A Note on Crystallization of Polymers

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Mathematic formulation of the crystallization kinetics of polymers is briefly reviewed and a modified equation is proposed applicable to polymers having very low crystallinity or to the crystallization under the condition that only a limited amount of mass fraction in the total mass can be transformed into the crystalline phase.

INTRODUCTION

Up to the present time many important and useful informations of the inherent nature of crystalline polymers have been obtained under the fundamental concept that mutual transformation between the melt and crystalline states of them should be a first order phase change which can thermodynamically be well defined. For example it is widely known that generally the isothermal crystallization of homo-polymers from the melt can be described sufficiently by the nucleation theory which has been developed for polymers under that concept in a very similar way as for monomeric substances, despite the resulting crystalline structure of polymers is extremely complicate in comparison with that of monomeric substances. The mathematic formulation of the crystallization kinetics of polymers has been obtained by taking account of the fact that the transformation of polymers from the melt to the crystalline state can not be completed; that is, the degree of the crystallinity never goes to unity, but only reaches an equilibrium level depending on the crystallization condition and inherent properties of a polymer in question, while that of monomeric substances substantially goes to unity. Thus the kinetic equation of the isothermal crystallization for polymers is given in a formula, solely substituting the relative development of the crystalline phase for the actual development of it in the kinetic equation developed for monomeric substances.

The validity of the equation thus developed for polymers has hitherto been assured by many collections of experimental results of the isothermal crystal-lization for homopolymers having high crystallinity, so far as the crystallization is conducted under such moderate conditions as the degree of crystallinity can reach an relatively high level at the equilibrium final stage. However, the validity of this equation should become to be questionable for homopolymers having low crystallinity or even for those having high crystallinity if the crystallization was conducted under such mild condition in a temperature range near to the melting

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temperature as an only limited amount of mass fraction of the total mass could crystallize. In this short note, the author would briefly review the mathematic formulation of kinetics of isothermal crystallization for polymers and present a modified equation applicable to such cases where an only limited amount of mass fraction could be transformed to the crystalline phase.

BRIEF REVIEW OF THE MATHEMATIC FORMULATION OF THE CRYSTALLIZATION KINETICS FOR MONOMERIC AND POLYMERIC SUBSTANCES

The basic relation to develop the mathematic formulation of the isothermal crystallization by the nucleation mechanism for monomeric substances was given by Avrami[1] as,

$$dX/dX' = 1 - X \qquad (1)$$

where X is the actual mass fraction transformed of the total mass at time t and it is assumed that the nucleation of crystallites is allowed to occur only in the mass untransformed and the growing of nuclei born is ceased by the mutual impingement of themselves. X' is the fictitious mass fraction transformed at time t when all restrictions to the nucleation and growing of crystallites are removed, and was given by Von Goler and Sachs[2] into the next general formula.

$$X' = \frac{\rho_c}{\rho_l} \int_o^t v(t,\tau)\dot{N}(\tau)d\tau \qquad (2)$$

where ρ_c and ρ_l are the densities of the crystalline and liquid phases, respectively. $\dot{N}$ is the nucleation frequency per unit of untransformed volume and $v(t,\tau)$ is the volume of a growing center at t, which was initiated at time τ $(\tau \leq t)$. If $v(t,\tau)$ tnd $\dot{N}(\tau)$ are appropriately specified as functions of time, eq. (2) can be calculated and reduced or approximated to the following general form,

$$X' = k\,t^n \qquad (3)$$

where n is a constant dependent on the specification of the nucleation, k rate constant independent of it. Thus, eqs. (1) and (2) imediately follow the general formula of the crystallization kinetics,

$$ln\frac{1}{1-X} = kt^n \qquad (4)$$

On the other hand the basic relation to develop the mathematic formulation of the isothermal crystallization for polymers was given by Mandelkern and Flory et al.[3,4,5] in an analogous form to eq. (1),

$$dX/dX' = 1 - U(t) \qquad (5)$$

where $U(t)$ is the *"effective fraction"* of the mass transformed at time t; it is that fraction of the total mass in which further crystal growth can not occur. This quantity includes the actual mass transformed as well as the amorphous chain segments which are in a noncrystallizable situation at time t. Mandelkern et al.

