

# Macrokinetics of polymer crystallization

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A new macrokinetic equation of autocatalytic type describing polymer crystallization is proposed. This equation was introduced for the mathematical description of non-isothermal crystallization, and it was proved with the use of isothermal experimental data. The agreement of the macrokinetic equation with the experimental data is shown. The temperature dependence of constants in the macrokinetic equation was studied.

**Keywords** Polymer; crystallization; kinetics; isotherms; non-isothermal

## INTRODUCTION

The universal method for describing the kinetics of polymer crystallization which is adopted at present in the majority of publications is the use of the Avrami equation. Practical application of the Avrami equation for analysis of real crystallization isotherms, however, shows that for a number of polymers it describes the kinetics of crystallization insufficiently. The most typical deviations from the canonical form of the description are fractional powers in the Avrami equation, which have no clear physical meaning, and the variation of the exponent in the Avrami equation with the development of crystallization. Some limitations of the Avrami method have already been pointed out in the literature<sup>1</sup>.

## THEORY

The use of the Avrami equation becomes very complicated in the description of non-isothermal crystallization of polymers. Hence it is evident that, for the solution of various practical problems where the analytical description of crystallization is required, a macrokinetic equation should be found, which would be convenient for calculations and agree with experimental data. This equation, in contrast to the Avrami equation, could be written in the differential form:

$$\dot{\alpha} = \dot{\alpha}(T, \alpha) \quad (1)$$

where  $\dot{\alpha}$  is the rate of crystallization, and  $\alpha$  is the degree of crystallinity varying from 0 to the equilibrium value.

Such a method of analytical description is identical in form to the conventional macrokinetic description of chemical reactions whose rate depends on the degree of conversion and temperature<sup>2</sup>. The aim of the present work is to determine the form of equation (1). The analogy above is intentional, and is mentioned because of the necessity to solve analytically problems in which polymerization and crystallization occur simultaneously (see, for example, ref. 3).

The development of a crystalline phase in a polymer melt includes two stages: the appearance of primary nuclei and subsequent growth of the crystals formed from them. Equation (1) can therefore be written as follows:

$$\dot{\alpha}(T, \alpha) = \dot{\alpha}_1(T, \alpha) + \dot{\alpha}_2(T, \alpha) \quad (2)$$

where  $\dot{\alpha}_1$  is the rate of variation of the degree of crystallinity due to the appearance of primary nuclei, and  $\dot{\alpha}_2$  is the rate of variation of the degree of crystallinity due to crystal growth.

To determine the form of the functions  $\dot{\alpha}_1$  and  $\dot{\alpha}_2$  we can use the approach adopted in the macrokinetics of chemical reactions, which is based on the representation of a function of two variables as the product of two functions each of which depends only on one variable:

$$\dot{\alpha}_1(T, \alpha) = f_1(T)f_2(\alpha) \quad (3)$$

$$\dot{\alpha}_2(T, \alpha) = f_3(T)f_4(\alpha)$$

The function  $\dot{\alpha}_1$  is determined by two principal parameters: the rate of formation of primary nuclei,  $I(T)$ , and the volume of the critical equilibrium nucleus,  $V_*(T)$ . As is known, the temperature dependence of the rate of formation of nuclei is bell-shaped and can be expressed as:

$$I(T) = I_0 \exp\left(-\frac{E}{RT} - \frac{\psi_1 (T_m^\circ)^m}{T(T_m^\circ - T)}\right) \quad (4)$$

where  $I$  is the number of nuclei formed per unit time per unit volume;  $I_0$ ,  $\psi_1$  and  $m$  are constants;  $E$  is the activation energy of transfer of a segment through the nucleus-melt interface;  $R$  is the gas constant; and  $T_m^\circ$  is the equilibrium melt temperature.

We suggest that the kinetics of nuclei formation be described as an analogue of the first-order chemical reaction so that the decrease in the rate of nuclei formation with increasing degree of crystallinity of a

material in the process is described by a function of the form:

$$f_2(\alpha) = \alpha_{\text{eq}} - \alpha \quad (5)$$

where  $\alpha_{\text{eq}}$  is the equilibrium degree of crystallinity which depends on the temperature and molecular mass.

For typical degrees of supercooling (up to  $\sim 50^\circ\text{C}$ ) the volume of a critical equilibrium nucleus can be assumed constant<sup>4</sup>. The function  $\dot{\alpha}_1(T, \alpha)$  can thus be written as follows:

$$\dot{\alpha}_1(T, \alpha) = k_1 \exp\left(-\frac{E}{RT} - \frac{\psi_1 (T_m^\circ)^m}{T(T_m^\circ - T)^m}\right) (\alpha_{\text{eq}} - \alpha) \quad (6)$$

where  $k_1$  is a constant.

