

Crystallization of poly(ϵ -caprolactone)

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The isothermal crystallization behaviour of poly(ϵ -caprolactone), PCL, has been investigated by dilatometry and optical microscopy. Nucleation rates and spherulitic growth rates have been measured. At all temperatures tested a change in nucleation rate was observed early during the crystallization. Growth rates were linear over the whole of the crystallization range. The experimental results were analysed using the Avrami equation in which the experimentally observed time dependence of nucleation is used. The equation contains integer values of the Avrami exponent and describes adequately the crystallization behaviour of PCL. The difference between the apparent and true nucleation rates is emphasized, and difficulties in the calculation of rate constants are discussed.

(Keywords: crystallization; kinetics; dilatometry; microscopy; nucleation)

INTRODUCTION

The many difficulties¹ associated with the use of the Avrami equation² in the analysis of crystallization behaviour of polymers have not diminished the popularity of the method over many years³⁻⁶.

Crystallizing polymer melts are often reported as either sporadically or instantaneously nucleated systems containing spherulites growing at a constant rate. In these cases, fractional powers occurring in the Avrami equation have no clear physical meaning and yet they are meticulously reported, often with disregard for the significant associated errors.

Deviations from the Avrami equation are generally attributed to inaccuracies in assumptions presumed in the derivation of the equation. For example, variation in spherulitic growth geometry or density, and the uncertainty of the time of onset of secondary crystallization have been used to explain fractional values of the Avrami exponent¹⁻⁹.

Little, if any, attention has been given to variation in nucleation rates during crystallization.

It is proposed here that the crystallization of PCL can be satisfactorily described by the Avrami equation if it is recognized that the overall rate is not necessarily characterized by a single rate constant. More specifically, we have observed changes in nucleation rates during isothermal crystallization which, when used appropriately in the Avrami equation, lead to a satisfactory description of the overall crystallization behaviour.

THEORY

The classical equation describing the time dependence of the liquid to solid transformation was derived by Avrami^{2,7,9}

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

where $X(t)$ is the mass fraction transformed to solid by time t . The exponent m contains contributions related to the crystal growth geometry and the time dependence of

the nucleation rate, and k is the overall crystallization rate constant involving contributions from crystal growth and nucleation.

For three dimensional growth at a constant rate the mass fraction of molten material, transformed into solid at time t , is given by

$$X(t) = 1 - \exp(-\pi/3\rho_s/\rho_l NG^3 t) \quad (2)$$

where ρ_s and ρ_l are the solid and molten densities, G is the spherulitic growth rate and N is the number of nuclei per unit volume of untransformed liquid present at time t . If N is linearly dependent on t ($N = \dot{N}t$), equation (2) can be written as

$$X(t) = 1 - \exp(-k_1 t^4) \quad (3)$$

where

$$k_1 = \pi/3\rho_s/\rho_l \dot{N} G^3 \quad (4)$$

and \dot{N} is the nucleation rate per unit volume of untransformed liquid. Under the same growth conditions but with instantaneous nucleation the mass fraction transformed into solid can be written as

$$X(t) = 1 - \exp(-k_2 t^3) \quad (5)$$

where

$$k_2 = 4\pi/3\rho_s/\rho_l \dot{N} G^3 \quad (6)$$

In both equations (3) and (5) k_1 and k_2 are the overall rate constants and make no allowance for changes in rate during the course of crystallization.

A particular variation in nucleation rate, frequently observed in experiments¹⁰⁻¹⁴, is the case when an initial linear nucleation rate changes to a lower value at some time during the process of crystallization. Let \dot{N}_1 and \dot{N}_2 be the two linear nucleation rate constants, and t_c be the time at which the nucleation rate changes. At time $t < t_c$, $\dot{N}_2 = 0$, and the crystallization behaviour is described by

equation (3). At time $t \geq t_c$ we have crystals, formed before t_c , continuing to grow, and new nuclei forming with nucleation rate constant \dot{N}_2 .

