

## Some Aspects of Nonisothermal Crystallization of Polymers. III. Crystallization During Melt Spinning

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### Synopsis

Crystallization during melt spinning is studied as an example of the nonisothermal crystallization of polymers. The following equation is derived, taking the temperature distribution within a filament into consideration:

$$\kappa \nabla^2 T = \mathbf{V} \cdot \text{grad } T - \frac{\Delta H}{C_p} \mathbf{V} \cdot \text{grad } X$$

where  $T$  = temperature,  $X$  = crystallinity,  $\kappa$  = thermal diffusivity,  $\mathbf{V}$  = velocity,  $\Delta H$  = heat of crystallization, and  $C_p$  = specific heat at constant pressure. The assumptions and the procedure for a numerical calculation of crystallinity and temperature within a running filament are described, and some results of calculation are illustrated. The results are compared with those obtained by a simpler calculation in which the radial temperature distribution is neglected. The simpler method proved useful in connection with x-ray measurements.

### INTRODUCTION

Previous papers<sup>1,2</sup> afforded a basis, both theoretical and experimental, for an analysis of nonisothermal crystallization of polymers. Changes in crystallinity and temperature were calculated in the course of the nonisothermal process under some important assumptions, that is, Newton's law of cooling, uniform temperature distribution in the sample, and isokinetic crystallization. In terms of the results obtained, the relationship between crystallization and temperature during melt spinning was discussed briefly.

Several papers<sup>3-8</sup> have been published on the temperature change during melt spinning. However, the problem was solved simply as heat transfer in a cooling filament. These calculations took no account of the kinetics of crystallization of polymers.

The purpose of this paper was to evaluate crystallinity and temperature along the spinline as a function of the position in the running filament, considering crystallization kinetics when crystallization occurs during the

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process. Proper treatment is very complicated because of the following reasons:

1. Polymer molecules become oriented in the course of elongational flow. At present, the orientation cannot be fully predicted, although efforts are being made to this end.

2. The morphology and the kinetics of crystallization vary with the development of molecular orientation. Especially, the kinetic crystallizability under molecular orientation becomes much larger by several orders of magnitude than that in a randomly oriented state.<sup>1</sup> The change in crystallization rate can not be quantitatively predicted because of the lack of detailed information on the strain induced crystallization.

3. The surface temperature of a running filament is lower than the temperature in the central part of the filament. Therefore, the stress is not uniform in a cross-sectional area but tends to concentrate in the vicinity of the surface.

These effects must be simultaneously taken into consideration for the thorough prediction of the crystallization during melt spinning. In the present work, however, the effect of stress concentration was neglected, and interest was chiefly confined to the calculation of the distribution of temperature and crystallinity within a filament, assuming appropriate crystallization kinetics which did not conflict with the experimental results. The results thus obtained were compared with those calculated without considering the radial temperature distribution in the filament. Radial distribution of crystallinity and temperature cannot be measured in experiment, but an average throughout the cross section is obtained. The calculation without considering the radial temperature distribution avails to simplify the analysis of crystallization during melt spinning.

## THEORETICAL

### Fundamental Equations

Consider an arbitrary small volume element,  $d\tau$ , fixed in space of the spinning way. Heat is transferred to this element through heat conduction and mass transport. If the thermal conductivity of a polymer,  $K_c$ , is independent of temperature  $T$ , heat conducted into the volume element  $d\tau$  per unit time across its surface is expressed by

$$K_c \nabla^2 T d\tau. \quad (1)$$

Heat transferred to the same volume element per unit time by mass transport is given by

$$-\operatorname{div}(H\rho\mathbf{V})d\tau \quad (2)$$

where  $H$ ,  $\rho$ , and  $\mathbf{V}$  are enthalpy per unit mass, density, and velocity of the polymer, respectively. From expressions (1) and (2), the enthalpy change per unit volume can be shown in the following equation, by the use of the

equation of continuity  $\partial\rho/\partial t = -\text{div}(\rho\mathbf{V})$  and the assumption of constant  $\rho$ :

$$\rho \frac{\partial H}{\partial t} = K_c \nabla^2 T - \rho \mathbf{V} \cdot \text{grad } H. \quad (3)$$

Since enthalpy is a function of temperature and crystallinity  $X$ , which was defined previously,<sup>1,2</sup> one obtains

$$\text{grad } H = C_p \text{ grad } T - \Delta H \text{ grad } X \quad (4)$$

where  $C_p$  is the specific heat at constant pressure and  $\Delta H$  is the heat of crystallization per unit mass.

