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A non-isothermal differential scanning calorimetry method for the determination of specific surface energies in polymer crystals

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Abstract

A non-isothermal DSC method for the determination of the lateral and end surface energies at the polymer crystal/melt interface has been developed. It is based on the analysis of the overall crystallization process which takes place under sporadic and athermal conditions. The validity of the suggested method is tested for the case of polypropylene, polydemethylene terephthalate and polyethylene terephthalate. The calculated values of the lateral and end surface energies are compared with literature data from isothermal experiments. It is found that the agreement is quite satisfactory.

Keywords: Crystal; DSC; Melt; Polymer; Surface energy

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1. Introduction

One of the main features of crystallization in polymer melts is that the phase formation processes have to be described by two surface energies – lateral surface energy σ, corresponding to the unstrained part of the polymer lamella, and end surface energy σ_e, relevant to the folded surface perpendicular to the chain axis [1–4]. In all physical models describing crystallization, a combination of both surface energies appears ($\sigma^2\sigma_e$ or $\sigma\sigma_e$). As far as separate measurements of nucleation and growth

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kinetics can be performed, the ratio of the work of three-dimensional (3D) and two-dimensional (2D) nucleation should give a possibility for evaluating both surface energies. However, this is a very tedious process because it requires prolonged measurements of the steady-state nucleation rate and of the linear growth velocity in a broader temperature interval. All these measurements are connected with considerable difficulties, for example direct microscopic determinations at lower temperatures are hampered by the small grain size of the spherulites. The determination of the rate of the homogeneous formation of 3D nuclei is also a formidable task and has been performed in only a few cases [5, 6]. Most authors confine their investigations to the measurement of the rate of overall isothermal crystallization which is relatively easily performed by using either density measurements or differential scanning calorimetry (DSC) technique. The kinetics of crystal growth can be evaluated if nucleation measurements are conducted in parallel experiments. This approach, however, is indirect and implies distinct assumptions.

The aim of the present contribution is to develop a simple alternative method for determination of the lateral and end surface energies at the polymer crystal/melt interface by using a non-isothermal DSC technique for measuring the overall crystallization kinetics. According to this method, two types of experiments have to be performed – experiments in which sporadic nucleation is guaranteed and experiments in which only growth of athermal nuclei takes place. It has been shown [7, 8] that sporadic nucleation can be observed in samples which have been treated at temperatures above the melting point T_m. Athermal crystallization takes place when the sample is not heated above the T_m. The validity of this method is tested for polypropylene (PP), polydecamethylene terephthalate (PDMT) and polyethylene terephthalate (PET). A comparison with experimental data is also given.

2. Theoretical description

The kinetics of overall isothermal crystallization is described by the Kolmogorov–Avrami equation [9]

$$\alpha(t) = 1 - \exp(-Kt^n) \tag{1}$$

where $\alpha(t)$ is the fraction of the material transformed at time t elapsed from the beginning of the process, and n is a constant which reflects the growth morphology, e.g. $n = 2, 3, 4$. The overall crystallization rate coefficient K depends on the nucleation rate I and on the linear growth velocity G

$$K_S = \omega G^{n-1} I \tag{2a}$$

When athermal nuclei are present in the system, the kinetic rate coefficient is determined only by their growth rate as

$$K_a = \omega N G^n \tag{2b}$$

In above equations, ω is a shape factor and N is the density of athermal nuclei. The subscripts s and a will be used to denote sporadic and athermal crystallization, respectively.

The rate of isothermal overall crystallization $\mathrm{d}\alpha/\mathrm{d}t$ is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = nKt^{n-1}\exp(-Kt^n) \tag{3}$$

or with Eq. (1)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = nK^{1/n}f(\alpha) \tag{4}$$

where $f(\alpha) = (1-\alpha)[\ln(1-\alpha)]^{-(n-1)/n}$.

Eq. (1) was derived for constant T. Nevertheless, it has served as a basis for nearly all treatments of non-isothermal kinetics of crystallization. A thorough discussion of this subject can be found in the paper by de Brujin et al. [10] where the applicability of Eq. (1) under non-isothermal conditions is considered.