treated the case that this effective fraction was proportional to the actual mass transformed, the proportionality factor being $1/X(\infty)$. ($X(\infty)$ was the actual mass fraction transformed at infinite time); *i.e.* $U(t)$ was taken as,

$$U(t) = X/X(\infty) \qquad (6)$$

Then, eqs. (5) and (3) follow the general formula for polymers,

$$ln\frac{1}{1-X/X(\infty)} = \frac{1}{X(\infty)} k\,t^n \qquad (7)$$

This equation reduces to eq. (4) if $X(\infty)$ goes to unity and has been assured as mentioned above by many collections of experimenal results of the isothermal crystallization for homopolymers having high crystallinity.

A MODIFICATION OF THE MATHEMATIC FORMULA OF THE CRYSTALLIZATION KINETICS FOR POLYMERS HAVING VERY LOW CRYSTALLINITY

However, for polymers having very low crystallinity or if $X(\infty)$ is far lower than unity, eq. (7) occationally fails to hit the experimental results. This incoincidence between the theory and experimental results should be caused by the rather arbitrary assumption for eq. (6). For such cases the effective mass fraction transformed $U(t)$ should be taken as a more complicate function of time or the actual mass fraction transformed. In order to develope an equation to describe more exactly the experimental results of the isothermal crystallization for polymers in such cases, the effective mass fraction $U(t)$ should be reinvestigated as a function of time. Since the amorphous chain segments to be brought into a noncrystallizable situation with the transformation are thought to be negligible in an incipient step of the transformation, the effective mass fraction transformed $U(t)$ should be taken as to be equal to the actual mass fraction transformed X itself in that step. On the contrary in a final equilibrium step of the transformation at infinite time since all chain segments remained in the amorphous phase are to be brought into a noncrystallizable situation, $U(t)$ is to be equal to $X/X(\infty)$ as dictated by eq. (6). Therefore, $U(t)$ should be taken as a function of time, varying from $X(t)$ to $X(t)/X(\infty)$ as the transformation proceeded.

The general equation of the crystallization kinetics for polymers, eq. (7) was obtained as mentioned above under the rather arbitrary assumption dictated by eq. (6). This assumption will be accepted approximately, if $X(\infty)$ is almost equal to unity or not so lower than it, because in such cases there is no enhanced difference in value between $X(t)$ and $X(t)/X(\infty)$. However, if $X(\infty)$ is very far from unity so that $X(t)/X(\infty)$ is much greater than $X(t)$, $U(t)$ could no longer be expressed by eq. (6). The form of $U(t)$ as a function of time would depend on the inherent nature of a polymer in question as well as the mechanism and condition for the crystallization, and could not monistically be defined, although its limiting values were expected as $X(t)$ and $X(t)/X(\infty)$ in the incipient and final equilibrium steps of the crystallization, respectively. Hence, for the time being the function $U(t)$ is to be appropriately assumed so as to hit the experimental results. For this purpose a variety of forms assumed for $U(t)$ should be

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examined, but only one arbitrary case dictated by eq. (6) has hitherto been inquired. In this note I would examine another assumption than eq. (6).

If it is assumed that dU/dX increases linearly with X $(dU/dX=a+bX$, where a and b are constants) from unity to a finite value so as to hit the condition that $\lim_{X\to 0} dU/dX=1$ and $\lim_{X\to X(\infty)} U(X)=1$, U can be expressed as a function of X as follow,

$$U(X)=X\left[1+\frac{1-X(\infty)}{X(\infty)^2}X\right] \tag{8}$$

Then the integration of eq. (5) with (8) and (7) imediately follow the next general formula of the crystallization kinetics for this case,

$$ln\frac{1}{1-X/X(\infty)}+ln\left[1+\frac{1-X(\infty)}{X(\infty)}X\right]=\frac{2-X(\infty)}{X(\infty)}kt^n \tag{9}$$