For the steady state, eq. (3) becomes

$$\kappa \nabla^2 T = \mathbf{V} \cdot \text{grad } T - \frac{\Delta H}{C_p} \mathbf{V} \cdot \text{grad } X \quad (5)$$

where  $\kappa = K_c/\rho C_p$ , the thermal diffusivity. Equation (5) is one of the fundamental equations on which the following calculations are based.

Another fundamental equation is concerned with the kinetics of crystallization under nonisothermal conditions, which was discussed in the previous papers.<sup>1,2</sup> That is,

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

where  $n$  is the Avrami index and  $K(T)$  is a sort of crystallization rate constant. The simultaneous solution of eqs. (5) and (6) under given initial and boundary conditions gives the crystallinity and temperature at any point within the filament.

### Assumptions for Calculation

In the calculation of the crystallinity and temperature during the melt spinning, the following assumptions are made in addition to those mentioned above, because not all the information necessary for the calculation can be obtained at present.

1. Temperature dependence of the crystallization rate constant is obtained from the data of melt spinning experiments. Therefore, the effect of molecular orientation is introduced implicitly in the formula of crystallization kinetics.

2. Temperature dependence of the density, the specific heat, and the thermal conductivity is neglected.

3. Heat loss from the surface of the filament is calculated in terms of Kase-Matsuo's equation.<sup>9</sup>

4. Change in the diameter of the filament is calculated, assuming the polymer melt as a Newtonian fluid with Arrhenius-type temperature dependence of the coefficient of viscosity.

5. Secondary crystallization is not taken into account. Taking polyethylene (Sholex 6050,  $M_v = 6.24 \times 10^4$ ) as an example, the following spinning conditions and physical constants are adopted: melt tempera-

ture, 170°C; die diameter, 0.6 mm; diameter of spun filament, 0.1 mm; mass output, 0.4 g/min; takeup velocity, 60 m/min; heat of crystallization, 40 cal/g; density, 0.833 g/cm<sup>3</sup>; specific heat at constant pressure, 0.55 cal/g-deg; heat conductivity,  $8.7 \times 10^{-4}$  cal/cm-sec-deg; melting point 160°C. The melting point is assumed to be 160°C instead of 140°C, because the temperature of equilibrium between crystalline and amorphous phases increases with molecular orientation.

### Procedure for Calculation

The calculation is simplified by consideration of dimensionless variables,  $\theta = (T - T_e)/(T_0 - T_e)$ ,  $\xi = \kappa x/R^2 V_z$ , and  $\eta = r/R$ , and a constant

