

Some Aspects of Nonisothermal Crystallization of Polymers. I. Relationship Between Crystallization Temperature, Crystallinity, and Cooling Conditions

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Synopsis

The changes in temperature and crystallinity of polymer during nonisothermal crystallization were theoretically analyzed assuming a cooling condition under which heat transfer occurs at a rate proportional to the difference in temperature between polymer and the environment. When a plateau appears in the temperature change during crystallization, crystallization temperature can be predicted by a simple method. This method gives nearly the same value as that obtained by successive calculations of temperature and crystallinity throughout the whole process. In addition, a graphic method is presented to predict crystallization temperature. By using the plateau temperature observed in melt-spinning experiments, the crystallization rate under molecular orientation is evaluated. Furthermore, a method applicable to estimating the ultimate crystallinity is proposed. A rough estimation of the increase in the rate of crystallization under molecular orientation was carried out for very high-speed spinning of poly(ethylene terephthalate).

INTRODUCTION

Numerous investigations, both theoretical and experimental, have been made of crystallization of polymeric materials. Main interest has been focused on the kinetics and morphology under isothermal conditions. These studies have led to a better understanding of the fundamental features of polymer crystallization, but do not provide adequate information for polymer processing. Crystallization during polymer processing occurs nonisothermally, except for some special cases. Examples of typical nonisothermal crystallization process include melt-spinning. Results from various experiments of melt-spinning indicated that the structure formed during the process is due to a nonisothermal crystallization under molecular orientation. The effects of molecular orientation on the crystallization from both melts and solution have stimulated current studies. On the other hand, only few works on nonisothermal crystallization can be found until recently. Hence, the nonisothermal crystallization should be studied

for the analysis of the practical processes in terms of polymer characteristics and cooling conditions.

Ziabicki¹ has dealt with the process in a theoretical treatment of melt-spinning and has proposed a new parameter, "kinetic crystallizability." By using the parameter, the crystallinity of as-spun filaments was successfully, but rather roughly, related to the polymer characteristics and cooling conditions. Ishibashi, Aoki, and Ishii² have investigated nonisothermal crystallization taking place in the course of the solidification process of quenched nylon 6 gut. A numerical calculation for estimating apparent crystallinity was performed with some assumptions and was compared with experimental data. The modified equation for homogeneous nucleation and spherulitic growth was applied in their calculation. The rates of nucleation and spherulitic growth were both obtained from the data of isothermal crystallization. Both treatments, however, take no account of the heat of crystallization. Gornick³ has carried out a computer analysis of DTA thermograms with consideration for the heat of crystallization. The temperature during crystallization is governed by the competition between heat generated by the crystallization and heat lost as a result of continuous cooling. The exact analysis of the process, therefore, requires not only the kinetics of crystallization, but also precise information of cooling over a whole range of the process. Complete mathematical description of the process would be too complex in procedure, even if all the data were available.

This paper proposes an approach to the analysis of nonisothermal crystallization under special cooling conditions. The conditions are that heat transfer occurs in proportion to the difference in temperature between polymer and the environment. In practice, polymer melts often encounter this sort of cooling. For example, heat transfer in crystallization during melt-spinning seems to satisfy this condition.

An attempt was made to estimate crystallization temperature and crystallinity of polymer. An analysis of relationships between cooling conditions and crystallization characteristics, such as rate of crystallization and crystallization temperature, forms the main part of the present study. The results obtained were compared with those calculated by using the Avrami equation which was modified to apply to the nonisothermal process under certain assumptions. The purpose of this work was to find a clue for understanding the features of nonisothermal crystallization, in particular, how crystallization during melt-spinning process occurs.

