

# Parameters characterizing the kinetics of the non-isothermal crystallization of poly(ethylene terephthalate) determined by d.s.c.

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A method of determining the parameters characterizing the kinetics of non-isothermal crystallization on the basis of d.s.c. thermograms is presented. One of these parameters, called 'kinetic crystallizability'<sup>8,9</sup>, is particularly commendable on account of its non-dimensional character and simplicity of determination. The values of the Avrami exponent have been determined, based on data obtained from the thermograms. The non-integral values  $n > 2$  obtained, testify to the existence of a specific number of three-dimensional spherulites which form as a result of athermal nucleation. Their number increases with an increase in cooling rate. In the extreme case of  $dT/dt = 25$  K/min the crystalline part of the polymer consists entirely of the above-mentioned structural forms. Thus, by changing the cooling rate, the morphology of the crystalline structure forming as a result of the non-isothermal crystallization can be determined in a controlled manner.

## INTRODUCTION

Investigation of the kinetics of polymer crystallization is significant both from the theoretical and practical point of view. Of theoretical importance is the mechanism of formation of the polymer fine structure during crystallization. The practical importance arises from the effect of the degree of polymer crystallinity on the physical and chemical properties of polymer.

The technique of thermal analysis<sup>1</sup>, particularly that of differential scanning calorimetry (d.s.c.)<sup>2,3</sup> has frequently been used. The d.s.c. method enables calorimetric measurements to be carried out in a relatively simple, quick and at the same time precise manner. But investigations of this type are most frequently carried out with respect to crystallization occurring under isothermal conditions<sup>4-6</sup>. Meanwhile it is known that in practice crystallization frequently occurs under non-isothermal conditions. Such processes take place particularly in the case of the melt-spinning of chemical fibres. The typical example is poly(ethylene terephthalate) fibre. The quantitative evaluation of the kinetics of non-isothermal crystallization is of great significance in the manufacture of these fibres. The possibility of characterizing such processes by appropriate parameters, which can be determined by means of differential scanning calorimetry, was the main purpose of this study.

## CHARACTERISTICS OF THE KINETICS OF NON-ISOTHERMAL CRYSTALLIZATION

The kinetics of non-isothermal crystallization can be characterized by the application of two procedures. The former is based on the acceptance of the simplifying assumption that crystallization occurs under constant temperature. In

this case, the parameter determining the crystallization kinetics is the constant  $Z_t$  occurring in the Avrami equation for polymers<sup>7</sup>:

$$[1 - X] = \exp[-Z_t t^n] \quad (1)$$

where  $X = X_t/X_E$ , the degree of polymer transformation:  $X_t$  is the degree of crystallinity after time  $t$  of the crystallization process; and  $X_E$  is the maximum degree of crystallinity as a result of crystallization. After conversion, equation (1) takes the well-known form:

$$\log[-\ln(1 - X)] = n \log t + \log Z_t \quad (2)$$

Drawing the straight line given by equation (2) enables us to determine  $\log Z_t$ . But considering the non-isothermal character of the process investigated, the value determined should be adequately corrected. The factor which should be considered is the cooling rate of the polymer. Assuming constant or approximately constant cooling rate, the final form of the parameter characterizing the kinetics of non-isothermal crystallization is given as follows:

$$\log Z_c = \frac{\log Z_t}{dT/dt} \quad (3)$$

The latter procedure enables the characterization of the kinetics of non-isothermal crystallization, based directly on the approximate theory formulated by Ziabicki<sup>8,9</sup>. This theory is based on the assumption that crystallization can be presented by means of the equation for first order kinetics:

$$dX/dt = [1 - X] K(T) \quad (4)$$

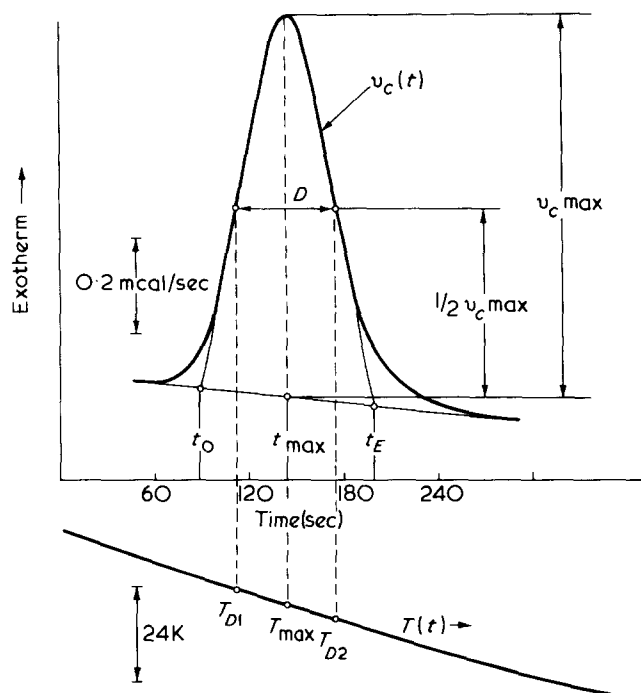


Figure 1 Typical d.s.c. thermogram of non-isothermal crystallization of poly(ethylene terephthalate). Cooling rate,  $dT/dt = 8.5$  K/min; sample mass,  $m = 2.28$  mg; crystallization rate,  $v_c$ ; cooling program,  $T(t)$ ;  $T_{D1} = 486$  K;  $T_{D2} = 479$  K;  $T_{max} = 483$  K

where the rate constant,  $K(T)$ , is dependent only on temperature.

Changes in the rate constant as a function of temperature are illustrated by a curve resembling a Gaussian. This curve can be described by the following equation:

$$K(T) \approx K_{max} \exp[-4 \ln^2(T - T_m)^2 / D^2] \quad (5)$$

where  $K_{max}$  is the maximum value of the rate constant corresponding to the temperature  $T_{max}$ ;  $D$  is the half width of the crystallization curve; and  $T_m$  is the melting temperature of the polymer.

Equation (5) enables us to calculate the quantity  $G$ , known as 'the kinetic crystallizability':

$$G = \int_{T_g}^{T_m} K(T) dT = (\pi / \ln 2)^{1/2} K_{max} D / 2 \quad (6)$$

where  $T_g$  is the glass transition temperature of the polymer.

The kinetic crystallizability ( $G$ ) characterizes the degree of transformation obtained over the entire crystallization range ( $T_m T_g$ ) with unit cooling rate.

The kinetic crystallizability is the parameter characterizing the kinetics of non-isothermal crystallization. This parameter, like the previous one, requires proper correction, considering the cooling rate of the polymer. The final form of this parameter will thus be as follows:

$$G_c = \frac{G}{dT/dt} \quad (7)$$

## EXPERIMENTAL

### Materials

Poly(ethylene terephthalate), produced in granular form

in Poland, was used for the investigation into non-isothermal crystallization in polymers. The viscosity-average molecular weight, determined from the Conix<sup>10</sup> formula was taken as a parameter characterizing the molecular structure of the polymer examined. The value of this index was  $\bar{M} = 17\,600$ .

### D.s.c. procedure

Investigations by the d.s.c. technique were carried out using a Du Pont 990 thermal analyser. The following apparatus parameters were used: heating rate, 20 K/min; Y-axis range, 0.2 mcal/sec; time base setting, 1 min/in; mass of the samples investigated,  $m = 2-3$  mg.

Melting thermograms were drawn during the first run, by heating the sample over the temperature range  $T_s = 298$  K,  $T_L = 548$  K. The melted sample was kept for 10 min at a temperature of 548 K: it was then cooled and the crystallization thermogram was recorded. Three different cooling rates were used:  $dT/dt = 8.5, 12$  or  $17$  K/min. Three crystallization thermograms were taken for each cooling variant. Three corresponding analytical quantities were determined from the thermograms. Their average values, taken from three measurements, were the basis for calculating the kinetic parameters of crystallization.

### Method of determining analytical quantities

A typical d.s.c. crystallization thermogram obtained for the examined polymer is shown in Figure 1. Thermograms similar to the one presented were the basis for determining the analytical quantities required. These analytical quantities were then used to determine the parameters  $Z_c$  and  $G_c$ .

$Z_c$  was calculated by equation (3). The value used for calculations was determined directly from the plot described by equation (2). The values of the Avrami exponent  $n$  were also determined from this plot.

$X$  values, required for drawing this diagram, were determined according to the rules operating in this system by means of the equation<sup>11</sup>:

$$X = \frac{\int_{t_0}^t v_c(t) dt}{\int_{t_0}^{t_E} v_c(t) dt} \quad (8)$$

Points corresponding to the initial and final times,  $t_0$  and  $t_E$ , respectively, of the crystallization process were determined in the thermogram by the procedure shown in Figure 1.

Calculation of the  $G_c$  parameter was made possible by knowing the values of  $K_{max}$  and  $D$  appearing in equation (6). The half-width  $D = T_{D1} - T_{D2}$  can easily be determined directly from the crystallization thermogram. A simple diagram of the corresponding procedure is shown in Figure 1.

