

A numerical method for the evaluation of data on the kinetics of polymer crystallization

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SUMMARY

Avrami's model of the kinetics of crystallization is the generally accepted starting point for the analysis of nucleation and primary crystallization in the growth step. However, in most cases, the experimental situation is complicated by additional phenomena such as incubation and secondary growth although, as yet, no simple analytical method, that takes these effects into account, has been described. An iterative procedure that deals with this problem is presented here and is based on the observation that, in most crystallization experiments, a plot of the kinetic data shows an inflexion point, the ordinate value of which is only marginally influenced by incubation and secondary crystallization. The reliability of the method is demonstrated by both simulation and experiment.

INTRODUCTION

A new, simple, numerical method for the evaluation of the kinetics of polymer crystallization has been elucidated. The theoretical basis of this method was originally described by Avrami (1) and others (2-6) for the ideal case where the growing morphological units (spherulites) do not interfere with one another's growth kinetics and show no incubation or secondary crystallization phenomena. This model separates the nucleation and growth steps: nucleation is considered to occur either thermally, in which case the number of nuclei changes with time, or spontaneously, under sufficient supercooling of the melt, in which case the number of nuclei does not change with time. The growing unit is a complex entity containing crystal lamellae and amorphous material and growth kinetics may be limited by either the rate of incorporation of molecules into the crystalline phase or by the diffusional transport of the molecules to the crystalline-melt interface. A simple mathematical description of the kinetics can be derived from this model:

$$X(t) = 1 - \exp(-kt^n) \quad (1)$$

where $X(t)$ is the degree of crystallinity given by the ratio of the volume of crystallized material at time t to the total vo-

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lume, k is the crystallization rate constant and n is the Avrami exponent. The Avrami exponent contains information about the mode of nucleation and growth control and about the geometry of the primary crystallization (i.e. whether the growing unit is of rod, disc or spherical shape). In most cases, following initial supercooling (and the transformation of the melt into a metastable state), some incubation time (τ) is required prior to isothermal polymer crystallization. To take this into account, the original Avrami equation must be modified: $X(t) = 1 - \exp(-k(t-\tau)^n)$ (2)

The incubation time depends on the experimental conditions such as the degree of supercooling employed, and on the purity of the sample. A further complication in the polymer crystallization process is the occurrence of secondary crystallization, the effects of which are superimposed upon the function $X(t)$ and its contribution $X'(t)$ must be deconvoluted from the observed function $X''(t)$: $X''(t) = X'(t) + X(t)$ (3)

in order to apply eq (2) to the main crystallization process. In reality, a property, $I(t)$, sensitive to the degree of crystallinity (such as volume, specific heat, optical retardation etc) is measured. The degree of crystallinity, $X(t_i)$ is defined as:

$$X(t_i) = (I(t_i) - I(0)) / (I(\infty) - I(0)) \quad (4)$$

The purpose of the present paper is to describe a method for the determination of τ , $X(t)$ and hence n .

BASIS OF THE EVALUATION

The time difference between subsequent observations of I , Δt_i is given by: $t_i = t'_{i+1} - t'_i$ with $t'_i = t_i - \tau$ (5)

Inverting (2) makes it obvious that t is a function of X, n, k and τ whereas Δt is only a function of X, n and k . The time difference Δt_i can be calculated without a priori knowledge of the incubation time τ . The quotient $Q_i = \Delta t_i / \Delta t_{i+1}$ (6)

is independent of k and thus only a function of X and n and can be calculated from eqs (2), (5) & (6):

$$Q(n) = \left[1 - \frac{\left[\ln \{1 - X(t_{i+1})\} \right]^{1/n}}{\left[\ln \{1 - X(t_i)\} \right]^{1/n}} \right] * \left[\frac{\left[\ln \{1 - X(t_{i+2})\} \right]^{1/n}}{\left[\ln \{1 - X(t_{i+1})\} \right]^{1/n}} - 1 \right]^{-1} \quad (7)$$

The form of this equation does not allow an explicit solution for n which must be found by iteration.