THEORETICAL

As cooling condition, it is first assumed that rate of heat transfer from polymer into the environment is proportional to the difference in temperature between them. If the changes in temperature and crystallinity of the polymer during a time interval ($t, t + dt$) are dT and dX , respectively, then the heat balance in unit mass of polymer can be written as follows:

$$\Delta H dX - R(T - T_s)dt = C_p dT.$$

where C_p is the specific heat at constant pressure, and T and T_s are the temperature of the polymer and of the environment, respectively. Crystallinity means degree of phase transformation, unless otherwise specified. This quantity should be distinguished from absolute crystallinity. Even if the phase transformation is completed, the absolute crystallinity will always be less than 100% for polymers. Consequently, ΔH is the heat of crystallization per unit mass of a partially crystalline polymer. The explicit expression for the rate of crystallization, dX/dt , and the cooling rate, dT/dt , is

$$\frac{dX}{dt} = \frac{R(T - T_s)}{\Delta H} + \frac{C_p}{\Delta H} \cdot \frac{dT}{dt} \quad (1)$$

where R is a constant (cal/g-deg-sec). The cooling of polymer is governed by R . Hence, this quantity is here designated as "cooling parameter." The cooling parameter is dependent upon the environment and the external shape of the samples.

Integrating eq. (1), one obtains in the region before crystallization begins,

$$T = T_s + (T_0 - T_s) \exp \left(-\frac{R}{C_p} t \right) \quad (2)$$

and in the region after crystallization has finished,

$$T = T_s + (T_0 - T_s) \exp \left\{ -\frac{R}{C_p} (t - \Delta t) \right\} \quad (3)$$

where T_0 is the initial temperature and Δt is an integral constant relating to a crystallization condition. The temperature-time curve under the cooling condition assumed is shown in Figure 1. The temperature of the polymer decreases along curve A before the onset of crystallization and along curve B after the end of it. Experimental results often show that a plateau in temperature change is observed during the crystallization pro-

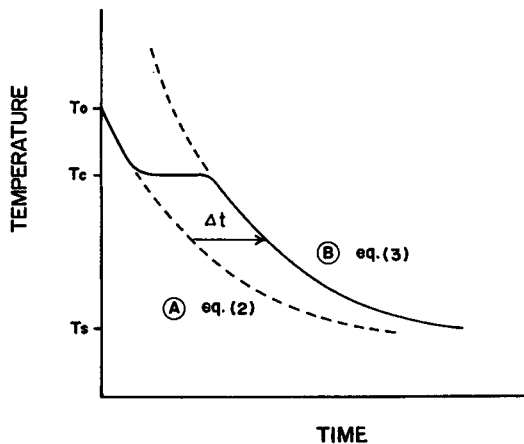


Fig. 1. Schematic plots of eq.(2) and eq. (3) as function of time.

cess, as shown in Figure 2. The plateau is due to the transient balance between heat released by crystallization and that lost by cooling. The crystallization, therefore, is considered to proceed isothermally at the temperature throughout the main part of the process, especially in the neighborhood of the point at which crystallinity is just half. It can be said that a polymer finds its own crystallization temperature or the rate of crystallization to fit the cooling parameter. In this case, the shift in abscissa between two curves approximates

$$\frac{\Delta H}{R(T_c - T_s)}$$

where T_c represents the crystallization temperature in the process. The concept of temperature-time curves is widely used in elementary physical chemistry to analyze the phase change for low molecular weight materials. For polymers, however, the shape of the temperature-time curve is much more influenced by cooling conditions, since polymers, even if molecular weight distribution is extremely narrow, are different from low molecular weight materials in crystallization kinetics. The plateau in temperature-time curves due to crystallization often appears fairly below the melting point and becomes more diffuse even at low cooling rates. In addition, molecular weight distribution will accelerate the peculiarities in polymer crystallization.

The plateau in the temperature-time curve may be expressed mathematically as

$$\left(\frac{dT}{dt}\right)_{X=1/2} \simeq 0.$$

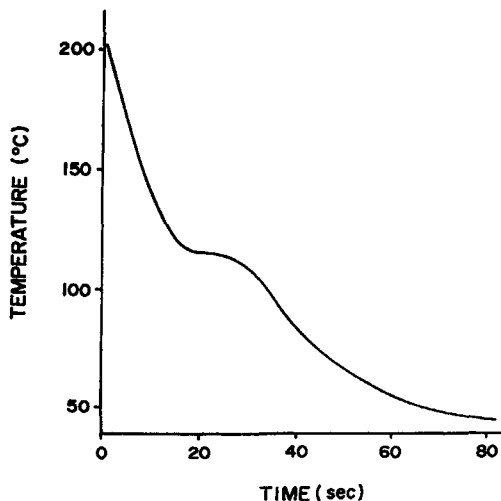


Fig. 2. Change in temperature during cooling process measured by a thermocouple embedded in the sample. High-density polyethylene (Sholex 6050), a thin film of $100\ \mu$ thickness, was melted at 210°C , then cooled.