At constant cooling rate $q = -\mathrm{d}T/\mathrm{d}t$, the decrease in the temperature is

$$T = T_\mathrm{m} - \mathrm{q}\mathrm{t} \tag{5a}$$

and the increase of the undercooling ΔT is

$$\Delta T = qt \tag{5b}$$

Eq. (4) is separable in α and T (see Ref. [11]) and at $q = \text{const.}$ it can be integrated directly

$$\int_0^{\alpha_\mathrm{p}} \frac{\mathrm{d}\alpha}{f(\alpha)} = n\int_0^{\Delta T_\mathrm{p}} K^{1/n}\frac{\mathrm{d}T}{q} = n\int_0^{t_\mathrm{p}} K^{1/n}\mathrm{d}t \tag{6}$$

Here ΔT_p is the undercooling at which the $\mathrm{d}\alpha/\mathrm{d}t$ curve reaches its peak value, α_p being the melt fraction crystallized up to this maximum. Thus, α_p is also determined as the inflection point of the $\alpha(T)$ or the $\alpha(t)$ dependence; T_p and t_p are the temperature and time at which the peak value of the $\mathrm{d}\alpha/\mathrm{d}t$ curve is reached.

For $t = t_\mathrm{p}$, Eqs. (5) give

$$T_\mathrm{p} = T_\mathrm{m} - qt_\mathrm{p} \tag{7a}$$

and

$$\Delta T_\mathrm{p} = qt_\mathrm{p} \tag{7b}$$

The temperature dependence of the nucleation rate I, and the linear growth velocity G, appearing in Eqs. (2), according to the classical capillary theory of phase formation [12] are

$$I = \text{const}\,\frac{1}{\eta}\exp\left[-\frac{A_{\mathrm{k}3}}{kT}\right] \tag{8a}$$

and

$$G = \text{const}\,\frac{1}{\eta}\exp\left[-\frac{A_{\mathrm{k}2}}{kT}\right] \tag{8b}$$

where η is the bulk viscosity of the melt at temperature T and k denotes the Boltzmann constant

$$A_{k3} = \tfrac{16}{3}\pi\frac{\sigma^2\sigma_e V_m}{\Delta S_m^2 \Delta T^2} \tag{9a}$$

is the work of formation of 3D nuclei, while

$$A_{k2} = \frac{4b_0\sigma\sigma_e V_m}{\Delta S_m \Delta T} \tag{9b}$$

is the work of formation of 2D nuclei. In writing Eq. (8b) it is assumed that the most probable mechanism of growth proceeds via formation of 2D nuclei as has in fact always been observed in polymers [13]. In the above equations, V_m is the molar volume of the crystallizing substance, ΔS_m is the entropy of melting and b_0 is the lattice parameter of the growing crystal.

Substituting Eqs. (8 and 9) into Eqs. (2), we obtain the following expression for the temperature dependence of the crystallization rate coefficient

$$K_S \approx \mathrm{const}\exp\left[-\frac{A_{k3}}{\mathrm{kT}}\left(1+\frac{(n-1)A_{k2}}{A_{k3}}\right)\right] \approx \mathrm{const}\exp\left[-\frac{A_{k3}}{kT}\right] \tag{10a}$$

under conditions of sporadic nucleation and

$$K_a \approx \mathrm{const}\exp\left[-\frac{A_{k2}}{kT}\right] \tag{10b}$$

In Eqs. (10) it is assumed that for narrow temperature intervals in the vicinity of T_m, the viscosity η is a constant. It follows from Eqs. (9) that at $T \rightarrow T_m$, $A_{k2}/A_{k3} \ll 1$, i.e. that K_s in Eq. (10a) is determined by the temperature dependence for 3D nucleation.

Taking into account Eqs. (7), (9), and (10), we can write Eq. (6) in the form

$$\int_0^{\alpha_p}\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = n\int_0^{t_p}\exp\left[-\frac{B_s}{(qt)^2}\right]\mathrm{d}t \tag{11a}$$

and

$$\int_0^{\alpha_p}\frac{\mathrm{d}\alpha}{f(\alpha)} = n\int_0^{t_p}\exp\left[-\frac{B_a}{(qt)}\right]\mathrm{d}t \tag{11b}$$

where

$$B_s = \tfrac{16}{3}\pi\frac{\sigma^2\sigma_e V_m^2 1}{\Delta S_m^2 k T_m n} \tag{12a}$$

and

$$B_a = \frac{4b_0\sigma\sigma_e V_m}{\Delta S_m k T_m} \tag{12b}$$

The analytical solutions of Eqs. (11a) and (11b) can be found by introducing the error function and the integral exponential function, respectively, as done by one of the authors in a previous work [14]. Here the detailed solution will not be given. Only the final simplified expressions will be used. In Ref. [14], it was shown that assuming $\int_0^{\alpha_p} d\alpha/f(\alpha) = \text{const.}$, the solution of Eq. (11a) can be approximated by the expression

$$\log q \approx \text{const} - \frac{B_S}{2.3 \Delta T_p^2} \tag{13a}$$

For athermal crystallization, the approximate solution of Eq. (11b) reads [14] (see also Ref. [15])

$$\log q \approx \text{const} - \frac{B_a}{2.3 \Delta T_p} \tag{13b}$$

Thus in coordinates $\log q$ vs. $1/\Delta T_p^2$ and $\log q$ vs. $1/\Delta T_p$ for sporadic and athermal crystallization, straight lines should be expected, the slopes of which should give the values B_s and B_a. The ratio of the two quantities determines the value of the lateral surface energy σ. Knowing the value of σ, the end surface energy σ_e can be calculated from Eq. (12b).