The number of nuclei per unit volume of untransformed liquid present at any time $t \geq t_c$ is then given by

$$N(t) = \dot{N}_1 t_c + \dot{N}_2 (t - t_c) \quad (7)$$

The mass fraction of material transformed to solid at time t can now be written as

$$X(t) = 1 - \exp(-\pi/3 \rho_s / \rho_l G^3 (\dot{N}_1 t_c + \dot{N}_2 t - \dot{N}_2 t_c) t^3) \quad (8)$$

The determination of the quantity $X(t)$ by dilatometry relies on the relationship:

$$X(t) = \frac{h_0 - h_t}{h_0 - h_\infty} \quad (9)$$

where h_t is the height of the mercury level measured at time t , h_0 is measured at the beginning, and h_∞ is obtained at a sufficiently long time after the completion of crystallization.

Observation of crystallization under an optical microscope provides means for the determination of the growth and nucleation rates. The spherulite growth rate is given by $G = dR/dt$, where R is the radius of the spherulite measured as a function of time.

Counting the number, n , of visible spherulites as a function of time, gives a measure of the apparent nucleation rate, dn/dt . The true nucleation rate \dot{N}' per unit mass of untransformed (molten) material is related to the measured quantity by:

$$\dot{N}' = \frac{1}{[1 - X(t)]} \frac{dn}{dt} \quad (10)$$

The densities ρ_s and ρ_l were taken from published data²².

EXPERIMENTAL

Sample preparation

Commercial poly(ϵ -caprolactone), PCL, (Aldrich Chemical Company, Inc.) in pellet form was ground in a nitrogen cooled mill to a fine powder (ASTM Sieve No. 45). This powder was Soxhlet extracted with dry diethyl ether for 5 days and then dried in a fluidized bed with nitrogen. The purified PCL was characterized by g.p.c. and gave $M_w = 85\,000$ and $M_n = 48\,000$ using polystyrene standards. Cylindrical plugs of pure PCL were moulded, following a method described earlier¹⁵, in a suitable die after a period of degassing.

Suitably sized samples were cut from these plugs for use in the dilatometric studies and thin sections were microtomed for use in the optical studies.

Dilatometry

Samples (2 g) were used in a mercury filled dilatometer held initially in a water bath at 80°C for 15 min. Subsequently the crystallization behaviour of the sample was followed by monitoring the mercury level as a function of time in water baths controlled at 51.0, 49.5, 47.6 and 46.5°C \pm 0.1°C. It was possible to use the same sample for all measurements as continued repetition of

the melting/crystallizing cycle caused no obvious variations in the crystallization behaviour of the PCL material. In all cases a blank was run to minimize errors in dilatometer readings due to thermal effects.

Optical microscopy

A Zeiss polarizing microscope fitted with a Mettler FP82 Hot Stage and an Olympus 35 mm camera was used to observe the nucleation and growth behaviour of 10 μ films of PCL, between glass plates, under the same melting/crystallizing cycles as used in the dilatometric studies. Approximately 15 micrographs were taken at suitably spaced time intervals during the course of each crystallization. Growth rates were measured directly and nucleation rates were determined by first counting on the photographs the number of nuclei present at any time with radius $\geq 5 \mu$. This observed number of nuclei per unit volume of crystallizing mixture was then converted to the number of nuclei per unit volume of untransformed molten polymer using the appropriate dilatometric data. In applying these data to equation (8) the experimental value of t_c has been corrected on the assumption that only spherulitic growth occurred from the nucleus. In making this correction it is of no importance at which size the nucleus began spherulitic growth. The magnitude of the growth rates ensure that errors in this correction are small.

Errors

Random and systemic errors associated with dilatometric measurements accumulated a total error of approximately 5% in the measured fraction of solid present at time t .

Growth rates were easily measured and the errors were approximately 3%. Errors in the nucleation rates were mainly due to the uncertainties in the determination of the polymer film thickness. These errors ranged from approximately 12% during rapid crystallization to approximately 5% at slower crystallization rates.