Introducing the relation into eq. (1) gives

$$\left(\frac{dX}{dt}\right)_{X=1/2} = \frac{R(T - T_s)}{\Delta H} \quad (4)$$

where $\left(\frac{dX}{dt}\right)_{X=1/2}$ ($= \dot{X}_{1/2}$) is the rate of crystallization at the point where crystallinity is one half. Equation (4) gives the relation between $\dot{X}_{1/2}$, the cooling parameter R , and the crystallization temperature. By introducing temperature dependence of $\dot{X}_{1/2}$ obtained from experimental data of isothermal crystallization into eq. (4), the crystallization temperature can be estimated for given values of R and ΔH . The derivation of the above relation is entirely independent of any kinetics for nonisothermal crystallization. Under given cooling conditions, therefore, eq. (4) is widely applicable to the estimation of crystallization temperature.

In principle, the transformation theory of phase change^{4,5} gives the following equation:

$$X(t) = 1 - \exp \{-E(t)\} \quad (5)$$

where

$$E(t) = \frac{\rho_c}{\rho_l} \int_0^t \dot{N}'(\tau) v(t, \tau) d\tau$$

and ρ_c and ρ_l are the densities of the crystalline and liquid phase, respectively. $\dot{N}'(\tau)$ is the rate of nucleation at time τ and is written in the following form:

$$\dot{N}'(\tau) = \nu(\tau)N(\tau)$$

where $\nu(\tau)$ is the probability of formation of growth nucleus per germ nucleus per unit time; $N(\tau)$ is the number of germ nuclei per unit volume at time τ ; $v(t, \tau)$ is the volume at time t of a growing grain formed at time τ and determined by the linear growth rate G and the geometry of the growing grain; and $E(t)$ means the total volume of growing grains, if overlapping is neglected. An exact analysis of nonisothermal crystallization is reduced to calculate $E(t)$ in eq. (5); that is, in general, temperature dependence of nucleation and growth rate must be evaluated separately. However, only an overall rate of crystallization is obtained, except for polymers that crystallize very slowly. It is here assumed that G/ν is an invariance of the phenomena (isokinetic⁴), and absolute crystallinity should get to the same maximum value throughout a temperature range considered now if the polymer is kept at the temperature for an extremely long period. These assumptions, which are plausible in a limited range of temperature, will be further discussed and verified in experiment in the following paper.⁶

On the above assumptions, the transformed weight fraction $X(t)$ in nonisothermal crystallization is reduced to resemble the Avrami equation:

$$X(t) = 1 - \exp \left[- \left\{ \int_0^t K(T(\tau)) d\tau \right\}^n \right] \quad (6)$$

where $K(T) = k(T)^{1/n}$, and n and $k(T)$ are the Avrami index and the isothermal crystallization rate constant, respectively. Temperature dependence of $k(T)$ is given by the following form according to Takayanagi and Kusumoto⁷:

$$\ln k(T) = A - \frac{BT}{(T - T_g - 51.6)^2} - \frac{CT_m}{T(T_m - T)}$$

where A , B , and C are constants relevant to the polymer, and T_m and T_g are the melting point and the glass transition temperature of the polymer, respectively.

Solving eqs. (1) and (6) simultaneously, the temperature and crystallinity of the polymer in the course of crystallization under given conditions can be obtained. Numerical calculation is easily carried out with the aid of a computer.

DISCUSSION

Crystallization Temperature

A polymer with a high crystallization rate crystallizes to the same degree of absolute crystallinity in nonisothermal crystallization, except at extremely high cooling rate. In such cases, therefore, the prediction of the crystallization temperature is required in terms of polymer characteristics and cooling conditions. Calculation was carried out for polyethylene as a typical example. Equation (4) is just applicable to this problem. On the other hand, the crystallization temperature is obtained from the calculation of changes in temperature and crystallinity throughout the process by use of eqs. (1) and (6).