The applicability of this theoretical algorithm for determining the lateral and end surface energies will be checked in the following section.

3. Experimental technique and results

Polypropylene, polydecamethylene terephthalate, and polyethylene terephthalate were employed as model systems.

Polypropylene, used was a commercial polymer, designated PP051, was provided by Repsol Quimica (Spain). Its molecular characteristics are: $M_w = 248\,297$, $M_w/M_n = 6.24$, isotacticity = 97% (from ^{13}C NMR data).

The polydecamethylene terephthalate employed was kindly supplied by Agfa Gavaert. The inherent viscosity of a 0.5% solution of PDMT in a mixture of phenol and orthodichlorobenzene (60/40) was measured as 0.55.

The polyethylene terephthalate used was of industrial grade with an average molecular weight of 18 400.

The melting point of the samples was determined as the temperature at which the last crystals melted. Thus, measured values of T_m were found to be 439 K for PP, 419 K for PDMT and 548 K for PET.

DSC measurements were carried out with a Mettler calorimeter, model TA 4000, DSC-30, controlled by a computer. Calibration was done following standard procedures. The measurements were performed with several constant cooling rates: 5, 10, 20, 30, 40, and 80°C min^{-1}. All runs were carried out in a stream of dried nirogen. The sporadic crystallization experiments were preceded by an isothermal period of 4 min at approximately 20°C above the respective melting temperatures, while the samples in which isothermal crystallization is expected were held for 4 min at the melting point. These thermal regimes were chosen in accordance with our previous experiments [14] as well as with literature data [7, 8].

Each experimental determination was repeated at least three times. The temperature T_p was determined as the temperature corresponding to the peak of the respective crystallization curve.

The results obtained for the rate dependence in coordinates $\log q$ vs. $1/\Delta T_p^2$ and $\log q$ vs. $1/\Delta T_p$ according to Eqs. (13) for the three systems studied are presented in Fig. 1. The values of B_s and B_a determined from the slopes of these dependences are summarized in Table 1. In performing the calculations for the lateral and end surface energies (see Eqs. (12)), the following values for ΔS_m have been used: 24.2 J K^{-1}mol^{-1} for PP; 113 JK^{-1}mol^{-1} for PDMT and 42.7 JK^{-1}mol^{-1} for PET. The lattice parameter b_0, appearing in Eq. (9b), is calculated as a mean lattice parameter using the expression $b_0 = (V_m/N_a)^{1/3}$, N_a being Avogadro's number. Such an estimate when compared with existing data for lattice cell parameters (compiled by Wunderlich [16]) gives quite satisfactory results for polymer crystals if we calculate V_m as $V_m = M_1/\rho$, where M_1 is the molecular weight per repeatable unit and ρ is the density of the crystalline material. It was found that $V_m = 28\,\mathrm{cm^3\,mol^{-1}}$ for PP, $V_m = 277\,\mathrm{cm^3\,mol^{-1}}$ for PDMT, $V_m = 146.6\,\mathrm{cm^3\,mol^{-1}}$ for PET, and $b_0 = 3.59 \times 10^{-8}$ cm for PP, $b_0 = 7.77 \times 10^{-8}$ cm for PDMT and $b_0 = 6.24 \times 10^{-8}$ cm for PET. The values of the lateral and end surface energies calculated according to Eqs. (12) are given in Table 1.