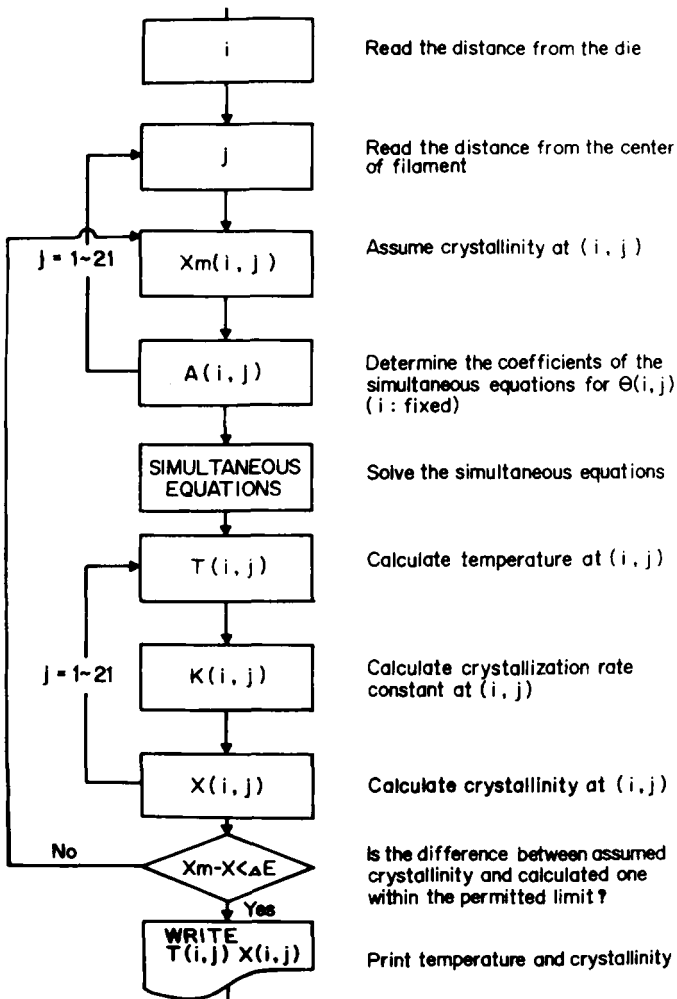


Fig. 1. Flow chart of numerical calculation for temperature and crystallinity in a filament.

$\mu = \Delta H/C_p(T_0 - T_e)$ , where  $T_e$  is the temperature of the environment,  $T_0$  is the melting temperature,  $x$  is the distance from die,  $r$  is the distance from the center of a filament,  $R$  is the radius of the filament, and  $V_x$  is the velocity in the flow direction. Incorporation of these variables into eq. (5) leads to

$$\frac{\partial \theta}{\partial \xi} - \frac{1}{\eta} \frac{\partial \theta}{\partial \eta} - \frac{\partial^2 \theta}{\partial \eta^2} = \mu \frac{\partial X}{\partial \xi}. \quad (7)$$

In this equation,  $\partial^2 \theta / \partial \xi^2$  is dropped since it is usually small in comparison with other terms.

In order to proceed to a numerical calculation, a difference grid is made in the domain of the variables  $\xi$  and  $\eta$ . Any point  $(i, j)$  represents a point at which  $\xi = (i - 1)h$ ,  $\eta = (j - 1)k$ , where  $h$  and  $k$  are the grid spacings. In this treatment,  $k$  is chosen as 0.05. Flow chart of a procedure for the calculation of crystallinity and temperature is shown in Figure 1. Crystallinity  $X_m(i, j)$  at a point  $(i, j)$  is first obtained by extrapolation from the past successive three values  $X(i - 1, j)$ ,  $X(i - 2, j)$ , and  $X(i - 3, j)$ . The temperature at each point with the same  $i$ -value is obtained solving simultaneous difference equations derived from eq. (7) and the boundary condition. The system consists of 21 linear equations with 21 variables  $\theta(i, j)$  ( $j = 1, 2, \dots, 21$ ). Then, the crystallization rate constant  $K(i, j)$  is acquired and  $X(i, j)$  is calculated with the aid of eq. (6).  $X_m(i, j)$  must be equal to  $X(i, j)$ , provided that the assumed value  $X_m(i, j)$  is a proper one. If their difference is larger than a permitted limit, a new crystallinity is defined by the equation

$$X'_m(i, j) = \frac{X(i, j) + X_m(i, j)}{2}.$$

This reassumed value is used instead of the original one, and the calculation is repeated until the difference between  $X(i, j)$  and  $X_m(i, j)$  becomes smaller than the permitted limit.