The physical constants for the calculation are summarized below:

heat of crystallization ΔH , 20, 40, 60 cal/g
 specific heat at constant pressure C_p , 0.55 cal/g-deg
 melting point T_m , 140°C
 glass transition temperature T_g , -40.0°C

Mandelkern's data⁸ were used for expressing an empirical formula of $k(T)$. Using the formula, the numerical calculations of both procedures were performed. Temperature and crystallinity are illustrated in Figure 3 as a function of $\frac{R}{C_p} t$ for various parameters, such as heat of crystallization, the Avrami index, and the cooling parameter. The results indicate that with increasing cooling parameter, crystallization rate increases proportionately, while crystallization temperature decreases. Comparison between results of eq. (4) and of eqs. (1) and (6) is made in Table I. Crystallization temperatures calculated from eq. (4) are shown in the odd lines in the table, and temperatures at which crystallization proceeds to just one half, obtained from eqs. (1) and (6) under the same crystallization conditions, are shown in the even lines in the table. On the whole, both results coincide rather well. When the cooling parameter is large and ΔH and n

are small, the difference becomes appreciable. In such a case, $\left(\frac{dT}{dt}\right)_{X=1/2} \simeq 0$ does not hold and this is clearly seen in Figure 3.

The above results suggest an interesting conclusion that $\dot{X}_{1/2}$ is well estimated by using eq. (4), if the cooling parameter R and the temperature of the plateau can be measured. It should be emphasized that eq. (4) requires no information of crystallization kinetics and that this estimation is made without it. Even in crystallization with molecular orientation, $\dot{X}_{1/2}$ can be determined by measurement of the plateau temperature and the cooling parameter. This value, $\dot{X}_{1/2}$, thus obtained includes the effect of molecular orientation implicitly and can be used as a characteristic of the crystallization under molecular orientation.

The relationship between crystallization temperature and cooling condition is studied by employing an intuitive graphic method. When a polymer is cooled at the cooling parameter R_r , the crystallization temperature is schematically determined in Figure 4. The $\dot{X}_{1/2}$ on the left side of eq. (4) exhibits a maximum between melting point and glass transition temperature. The intersection of the straight line passing through T_s , with slope R_r , and the profile of $\dot{X}_{1/2}(T)$ determines the crystallization temperature T_r .

If $R_i < R_r$, then $T_i > T_r$; that is, the larger cooling parameter, the lower crystallization temperature. If molecules are oriented, the profile of $\dot{X}_{1/2}(T)$ shifts to the higher temperature side and the maximum value increases. In this case, $T_r < T_r'$, for a given cooling parameter R_r , as shown in Figure 4.

The change in the $\dot{X}_{1/2}$ profile may be explained from the viewpoints of thermodynamics and the transition rate theory.⁹ One is that a decrease of the entropy of the liquid phase due to the elongation of chain molecules causes an increase in the melting point. The other is that molecular orientation lowers the free energy of activation for autodiffusion across the crystalline-liquid interfaces.

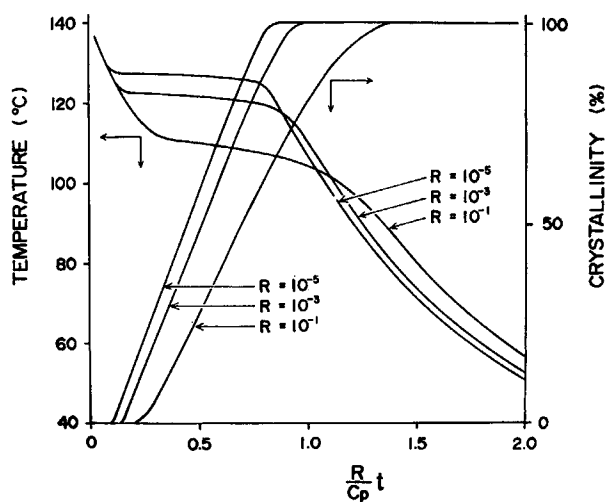
Ultimate Crystallinity

A polymer with a low crystallization rate does not always accomplish the phase transformation completely. The degree of phase transformation, in this case, is defined as the ultimate crystallinity. Cooling condition plays an important role in determining this quantity. Attention is especially focused on how the ultimate crystallinity varies with cooling conditions. Poly(ethylene terephthalate) (PET) shows such a typical characteristic in nonisothermal crystallization. Change in temperature and crystallinity in the course of crystallization is calculated as in the case of polyethylene. Temperature dependence of $k(T)$ is empirically given by Cobbs and Burton's data.¹⁰ Physical constants used in the calculation are as follows:

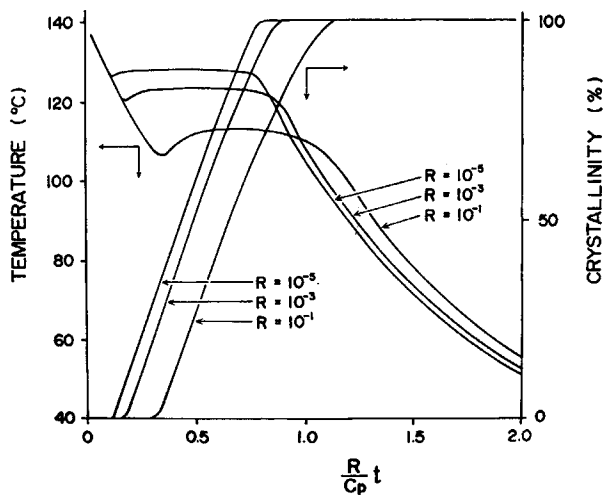
heat of crystallization ΔH , 15 cal/g
 specific heat at constant pressure C_p , 0.40 cal/g-deg
 melting point T_m , 265°C
 glass transition temperature T_g , 66.0°C

The solid lines in Figure 5 show the relationship between ultimate crystallinity and cooling parameter calculated from eqs. (1) and (6). The variation of ultimate crystallinity is highly dependent upon the Avrami index. When the Avrami index is 1, the ultimate crystallinity varies over a wide range of cooling parameter, but for a large n , it varies rather critically with the cooling parameter.

The above calculation of ultimate crystallinity requires all informations on changes in temperature and crystallinity during the course of the crystallization. Under the assumed cooling condition in eq. (1), it is possible to



(a)

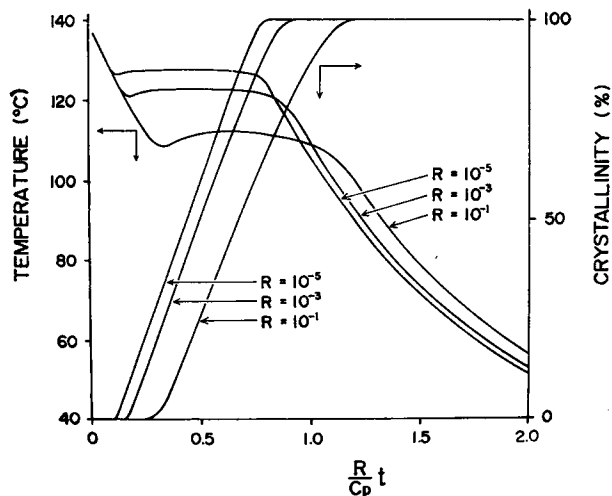


(b)

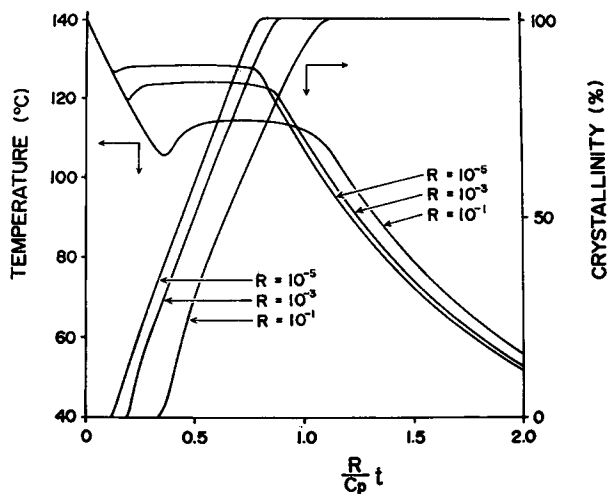
Fig. 3 (continued)

make a direct estimation for ultimate crystallinity. Substituting eq. (1) into eq. (6), one obtains, on the assumption that $T_g > T_s$,

$$X_{\infty} = 1 - \exp \left[- \left\{ - \frac{C_p}{R} \int_{T_m}^{T_g} \frac{K(T)}{T - T_s} dT + \frac{\Delta H}{R} \int_{T_m}^{T_g} \frac{K(T)}{T - T_s} \cdot \frac{dX}{dT} \cdot dT \right\}^n \right] \quad (7)$$