DISCUSSION

The optical micrograph (Figure 1) and the growth rate curves (Figure 2) demonstrate, that in this study, crystalline growth in PCL is spherulitic and linear with time as previously reported for solvent cast films of PCL⁴. This means that the growth process is interface- rather than diffusion-controlled. The micrographs also show a size distribution of spherulites which, in view of the results in Figure 2, implies time dependent nucleation.

Optical measurements of the apparent nucleation rates (Figure 3) show a non-linear time dependence, which to a first approximation can be represented by two linear regions. Such changes in nucleation rates are well documented⁹⁻¹⁴. For example in poly(ethylene oxide) crystallized at 47°C and 49°C similar changes in nucleation rates occur at approximately 60% and 25% transformation to solid respectively¹⁰.

The true nucleation rates, \dot{N}_1 and \dot{N}_2 , were obtained from the data shown in Figure 3 by the use of the relationship given in equation (10).

In earlier publications^{10,11} a single constant value of \dot{N}' or \dot{N} was assumed. It was evaluated either from the slope of a number of nuclei versus time plot, or from the initial slope of one of these plots. It appears that the observed

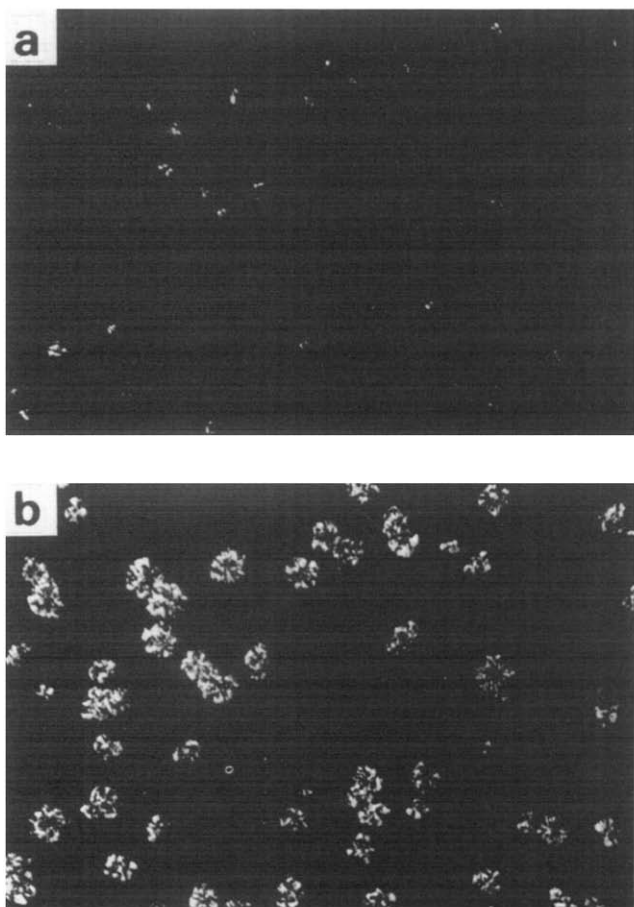


Figure 1 Optical micrographs of the same area of PCL showing spherulitic growth and time dependence of nucleation. Crystallized at 47.6°C. (a) after 20 min, (b) after 36 min

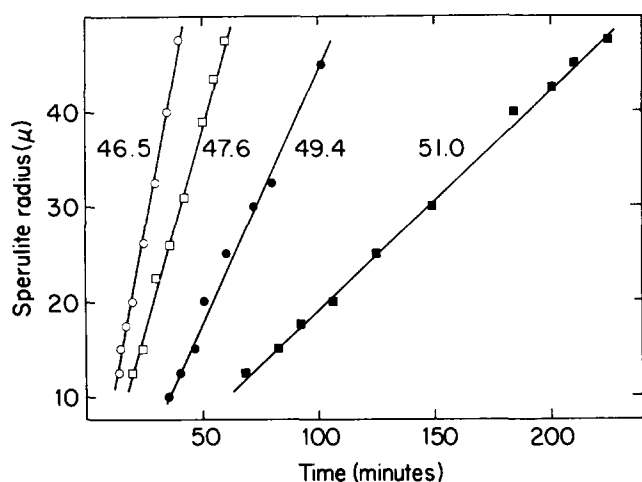


Figure 2 Observed spherulite radius as a function of time for the isothermal crystallization of PCL: 46.5°C, 47.6°C, 49.4°C, 51.0°C

