

Some Problems in Melt Spinning Processes. II. Molecular Orientation in the Course of Melt Spinning

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Synopsis

The approximate solutions of the three-dimensional, fundamental equation for the molecular orientation of a spun fiber are obtained, a rigid ellipsoid model for the molecular segments or the paracrystalline structure being assumed. A rate of strain G (sec.⁻¹) of a molten fiber and a rotational diffusion constant D (sec.⁻¹) of the segment are approximated as a function of time t (sec.) as follows:

$$\begin{aligned} G &= G_0 + G_1t + G_2t^2 + \dots \\ D &= D_0 + D_1t + \dots \end{aligned}$$

Under the conditions, $1 \gg G_0t \gg G_1t^2 \gg G_2t^3 \gg \dots$ and $1 \gg D_0t \gg D_1t^2 \gg \dots$, a coefficient of the molecular orientation f of spun fiber is found to be:

$$\begin{aligned} f &= \frac{2}{5} \int_0^t G dt - \frac{6}{5} G_0 \left(D_0 - \frac{1}{21} G_0 \right) t^2 \\ &\quad - \frac{2}{5} \left(\frac{2}{21} G_0^3 + \frac{4}{7} G_0^2 D_0 - 6G_0 D_0^2 - \frac{1}{7} G_0 G_1 + 2G_0 D_1 + G_1 D_0 \right) t^3 + \dots \end{aligned}$$

The applicability of these approximate, theoretical results is extremely limited in the neighborhood of the spinneret under practical melt spinning conditions. However, the theory should be useful in the case where the polymer temperature is near its melting temperature and the extension rate of spinning fiber is small.

INTRODUCTION

In the course of a melt spinning process, polymer molecules are oriented with an extension of a melt fiber. The molecular orientation of a spun fiber is determined both from the orientation which is due to the extension of the fiber and from the orientation relaxation due to a rotational diffusion of the polymer molecules.¹

Several experimental studies²⁻⁴ have been carried out on the molecular orientation of the spun fiber, and some empirical laws have been discovered.²⁻⁴

Ziabicki¹ presented two fundamental differential equations which governed the orientation of the polymer molecules in a molten fiber. One of which is concerned with a rigid ellipsoid model, and the other is related to a flexible coiled chain model. The solutions of these differential equations

were not obtained. Moreover, some corrections should be made to the fundamental differential equation for the rigid ellipsoid model, because this equation treats the two-dimensional problems disregarding the fact that the melt spinning involves a three-dimensional system.

The objectives of this paper are (1) to present a new fundamental differential equation which governs the orientation of the polymer molecules or the paracrystalline structure as to the rigid ellipsoid model in a three-dimensional space, (2) to obtain the approximate mathematical solutions, and (3) to discuss the scope of the applicability of the solutions.

In the following section, we use the term "segment" in the sense of the polymer segment or the crystallite of the paracrystalline structure.

THEORY

1. Rotation of Segments in a Flow of Velocity Gradient

First of all, the molecular model should be described. The following assumptions are made.

(1) A freely jointed chain model⁵ can be used as the model of both the polymer molecule and the paracrystalline structure.^{6,7} In this model, rotational ellipsoidlike segments are freely joined as shown in Figure 1, and the effects of interactions through the both ends of the segment are negligible.

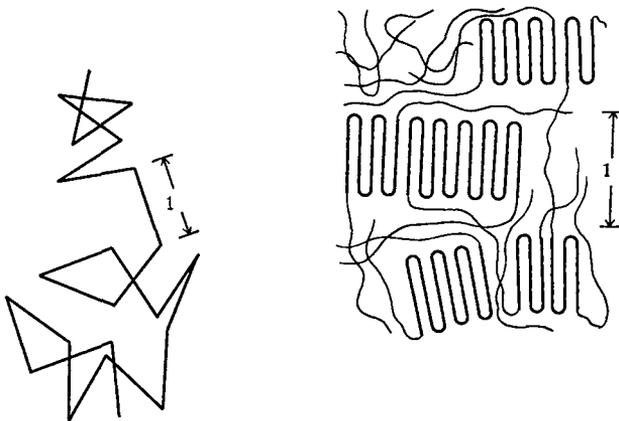


Fig. 1. Models assumed in the theory for (a) a molecule⁵ and (b) a paracrystalline structure.

(2) At first, the segments are randomly oriented; then the segments are forced to orient only through a deformation of the medium. The orientation of the segments relaxes only through a rotational diffusion.

(3) The effects of the crystallization on the segment orientation are negligible. The assumption is correct whenever the crystallinity level of the spun fiber is negligibly small.

For a molten polymer stream in the melt spinning process, we make the following assumptions.

(4) The polymer stream is in the steady state. In other words, the profile of the stream does not change with time.

(5) The velocity profile can be expressed only as a function of the distance from the spinneret orifice.