The assumption has been made that secondary crystallization has no influence on the crystallization progression curve in the neighbourhood of the inflexion point $X(t_\psi)$ so that

$$X(t_\psi) = X''(t_\psi) \quad (8)$$

Bearing in mind that the criterion $n > 1$ must be fulfilled (otherwise there exists no inflexion point), the value of the inflexion point $t'_\psi = t_\psi - \tau$ can be calculated from eq (2) as:

$$\frac{d^2(1 - X(t'))}{d t'^2} \Big|_{t' = t'_\psi} = 0 \quad (9)$$

With $t' = t - \tau$ and resolving eq (9) for t'_ψ gives

$$t'_\psi = (n-1/nk)^{1/n} \quad (10)$$

and by substitution in eq (2), it follows that $X(t\psi)$ is only a function of n : $X(t\psi) = 1 - \exp((1-n)/n)$ (11)

NUMERICAL METHODS FOR THE CALCULATION OF THE KINETIC PARAMETERS

Using Newton's approximation $n_{k+1} = n_k - Q(n_k)/(dQ(n_k)/dn_k)$ (12) an estimated value of n can be found. This value when substituted into eq (11) enables an iteration. The iterative procedure is repeated until the difference between successive values of n_k and n_{k+1} is sufficiently small, giving a final estimate of n .

EXPERIMENTAL METHODS

Isothermal crystallization kinetics were followed by observing the increase in birefringence upon crystallization using a Zeiss Photopol III polarization microscope equipped with a Mettler FP82 hot-stage. The degree of crystallinity was defined (eq (4)) as being proportional to the light intensity transmitted $I(t)$ by the sample, which was inserted between closed polarizers. Light-intensity was measured with a photometer and the output current amplified by a Mettler FP80 processor. The same processor was used to control the temperature of the hot-stage. The crystallizing melt of a sample of highly purified polypropylene was sandwiched (thickness about $10\mu\text{m}$) between a microscope slide and a cover slip, conditions under which growth can take place in 3 dimensions. In a typical experiment the temperature of the sample was cooled from 200°C to 128°C at a rate of $10^\circ\text{C}/\text{min}$. Numerical calculations were performed on a programmable pocket calculator.

RESULTS

Table 1 lists the results of applying the iteration procedure to real data using the starting parameters $n_1=2.242$, $k_1=5.546\text{E}-8$ and $I(\infty)=51.553$

Table 1:

Input data					Results			
$I(t\psi)$	$t\psi$	$X(t_1)$	$X(t_2)$	$X(t_3)$	$n(\tau)$	$k(\tau)$	$I(\infty)$	τ
[mV]	[sec]	start	start	start		[sec^{-1}]	[mV]	[sec]
22.5	990	0.1	0.2	0.3	2.44	4.96E-8	50.4	197
		0.1	0.25	0.5	2.47	4.14E-8	50.1	192
21.0	960	0.1	0.2	0.3	2.53	2.84E-8	46.2	183
		0.1	0.25	0.5	2.65	1.24E-8	45.2	162
25.0	1045	0.1	0.2	0.3	2.29	1.21E-7	58.0	220
		0.1	0.25	0.5	2.15	3.18E-7	60.3	249

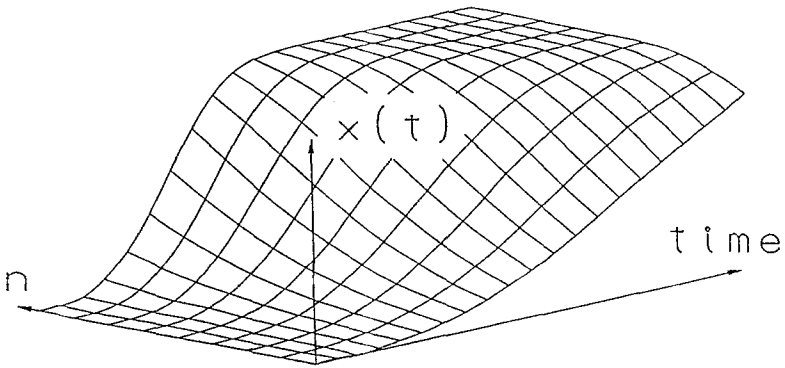


Figure 1: The shape of the Avrami function for different values of n in a 3-dimensional representation

