

Some Aspects of Nonisothermal Crystallization of Polymers. II. Consideration of the Isokinetic Condition

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Synopsis

In the previous paper a practical method has been applied for an analysis of non-isothermal crystallization in terms of data of isothermal crystallization. The fundamental equation was written on the assumption of the isokinetic conditions in the following form:

$$X(t) = 1 - \exp \left[- \left(\int_0^t K(T) d\tau \right)^n \right]$$

where $X(t)$ is the degree of phase transformation at time t , and n is the Avrami index determined in the isothermal experiments; $K(T)$ is connected with the crystallization rate constant of the isothermal crystallization, $k(T)$, through the relation $K(T) = k(T)^{1/n}$. The equation is derived on the basis of the well-known theory of phase transformation. Experiments of nonisothermal crystallization of high-density polyethylene were carried out under various cooling conditions. The change in crystallinity during the process was followed by using the above equation in the course of the primary crystallization. A procedure of the analysis of the whole, including both the primary and secondary processes, is suggested as an eminently practical one on a more general assumption.

INTRODUCTION

Nucleation rate, growth rate, and growth morphology are essential to a full understanding of crystallization. However, the degree of phase transformation of polymers from the amorphous to the crystalline phase is, in general, the only available parameter for the analysis of polymer crystallization. Direct observation of the process of spherulitic growth improves the situation since the rate of nucleation and/or the rate of growth can be directly observed. The observation, however, is limited to very slow crystallization.

In the previous paper,¹ a practical method was proposed for an analysis of nonisothermal crystallization. Using the method, the relationship between crystallization temperature, crystallinity, and cooling rate was discussed in terms of the data of the isothermal crystallization. In the cal-

ulation of crystallinity, it was assumed that the characteristic kinetics of phase change remain the same during crystallization (isokinetic). The object of the present work was, therefore, to verify this assumption by experiment. At first, the phase transformation theory for the isothermal crystallization developed by Avrami² and Evans³ was extended to derive a fundamental expression of the nonisothermal process on the isokinetic condition. Then, experiments were carried out to follow the change in the degree of phase transformation as a function of time or temperature. The experimental results were compared with theoretical predictions.

THEORETICAL

Isotherms of polymer crystallization show an S-shape which is characteristic of the transformation-time curve. The degree of phase transformation, $X(t)$, is related to time t by the general Avrami equation

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

where k is the crystallization rate constant containing nucleation and growth rates, and n is a constant called the Avrami index. Both constants are characteristics of crystallization. On the application of the Avrami equation to the analysis of polymer crystallization isotherms, there are many limitations. The Avrami index is often found fractional and nonconstant. The isotherms do not always terminate in the way predicted by the Avrami equation. This fact shows that polymer crystallization cannot be interpreted in a simple manner. An isotherm is generally divided at least into two portions owing to primary and secondary crystallization. Primary crystallization, which is the main part of the whole process, is described by a general Avrami equation. Secondary crystallization becomes dominant in the terminal stage, and can be considered to occur simultaneously with or consecutive to primary crystallization for several reasons, such as lamellar thickening, crystallization of segregated molecules, some kinds of reorganization in already transformed portions, and so on. The analysis of the crystallization isotherms is, in practice, much complicated by the fact that primary crystallization is not readily separable from secondary crystallization in a theoretically meaningful way. Therefore, primary crystallization in this paper is simply regarded as the crystallization which apparently follows the Avrami equation. According to a rule described later, the contribution of the secondary crystallization is separated from the isotherms in a practical sense.

The transformation theory of phase change is here further extended so as to describe nonisothermal crystallization in practical processes. A basic assumption in the analysis is that the growth of a crystal ceases when that crystal impinges on another. The Avrami theory results in the following equation:

$$X(t) = 1 - \exp[-E(t)] \quad (2)$$

where

$$E(t) = \frac{\rho_c}{\rho_l} \left[\int_0^t \dot{N}'(\tau) v(t, \tau) d\tau \right], \quad (3)$$

ρ_c and ρ_l are the densities of the crystalline and liquid phases, respectively; $\dot{N}'(\tau)$ is the rate of nucleation at time τ ; and $v(t, \tau)$ is the volume at time t of a growing grain formed at time τ . Therefore, $E(t)$ is the total volume of growing grains if the overlapping of them is neglected. An exact analysis of crystallization is reduced to a calculation of $E(t)$ in eq. (3), whether the process is isothermal or nonisothermal. If the temperature dependence of nucleation rate and that of the growth rate are separately obtained, $E(t)$ can be easily determined by the integration of eq. (3). In consequence, main efforts should be focused on the evaluation of eq. (3).