## RESULTS AND DISCUSSION

As an example of the calculation in the case of  $n = 2$ , Figure 2 shows isothermal lines and equicrystallinity contours in the running filament being spun under given spinning conditions. At the crystallization point, the temperature gradient of about 300°C/cm in the radial direction is much larger than that of about 3°C/cm in the flow direction. It is obviously shown that the temperature is lower on the surface, and crystallization proceeds from the surface to the center of the filament. Crystallinity and temperature both on the surface and at the center of the filament as well as their averages throughout the cross section are plotted in Figure 3 against the distance from the die. A characteristic change in temperature during crystallization is due to the transient balance between heat released by crystallization and heat lost by cooling. The crystallization temperature on the surface is several degrees lower than that at the center.

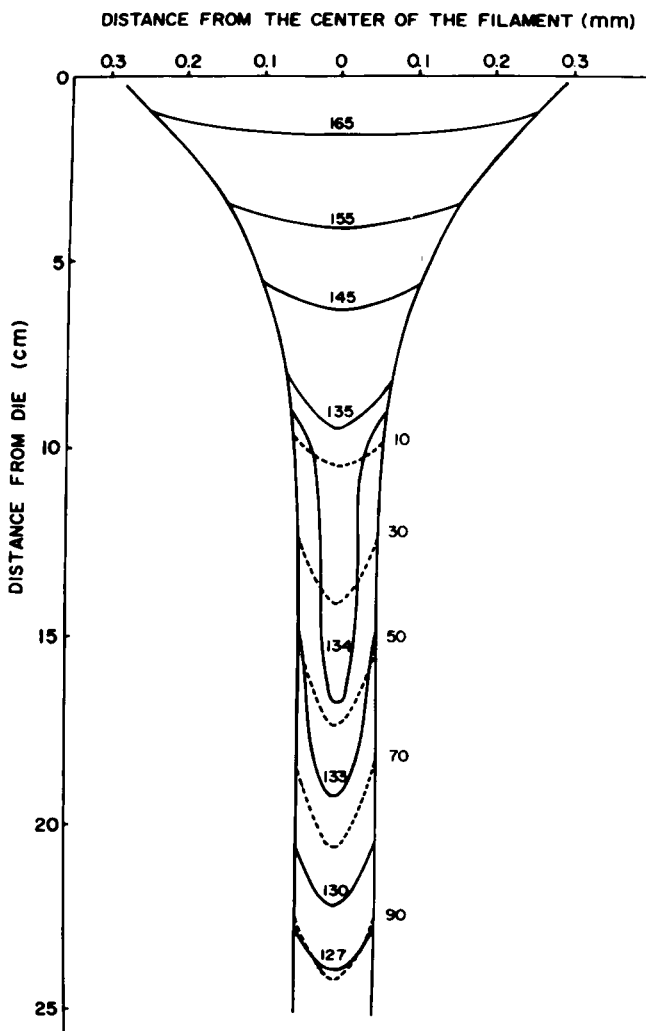


Fig. 2. Isothermal lines and equicrystallinity contours in a filament during melt spinning process ( $n = 2$ ): solid line, isothermal line ( $^{\circ}\text{C}$ ); broken line, equicrystallinity contour (%).

In practice, the average crystallinity and the temperature on the surface are measured. Therefore, a simpler method for a direct prediction of the average crystallinity is not meaningful. If the temperature distribution in the cross section of a filament is neglected, the calculation becomes much simpler than that based on eq. (5). In this case, we get eq. (8) instead of eq. (7):

$$\frac{d\theta}{d\xi} + 2\text{Bi} \theta = \mu \frac{dX}{d\xi} \quad (8)$$

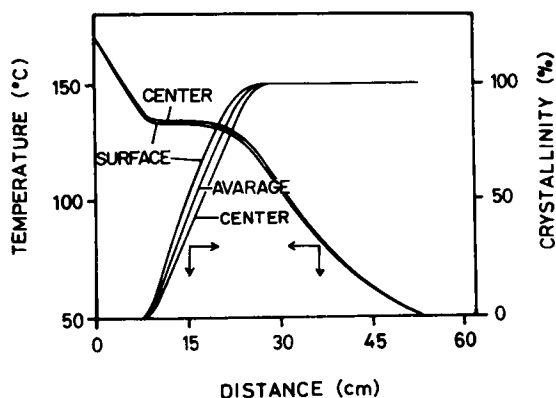


Fig. 3. Change in temperature and crystallinity along the spinline, calculated using eqs. (6) and (7) ( $n = 2$ ).