(c)



(d)

Fig. 3. Temperature and crystallinity vs. $R/C_p t$ for various cooling parameter calculated from eqs. (1) and (6): (a) for $\Delta H = 40$ cal/g and $n = 1$; (b) for $\Delta H = 40$ cal/g and $n = 2$. (c) for $\Delta H = 40$ cal/g and $n = 3$. (d) for $\Delta H = 40$ cal/g and $n = 4$.

TABLE I
Crystallization Temperature for Various Value of n , ΔH (cal/g), and R (cal/g-deg-sec)

R	Crystallization temp., °C		
	$\Delta H = 20$	40	60
$n = 1$			
10^{-5}	126.5 ^a	127.1	127.5
	126.6 ^b	127.2	127.5
10^{-3}	120.5	121.7	122.4
	120.6	121.6	122.4
10^{-1}	104.3	108.3	110.2
	105.8	108.8	110.5
$n = 2$			
10^{-5}	127.2	127.7	128.0
	127.2	127.7	128.0
10^{-3}	121.7	122.8	123.4
	121.7	122.8	123.4
10^{-1}	108.3	111.5	113.1
	108.2	111.5	113.1
$n = 3$			
10^{-5}	127.5	128.0	128.3
	127.5	128.0	128.3
10^{-3}	122.4	123.4	123.9
	122.4	123.4	123.9
10^{-1}	110.2	113.0	114.4
	109.5	113.0	114.4
$n = 4$			
10^{-5}	127.7	128.2	128.4
	127.7	128.2	128.5
10^{-3}	122.8	123.7	124.3
	122.8	123.8	124.3
10^{-1}	111.4	114.0	115.3
	110.5	114.0	115.3

^a Value calculated from eq. (4).

^b Value calculated from eqs. (1) and (6).

where X_{∞} is the ultimate crystallinity. In eq. (7), the term $\frac{K(T)}{T - T_s}$ changes more slowly than the term $\frac{dX}{dT}$ with temperature. By using the maximum value of the term $\frac{K(T)}{T - T_s}$, eq. (7) is rewritten as follows:

$$X_{\infty} = 1 - \exp \left[- \left\{ \frac{a}{R} (1 + bX_{\infty}) \right\}^n \right] \quad (8)$$

$$a = C_p \int_{T_g}^{T_m} \frac{K(T)}{T - T_s} dT \simeq \frac{C_p}{T_p - T_s} \int_{T_g}^{T_m} K(T) dT$$

$$b = \frac{\Delta H}{C_p} \cdot \frac{1}{\delta T}$$

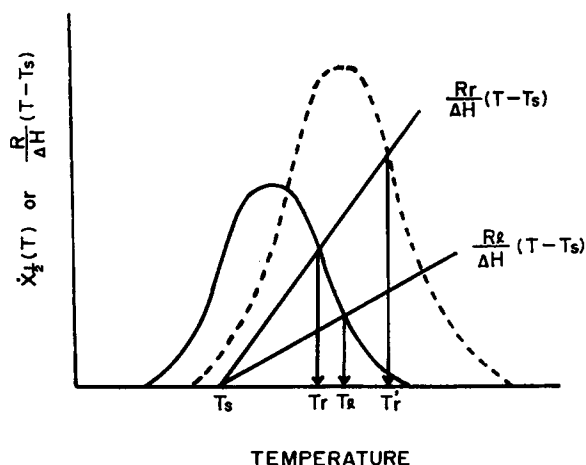


Fig. 4. Schematic diagram of relationship between crystallization temperature and $\dot{X}_{1/2}(T)$ or $R/\Delta H(T - T_s)$. Solid line: $\dot{X}_{1/2}(T)$ for unoriented state; dotted line: $\dot{X}_{1/2}(T)$ for oriented state.