This equation reduces to eq. (7) and further to (4), according as the equilibrium mass fraction transformed at infinite time $X(\infty)$ approaches unity. But if $X(\infty)$ is far lower than unity, it significantly deviates from eq. (7). It is clear by examining this equation that if the relative development of the crystallinity $1-X/X(\infty)$ is plotted against the logarithm of time with different values in rate
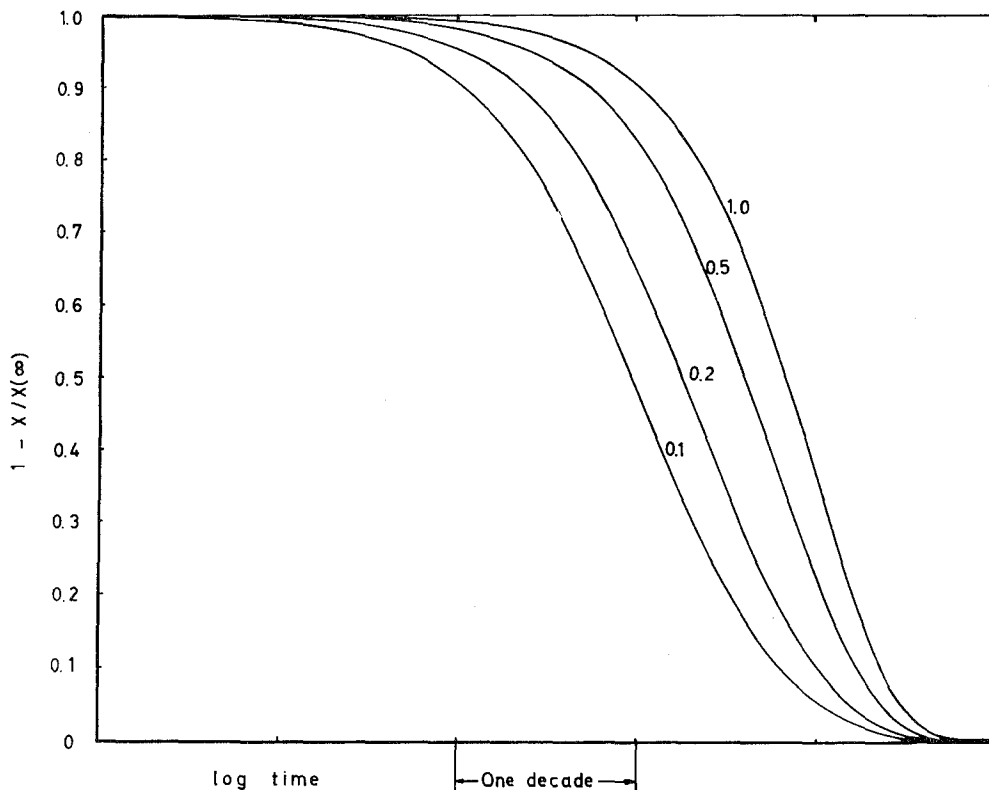

Fig. 1. The relative development of the crystallinity $1-X/X(\infty)$ against the logarithm of time according to eq. (9). Here $n=1$, and the value of $X(\infty)$ is indicated for each of curves.
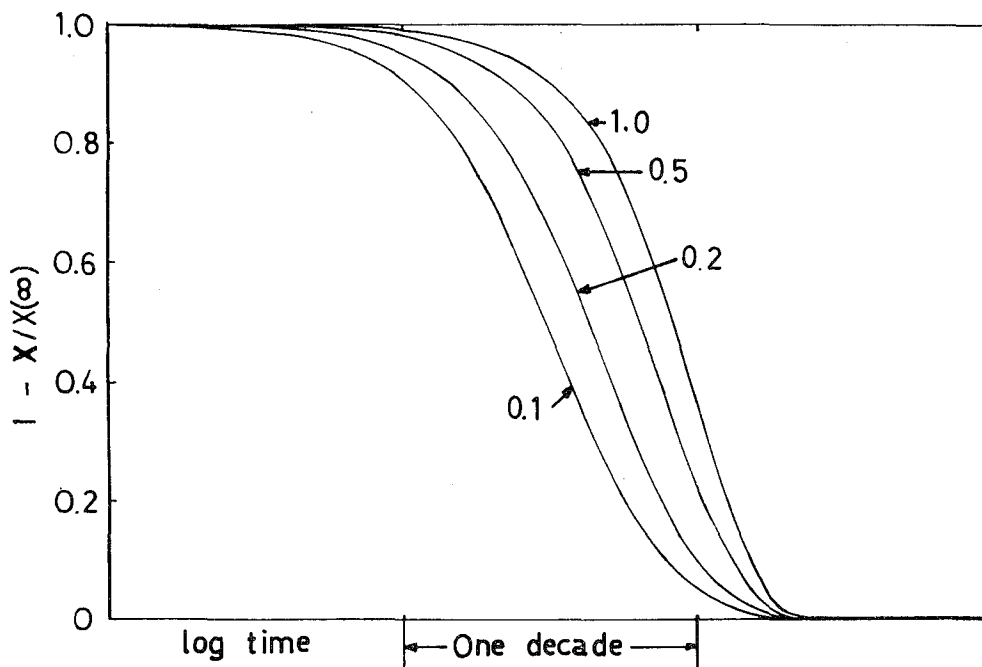
Fig. 2. The relative development of the crystallinity $1-X/X(\infty)$ against the logarithm of time according to eq. (9). Here $n=2$, and $X(\infty)$ is indicated for each of curves.