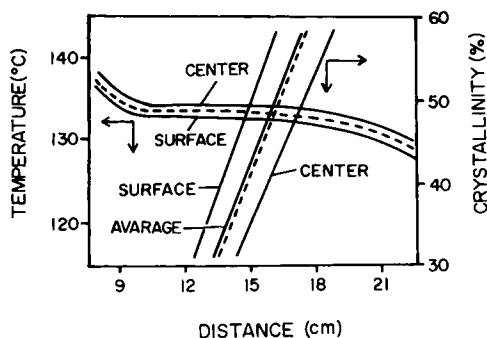
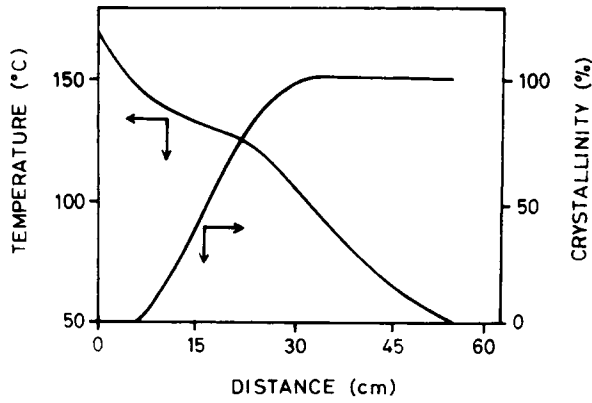


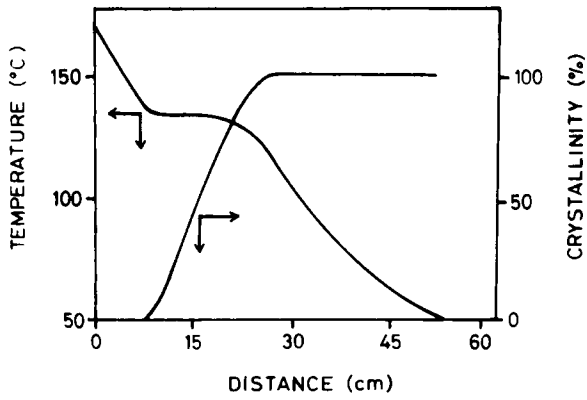
Fig. 4. Detail of Fig. 3: broken line, results calculated without considering temperature distribution in cross section.

where  $Bi$  represents the Biot number  $\alpha R/K_c$ ,  $\alpha$  being the heat transfer coefficient on the surface. The results of such calculations were compared with the average value obtained in consideration of the temperature distribution. As shown in Figure 4, the difference between the two crystallinity curves is fairly small, and the starting and terminating points of crystallization do not differ appreciably in the two calculations. Therefore, the complex calculation can be replaced by the simpler one for the analysis of crystallization in connection with the x-ray measurement, which gives the average crystallinity through the cross section.

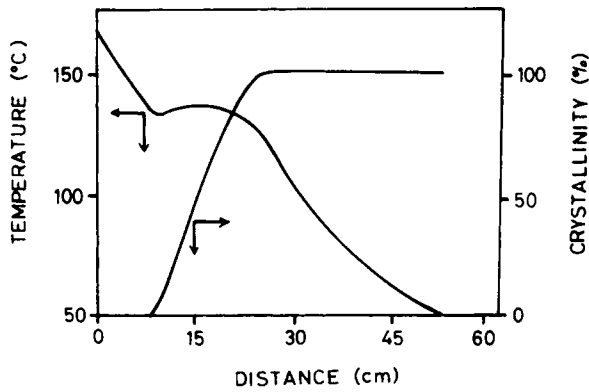
The changes in crystallinity and temperature are influenced by the Avrami index  $n$ , even though  $\dot{X}_{1/2}(T)$ , the crystallization rate at  $X = 1/2$ , remains the same. Figures 5a, 5b, and 5c show the results of calculations for  $n = 1, 2$ , and 3, respectively. Experimental results of changes in temperature and crystallinity are shown in Figure 6.<sup>10</sup> There is a similarity between the crystallinity curves in Figure 5b ( $n = 2$ ) and Figure 6, at least in the early stages of crystallization. The discrepancy between the two curves in the later stages of crystallization is due to secondary crystalliza-