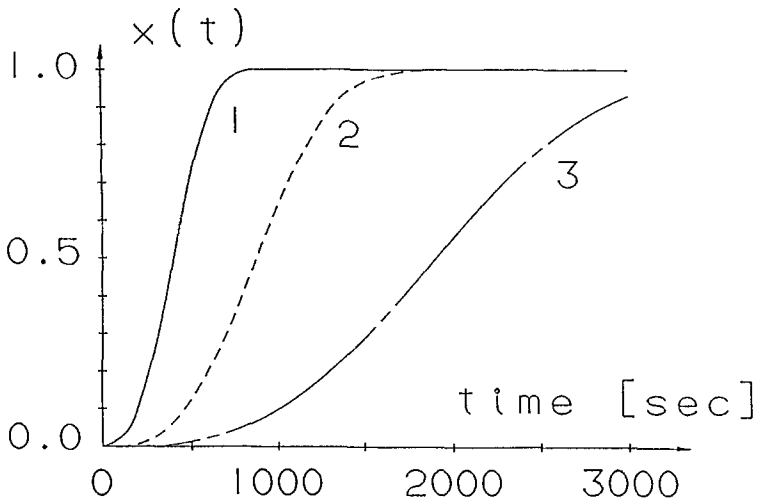


Figure 2: The inflexion point of the kinetic curve is independent of the crystallisation rate constant k .

- 1: $k=1.00E-8$
- 2: $k=1.00E-9$
- 3: $k=1.00E-10$

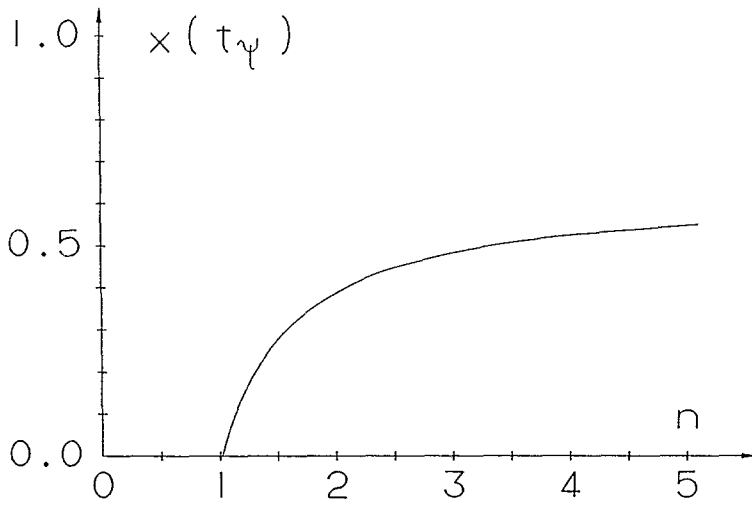


Figure 3: The dependence of $X(t_\psi)$ upon the Avrami exponent n plotted according to (eq 11).

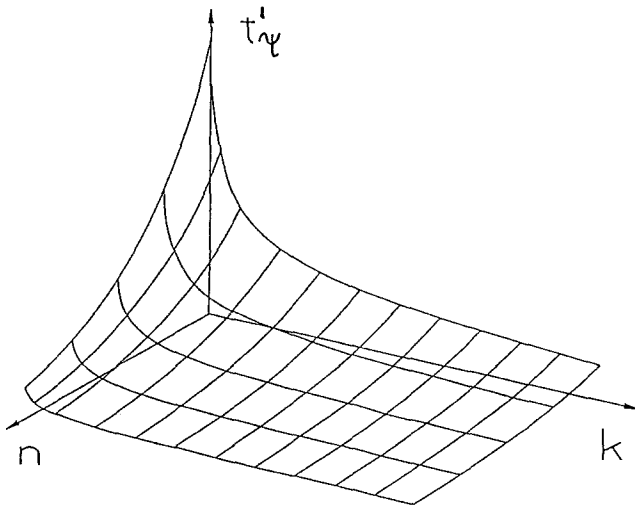


Figure 4: The influence of n and k on the position of the inflexionpoint t'_ψ (eq 10).