constant k, the curves obtained will be mutually superposable solely by shifting each of them an appropriate distance along the time axis as similarly as in the case of eq. (4), provided a same value of n is hold throughout the transformation. Hence the development of the crystallinity with different values of $X(\infty)$ can be compared according to eq. (9). Such attempts are made in Figures 1 and 2.

In Figures 1 and 2 the relative development of the crystallinity $1-X/X(\infty)$ is plotted against the logarithm of time for different values of $X(\infty)$ according to eq. (9), where n is taken as *1* aud *2*, respectively. In these figures, the curves for $X(\infty)=1.0$ are no other than the theoretical curves according to the usual equation of the crystallization kinetics for polymers eq. (7), but it is apparently recognized that they deviate the theoretical curves by eq. (7) and the retardation of the transformation becomes to be enhanced as $X(\infty)$ becomes lower than unity. In fact in an attempt to elucidate the crystalline structure of polymers, the crystallization kinetics conducted under the condition that only a small limited amount of the mass fraction can be transformed into the crystalline phase would be of great importance. In such cases the crystallization kinetics should be described and interpreted according to eq. (9) but not to eq. (7), because in expressing the effective mass fraction transformed as a function of time eq. (8) has been more plausibly defined than eq. (6).

AN APPLICATION OF THE MODIFIFD EQUATION TO AN EXPERIMENTAL RESULT

As mentioned in the foregoing section, if the crystallization of polymers is

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conducted under the condition that $X(\infty)$ is not so lower than unity, eq. (7) can describe its kinetics. However, a great deal of the crystallization of polymers of importance has hitherto been conducted in the temperature range relatively close to the equilibrium melting temperature since the crystallization in that temperature range should be of great importance on a standpoint that the mutual transformation of the crystalline and amorphous phases of polymers is a thermodynamically well defined phase change of first order. In such cases the value of $X(\infty)$ often becomes to be very lower than unity as small as *0.2* or *0.1* for example.[6]* Therefore, unless a proper correction is made for such cases, an
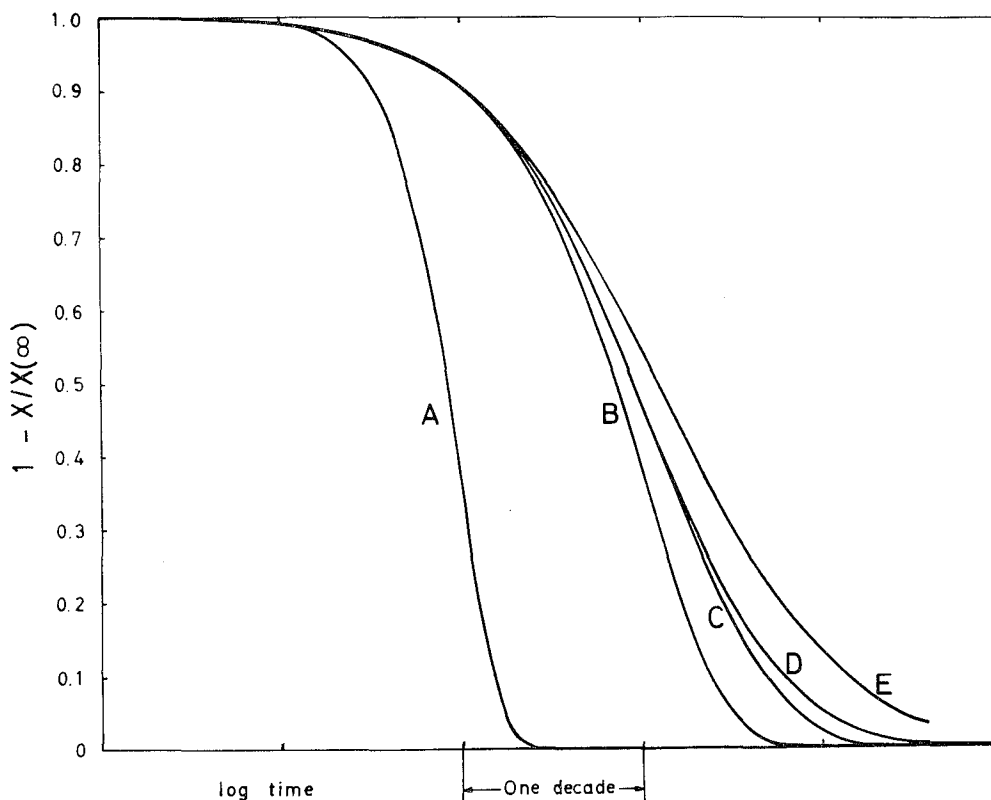