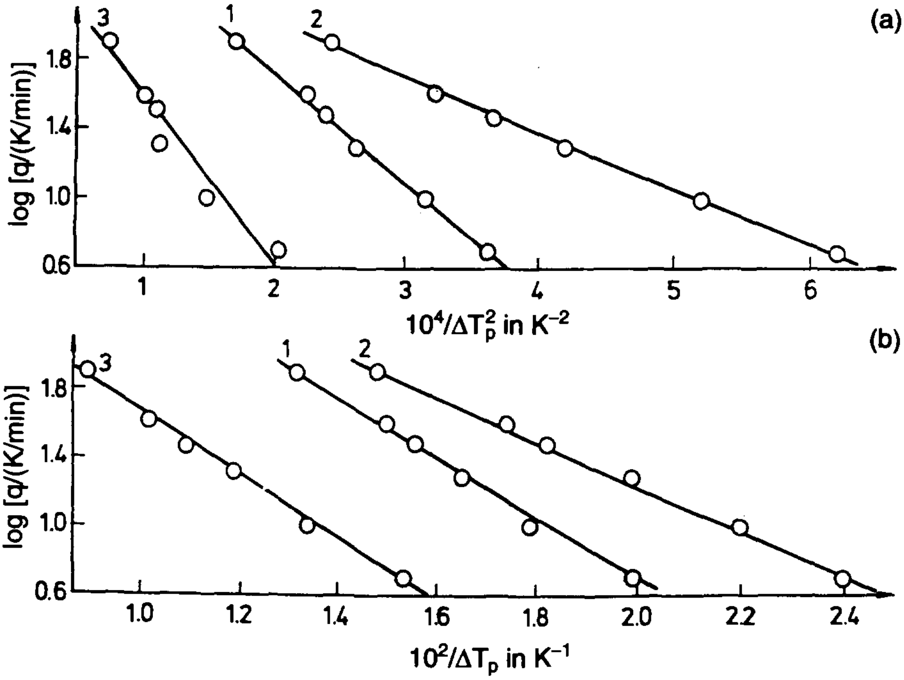

Fig. 1. (a) Rate dependence of the crystallization temperature in the coordinates $\log q$ vs. $1/\Delta T_p^2$ according to Eq. (13a). (b) Rate dependence of the crystallization temperature in the coordinates $\log q$ vs. $1/\Delta T_p$ according to Eq. (13b). 1, Polypropylene; 2, polydecamethylene terephthalate; 3, polyethylene terephthalate.

Table 1
Values of the kinetic parameters B_s and B_a determined from the slopes of the straight lines in Fig. 1 according to Eq. (13). Values of the lateral and end surface energies are calculated according to Eq. (12)

Polymer	B_s	B_a	σ erg cm^{-2}	σ_e erg cm^{-2}
PP	14 350	368	10.0	120.0
PDMT	7 254	298	5.7	39.2
PET	21 160	493	6.5	59.5

The value of n in Eq. (12a) is taken from literature data for experiments performed under similar but isothermal conditions. Khunova et al. [17] have found that for PP crystallized in the vicinity of T_m, n is 3. Keller et al. [7] report that for PET, $n = 3$ in the temperature range under investigation. Sharples and Swinton [18] have obtained $n = 3$ for PDMT by studying the overall isothermal crystallization from undercooled PDMT melts by density measurements. The analysis of the kinetics of isothermal crystallization in PET and PDMT, performed by Dobreva [19], also shows that at $T \to T_m$, n is 3.

4. Discussion

The straight lines in Fig. 1 show that in the vicinity of the melting point, the developed theoretical scheme, based on the concepts of the classical steady-state nucleation theory, gives satisfactory results.

It is seen from Table 1 that the values of the lateral and end surface energies are quite reasonable. Burns and Turnbull [6] have found by conducting optical microscopic observations of PP droplets that the value of the end surface energy σ_e is between 60 and 90 erg cm^{-2}. They have stated that it is reasonable to assume that the lateral surface energy for PP has to be approximately equal to that of polyethylene and n-alkanes. Turnbull and Cormia [5] reported that for polyethylene σ is 9.6 erg cm^{-2}.

The kinetics of overall crystallization of PET and PDMT melts have been studied in Ref. [19] by using isothermal DSC experiments. By combining sporadic and athermal conditions in the vicinity of the melting point it has been calculated that $\sigma = 5.2$ erg cm^{-2} and $\sigma_e = 31$ erg cm^{-2} for PDMT, and $\sigma = 4$ erg cm^{-2} and $\sigma_e = 39$ erg cm^{-2} for PET.

In the crystallization of undercooled melts, non-steady-state effects may be of major importance [20]. In this respect, Eqs. (8) may be used in their steady-state formulation only under distinct limitations [21]. In the investigated temperature interval ($\Delta T/T_m \to 0.1$) the non-steady-state time lag τ has usually such small values for the process of melt crystallization that it can be neglected. Non-steady-state effects have not been experimentally found so far at $\Delta T/T_m < 0.1$ [21].

5. Conclusions

The results of the present investigation show that the formalism developed here gives a useful method for analysing non-isothermal cooling-run experiments and for determining the lateral and end surface energies. From a general physical point of view, σ and σ_e are quite reasonable and correspond to values known from the literature. The gain of experimental time using our approach is obvious and we hope that the method described here can be not only of theoretical but also of technical significance.

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