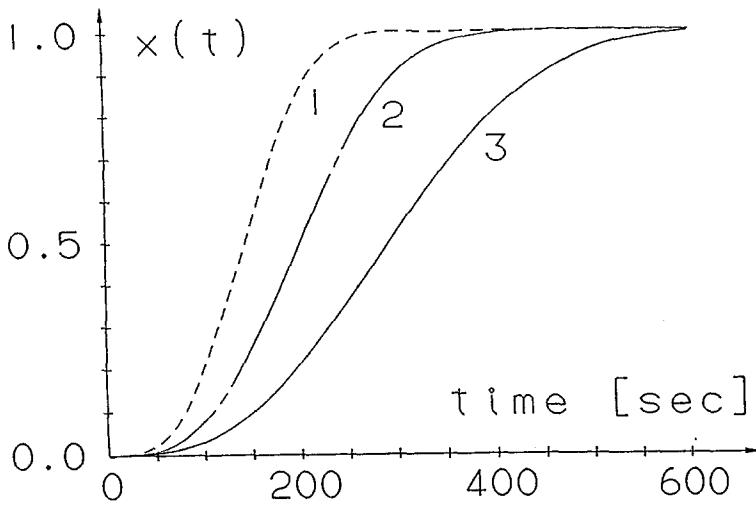


Figure 5: The influence of varying the exponent n on the basic form of the Avrami curve (eq 1). Curves 1, 2 and 3 are calculated for $n=2.80$, $n=3.00$ and $n=3.20$.

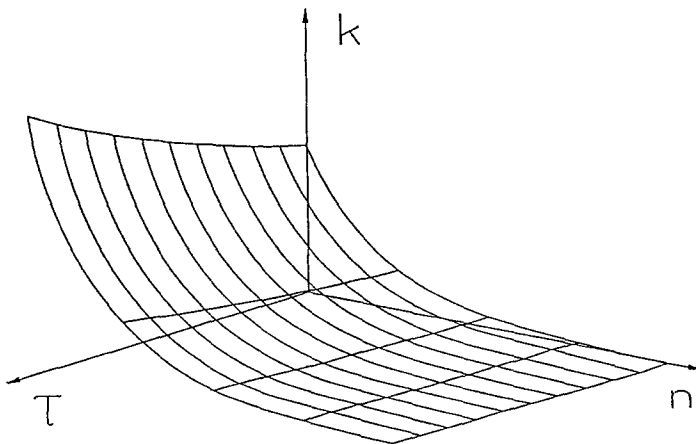


Figure 6: Simulated values of k by given n and τ .

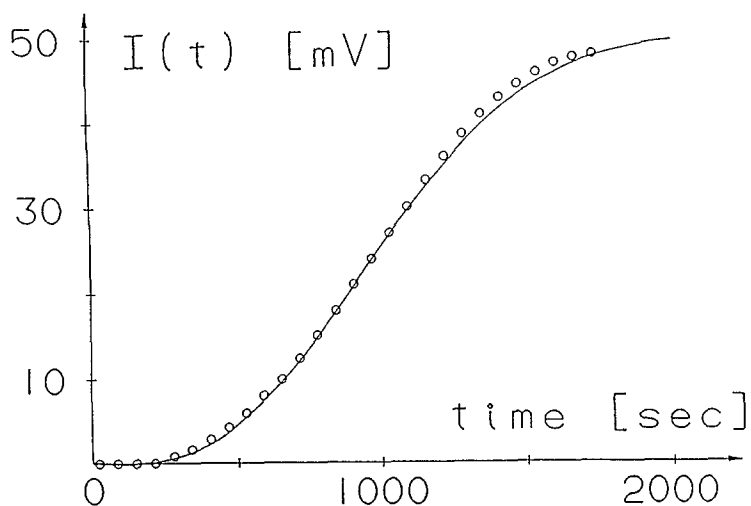


Figure 7: Typical experimental values from the crystallization of polypropylene under isothermal conditions (120.8°C). (See table 1)