As was mentioned above, the second stage of formation of the crystalline phase in polymer melts is associated with the growth of primary nuclei. The generalized equation for the growth rate has the form<sup>5</sup>:

$$G(T) = G_0 \exp\left(-\frac{E}{RT} - \frac{\psi_2 (T_m^\circ)^l}{T(T_m^\circ - T)^l}\right) \quad (7)$$

where  $G_0$ ,  $\psi_2$  and  $l$  are constants.

The suppression of the rate of crystal growth depending on the degree of crystallinity can be presented by the first-order kinetic equation, i.e. in the same form as for the function  $\dot{\alpha}_1(T, \alpha)$ :

$$f_4(\alpha) = \alpha_{\text{eq}} - \alpha \quad (8)$$

Then the equation for  $\dot{\alpha}_2(T, \alpha)$  is written as:

$$\dot{\alpha}_2(T, \alpha) = k'_2 \exp\left(-\frac{E}{RT} - \frac{\psi_2 (T_m^\circ)^l}{T(T_m^\circ - T)^l}\right) S(\alpha) (\alpha_{\text{eq}} - \alpha) \quad (9)$$

where  $k'_2 = G_0$ , and  $S(\alpha)$  is the total surface area over which crystal formation occurs.

Substituting the values of  $\dot{\alpha}_1$  and  $\dot{\alpha}_2$  into equation (2), we can determine  $\dot{\alpha}$ :

$$\frac{d\alpha}{dt} = \left[ k_1 \exp\left(-\frac{E}{RT} - \frac{\psi_1 (T_m^\circ)^m}{T(T_m^\circ - T)^m}\right) + k'_2 \exp\left(-\frac{E}{RT} - \frac{\psi_2 (T_m^\circ)^l}{T(T_m^\circ - T)^l}\right) S(\alpha) \right] (\alpha_{\text{eq}} - \alpha) \quad (10)$$

where  $k_1 = I_0 V_*$ .

Equation (10) is the general macrokinetic equation for polymer crystallization, since it was obtained without essential strict limitations. For practical purposes, however, some simplifications are possible, which make the use of this equation simpler. For example, in most cases<sup>4</sup> it was found experimentally that polymers exhibit heterogeneous nucleation of crystalline structures ( $m = 1$ ), and crystal growth occurs via the formation of two-dimensional surface nuclei ( $l = 1$ ). The function  $S(\alpha)$  is, generally speaking, a non-linear function of its argument; its form is determined by the geometry of the growing crystals. If one assumes the linear form of the function  $S(\alpha)$ , i.e.  $S(\alpha) = D\alpha$ , then equation (10) can be written in a simple form:

$$\frac{d\alpha}{dt} = \left[ k_1 \exp\left(-\frac{E}{RT} - \frac{\psi_1 T_m^\circ}{T(T_m^\circ - T)}\right) + k_2 \exp\left(-\frac{E}{RT} - \frac{\psi_2 T_m^\circ}{T(T_m^\circ - T)}\right) \alpha \right] (\alpha_{\text{eq}} - \alpha) \quad (11)$$

where  $k_2 = G_0 D$ . It simplifies the description of the process of non-isothermal crystallization and makes it possible to apply numerical methods for the solution of non-isothermal problems.

In the present work we aim to verify the possible use of equation (11) for the description of experimental results. Most simply this can be done for isothermal conditions, when the heat transfer equation is excluded from the system of macrokinetic equations. In this case equation (11) has the form:

$$\frac{d\alpha}{dt} = (A_1 + A_2 \alpha)(A_3 - \alpha) \quad (12)$$

where  $A_1$ ,  $A_2$  and  $A_3$  are different functions of temperature, whose forms are determined by the equations cited above.

If we introduce a 'reduced' degree of crystallinity  $\alpha_* = \alpha/A_3$  (since the physical meaning of  $A_3$  is the equilibrium degree of crystallinity) and the notation  $C_0 = A_2 A_3/A_1$ , and  $k_0 = A_1$ , then equation (12) will take the form typical of ordinary macrokinetic equations of chemical kinetics of autocatalytic type:

$$\frac{d\alpha_*}{dt} = k_0 (1 + C_0 \alpha_*) (1 - \alpha_*) \quad (13)$$

The solution of this equation for the isothermal case can easily be found. It has the form:

$$\alpha_*(t) = 1 - \frac{C_0 + 1}{C_0 + \exp(C_1 t)} \quad (14)$$

where  $C_1 = (C_0 + 1)k_0$ .

