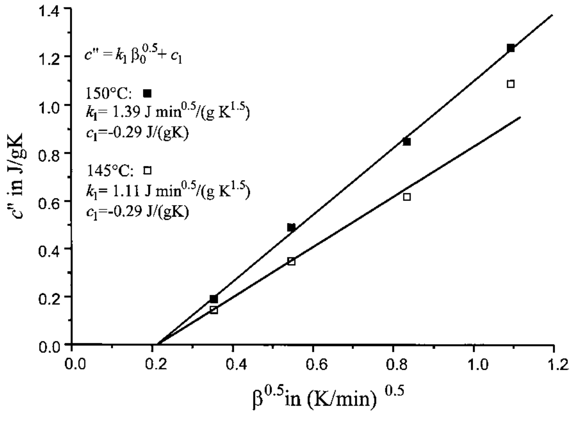

Fig. 4. The imaginary part of the complex specific heat capacity of s-PP as a function of the square root of the underlying heating rate for different temperatures (data from Fig. 2).

$$c'' = k_2\beta_0^{0.5} + c_2, \tag{17}$$

where k_2 and c_2 are constants.

For discussion of the heating rate dependence of c', kinetic processes during melting which are described in [8,12] must be considered. Then Eq. (13) can be modified by a time dependent function $a(t)$:

$$\dot{\zeta}(T,t) = a(t)\left(\frac{\partial\dot{\zeta}}{\partial T}\right)_{T_f}(T - T_f). \tag{18}$$

If $a(t)$ is the step function $\Theta(t-0)$ Eq. (18) is identical to Eq. (13) and c'=c_{st}. In a more general case we can assume that $a(t)$ is proportional to $\dot{\zeta}(t)$ in Eq. (11). In this case c' yields to

$$c' = c_{st} + k_1\beta_0^{0.5}, \tag{19}$$

where k_1 is proportional to the real part of the Fourier transformation of $a(t)$ (see Eqs. (12a) and (12b)).

4.2. Quasi isothermal TMDSC measurements

A quasi isothermal TMDSC experiment in the melting region of polymers can be separated into an initial non-isothermal step and the quasi isothermal measurement. In the initial step the sample is slowly heated from an initial temperature to the constant temperature of investigation T_{ex}. T_{ex} is the averaged temperature for the measurement. The sample response during a small periodic temperature perturbation is measured as a function of time. In the initial step, the state of the sample becomes a (stationary) non-equilibrium. During the measurement the sample state relaxes into a (meta stable) equilibrium. The measured signal depends on the initial step. This should be considered in the interpretation of the experimental results of the quasi isothermal measurements. It is possible to describe the time dependence of the complex heat capacity using empirical functions. On the example of the stretched exponential function this is shown in [3]:

$$|c| = c_{\mathrm{st}} + c_0 \exp(-(t/\tau)^{\beta_{\mathrm{KWW}}}). \tag{20}$$

Besides of the interpretation of the empirical parameters τ and β_{KWW} the problem is to find a physical explanation of the fundamental relaxation process of Eq. (20) that is consistent to other experimental results. In this paper, we recommend an other empirical function for the time dependence of $|c|$ in the case of quasi isothermal TMDSC measurements. The results of the scanning experiments lead to this function.

For simplification, we discuss only one type of crystal. The initial step of the experiment starts with heating the sample with the initial heating rate β_{i} from the equilibrium at T_{eq} to T_{ex}. If the actual temperature is lower than T_{f} the crystals do not melt. During this heating the sample goes into a non-equilibrium state and melts corresponding to Eqs. (17) and (19). To describe the measurement after the initial step we introduce a time dependent effective heating rate $\beta_{\mathrm{eff}}(t_{\mathrm{m}})$ by

$$\beta_{\mathrm{eff}}(t_{\mathrm{m}}) = \frac{\Delta T}{\Delta t} = \frac{T_{\mathrm{ex}} - T_{\mathrm{eq}}}{t_{\mathrm{m}} + t_{\mathrm{i}} - t_0}, \tag{21}$$

where t_{m} is the measuring time, t_{i} the time after the initial step and t_0 the time on that the experiment starts. The meaning of $\beta_{\mathrm{eff}}(t_{\mathrm{m}})$ and the relating properties are explained in Fig. 5.