In the neighborhood of the orifice, the polymer velocity is also a function of the radial coordinate, in which case assumption (5) is not valid. However, the above assumption is correct except very near the spinneret orifice.

(6) The temperature of the molten polymer stream can be expressed only as a function of the distance from the spinneret orifice. In other words, the rotational diffusion constant can be expressed only as a

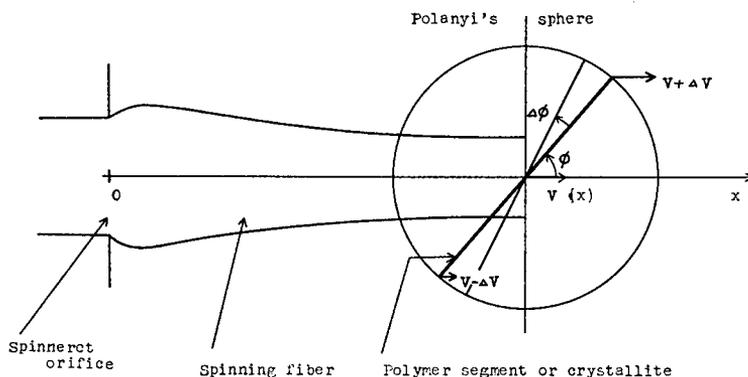


Fig. 2. Orientation of a polymer segment or a crystallite according to an extension of a molten polymer stream.

function of the distance, because the rotational diffusion constant is a function of the temperature. Actually, the temperature is also a function of the radial coordinate. However, the assumption (?) is correct in the case where the molten polymer stream is extremely thin and the temperature difference between the polymer and the surrounding cooling gas is extremely small.

We can discuss the orientation of the polymer segments or the crystallites through the above models and the assumptions. We consider the polymer molecule segment, which rotates in a flow where a velocity gradient exists in the x direction as shown in Figure 2.

The following quantities are also defined: V = velocity of flow in the x direction at $x = x$ (centimeters per second); G = velocity gradient of flow at $x = x$ (per second); ϕ = angle between the segment and the x axis (radians); $\dot{\phi}$ = rate of rotation of the segment (radians per second); t = time (seconds); x = distance from the spinneret orifice ($x = 0$, at $t = 0$) (centimeters).

The above quantities, G and $\dot{\phi}$ are expressed as:

$$G = dV/dx \quad (1)$$

$$\dot{\phi} = d\phi/dt \quad (2)$$

The rate of the segment rotation is calculated as:^{1,8}

$$\dot{\phi} = -G \sin \phi \cos \phi \quad (3)$$

2. Probability Distribution Function of Segment

In this section, we derive the fundamental differential equation for the segment rotation; then we obtain the approximate solutions of the equation.

We define the following $\rho(\phi, t)$ and D as: $\rho(\phi, t)$ = probability distribution function attributed to the segment making an angle ϕ with the x axis at a time t ; D = rotational diffusion constant of the segment (per second).

It is clear in Figure 2 that a number dN of segments which lie in the angular interval $[\phi, \phi + d\phi]$ is given as:

$$dN = N_0 \rho(\phi, t) \sin \phi d\phi \quad (4)$$

because the distribution function is of axial symmetry with respect to the x axis, where N_0 is the total number of segments.

We obtain the following equation from eq. (4).

$$\int_0^{\pi/2} \rho(\phi, t) \sin \phi d\phi = 1 \quad (5)$$

The fundamental differential equation for the probability distribution function is then as follows.

$$\frac{\partial}{\partial t} (\rho \sin \phi) = - \frac{\partial}{\partial \phi} \left(\rho \dot{\phi} \sin \phi - D \sin \phi \frac{\partial \rho}{\partial \phi} \right) \quad (6)$$

Ziabicki¹ discussed the same problem using the following equation.

$$\frac{\partial}{\partial t} = - \frac{\partial}{\partial \phi} \left(\rho \dot{\phi} - D \frac{\partial \rho}{\partial \phi} \right)$$

However, the above equation should be used for the two-dimensional problem. As our problem is three-dimensional character, eq. (6) should be used.

The general solution of eq. (6) may be impossible to obtain in practice. Therefore, we must be satisfied with an approximate solution.

In order to obtain an approximate solution of eq. (6), we make the following further assumptions for the polymer stream.

(7) The duration of the fiber deformation is sufficiently short.

(8) Both the velocity gradient G and the rotational diffusion constant D are approximately constant as to the distance from the spinneret orifice.

When we express G and D as follows:

$$G(t) = G_0 + G_1 t + G_2 t^2 + \dots \quad (7)$$

$$D(t) = D_0 + D_1 t + \dots \quad (8)$$

the probability distribution function $\rho(\phi, t)$ should be expressed as follows:

$$\rho(\phi, t) = \rho_0 + \rho_1(\phi)t + \rho_2(\phi)t^2 + \rho_3(\phi)t^3 + \dots \quad (9)$$

where, $G_0, G_1, G_2, \dots, D_0, D_1, \dots$ are constant. Taking the assumptions (7) and (8) into account, we assume that:

$$1 \gg G_0 t \gg G_1 t^2 \gg G_2 t^3 \dots$$

$$1 \gg D_0 t \gg D_1 t^2 \dots \quad (10)$$

From eqs. (5)–(9), we determine $\rho_0, \rho_1(\phi), \rho_2(\phi), \rho_3(\phi)$.