(a)



(b)



(c)

Fig. 5. Changes in temperature and crystallinity along the spinline, calculated using eqs. (6) and (8): (a)  $n = 1$ ; (b)  $n = 2$ ; (c)  $n = 3$ .



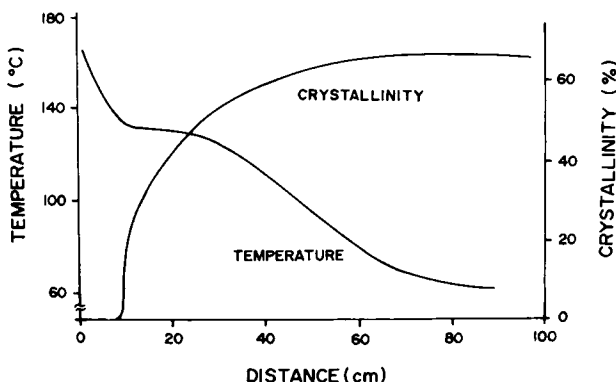


Fig. 6. Changes in temperature and crystallinity along the spinline, observed in melt spinning experiment for high-density polyethylene. Spinning condition: melt temperature, 170°C; flow rate, 0.4 g/min; takeup velocity, 60 m/min.

tion which is neglected in the calculation. It is worth noting that the Avrami index tends to decrease with increase in molecular orientation, for the index in the quiescent state is 3.35 for the same sample.<sup>2</sup> This fact has been pointed out in the studies on crystallization of natural rubber<sup>11</sup> and crosslinked polyethylene under stress.<sup>12,13</sup>

The calculations in this paper are based on many assumptions. However, a general outline of crystallization during melt spinning can be predicted. If more detailed information on the development of molecular orientation during elongational flow and the kinetics of crystallization under stress is acquired, a more accurate prediction will be established using the method described above.

The authors are indebted to Mr. Higuchi of the Computer Division for executing the numerical calculations.

### References

1. K. Nakamura, T. Watanabe, K. Katayama, and T. Amano, *J. Appl. Polym. Sci.*, **16**, 1077 (1972).
2. K. Nakamura, K. Katayama, and T. Amano, *J. Appl. Polym. Sci.*, **17**, 1031 (1973).
3. A. Ziabicki, *Faserforsch. Textiltech.*, **8**, 467 (1957).
4. E. H. Andrews, *Brit. J. Appl. Phys.*, **10**, 39 (1959).
5. V. Pechoc, *Faserforsch. Textiltech.*, **10**, 62 (1959).
6. N. Yamada, Y. Sano, and T. Nanbu, *Sen-i Gakkaishi*, **22**, 197 (1966).
7. G. Wilhelm, *Kolloid-Z. Z. Polym.*, **208**, 97 (1966).
8. M. E. Morrison, *A.I.Ch.E. J.*, **16**, 57 (1970).
9. S. Kase and T. Matsuo, *J. Polym. Sci., A*, **3**, 2541 (1965).
10. K. Katayama, T. Amano, and K. Nakamura, *Kolloid-Z. Z. Polym.*, **226**, 125 (1968).
11. A. Gent, *Trans. Faraday Soc.*, **50**, 521 (1954).
12. T. Kawai, I. Iguchi, and H. Tonami, *Kolloid-Z. Z. Polym.*, **221**, 28 (1968).
13. R. Kitamaru and H. D. Chu, *Bull. Inst. Chem. Res. Kyoto Univ.*, **46**, 97 (1968).

Received June 1, 1973