## DISCUSSION

The experimental verification of the equations obtained was carried out using the results of isothermal experiments on crystallization of poly(propylene)<sup>6</sup>, poly(ethylene terephthalate)<sup>4</sup> and poly(propylene oxide)<sup>7</sup>. For this purpose the data presented in the original works and processed according to the Avrami equation were plotted in

$$\frac{1}{1 - \alpha_*} \frac{d\alpha_*}{dt} \text{ vs. } \alpha_*$$

coordinates. The resultant curves for poly(ethylene terephthalate) are shown in *Figures 1a* and *2a*. As can be seen, the experimental data are described by this method in a wide range of variables, except for the terminal part. It is known, however<sup>5</sup>, that the Avrami equation agrees less well with experiment, particularly at the end of the process, and gives overestimates in comparison with experimental data. Therefore, the divergence between

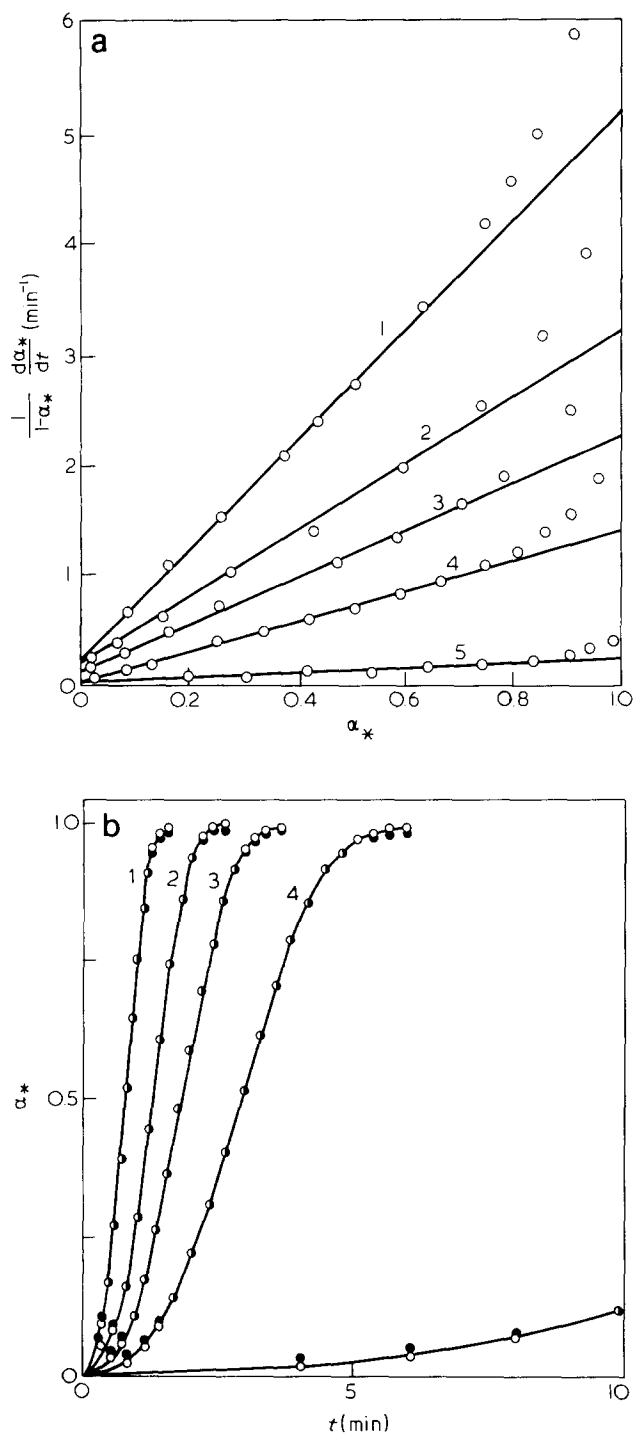


Figure 1 Crystallization isotherms for poly(ethylene terephthalate): (1) 180°C; (2) 200°C; (3) 210°C; (4) 220°C; (5) 230°C: (a)  $\ln 1/(1-\alpha_*) d\alpha_*/dt$  vs.  $\alpha_*$  coordinates; — calculated results using equation (13);  $\circ$  using the Avrami equation. (b)  $\ln \alpha_*$  vs.  $t$  coordinates;  $\bullet$  calculated using equation (14);  $\circ$ — using the Avrami equation

experimental and calculated 'points' in Figures 1a and 2a speaks rather in favour of equation (14).