From eq. (9), it is clear that:

$$\rho(\phi, 0) = \rho_0$$

Taking assumption (2) into account, ρ_0 is a constant. In other words, ρ_0

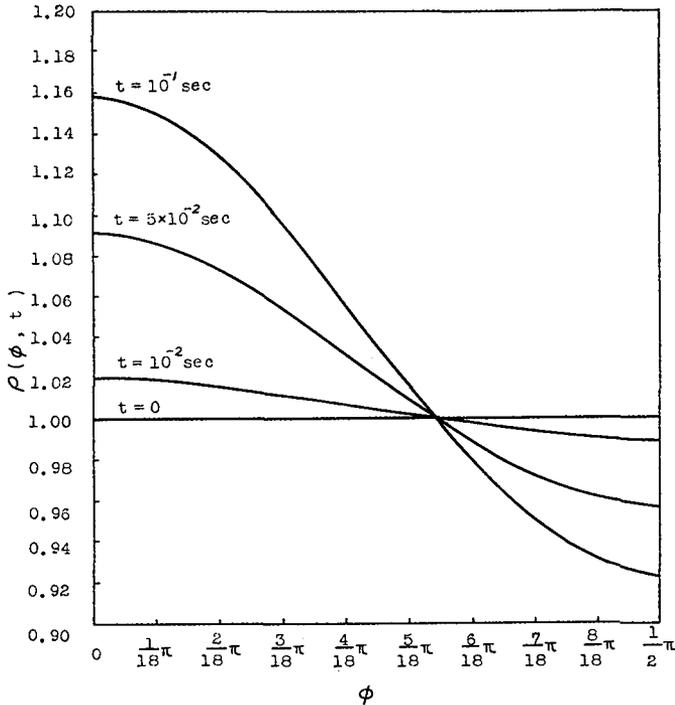


Fig. 3. Probability distribution function $\rho(\phi, t)$ as a function of time t . Calculation was made by eq. (14) assuming that $G_0 = 1 \text{ sec.}^{-1}$; $G_1 = G_2 = \dots = 0$; $D_0 = 1 \text{ sec.}^{-1}$; $D_1 = D_2 = \dots = 0$; $t = 0, 10^{-2}, 5 \times 10^{-2}, 10^{-1} \text{ sec}$.

is independent of ϕ . Considering this fact we obtain ρ_0 as follows, eq. (5) being used.

$$\rho_0 = 1 \quad (11)$$

Substituting eqs. (9) and (11) into eq. (5), and considering that eq. (5) should hold true at any time, we obtain

$$\int_0^{\pi/2} \rho_i(\phi) \sin \phi d\phi = 0 \quad i = 1, 2, 3, \dots \quad (12)$$

Substituting eqs. (3), (7), (8), (9), and (11) into eq. (6), and considering that eq. (6) should hold true at any time, we obtain

$$\rho_1 = G_0(3 \cos^2 \phi - 1)$$

$$2\rho_2 = (G_0\rho_1 + G_1)(3 \cos^2 \phi - 1) + G_0\rho_1' \sin \phi \cos \phi + D_0\rho_1' \cot \phi + D_0\rho_1''$$

$$3\rho_3 = (G_0\rho_2' + G_1\rho_1') \sin \phi \cos \phi + (G_0\rho_2 + G_1\rho_1 + G_2)(3 \cos^2 \phi - 1) \\ + (D_0\rho_2' + D_1\rho_1') \cot \phi + D_0\rho_2'' + D_1\rho_1''$$

where, ρ_1' , ρ_1'' , ρ_2' , and ρ_2'' stand for $d\rho_1/d\phi$, $d^2\rho_1/d\phi^2$, $d\rho_2/d\phi$, and $d^2\rho_2/d\phi^2$, respectively. From the above equations, we obtain

$$\rho_1(\phi) = -G_0 + 3G_0 \cos^2 \phi$$

$$\rho_2(\phi) = \frac{1}{2} G_0^2 - \frac{1}{2} G_1 + 3G_0D_0 - 3 \left(2G_0^2 - \frac{1}{2} G_1 + 3G_0D_0 \right) \cos^2 \phi \\ + \frac{15}{2} G_0^2 \cos^4 \phi$$

$$\rho_3(\phi) = -\frac{1}{6} G_0^3 + \frac{1}{2} G_0G_1 - \frac{1}{3} G_2 - 5G_0^2D_0 - 6G_0D_0^2 + 2G_0D_1 + G_1D_0 \\ + \left(\frac{13}{2} G_0^3 - 6G_0G_1 + G_2 + 54G_0^2D_0 + 18G_0D_0^2 - 6G_0D_1 - 3G_1D_0 \right) \cos^2 \phi \\ - 5 \left(\frac{9}{2} G_0^3 - \frac{3}{2} G_0G_1 + 13G_0^2D_0 \right) \cos^4 \phi + \frac{35}{2} G_0^3 \cos^6 \phi \quad (13)$$