number of nuclei rather than a corrected number of nuclei per unit of remaining liquid polymer was used to evaluate a nucleation rate. If this is so then dn/dt has been evaluated rather than N' . We emphasize this point here, since on reading a number of publications on this subject we observed that the distinction between these quantities is not generally understood, even though it is clearly and accurately defined⁹.

It should be noted that the extrapolated corrected nucleation rates do not pass through the origin (Figure 3).

Firstly, this is largely accounted for by the time needed to grow from critical nucleus size (around 20 nm) to the visible size of 5 μ , as measured by our method. Secondly, in view of the demonstrated time dependence of the nucleation rates, it is possibly due to low initial growth rates before spherulitic geometry is achieved¹⁶ or an incubation period¹⁷ proposed by some workers. Of course there is no certainty of this and the absence or presence of an incubation period or a different species growing at a different rate early in the crystallization process, will have a marked effect on the subsequent crystallization behaviour.

Next it is important to consider whether the crystal growth processes on the microscope slide and in the dilatometer are related. It has been suggested that attempts to correlate dilatometric and microscopic kinetic data is of little value because of the observed dependence of nucleation and growth rates on sample thickness of poly(ethylene oxide)¹⁰, and for polyethylene¹³ although no such dependence has been observed for nucleation rates in poly(decamethylene