First Approach

Avrami described the nucleation rate in a very skillful manner for the analysis of eq. (3) as follows²:

$$\dot{N}'(t) = \nu(t)N(t) \quad (4)$$

where $\nu(t)$ is the probability of the formation of a growth nucleus per germ nucleus per unit time, and $N(t)$ is the number of germ nuclei per unit volume at time t which decreases from the number of germ nuclei \bar{N} per unit volume of the liquid phase before crystallization.

For convenience of the analysis, a characteristic time was introduced after Avrami through the following transformation²:

$$\xi(t) = \int_0^t \nu(\tau) d\tau.$$

By using the characteristic time ξ , eq. (3) yields for three-dimensional growth with growth rate $G(t)$ at time t the following:

$$E(\xi) = \frac{\rho_c}{\rho_l} \left[\bar{N} \int_0^\xi \exp(-\xi') \sigma \left(\int_{\xi'}^\xi \frac{G}{\nu} du \right)^3 d\xi' \right] \quad (5)$$

where σ is a shape factor equal to $4\pi/3$ for a sphere, and G/ν is a function of temperature. It is worth noticing that the transformed volume v in the characteristic time scale depends upon ν and G only through the ratio G/ν .

Since G/ν is constant in the isothermal crystallization, eq. (5) can be readily integrated.^{2,4} One obtains

$$E(\xi) = 6 \frac{\rho_c}{\rho_l} \sigma \bar{N} \left(\frac{G}{\nu} \right)^3 \left(\exp(-\xi) - 1 + \xi - \frac{\xi^2}{2!} + \frac{\xi^3}{3!} \right). \quad (6)$$

The observable range of the degree of transformation is limited to between 0.01 and 0.99 in actual experiments; $E(\xi)$ is, therefore, expected to vary between 0.01 and 5. In the most significant range, the function $E(\xi)$ can be described in the approximate form

$$E(\xi) = k_1 \xi^n \quad (7)$$

where k_1 is a constant and n corresponds to an Avrami index the value of which is between 3 and 4. Both constants are determined through a time-independent factor, $(\rho_c/\rho_l)\sigma\bar{N}(G/\nu)^3$, in eq. (6). Equation (7) directly leads to the general Avrami equation shown in eq. (1). The crystallization rate constant k is related to k_1 in eq. (7) by

$$k = k_1\nu^n.$$

If the temperature varies during the phase change (nonisothermal), the description in eq. (5) is still the same, but the unit of measure of ξ in terms of the real time t is variable during the process. Equation (5) thus formally describes nonisothermal crystallization. For the performance of the calculation, however, some assumptions are required, since G/ν and \bar{N} are rarely obtained in practice. The first assumption is that \bar{N} is a constant and G/ν is independent of temperature, though ν and G change with external conditions (isokinetic). It is concluded from this assumption that the crystallization isotherms for various crystallization temperatures are entirely superposable upon each other when shifted along the time scale. The second assumption is that the final absolute crystallinity is also independent of the cooling process.

On the above assumptions, the characteristic kinetics of phase change in a nonisothermal process is expressed by eqs. (2) and (6) in terms of the characteristic time. Therefore, the transformed weight fraction is written resembling the Avrami equation of isothermal crystallization:

$$X(t) = 1 - \exp\left[-\left(\int_0^t K(T)d\tau\right)^n\right] \quad (8)$$

where n is the Avrami index determined from the data of the isothermal crystallization; $K(T)$ is related to $k(T)$ in eq. (1) through the following relation:

$$K(T) = k(T)^{1/n}.$$

By calculating eq. (8), the crystallinity-time relation in the nonisothermal crystallization can be predicted from the data of the isothermal crystallization. Strictly speaking, the assumption of the isokinetic condition is not likely to hold because the nucleation and growth processes involve quite different factors.⁵ However, the Avrami index in eq. (1) is fortunately not so sensitive to the change in G/ν with temperature.

Second Approach

The particular manner of nucleation expressed by eq. (4) was assumed in the first approach. The nucleation is characterized by the probability ν and the number of germ nuclei \bar{N} in this expression. The concept of germ nuclei which exist in the liquid phase is ambiguous in the physical meaning, and the number of them, \bar{N} , is not observable. The approach seems rather to incline toward a better mathematical expression than the consideration on a physical basis.