From eqs. (9), (11), and (13), we obtain the approximate solution of the fundamental differential eq. (6) under the approximation of eq. (10), as follows:

$$\rho(\phi, t) = 1 - G_0(1 - 3 \cos^2 \phi)t \\ + \left[\frac{1}{2} G_0^2 - \frac{1}{2} G_1 + 3G_0D_0 - 3 \left(2G_0^2 - \frac{1}{2} G_1 + 3G_0D_0 \right) \cos^2 \phi \right. \\ \left. + \frac{15}{2} G_0^2 \cos^4 \phi \right] t^2 - \left[\frac{1}{6} G_0^3 - \frac{1}{2} G_0G_1 + \frac{1}{3} G_2 + 5G_0^2D_0 + 6G_0D_0^2 \right. \\ \left. - 2G_0D_1 - G_1D_0 - \left(\frac{13}{2} G_0^3 - 6G_0G_1 + G_2 + 54G_0^2D_0 + 18G_0D_0^2 \right) \cos^2 \phi \right. \\ \left. - 5 \left(\frac{9}{2} G_0^3 - \frac{3}{2} G_0G_1 + 13G_0^2D_0 \right) \cos^4 \phi + \frac{35}{2} G_0^3 \cos^6 \phi \right] t^3$$

$$\begin{aligned}
 & - 6G_0D_1 - 3G_1D_0) \cos^2 \phi + 5 \left(\frac{9}{2} G_0^3 - \frac{3}{2} G_0G_1 + 13G_0^2D_0 \right) \cos^4 \phi \\
 & \quad - \frac{35}{2} G_0^3 \cos^6 \phi \Big] t^3 + \dots \quad (14)
 \end{aligned}$$

A numerical calculation was made for an example. The result is shown in Figure 3.

3. Coefficient of Fiber Orientation

We can calculate the coefficient of molecular orientation of spun fiber by using the probability distribution function $\rho(\phi, t)$. The coefficient can be compared easily with an experimental result, e.g., birefringence.^{9a}

The following quantities are defined: f = coefficient of molecular orientation of spun fiber at a time t ; n_{\parallel} = refractive index of a fiber in the direction of the fiber axis at a time t ; n_{\perp} = refractive index of a fiber in the direction perpendicular to the fiber axis at a time t ; σ_{\parallel} = refractive index of single molecular segment or crystallite in the direction of the axis of segment or crystallite; σ_{\perp} = refractive index of single molecular segment or crystallite in the direction perpendicular to the axis of segment or crystallite; $(n_{\parallel} - n_{\perp})_{\phi}$ = constituent of an optical anisotropy of a fiber from the anisotropy $(\sigma_{\parallel} - \sigma_{\perp})$ of a single segment or crystallite inclined to the fiber axis at an angle ϕ .

The constituent $(n_{\parallel} - n_{\perp})_{\phi}$ is calculated as:^{9b, 10}

$$(n_{\parallel} - n_{\perp})_{\phi} = (\sigma_{\parallel} - \sigma_{\perp}) [1 - (3/2) \sin^2 \phi] \quad (15)$$

The optical anisotropy $(n_{\parallel} - n_{\perp})$ of a fiber can be calculated by eq. (16):

$$n_{\parallel} - n_{\perp} = \int_0^{\pi/2} (n_{\parallel} - n_{\perp})_{\phi} \rho(\phi, t) \sin \phi d\phi \quad (16)$$

From eqs. (5), (15), and (16), we obtain

$$n_{\parallel} - n_{\perp} = (\sigma_{\parallel} - \sigma_{\perp}) \left[1 - \frac{3}{2} \int_0^{\pi/2} \rho(\phi, t) \sin^3 \phi d\phi \right] \quad (17)$$

As the coefficient of molecular orientation of spun fiber is defined as:

$$f = (n_{\parallel} - n_{\perp}) / (\sigma_{\parallel} - \sigma_{\perp}) \quad (18)$$

we obtain the following expression from eqs. (17) and (18).

$$f = 1 - \frac{3}{2} \int_0^{\pi/2} \rho(\phi, t) \sin^3 \phi d\phi \quad (19)$$

Substituting eq. (14) into eq. (19), we obtain

$$\begin{aligned}
 & = \frac{2}{5} G_0 t + \frac{1}{5} \left(\frac{2}{7} G_0^2 - 6G_0D_0 + G_1 \right) t^2 \\
 & - \frac{2}{5} \left(\frac{2}{21} G_0^3 + \frac{4}{7} G_0^2D_0 - 6G_0D_0^2 - \frac{1}{7} G_0G_1 + 2G_0D_1 + G_1D_0 - \frac{1}{3} G_2 \right) t^3 \\
 & \quad + \dots \quad (20)
 \end{aligned}$$

A numerical calculation was made for an example; the result is shown in Figure 4.