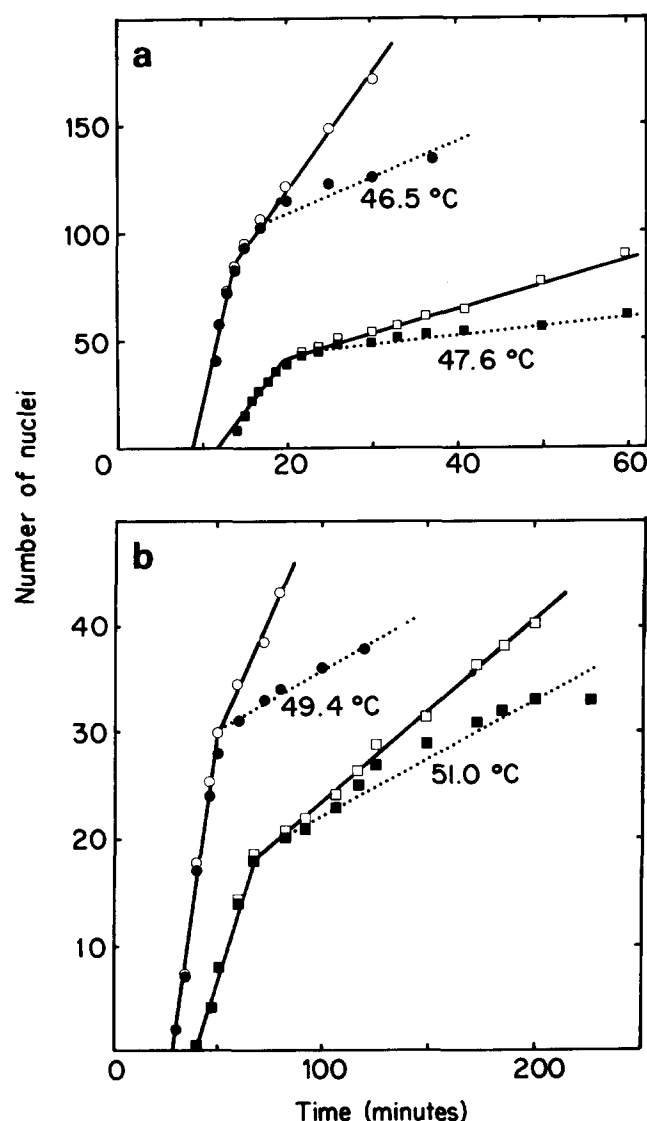


Figure 3 Observed number of nuclei (points) versus time for the isothermal crystallization of PCL: (a) 46.5°C, 47.6°C; (b) 49.4°C, 51.0°C. The apparent nucleation rates are equal to the gradients of the dotted lines. The true nucleation rate, according to equation (10), are given by the gradients of the solid lines

sebacate)¹⁶. Nevertheless the following points can be made.

It is well known that the spherulitic growth rate, G , for a given polymer is usually found to be the same at a constant temperature, therefore it is reasonable to assume the same value of G in both cases. In fact, comparison of crystallization behaviour in both types of experiment shows agreement between the times required to achieve marked slowing down of crystallization in each case.

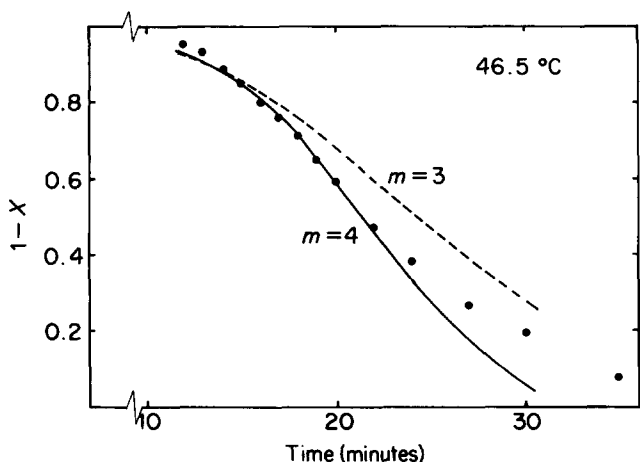


Figure 4 Isothermal crystallization data for PCL crystallized at 46.5°C: observed dilatometric data; calculated results using equation (3); calculated results using equation (5)

The question of similar nucleation rates is more difficult to resolve. Consider Figure 4 which shows a plot of $(1-X)$ versus time for PCL at 46.5°C. The experimental data, plotted as $(h_{\infty} - h_t)/(h_{\infty} - h_0)$ from dilatometry, are compared with curves calculated from equations (3) and (5) using growth rates and the initial nucleation rates as determined optically. The observed change in nucleation rate is neglected for the moment. The experimental data follow more closely the curve calculated by equation (3) during the early crystallization period. In fact the curve calculated by equation (5), corresponding to an instantaneous nucleation model, does not correlate with the dilatometric data at all. Assuming the growth in the dilatometer is spherulitic, nucleation in the dilatometer cannot be instantaneous, but must be time dependent. It is not yet possible to establish whether the mechanisms of nucleation are the same, but the time dependence of nucleation appears to be similar in both cases. This is further supported by the good agreement between the experimental and calculated values using equation (8) at all four crystallization temperatures up to about 80% conversion as shown in Figure 5. The least satisfactory agreement occurs for data obtained at 46.5°C which is the data subject to the greatest uncertainty (Table 1).

Although the comparison of dilatometry and optical microscopy results is subject to a number of difficulties, it offers a much greater insight into the underlying processes