For description of the measurements the underlying heating rate β_0 must be replaced in Eqs. (17) and (19) by $\beta_{\mathrm{eff}}(t_{\mathrm{m}})$. For substitution of t_{m} for β_{eff} we have to calculate the square root of the effective heating rate.

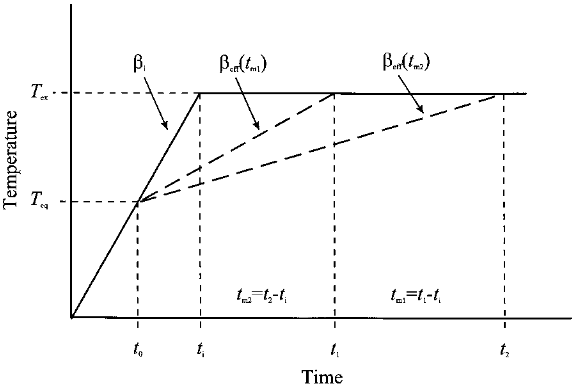

Fig. 5. Schema of the underlying temperature program (without the periodic temperature perturbation) and the effective underlying heating rate β_{eff} for quasi isothermal measurements at the times t_{m_1} and t_{m_2}.

From Eq. (21) follows:

$$\beta_{\mathrm{eff}}^{0.5} = \sqrt{\frac{1}{1 + (t_{\mathrm{i}} - t_0)/t_{\mathrm{m}}}} \left(\frac{\Delta T}{t_{\mathrm{m}}}\right)^{0.5} \simeq \Delta T^{0.5}\, t_{\mathrm{m}}^{-0.5}. \tag{22}$$

This approximation is valid for sufficient large t_{m}. By insertion of Eq. (22) into Eqs. (17) and (19) the complex specific heat capacity reads:

$$c' = c_{\mathrm{st}} + A_1 t_{\mathrm{m}}^{-0.5}, \tag{23a}$$

and

$$c'' = c_2 + A_2 t_m^{-0.5}. \tag{23b}$$

The constants A_1 and A_2 depend on the averaged superheating $T_{\mathrm{ex}} - T_{\mathrm{eq}}$ and the related constants in Eqs. (17) and (19). From Eqs. (23a) and (23b) follows the modulus of the complex specific heat capacity $|c|$:

$$|c| = \sqrt{\left(c_{\mathrm{st}} + A_1 t_{\mathrm{m}}^{-0.5}\right)^2 + \left(c_2 + A_2 t_{\mathrm{m}}^{-0.5}\right)^2}. \tag{24}$$

By introducing the new parameters $B_1 = 2(c_{\mathrm{st}}\, A_1 + c_2 A_2)$, $B_2^2 = A_1^2 + A_2^2$ and $c_{\mathrm{i}}^2 = c_{\mathrm{st}}^2 + c_2^2$ the final model function for quasi isothermal TMDSC measurements during polymer melting reads:

$$|c| = \sqrt{c_{\mathrm{i}}^2 + B_1 t_{\mathrm{m}}^{-0.5} + B_2 t_{\mathrm{m}}^{-1}}. \tag{25}$$