Considering eq. (21):

$$\int_0^t Gdt = G_0t + \frac{1}{2} G_1t^2 + \frac{1}{3} G_2t^3 + \dots \quad (21)$$

we obtain eq. (22) from eq. (20).

$$f = \frac{2}{5} \int_0^t Gdt - \frac{6}{5} G_0 \left(D_0 - \frac{1}{21} G_0 \right) t^2 - \frac{2}{5} \left(\frac{2}{21} G_0^3 + \frac{4}{7} G_0^2 D_0 - 6G_0 D_0^2 - \frac{1}{7} G_0 G_1 + 2G_0 D_1 + G_1 D_0 \right) t^3 + \dots \quad (22)$$

The integral in eq. (22) can be expressed as:

$$\int_0^t Gdt = \int_0^x \frac{G}{V} dx = \int_0^x \frac{1}{V} \left(\frac{dV}{dx} \right) dx = \int_0^x \frac{d \ln V}{dx} dx = \ln (V/V_0) \quad (23)$$

where V_0 is the initial velocity (at $x = 0$ or $t = 0$).

Considering eq. (23), we obtain from eq. (22):

$$f = \frac{2}{5} \ln \left(\frac{V}{V_0} \right) - \frac{6}{5} G_0 \left(D_0 - \frac{1}{21} G_0 \right) t^2 - \frac{2}{5} \left(\frac{2}{21} G_0^3 + \frac{4}{7} G_0^2 D_0 - 6G_0 D_0^2 - \frac{1}{7} G_0 G_1 + 2G_0 D_1 + G_1 D_0 \right) t^3 + \dots \quad (24)$$

4. Solution Expressed by the Space Coordinate as a Variable

Another approach can be considered in obtaining the solution of the fundamental equation. In this section we use the distance from a spinneret orifice as the variable.

Using the following relation as to the velocity V of a flow, we can change the variable from t to x :

$$V = dx/dt \quad (25)$$

If we take the above relation into account, the fundamental equation, eq. (6), becomes:

$$V \frac{\partial}{\partial x} (\rho \sin \phi) = - \frac{\partial}{\partial \phi} \left(\rho \phi \sin \phi - D \sin \phi \frac{\partial \rho}{\partial \phi} \right) \quad (6')$$

where, $\rho(\phi, x)$ is the probability distribution function at $x = x$.

When we express V , G , and D as follows:

$$V(x) = \bar{V}_0 + \bar{V}_1 x + \bar{V}_2 x^2 + \bar{V}_3 x^3 + \dots \quad (26)$$

$$G(x) = \bar{G}_0 + \bar{G}_1 x + \bar{G}_2 x^2 + \dots \quad (27)$$

$$= \bar{V}_1 + 2\bar{V}_2 x + 3\bar{V}_3 x^2 + \dots \quad (27)$$

$$D(x) = \bar{D}_0 + \bar{D}_1 x + \dots \quad (8')$$

The above discussion indicates that the applicability of the approximate, theoretical results is extremely limited in the neighborhood of spinneret under practical melt spinning conditions.

However, the theory should be useful in a case where the polymer temperature is near its melting temperature and the velocity gradient or the rate of extension is small.

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Résumé

Les solutions obtenues par approximation de l'équation fondamentale tridimensionnelle concernant l'orientation moléculaire d'une fibre filée, ont été obtenues en supposant un modèle ellipsoïdal rigide pour les segments moléculaires ou une structure paracristalline. On effectue une approximation de la vitesse d'extension G (sec^{-1}) d'une fibre fondue et de la constante de diffusion rotationnelle D (sec^{-1}) du segment en fonction du temps t (sec), comme suit:

$$G = G_0 + G_1 t + G_2 t^2 + \dots$$

$$D = D_0 = D_1 t + \dots$$

Dans les conditions ci-dessous: $1 \gg G_0 t \gg G_1 t^2 \gg G_2 t^3 \gg \dots$ and $1 \gg D_0 t \gg D_1 t^2 \gg \dots$, on trouve un coefficient f d'orientation moléculaire de la fibre fondue égale à:

$$f = \frac{2}{5} \int_0^t G dt - \frac{6}{5} G_0 \left(D_0 - \frac{1}{21} G_0 \right) t^2$$

$$- \frac{2}{5} \left(\frac{2}{21} G_0^3 + \frac{4}{7} G_0^2 D_0 - 6 G_0 D_0^2 - \frac{1}{7} G_0 G_1 + 2 G_0 D_1 + G_1 D_0 \right) t^3 + \dots$$

Le domaine d'application de l'approximation théorique ci-dessous est extrêmement limité ou voisinage de la filière dans les conditions pratiques du filage à l'état fondu. Cependant la théorie aurait son utilité dans le cas où la température du polymère serait proche de sa température de fusion et où la vitesse d'extension de la fibre filée serait faible.