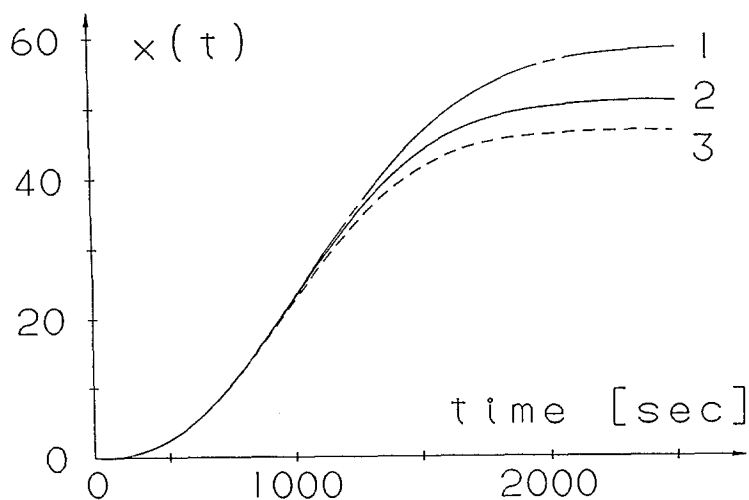


Figure 8: The influence of the selected $I(t\psi)$ values on the shape of the final portion of the curve in Figure 7.
 Curve 1: $I(t\psi)=25.0\text{mV}$ at 1045sec
 Curve 2: $I(t\psi)=22.5\text{mV}$ at 990sec
 Curve 3: $I(t\psi)=21.0\text{mV}$ at 960sec

Figures 1-6 were obtained by simulation of experimental data. The basic form of the Avrami curve is shown in figs. 1, 2 & 5. Fig. 2 demonstrates that $X(t\psi)$ is independent of k . In contrast, figs. 3 & 4 show that both $X(t\psi)$ and $t'\psi$ are dependent upon n . The influence of varying τ and n on k is depicted in fig. 6. In fig. 7 the results of a typical crystallization experiment are shown along with the calculated curve with the starting values of $X(t_1)$, $X(t_2)$, $X(t_3)$ set at 0.1, 0.2, 0.3 respectively and with $I(t\psi) = 22.5$. Fig. 8 shows the effect of varying $I(t\psi)$ on the shape of the final portion of the progress curve.

DISCUSSION

It has been assumed that the measured intensity $I(t)$ is proportional to the degree of crystallization although this only holds in the case of 2-dimensional crystallization. During 3-dimensional crystallization $I(t)$ is proportional to the 2-dimensional projection of the growing crystallites in the plane of the microscope objective. This may lead to significant over-estimation of the degree of crystallinity in the initial phase of the kinetic curve, especially when the sample thickness is greater than size of the spherulites. The value of the experimentally determined exponent n , of around 2.5, can be explained by athermal nucleation at the high cooling rates used and by the dimensionality (2 to 3) of the growing crystals at the sample thickness employed.

The fact that no secondary crystallization is apparent at the inflexion point $t\psi$ is critical to the success of this method as is the selection of appropriate starting values of $X(t_i)$ which should be in a range of t_i where the determination of $I(t_i)$ is accurate and unaffected by secondary crystallization.

REFERENCES

- (1) Avrami, M., J. Chem. Phys., 7, 1103 (1939)
8, 212 (1940)
9, 117 (1941)
- (2) Birch, F., a. J. Sci., 238, T92 (1940)
- (3) Darken, L.S. and Gurry, R.W., J. Met., 3, 1015 (1951)
- (4) Mehl, R.F., Hull, F.C. and Colten, R.A., Transactions AIME, 150, 185 (1943)
- (5) Burke, J.E. and Turnbull, D., Prog. Metallphys., 3, 220 (1960)
- (6) Mehl, R.F. and Hagel, U.K., Prog. Metallphys., 3, 88 (1960)