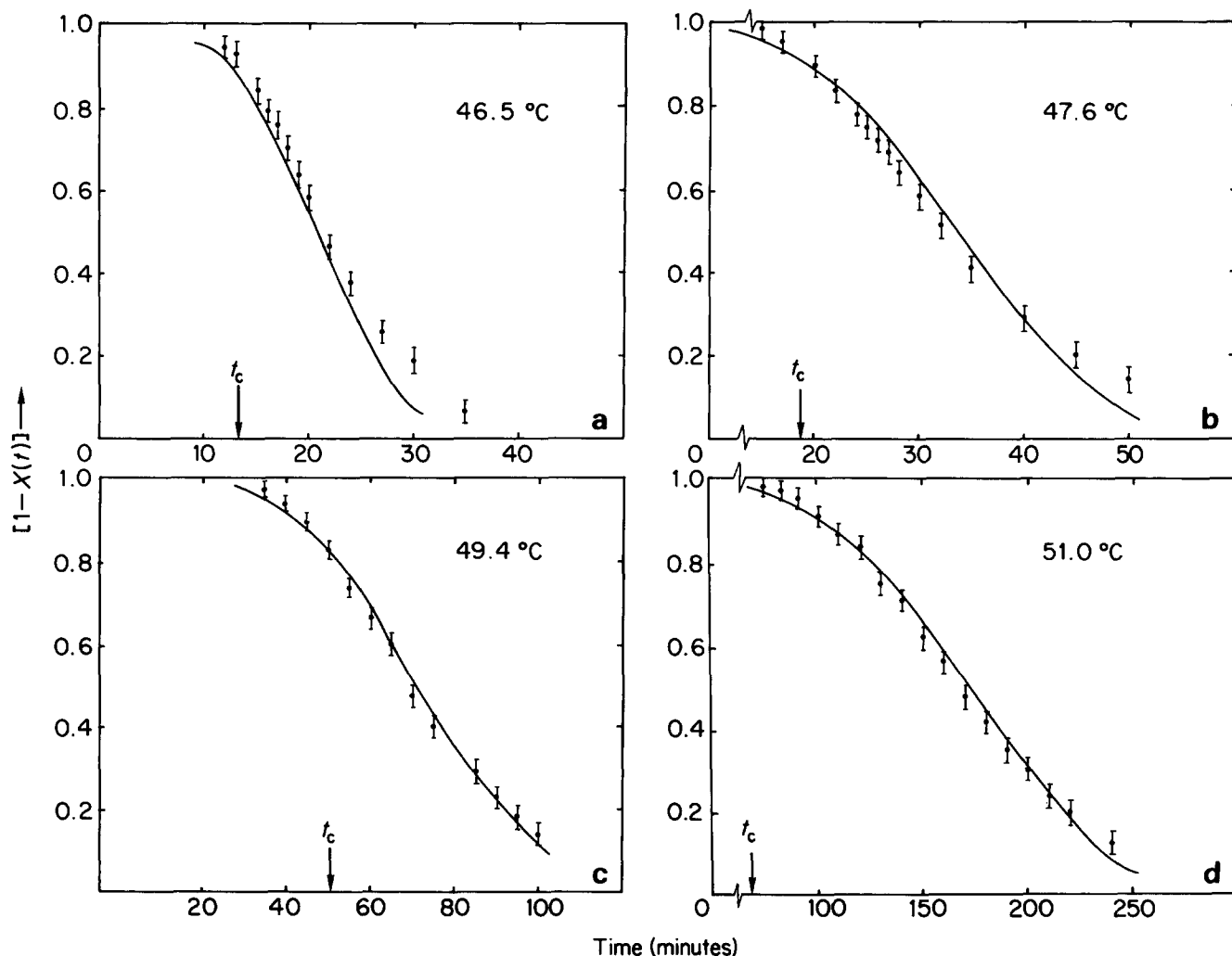


Figure 5 Isothermal crystallization data for PCL; observed dilatometric data; calculated results using equation (8) and data from Table 1: (a) 46.5°C, (b) 47.6°C, (c) 49.4°C, (d) 51.0°C