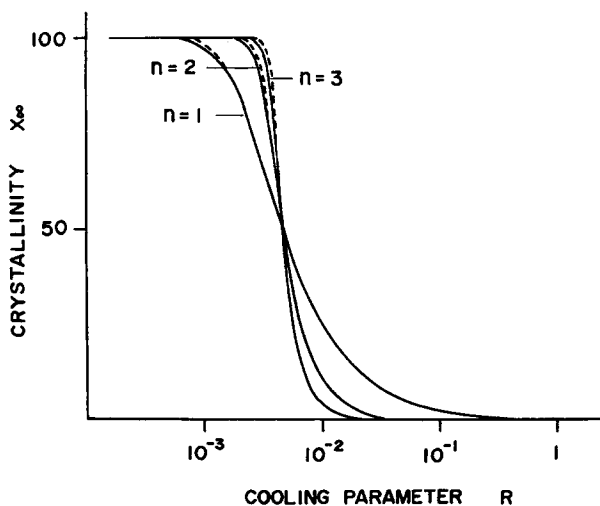


Fig. 5. Ultimate crystallinity of PET vs. cooling parameter. Solid line: calculated from eqs. (1) and (6); dotted line: calculated from eq. (8).

where T_p is the temperature at which $K(T)$ reaches its maximum K_{\max} ; and δT , the integral breadth of $\frac{K(T)}{T - T_s}$, is defined by the equation

$$\delta T = \int_{T_g}^{T_m} \frac{K(T)}{T - T_s} / \left(\frac{K(T)}{T - T_s} \right)_{\max} \simeq \int_{T_g}^{T_m} K(T) dT / K_{\max}$$

where a and b in eq. (8) are constants relevant to the polymer, and especially a is proportional to the "kinetic crystallizability" defined by Ziabicki.¹

Equation (8) gives the relation between X_∞ and R . Figure 5 shows a comparison between the results obtained from eq. (8) and those determined by using eqs. (1) and (6). Both curves coincide except for the range of large X_∞ values. This result suggests that the calculation of the whole process can be replaced by the solution of eq. (8).

Melt-Spinning Process

Data of numerous experiments have shown that melt-spinning is a process during which nonisothermal crystallization occurs under molecular orientation. Molecular orientation exerts a considerable influence on the kinetics and the morphology of polymer crystallization. The mechanism of the phenomenon, however, even in isothermal process, is yet to be fully known. Some treatment developed in this paper is here intended for an analysis of the crystallization during melt-spinning process.

When a plateau in temperature change during the process is observed,¹¹ the crystallization temperature is predicted in the same way as in Figure 4. The profile of $\dot{X}_{1/2}(T)$ varies with change in molecular orientation due to elongational deformation throughout the melt-spinning process. Furthermore, the cooling parameter increases with decreasing diameter of thread along the spinline. Crystallization begins at the temperature of the intersection of two curves: one is the trajectory of $\frac{R}{\Delta H}(T - T_s)$, and the other is the profile of $\dot{X}_{1/2}(T)$ (Fig. 6). After crystallization begins, the cooling parameter is kept constant because the diameter of the thread no longer changes. Therefore, the crystallization temperature during the process is determined from the intersection of the profile $\dot{X}_{1/2}(T)$ and the straight line defined by the final cooling parameter R_c .

It is uncertain whether crystallization temperature becomes higher or lower with spinning velocity without knowing which is more influential,

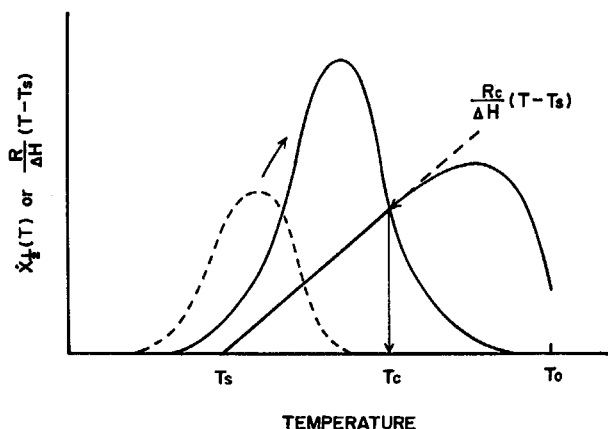


Fig. 6. Schematic determination of the crystallization temperature during melt-spinning process.