On the other hand, there is another approach for deriving the general Avrami equation. If there are predetermined nucleation and sporadic nucleation, the general expression of $E(t)$ corresponding to eq. (3) can be written for three-dimensional growth in the following form:

$$E(t) = \frac{\rho_c}{\rho_l} \left[N_s v(t, 0) + \int_0^t \mu(\tau) v(t, \tau) d\tau \right] \\ = \frac{\rho_c}{\rho_l} \left[N_s \sigma \left(\int_0^t G(x) dx \right)^3 + \int_0^t \mu(\tau) \sigma \left(\int_0^t G(x) dx \right)^3 d\tau \right] \quad (9)$$

where N_s is the number of predetermined nuclei and $\mu(t)$ is the rate of sporadic nucleation at time t . The first term of eq. (9) shows the crystal volume developing from predetermined nuclei, and the second shows that from sporadic nuclei. A characteristic time is also introduced through the following transformation⁶:

$$\eta(t) = \int_0^t G(\tau) d\tau.$$

The expression corresponding to eq. (5) is

$$E(\eta) = \frac{\rho_c}{\rho_l} \sigma \left[N_s \eta^3 + \int_0^\eta \frac{\mu(\eta')}{G(\eta')} (\eta - \eta')^3 d\eta' \right]. \quad (10)$$

Since G/μ is entirely independent of time in the isothermal crystallization, eq. (10) can be written in the following form by using the characteristic time η :

$$E(\eta) = \frac{\rho_c}{\rho_l} \sigma \left(N_s \eta^3 + \frac{\mu}{4G} \eta^4 \right). \quad (11)$$

In the case that both N_s and μ are not zero, eq. (11) can be closely approximated by the expression $k_2 \eta^n$, where k_2 is a constant and n corresponds to an Avrami index the value of which is between 3 and 4. If G/μ is independent of temperature, eq. (11) remains the same in terms of the characteristic time η in nonisothermal crystallization. Equation (8), therefore, is also proposed within the isokinetic range of temperature.

In consequence, both approaches lead to eq. (8) of the same fundamental equation which was used in the previous paper for the analysis of nonisothermal crystallization. This equation enables us to apply the results of isothermal crystallization analysis to the description of nonisothermal crystallization. In the above discussion, only three-dimensional growth was considered. The same approaches are possible for one- or two-dimensional growth.

EXPERIMENTAL

In crystallization experiments, the temperature of a sample should make an effective response to a change in temperature of the environment.

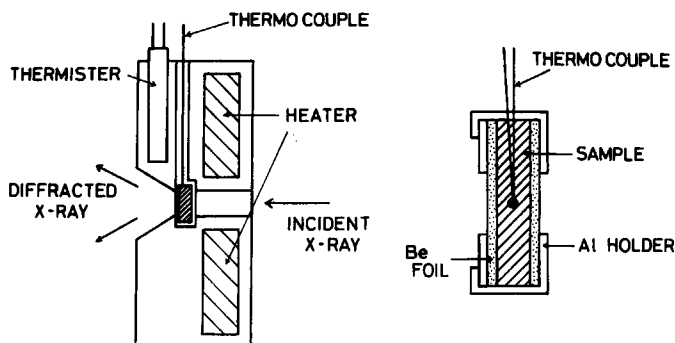


Fig. 1. Schematic diagram of the sample holder.

X-ray technique⁷ well satisfies the necessary conditions of the experiments if the shapes of the sample and the sample holder are suitable.

Samples used in this study were high-density polyethylene (Sholex 6050, $M_v = 6.24 \times 10^4$) in the form of a thin film thickness 50μ . The film was disc shaped with a diameter of 6 mm. The temperature of the sample was directly measured by using a copper-Constantan thermocouple embedded in the sample. The thermocouple was carefully placed in the sample so that the measurements of both the temperature and the crystallinity were performed on the same portion of the sample. Care was employed in avoiding the effect of inhomogeneity of temperature within the sample due to the small thermal conductivity of polymers. The sample holder and the heating stage are illustrated in Figure 1. An aluminum pan 6 mm in diameter and 0.1 mm in foil thickness was used as the sample holder, and its windows (diameter of 3 mm) were covered with beryllium foils 0.2 mm thick. The temperature of the heating stage made of brass was regulated to $\pm 0.05^\circ\text{C}$ by the use of a Thermistor in the stage block.