Table 1 PCL crystallization data obtained from Figures 2 and 3, and from ref. 22. These data were used to obtain curves shown in Figures 4 and 5

| Temperature of crystallization (°C) | Density of liquid (g cm ⁻³) | Density of solid (g cm ⁻³) | Growth rate G ($\mu\text{m min}^{-1}$) | Nucleation rate \dot{N}_1 ($\mu\text{m min}^{-1}$) | Nucleation rate \dot{N}_1 ($\mu\text{m min}^{-1}$) | Time t_c (min) |
|-------------------------------------|---|--|--|--|--|------------------|
| 51.0 | 1.072 | 1.138 | 0.23 ± 0.01 | 0.17 ± 0.02 | 0.05 ± 0.003 | 65 |
| 49.4 | 1.073 | 1.138 | 0.49 ± 0.02 | 0.40 ± 0.03 | 0.10 ± 0.01 | 50 |
| 47.6 | 1.075 | 1.138 | 0.89 ± 0.04 | 1.4 ± 0.2 | 0.37 ± 0.02 | 19 |
| 46.5 | 1.076 | 1.138 | 1.29 ± 0.03 | 4.0 ± 0.6 | 1.3 ± 0.2 | 14 |

of crystallization. Consequently, providing the correct nucleation rates are used, the crystallization of PCL can be described by the simply modified Avrami equation with integer values of the exponent.

Many workers have measured nucleation and growth rates in order to calculate overall rate constants for polymer crystallization using equations (4) or (6)¹⁰⁻¹⁴. The correlation between rate constants calculated by these equations and rate constants obtained by analysis of dilatometric data using equation (1) for similar samples shows considerable variation.

The reasons for these variations most likely lie in the assumptions on which the kinetic analysis are based¹⁸:

- (1) Nucleation is either instantaneous or sporadic (i.e. the number of nuclei is proportional to t^0 or t^1).
- (2) Growth is in either one, two or three dimensions.
- (3) The linear dimensions of the growing bodies are proportional to t^1 .
- (4) The nuclei are randomly spaced.
- (5) The density of the growing solid is independent of the extent of growth.

Assumptions (2), (3) and (4) can be supported by relatively simple microscopic observations, and (5) has received much attention^{11,19,20}. However there are a number of points that should be made regarding assumption (1), the nucleation behaviour.

The frequently made assumption of a constant nucleation rate during crystallization needs questioning. During the crystallization of polymers, there are a number of factors operating to upset the integrity of the system. If crystallization is rapid and thermal conductivity low then local temperature fluctuations may occur which will influence the rate of nucleation. Equally, the many different molecular species present in a polydisperse sample will have different activation energies for nucleation and the order in which these species crystallize or the randomness of the order will determine the value of \dot{N} during crystallization.

Changes in nucleation rates can also be explained in terms similar to those of Keith and Padden²¹ describing spherulitic fibrous branching.

A further point to be noted is in relation to the calculation of rate constants. Using the half life of crystallization, $t_{0.5}$, as a measure of the rate constant, produces a non linear Arrhenius plot for both the data reported here and some earlier data of Perret and Skoulios²². These latter workers presented dilatometric data for the crystallization of lower molecular weight samples of PCL at temperatures between 40°C and 58°C. It is clear that $t_{0.5}$ does not reflect the crystallization rate constants in these cases. This is to be expected since the changes in \dot{N} that we have observed all occur well before 50% of crystallization and therefore the crystallization rate is not constant over this time interval.

Using the time for 10% reaction, $t_{0.1}$, gives a linear Arrhenius plot for both sets of data. This indicates a

constant reaction rate in this time interval which is consistent with our observations. A similar analysis of kinetic data reported for the crystallization of poly(pivalolactone) (PPL) however, indicates no change in crystallization mechanism within the time interval $t_{0.1}$ to $t_{0.5}$.²³

Changes in nucleation rates during crystallization will cause changes in the overall rate constant k in equation (1) and will be accompanied by a corresponding change in the exponent m . Therefore, we conclude that the analysis of dilatometric data alone, for crystallizations in which the nucleation rate changes, cannot produce any reliable information about the crystallization mechanism. The dilatometric studies must be accompanied by measurements of nucleation rate and crystalline morphology. The popular practice of summarizing crystallization data with Avrami parameters can be misleading and may not contribute to an understanding of the crystallization mechanism. In the latter case much more useful information would be available if raw crystallization data were reported.

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