6. Velocity and Velocity Gradient of the Polymer Stream

The coefficient of fiber orientation can be calculated from eqs. (20), (22), (24), (20'), and (24'), using G , V , and D . The quantities G and V have been measured by several authors.^{11,12} The measurements of G and V are relatively easy. When we define the following quantities: σ = density of

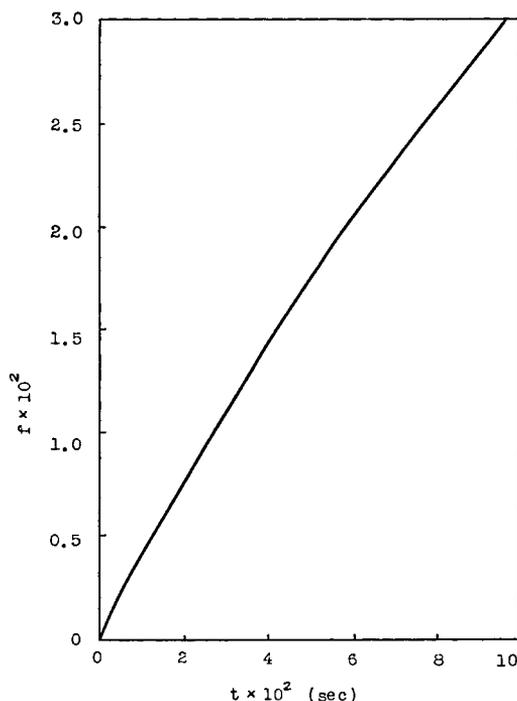


Fig. 4. Coefficient of molecular orientation f of spun fiber as a function of time t . Calculation was made by eq. (20) assuming that $G_0 = 1 \text{ sec.}^{-1}$; $G_1 = G_2 = \dots = 0$; $D_0 = 1 \text{ sec.}^{-1}$; $D_1 = \dots = 0$.

the fiber (grams per cubic centimeter), d = diameter of the fiber (centimeters), Q = mass extruded from a spinneret orifice in unit time (grams per second). The velocity of a fiber is given by:

$$V = 4Q/\pi\sigma\bar{d}^2 \quad (30)$$

and the velocity gradient is given by:

$$G = -(8Q/\pi\sigma\bar{d}^3)(d\bar{d}/dx) \quad (31)$$

We can calculate V and G from eqs. (30) and (31), respectively, whenever the diameter \bar{d} has been measured.

7. Rotational Diffusion Constant of Segment

The rotational diffusion constant D of rodlike segments is given as:¹³

$$D = 8kT/\pi\mu\bar{l}^3 \quad (32)$$

where l = length of the rodlike segment (centimeters), μ = microscopic, local, shear viscosity¹⁴ of a medium for the segment, (grams per centimeter per second), T = absolute temperature, k = Boltzmann's constant (1.38×10^{-16} erg. deg. $^{-1}$ molecule $^{-1}$).

The rodlike segment can be regarded as a kind of a rotational ellipsoid. The microscopic, local viscosity is somewhat different generally from the usual, macroscopic viscosity.¹⁴ However, these quantities may be of the same order of magnitude.

From eq. (32), we know that the rotational diffusion constant D is a function of l , μ , and T . As the viscosity is a function of both the molecular weight and the temperature of the medium (molten fiber), we can estimate the diffusion constant whenever we know an appropriate segment length, the molecular weight, and the temperature of the molten fiber.

DISCUSSION

In this section we compare the theory with results of an experiment published previously¹² and discuss the scope of applicability of the theory.

1. Velocity and Velocity Gradient Profiles

Ziabicki's data¹² for polycapronamide are used for the discussion. The spinning conditions (No. A8) were as follows: spinneret orifice diameter, 0.1 cm.; denier of spun fiber, 40 den.; initial polymer temperature, 275°C.; initial melt viscosity, 2000 g. cm. $^{-1}$ sec. $^{-1}$; spinning speed, 1093 cm. sec. $^{-1}$; initial stream speed, 5.73 cm. sec. $^{-1}$; distance where the stream speed saturates, 1400 cm.

As shown in Figure 5, the velocity gradient profile can be approximated as follows:

$$G(x) = 4.2 + 0.26x + 0.006x^2 + \dots, 0 < x < 30(\text{cm.}) \quad (33)$$

Another approximation of the velocity gradient profile for a wider range of x may be possible as follows:

$$G(x) = 4.2 + 0.79x - 0.012x^2 + \dots, 0 < x < 65(\text{cm.}) \quad (34)$$

However, the approximation expressed by eq. (34) should be inadequate for use in the approximate solution of eq. (6), because the approximate solution, eq. (20) or (20'), is valid only near the spinneret orifice where the conditions expressed by eq. (10) or (10') are realized.