Changes in crystallinity of the samples were followed by measuring the integrated intensity of the 2θ range, $20^\circ 15'$ to $22^\circ 15'$, in which the (110) reflection is located.⁸ The intensity was counted with the aid of a scintillation counter. The degree of crystallinity $X(t)$ at time t was calculated using the following equation:

$$X(t) = \frac{I_t - I_a}{I_\infty - I_a}$$

where I_t is the intensity at time t ; the suffix a indicates the completely amorphous state, and the suffix ∞ corresponds to the state with the saturated crystallinity. Therefore, I_a is the intensity measured before the crystallization begins. The value $X(t)$ thus obtained means the degree of transformation to the crystalline phase, which should be distinguished from the absolute crystallinity $X_{\text{abs}}(t)$ at time t . This quantity is readily obtained through the following relation:

$$X_{\text{abs}}(t) = X(t) \cdot X_{\text{abs},\infty}$$

where $X_{\text{abs},\infty}$ is the saturated value of absolute crystallinity. This value was determined after the method of Matthews, Peiser, and Richards.⁹

The sample with a thermocouple was tightly set in the sample holder and melted at 200°C previously in a preheating stage and kept there for 15 min. Then, it was instantly removed into the heating stage, the temperature of which was controlled at crystallization temperature. The time measurement started from the point at which the temperature of the sample was reduced to the crystallization temperature. The dead time, the time interval during which the temperature of the sample was higher than the preset temperature, was always less than 60 sec.

In order to gain the fundamental data, the samples used were isothermally crystallized in the temperature range of 121.8° to 125°C. The temperature of the sample often increases during the rapid crystallization because of the large heat of fusion of polyethylene. This phenomenon disturbs the isothermal condition and determines the lowest limit of the setting temperature in the isothermal crystallization. Nonisothermal conditions in this study were controlled by adjusting the heating current of the heating stage. The separation of the primary and secondary crystallization makes the analysis of the experimental data complicated. Although some procedures for the separation were proposed,¹⁰ the isotherms here obtained were separated into two parts in the following manner: (1) A level of crystallinity reached by the primary crystallization is first assumed. The parameters k and n are determined so that the Avrami equation fits the experimental data within the range assumed above. The Avrami equation thus obtained is checked according to the criterion that the calculated crystallinity should not exceed the corresponding experimental data within the range. (2) If the equation fulfills the criterion, the level is changed to a higher value. The procedure is repeated until the highest level of the primary process is obtained under the criterion. The Avrami equation finally obtained is considered to describe the primary crystallization. This procedure is not fully rigorous on a physical basis, but would not have any marked effect on the analysis in this study.

RESULTS AND DISCUSSION

Table I shows the final absolute crystallinities of the samples crystallized at various temperatures. These values approach almost the same in very long crystallization periods at various temperatures. The observation verifies the assumption that the final absolute crystallinity is kept constant within the range of temperature. Change in crystallinity at various crystallization temperatures is shown in Figure 2. Figure 3 shows the plots of crystallinity versus relative time t/t^* . The standard time t^* is the time when the crystallization proceeds to 50%. The superposition of these plots consequently was confined to the range up to 70% of crystallinity. The terminal portions of the curves seem to have larger scatters than those obtained in dilatometric measurements. It is presumed that x-ray

TABLE I
Temperature Dependence of Final Absolute Crystallinity

| Crystallization temp., °C | Final absolute crystallinity, % |
|---------------------------|---------------------------------|
| 121.8 | 60.0 |
| 122.2 | 61.3 |
| 123.0 | 61.4 |
| 124.3 | 59.5 |
| 125.0 | 59.4 |
| 125.9 | 60.8 |

measurements are sensitive to the structural changes during secondary crystallization. The portions of the isotherms up to 70% crystallinity are due to only primary crystallization and are superposable by the transformation of the time scale. This fact, therefore, points out that the primary crystallization of these isotherms could be described by the Avrami equation with a single Avrami index. The results of the analysis led to a common value of the Avrami index $n = 3.35$. The fit between the experimental data and calculated results of the Avrami equation with $n =$

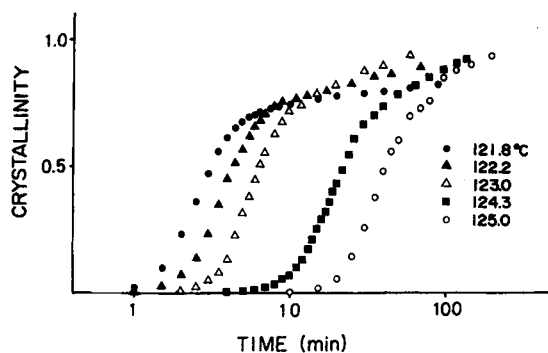


Fig. 2. Crystallinity-time curves in isothermal crystallization at various temperatures.