On the basis of the results obtained, the constants  $C_0$  and  $C_1$  were calculated for all of the above-mentioned materials (for each crystallization temperature) after which, using equation (14) and the determined values of  $C_0$  and  $C_1$ , crystallization isotherms were calculated and then compared with the results of calculation using the Avrami equation (Figures 1b, 2b and 3). These figures

show good agreement between the results obtained using equation (14) and the Avrami equation. It should be noted that Figure 3 gives the crystallization isotherms of poly(propylene oxide). Their distinctive feature is that crystallization of this polymer is described by the Avrami equation with the exponent varying with the development of crystallization, whereas Figure 4 gives the theoretical and experimental isotherms of poly(caproamide) crystallization, obtained during anionic activated polymerization of  $\epsilon$ -caprolactam in the temperature range where the total thermal effect is decomposed into components<sup>3</sup>.

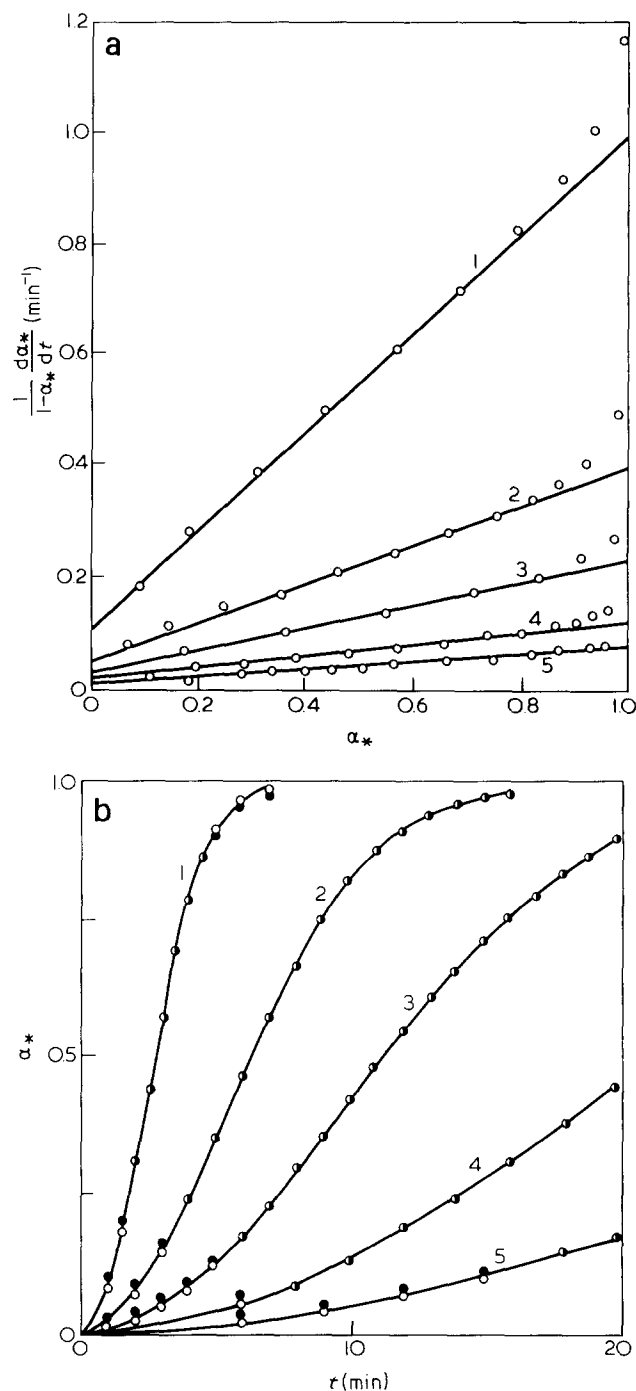


Figure 2 Crystallization isotherms for poly(propylene): (1) 117°C; (2) 125°C; (3) 130°C; (4) 132.5°C; (5) 135°C. (a)  $\ln 1/(1-\alpha_*) d\alpha_*/dt$  vs.  $\alpha_*$  coordinates; — calculated using equation (13);  $\circ$  using the Avrami equation. (b)  $\ln \alpha_*$  vs.  $t$  coordinates;  $\bullet$  calculated using equation (14);  $\circ$ — using the Avrami equation