From the spinning conditions and by comparing eq. (27) with eq. (33), we obtain the following values for the spinning.

$$\bar{V}_0 = 5.73 \text{ cm. sec.}^{-1}$$

$$\bar{V}_1 = 4.2 \text{ sec.}^{-1}$$

$$\bar{V}_2 = 0.13 \text{ cm.}^{-1} \text{ sec.}^{-1}$$

$$\bar{V}_3 = 0.002 \text{ cm.}^{-2} \text{ sec.}^{-1}$$

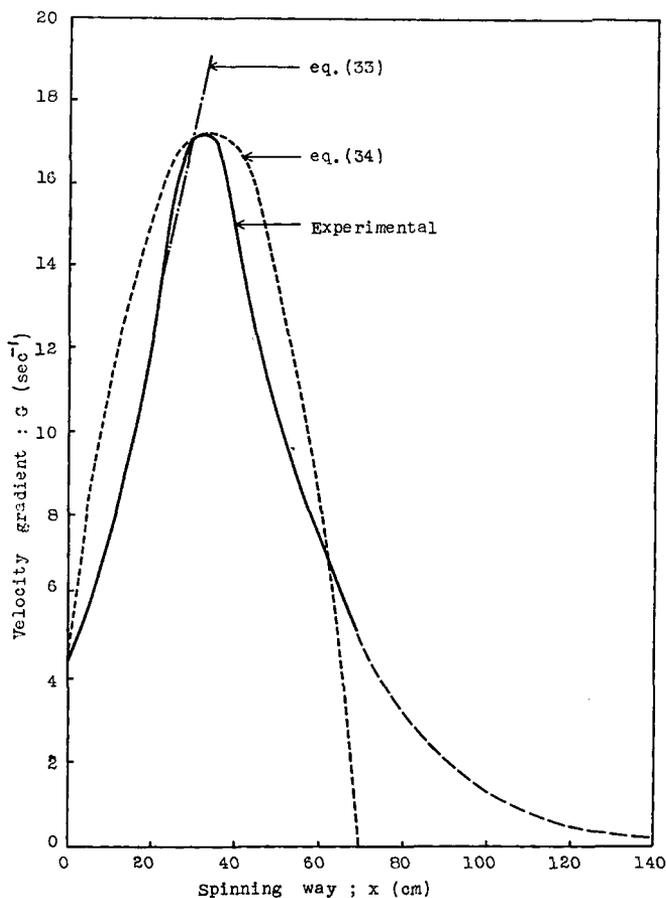


Fig. 5. Velocity gradient G as a function of the distance x from spinneret orifice, and its approximations:¹² eq. (33), adequate approximation; eq. (34), inadequate approximation.

The initial velocity \bar{V}_0 was calculated from the orifice diameter, spinning speed, spun fiber denier, and the density of the melt polymer (1.08 g. cm.^{-3}) disregarding the stream broadening¹⁵ in the neighborhood of the orifice. Then the true value of \bar{V}_0 is less than $5.73 \text{ cm. sec.}^{-1}$

2. Scope of Applicability of Approximate Solution Taking into Account the Velocity Profile

By substituting the values of \bar{V}_0 , \bar{V}_1 , \bar{V}_2 , and \bar{V}_3 into eq. (10'), we can determine the region where the approximate solution, eqs. (20') or (24'), is valid. We obtain the region as follows:

$$0 < x < 0.2 \text{ cm.}$$

We know that the approximate solution has poor applicability in practical melt spinning conditions.

3. Scope of Applicability of Approximate Solution Taking into Account the Rotational Diffusion Constant

We can estimate the dimensions of structural units by means of x-ray diffraction. The large-angle scattering suggests a unit cell with $a = 9.45$ Å., $b = 8.02$ Å., and $c = 17.08$ Å.¹⁶ in nylon 6 $[-\text{NH}(\text{CH}_2)_5\text{CO}-]_n$, where the dimension $c = 17.08$ Å. corresponds to two monomer units along the fiber axis.

On the other hand, another dimension of 73–76 Å. is suggested by the small-angle scattering in nylon 6.¹⁷ We could use these dimensions in the estimation of the rotational diffusion constant. We obtain the following values from eq. (32).

Case 1:

$$T = 548^\circ\text{K.}$$

$$\mu = 2000 \text{ g. cm.}^{-1} \text{ sec.}^{-1}$$

$$l = 1.7 \times 10^{-7} \text{ cm.}$$

$$D = 1.96 \times 10^4 \text{ sec.}^{-1}$$

Case 2:

$$T = 473^\circ\text{K.}$$

$$\mu = 10^5 \text{ g. cm.}^{-1} \text{ sec.}^{-1}$$

$$l = 7.5 \times 10^{-7} \text{ cm.}$$

$$D = 3.94 \text{ sec.}^{-1}$$

Case 1 may represent a polymer stream in the neighborhood of the spinneret orifice in a melt spinning of nylon 6, because the temperature is considerably higher than the melting temperature and the melt viscosity is suitable for a practical melt spinning and the dimension of the structural unit (polymer segment) is small.