The  $K_{max}$  value, corresponding to temperature  $T_{max}$ , in which the crystallization rate is maximum ( $\theta_{c,max}$ ), should now be calculated. It can be shown, using equation (4) as a starting point, that the formula required is as follows:

$$K_{max} = C_k (t_{max})^{-1} \quad (9)$$

where:

$$C_k = \frac{\int_{t_0}^{t_{max}} v_c(t) dt}{\int_{t_{max}}^{t_e} v_c(t) dt}$$

Table 1 Parameters characterizing the kinetics of non-isothermal poly(ethylene terephthalate) crystallization

Cooling rate, $dT/dt$ (K/min)	Avrami exponent $n$	Rate constant		Half-width, $D$ (K)	Rate constant, $K_{\max}$ (sec $^{-1}$ )	Kinetic crystallizability	
		$Z_t$ (min $^{-n}$ )	$Z_c$ (min $^{-n}/K$ )			$G$ (K/sec)	$G_c$
8.5	2.35	1.202	1.022	7.2	0.0184	0.1410	0.990
12	2.49	1.303	1.022	8.5	0.0219	0.1982	0.990
17	2.65	1.445	1.022	10.4	0.0254	0.2812	0.990

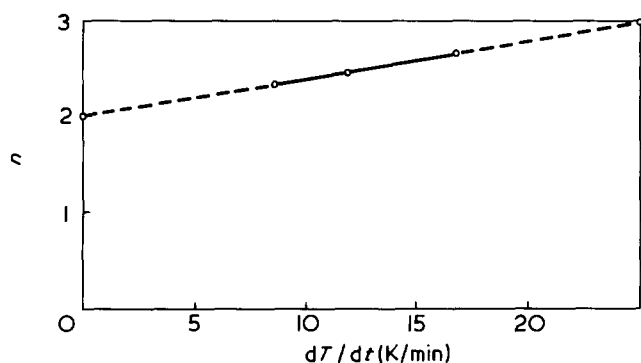


Figure 2 Avrami exponent as a function of cooling rate

$t_{\max}$  is the time from the start of crystallization upto reaching the maximum rate of reaction.

## RESULTS AND DISCUSSION

The results of the determination of parameters characterizing the non-isothermal crystallization of the polymer examined have been shown in Table 1.

The results show that both  $Z_c$  and  $G_c$  parameters can be successfully used for characterizing the kinetics of non-isothermal crystallization. This arises from the fact that values of these parameters are not dependent on the conditions of the crystallization process, and particularly on the cooling rate of the polymer. It may be presumed that the values discussed depend exclusively on the specific chemical features and molecular structure of the polymer investigated.  $G_c$  should be particularly recommended for investigations aiming at the determination of quantitative relations between the kinetics of polymer crystallization and the structural features. The advantages of this parameter, in comparison with  $Z_c$ , are the non-dimensional character and simplicity of procedure aiming at its determination.

Results in Table 1 show that in the case of the Avrami exponent, the values obtained are non-integral. The frequent occurrence of such values can, in practice, be explained in many ways. As a rule explanations are based on models of the nucleation mechanism<sup>12,13</sup>. In the case of the above work the interpretation of results must take into account the specificity of the non-isothermal crystallization process. This specificity arises from the fact that the only parameter which changes considerably in the successive measurements is the cooling rate of the polymer. Thus it can be claimed that the cooling rate is one of the factors res-

ponsible for the diversity of  $n$ -values. The evidence supporting the correctness of such an assumption is the linear character of the diagram illustrating the dependence  $n = f(dT/dt)$  shown in Figure 2.

The values of the cooling rate corresponding to the integer values of the Avrami exponent  $n = 2$  and  $3$ , respectively, can be determined from this diagram by the extrapolation method. It was found that the value  $n = 2$  is characteristic for the 'zero' cooling rate, i.e. for the isothermal conditions of crystallization. The result indicates that only two-dimensional crystallites of lamellar type form in the isothermal crystallization of the polymer examined.

From Figure 2 it is seen that the values  $n > 2$  are characteristic for the range of non-isothermal crystallization,  $dT/dt > 0$ . In an experimental case, however, the value of the Avrami exponent is determined by the cooling rate. The more rapid the cooling, the larger the value of  $n$ . It seems that this dependence is directly related to the increasing effect of the athermal nucleation process, which is connected with the increase in the cooling rate. In the extreme case,  $dT/dt = 25$  K/min, the morphology of the crystalline structures forming is exclusively conditioned by the athermal nucleation. The value of the Avrami exponent, corresponding to the given cooling conditions shows that these are three-dimensional spherulite structures.

Thus the morphology of crystalline structures forming as a result of non-isothermal crystallization, i.e. the amounts of the individual forms, is dependent on the processing conditions. The decisive factor is the cooling rate. By making appropriate changes in the cooling rate, the polymer morphology can be determined in a specific manner.

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