Fig. 3. Comparison between the theory and an experimental result in the crystallization kinetics for a polyethylene. Curves A and B are the theoretical curves according to eq. (7) for $n=2$ and 1, respectively. Curves C and D are the theoretical ones according to eq. (9) for $n=1$, and $X(\infty)=0.2$ & 0.1, respectively. Curve E is an experimental isotherm obtained from the isothermal crystallization in the temperature range of 119–$122°C$ for a very lightly cross-linked polyethylene (the viscosity average molecular weight prior to the crosslinking $=126,000$ and the cross-linking density $=5$ units per the equivalent units of the weight average molecular weight of the primary molecule).

* It was reported that even for linear polyethylene having high crystallizability, if a high molecular weight fraction of it was crystallized from the melt in the temperature range higher than $130°C$ the mass fraction crystallized at the final equilibrium stage was lower than 0.3.[7]

erroneous conclusion of the kinetic mechanism of the crystallization might be reached, although most interpretations of the crystallization for polymers have been limited to that in the relatively earliar step of the transformation so as to avoid the uncertainty caused by the arbitrary assumption for eq. (6).

The author lastly would like to cite an rather extreme example that $X(\infty)$ is very lower than unity so that the application of eq. (9) becomes to be necessary. The author et al.[6] studied the crystallization isotherm of a very lightly cross-linked polyethylene in the temperature range of $119-122°C$ and confirmed that the isotherms in that temperature range were mutually superposable solely shifting each of them an appropriate distance along the time axis and one composite isotherm could be obtained from all data in that temperature range. The composite isotherm thus obtained is re-depicted in Figure 3 with the theoretical ones according to eqs. (7) and (9). With the coincidence between the experimental isotherm E and the theoretical one B according eq. (7) for $n=1$ in the figure in the incipient step of the transformation, we formerly concluded[6] that the crystallization for this case should be conducted by a heterogeneous nucleation with 2-*dimensional diffusion-controlled growth*. However, as can be seen in the figure, since the coincidence between the theory and the experimental data is limited only to the very earliar step of the transformation, some distrust still resided in the conclusion. However, in this case the equilibrium mass fraction transformed $X(\infty)$ was ranged from 0.1 to 0.3 depending on the crystallization temperature. Hence eq. (9) instead of eq. (7) should be adopted to analize those results. In Figure 3 the theoretical isotherms according to eq. (9) for $n=1$ and $X(\infty)=0.2$ & 0.1 are also depicted by C and D. It is apparently ascertained that the coincidence of the experimental isotherm E with these theoretical ones C and D is now excellent up to the relatively latter step of the transformation. Therefore, by using the modified equation (9) with the corresponding value of $X(\infty)$ to the experimental data, the former conclusion would further be assured.

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