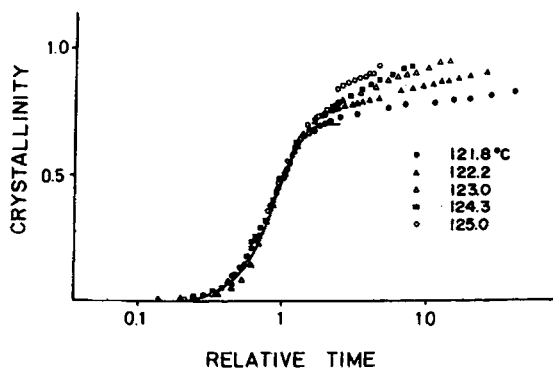


Fig. 3. Plots of crystallinity vs. relative time t/t^* , t^* is time when the crystallization proceeds to 50%.

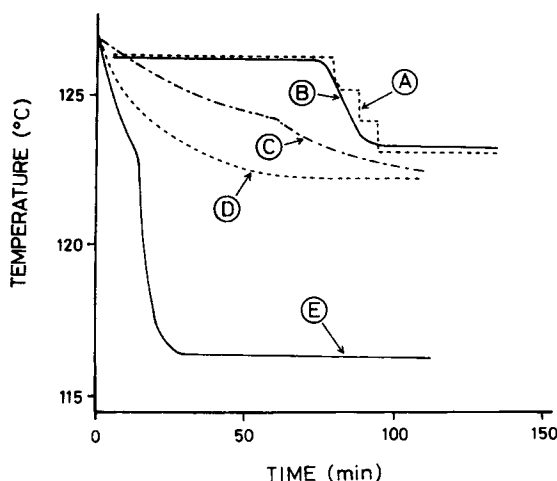


Fig. 4. Temperature of sample vs. time relations during nonisothermal crystallization.

3.35 was quite good. The crystallization rate constant $k(T)$ at a temperature is connected with the crystallization half-time $t_{1/2}$ of the primary process by the relation

$$k(T) = \frac{\ln 2}{t_{1/2}^n}$$

The $k(T)$ value plays an important role in the analysis of the nonisothermal crystallization in terms of the fundamental equation, eq. (8). Experiments of the nonisothermal crystallization were carried out under various cooling processes. The changes in temperature of the samples are shown in Figure 4. The solid lines in Figure 5 show crystallinity versus time curves according to eq. (8) for various cooling processes. The experimental data plots are in good agreement with the theoretical predictions in the course of primary crystallization, except for (A) and (B).

Accordingly, based on the assumption of the isokinetic condition, eq. (8) is available for the purpose of predicting the primary crystallization during the nonisothermal process from the data of the isothermal crystallization of polymers. The discrepancy between theory and experiment was appreciable at the early stage of processes (A) and (B). It is probably attributed to the lack of the data for the isothermal crystallization at very high temperatures. In this calculation, extrapolated values of $k(T)$ were used outside of the temperature range 121.8° to 125°C.

In practice, the secondary crystallization cannot be neglected in the analysis. Another procedure is suggested on a more general assumption. The assumption is that the rate of crystallization at time t depends only on the temperature and the crystallinity at the time, without relation to the history of the crystallization. This is equivalent to the fact that all the isotherms at various temperatures are superposable over the whole