The physical meaning of this function is that the

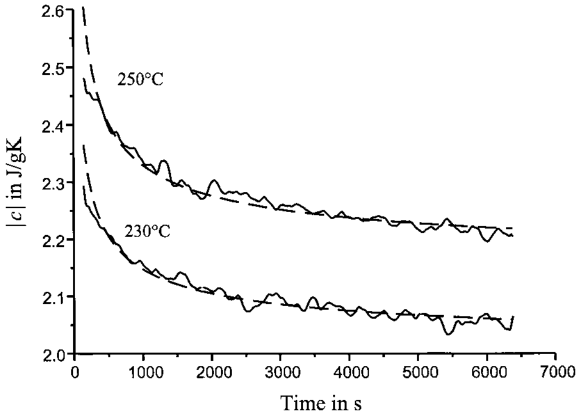

Fig. 6. The modulus of the complex specific heat capacity during quasi isothermal TMDSC measurements at 230°C and 250°C. (Sample: at 170°C crystallised PET; T_a=50 mK, t_p=48 s.) The dashed lines represent the fit with the model function Eq. (25). (230°C: c_i=2.00 J/gK, B_1=19.45 Js$^{0.5}$/gK, B_2=0.29 Js/gK; 250°C: c_i=2.14 J/gK, B_1=26.72 Js$^{0.5}$/gK, B_2=0.43 Js/gK.)

isothermal relaxation process during melting is mainly influenced by irreversible melting of the crystals. This processes can be described by a power law for the real and the imaginary part of the complex specific heat capacity.

The validity of the fit function Eq. (25) is verified on example of s-PP and PET with different morphology. The results are shown in Figs. 6–8. For all plots a good correspondence between the fits and the measured data can be seen. In the interesting time scale (t_m larger than 200s) the characteristic time dependence of |c| during quasi isothermal TMDSC measurements is caused by irreversible melting.

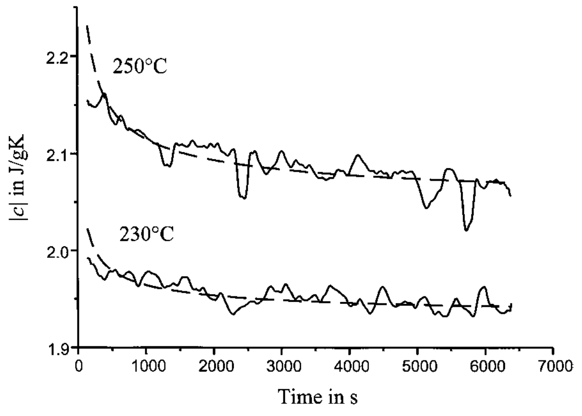

Fig. 7. The modulus of the complex specific heat capacity during quasi isothermal TMDSC measurements at 230°C and 250°C. (Sample: stepwise crystallised PET; T_a=50 mK, t_p=48 s.) The dashed lines represent the fit with the model function Eq. (25). (230°C: c_i=1.93 J/gK, B_1=4.56 Js$^{0.5}$/gK, B_2=0.09 Js/gK; 250°C: c_i=2.04 J/gK, B_1=9.95 Js$^{0.5}$/gK, B_2=0.16 Js/gK.)

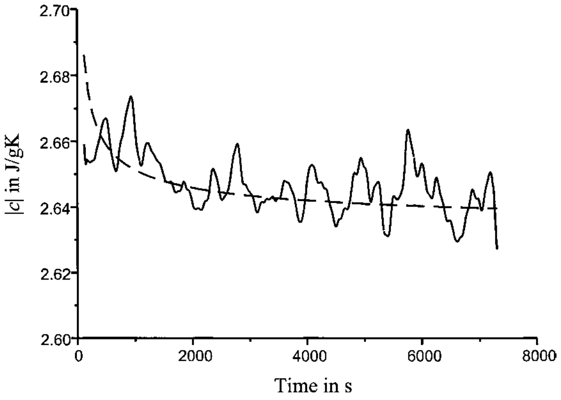

Fig. 8. The modulus of the complex specific heat capacity during quasi isothermal TMDSC measurements at 145°C. (Sample: s-PP; T_a=100 mK, t_p=48 s.) The dashed lines represent the fit with the model function Eq. (25). (230°C: c_i=2.63 J/gK, B_1=3.11 Js$^{0.5}$/gK, B_2=0.12 Js/gK.)