Case 2 may be considered to correspond to a polymer stream which is a considerable distance from the spinneret orifice in spinning of nylon 6, because the temperature is lower than the melting temperature and the viscosity is considerably high and the larger structure (crystallite) has been produced.

By substituting the values of \bar{V}_0 and \bar{D}_0 into eq. (10'), we can ascertain the region where the approximate solution, eqs. (20') or (24'), is valid. We obtain the region as follows:

For case 1:

$$0 < x < 6 \times 10^{-5} \text{ cm.}$$

For case 2:

$$0 < x < 0.3 \text{ cm.}$$

The above discussion indicates that the applicability of the approximate, theoretical results is extremely limited in the neighborhood of spinneret under practical melt spinning conditions.

However, the theory should be useful in a case where the polymer temperature is near its melting temperature and the velocity gradient or the rate of extension is small.

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Résumé

Les solutions obtenues par approximation de l'équation fondamentale tridimensionnelle concernant l'orientation moléculaire d'une fibre filée, ont été obtenues en supposant un modèle ellipsoïdal rigide pour les segments moléculaires ou une structure paracristalline. On effectue une approximation de la vitesse d'extension G (sec^{-1}) d'une fibre fondue et de la constante de diffusion rotationnelle D (sec^{-1}) du segment en fonction du temps t (sec), comme suit:

$$G = G_0 + G_1 t + G_2 t^2 + \dots$$

$$D = D_0 = D_1 t + \dots$$

Dans les conditions ci-dessous: $1 \gg G_0 t \gg G_1 t^2 \gg G_2 t^3 \gg \dots$ and $1 \gg D_0 t \gg D_1 t^2 \gg \dots$, on trouve un coefficient f d'orientation moléculaire de la fibre fondue égale à:

$$f = \frac{2}{5} \int_0^t G dt - \frac{6}{5} G_0 \left(D_0 - \frac{1}{21} G_0 \right) t^2$$

$$- \frac{2}{5} \left(\frac{2}{21} G_0^3 + \frac{4}{7} G_0^2 D_0 - 6 G_0 D_0^2 - \frac{1}{7} G_0 G_1 + 2 G_0 D_1 + G_1 D_0 \right) t^3 + \dots$$

Le domaine d'application de l'approximation théorique ci-dessous est extrêmement limité ou voisinage de la filière dans les conditions pratiques du filage à l'état fondu. Cependant la théorie aurait son utilité dans le cas où la température du polymère serait proche de sa température de fusion et où la vitesse d'extension de la fibre filée serait faible.

Zusammenfassung

Unter der Annahme eines starren Ellipsoides als Modell für die Molekülsegmente oder die parakristalline Struktur wurden Näherungslösungen der dreidimensionalen Fundamentalgleichung für die molekulare Orientierung einer gesponnenen Faser erhalten. Die Dehnungsgeschwindigkeit G (sec^{-1}) einer geschmolzenen Faser und die Rotations-Diffusions-konstante D (sec^{-1}) des Segmentes werden durch folgende Näherungsgleichungen als Funktionen der Zeit t (sec) wiedergegeben:

$$\begin{aligned} G &= G_0 + G_1 t + G_2 t^2 + \dots \\ D &= D_0 + D_1 t + \dots \end{aligned}$$

Unter Beachtung der Bedingungen $1 \gg G_0 t \gg G_1 t^2 \gg G_2 t^3 \gg \dots$ und $1 \gg D_0 t \gg D_1 t^2 \gg \dots$ findet man für den Koeffizienten der Molekülorientierung f der gesponnenen Faser:

$$\begin{aligned} f &= \frac{2}{5} \int_0^t G dt - \frac{6}{5} G_0 \left(D_0 - \frac{1}{21} G_0 \right) t^2 \\ &\quad - \frac{2}{5} \left(\frac{2}{21} G_0^3 + \frac{4}{7} G_0^2 D_0 - 6 G_0 D_0^2 - \frac{1}{7} G_0 G_1 + 2 G_0 D_1 + G_1 D_0 \right) t^3 + \dots \end{aligned}$$

Unter den technischen Schmelzspinnbedingungen ist die Anwendbarkeit dieser aus der Theorie hergeleiteten Näherungslösung in der Nähe der Spinn Düse sehr beschränkt. Die Theorie sollte aber für den Fall brauchbar sein, dass die Temperatur des Polymeren in der Nähe seines Schmelzpunktes liegt und die Dehnungsgeschwindigkeit beim Spinnen der Faser niedrig ist.

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