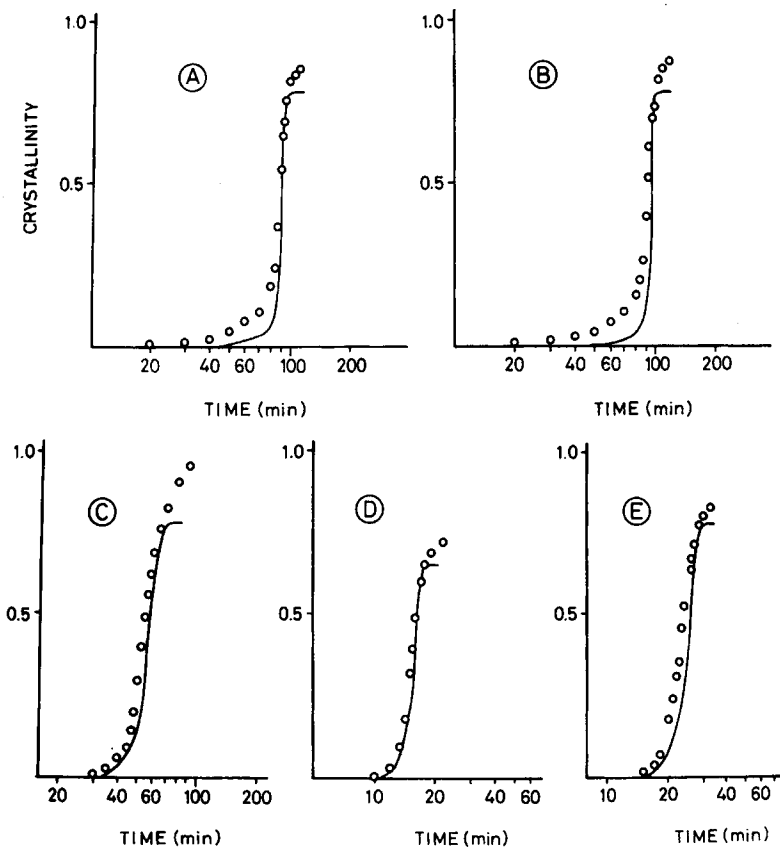


Fig. 5. Crystallinity-time relations under the cooling conditions shown in Figure 4: solid line, results calculated by using eq. (8); open circles, experimental data.

process of crystallization. The procedure can be described in the following mathematical form:

$$X(t) = \int_0^t \dot{X}_{\text{iso}}[T(\tau), X(\tau)] d\tau \quad (12)$$

where $\dot{X}_{\text{iso}}(T, X)$ is the rate of crystallization obtained from the analysis of the isotherms at temperature T and crystallinity X . Supposing any space where the coordinates are factors defining a microstructure, a crystallization process is shown in the space by a trajectory from one point corresponding to the melts to the other point corresponding to the final structure formed in the process. The assumption made in the above procedure signifies that the crystallization proceeds along the same trajectory, independent of cooling conditions. Over a wide range of temperature, the proposition clearly contradicts the experimental evidence. A polymer crystallizes at a high temperature near the melting point to form a small number of big spherulites, while a number of small spherulites are obtained under rapid cooling. Therefore, the procedure based on eq. (12) is nothing

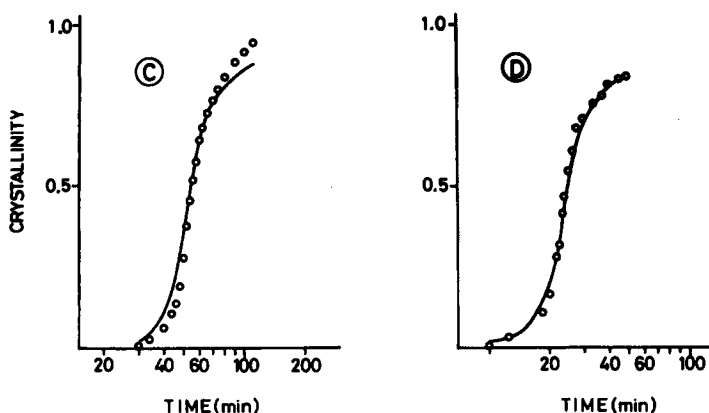


Fig. 6. Crystallinity–time relations under cooling conditions shown in Figure 4: solid line, results calculated by using eq. (12); open circles, experimental data.

but an eminently practical one, and possesses a distinct advantage in that the calculation can be carried out without considering any variation in growth kinetics. Equation (8) is derived from eq. (12) if the analysis is limited to the primary crystallization.

Figure 6 shows a comparison between experimental and calculated results. The solid line represents the crystallinity–time relation calculated using eq. (12) for the cooling processes (C) and (D) in Figure 4. The experimental data points are shown by open circles. The agreement between both results is good, even beyond the range of the primary crystallization. If the isothermal secondary crystallization is described by a single analytical expression with temperature-dependent parameters, the procedure will be more practical for the analysis of the whole crystallization process, including both the primary and secondary processes.

In a paper in preparation, crystallization during melt spinning will be discussed as an example of numerical calculation of nonisothermal crystallization.

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