In [2,4] in connection with quasi isothermal measurements reversible melting processes are discussed for PET and poly(ether-etherketone) (PEEK). Such reversible melting is the reason for a heat flow amplitude which is larger than expected from the heat capacity of the melt. The applicability of the model function for quasi isothermal melting data is an indication that the decrease of the reversible melting is caused by irreversible melting. In this sense irreversible melting means that the volume fraction which shows reversible effects decreases during the measurement. The causes for the decrease of the relevant volume fraction of the crystals can be both real reversible melting of crystals and reorganisation to crystals with a higher stability (melting temperature). The reorganisation of the crystals can be understood as a structural relaxation of native crystals into equilibrium crystals described by Strobl [11,21].

A prediction of the presented discussion is a rather small temperature amplitude (smaller than 0.1 K [15]). For larger temperature amplitudes the temperature perturbation leads to additional melting and recrystallisation effects. In such case the shape of the periodical heat flow component is affected and larger supercooling effects for crystallisation must be considered [22].

A comparison of the curves measured by the fast and the stepwise crystallised PET (Figs. 7 and 8) shows a dependence of the intensity of the $|c|$ changes on the stability of the crystals. It seems that the intensity increases with decreasing stability of the crystals.

5. Conclusion

Quasi isothermal TMDSC measurements in the melting region of partial crystalline polymers show a time dependence in c' and c''. This time dependence can be described using a simple kinetic model of the melting process, assuming that the melting rate depends on the actual local non-equilibrium situation on the lateral surfaces of the polymer crystals. In result, we evaluate power laws from this model which describe the dependence of the complex heat capacity on time and on the thermal history. The measured data are in good conjunction with these laws.

Acknowledgements

This work was financially supported by the European Commission (INCO-COPERNICUS PL 965136).

References

[1] I. Okazaki, B. Wunderlich, Macromolecules 30 (1997) 1758.
[2] I. Okazaki, B. Wunderlich, Macromol. Rapid Commun. 18 (1997) 313.
[3] C. Schick, M. Merzlyakov, B. Wunderlich, Polym. Bull. 40 (1998) 297.
[4] A. Wurm, M. Merzlyakov, C. Schick, Colloid Polym. Sci. 276 (1998) 289.
[5] W.J. Sichina, Proceedings of the 24th NATAS Conference, 1995, p. 123.
[6] J.E.K. Schawe, Thermochim. Acta 271 (1996) 127.
[7] Y. Saruyama, Thermochim. Acta 304–305 (1997) 171.
[8] J.E.K. Schawe, E. Bergmann, Thermochim. Acta 304–305 (1997) 179.
[9] J.E.K. Schawe, G.R. Strobl, Polymer 39 (1998) 3745.
[10] A. Toda, C. Tomita, M. Hikosaka, Y. Saruyama, Proceedings of the 25th NATAS Conference, 1997, p. 659.
[11] J. Schmidtke, G.R. Strobl, T. Thurn-Albrecht, Macromolecules 30 (1997) 5804.
[12] J.E.K. Schawe, in preparation.
[13] M. Reading, A. Luget, R. Wilson, Thermochim. Acta 238 (1994) 295.
[14] J.E.K. Schawe, Thermochim. Acta 261 (1995) 183.
[15] J.E.K. Schawe, E. Bergmann, W. Winter, J. Thermal. Anal. 54 (1998) 565.
[16] J.E.K. Schawe, Thermochim. Acta 271 (1996) 127.
[17] J.E.K. Schawe, W. Winter, Thermochim. Acta 298 (1997) 9.
[18] S. Weyer, A. Hensel, C. Schick, Thermochim. Acta 303–304 (1997) 267.
[19] R. Thomann, C. Wang, J. Kressler, S. Jüngling, R. Mühlhaupt, Polymer 36 (1995) 3795.
[20] J.E.K. Schawe, Thermochim. Acta 304– 305 (1997) 111.
[21] G. Strobl, Acta Polymerica 48 (1997) 562.
[22] K. Ishikiryama, B. Wunderlich, Macromolecules 30 (1997) 1877.