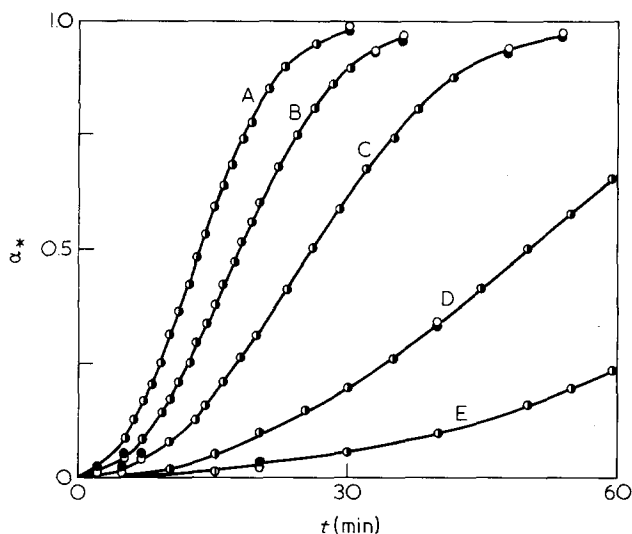


Figure 3 Crystallization isotherms for poly(propylene oxide): (A) 38.5°C; (B) 40°C; (C) 42.5°C; (D) 45°C; (E) 47.5°C; ●—calculated using equation (14); —○—using the Avrami equation

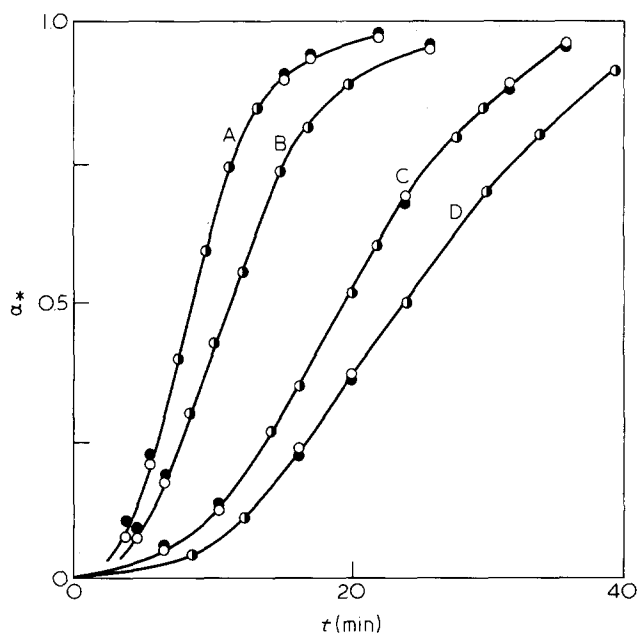


Figure 4 Crystallization isotherms for poly(caproamide): (A) 180°C; (B) 184°C; (C) 188°C; (D) 192°C; ●—calculated using equation (14); —○—experimental

The results obtained indicate the universal nature of equation (14) in the description of crystallization kinetics. Figure 5 shows temperature dependences of the quantities  $A_1$  and  $A_2$  for poly(ethylene terephthalate) from which the

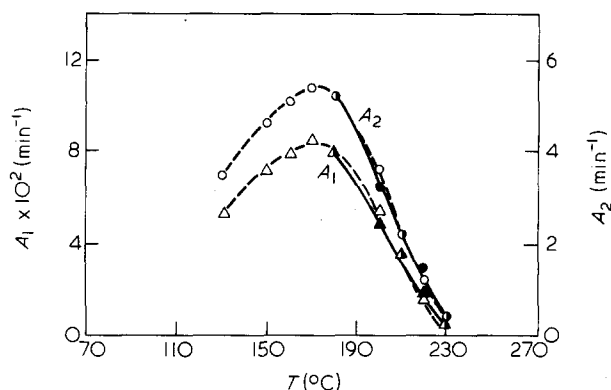


Figure 5 Temperature dependences of the quantities  $A_1$  and  $A_2$

constants entering equation (11) were determined:

$$E = 40.24 \text{ kJ mol}^{-1}; \quad T_m^\circ = 533 \text{ K (ref.);}$$

$$\psi_1 = 201 \text{ K}; \quad \psi_2 = 201 \text{ K;}$$

$$k_1 = I_0 V_* = 4.33 \times 10^6 \text{ min}^{-2};$$

$$k_2 = G_0 D = 6.6 \times 10^4 \text{ min}^{-1}$$

Temperature dependences of  $A_1$  and  $A_2$  calculated from equation (11) using the obtained values of the constants are shown by the broken lines in Figure 5. It can be seen that the maxima on these curves lie at  $\sim 170^\circ\text{C}$ , which corresponds to  $0.82T_m$ .

Equation (14) can thus be used to replace the conventional Avrami equation. The possibility of this replacement is justified by its agreement with experimental data and the expediency of such a replacement by the advantages of a simple differential form of equation (13) in comparison with possible generalizations of the Avrami equation for non-isothermal processes. In future it would be interesting to consider the problems associated with non-isothermal crystallization by simultaneously analysing the general equation (11) and the heat transfer equation.

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