TABLE II
Results from a Melt-Spinning Experiment with High-Density
Polyethylene (Sholex 6050)^a

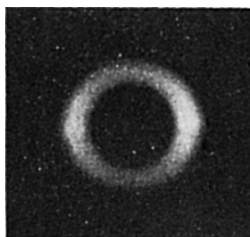
	Sp. vel. ^b 25 m/min	Sp. vel. ^b 60 m/min
Crystallization temperature, °C	137	132
Birefringence at crystallization point	0.62×10^{-3}	0.88×10^{-3}
Cooling parameter, cal/g-deg-sec	0.46	0.61
Rate of crystallization at $X = 1/2$, sec ⁻¹	1.28	1.62

^a Melt temperature, 170°C; flow rate, 0.4 g/min.

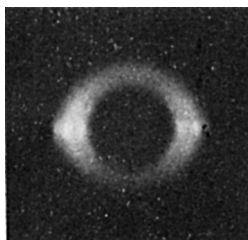
^b Spinning velocity.

molecular orientation or cooling condition. The results of a spinning experiment of high-density polyethylene¹¹ are shown in Table II. Crystallization temperature is lower for higher spinning velocity. (The reverse was also found in other experiments.^{12,13}) The extrapolated value of $\dot{X}_{1/2}$, which is determined from the data of isothermal crystallization for the same polymer, is less than 10^{-7} sec⁻¹ for the unoriented state above 130°C. Thus, the increase in crystallization rate with molecular orientation is clearly recognized.

Crystallization of PET during melt-spinning under normal conditions is situated at another extreme from that of polyethylene. PET does not crystallize usually during melt-spinning. However, very high-speed spinning leads to crystallization of PET. X-Ray photographs of as-spun PET fibers with high spinning velocity are shown in Figure 7. With in-



(a)



(b)

Fig. 7. X-Ray photographs of PET wound up with high spinning velocity: (a) 2040 m/min; (b) 2600 m/min.

creasing spinning velocity, more intense crystalline reflections appear and density of the fiber increases, too. Crystallinity of as-spun fibers of Figure 7b is calculated at 20% by using the value of 1.355 g/cc as the density of oriented amorphous.

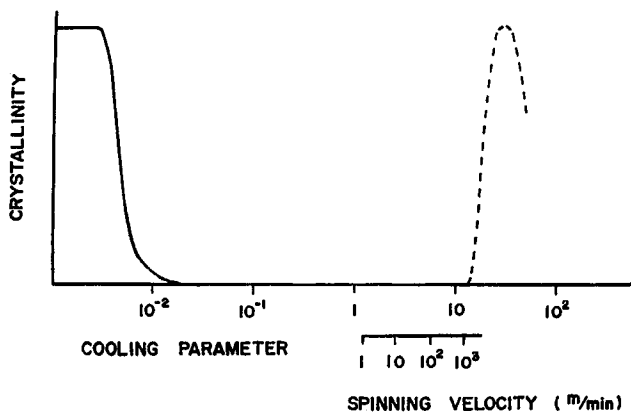


Fig. 8. Ultimate crystallinity vs. cooling parameter. Solid line: crystallinity change for $n = 2$ (shown in Fig. 5); dotted line: crystallinity change expected in high-speed spinning.

Figure 8 shows the cooling parameter versus ultimate crystallinity. The solid line represents the relation for $n = 2$ as shown in Figure 5 and the dotted line, for high-speed spinning. Spinning velocity corresponding to the cooling parameter is calculated for a thread $30\ \mu$ in diameter from the relation proposed by Kase and Matsuo.¹⁴ The crystallization of PET during high-speed melt-spinning is thus attributed to an increase in rate of crystallization as a consequence of molecular orientation. The increase in the rate of crystallization in this case can be estimated from eq. (8). If the value δT is not seriously influenced by molecular orientation, the kinetic crystallizability is about 10^4 times larger than that under the unoriented state.

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