

Melt Spinning of Polymers I. An Elementary Framework for Analyzing the Development of Orientation

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Synopsis

An elementary framework to describe the evolution of orientational order in melt spinning of polymers is presented. By dividing this process into fundamentally different zones of structure development (melt zone with $T >$ temperature of initiation of crystallization T_c ; crystallization zone with $T_c > T > T_g$; static zone with $T < T_g$), it is shown that a generalized framework can be developed into which different homopolymers can be fitted on the basis of their physical transition temperatures. Sources of deviation from the simplified framework are also discussed.

INTRODUCTION AND FRAMEWORK

The desired end product from a polymer fabrication process is a material possessing the geometric shape and size and the physical properties required for a specific end use. The process conditions determine the external geometric features as well as the internal organization of structural units (morphology) of the material produced. The physical properties of the product are derived from the intrinsic properties of the polymer and the morphology of the product. For example, one knows from experience that the properties of a fabric are derived from the spatial organization and the intrinsic properties of the structural units, namely, the yarns, in it. The properties of the yarns, in turn, are governed by those of the fibers and their organization, which includes the size and shape of filaments, the twist, and the nature of migration. Intuition and sophisticated indirect experience show that one can proceed further along these lines but one no longer has a clear visual image of the morphology supporting this effort. Building a description of the morphology based on experimental techniques, such as x-ray diffraction and electron microscopy, becomes somewhat subjective. Nevertheless, if the morphology of a fiber can be characterized quantitatively, it would be advantageous in establishing a rational basis of correlations between the parameters of a fiber formation process and the properties of the fibers produced in it. Considerable work in this field has been reported in the literature, and much of it is discussed in detail by Ziabicki.¹ The complex distribution of textures that can exist in a polymeric fiber produced under different conditions of processing makes it a formidable task to quantitatively relate the structure to the physical properties.

In this presentation we will set aside for the most part the question of the precise arrangement of morphological units and concentrate, instead, on a set

of measurable morphological parameters that may be relevant in providing a bridge between the process conditions and the properties of melt-spun fibers. In this connection we assume that a solid fiber contains:

1. Crystalline regions where the segments of molecules are packed in a repetitive three-dimensional array (sometimes only in two dimensions) of the atoms in the segments

2. Noncrystalline* regions where such repetitive order is absent.

The discussion here will be concentrated primarily on the relative extents of such regions and the orientations of chains within these regions with respect to the fiber axis. These parameters have been shown to provide a reasonable basis for obtaining morphology-property correlations in synthetic fibers.^{1,2} Since all the polymers of concern to us here are melted into an essentially isotropic amorphous mass[†] before being shaped into filaments, we consider initially some simple concepts of orientation induced by flow and possible crystallization of this oriented polymer in a melt spinning threadline. Experimental results from specific polymers will be reviewed in Part II of this sequence.

With the exception of recently developed high-speed spinning processes, a major portion of the high orientation, especially of the uncrystallized fibers, necessary in a useful fiber is introduced in a drawing operation subsequent to melt spinning. The orientation developed in melt spinning is, however, significant in the sense that small changes can cause large changes in the response in the drawing operation. Structural and dimensional variations in undrawn yarns are also major sources of undesirable variations in the ultimate drawn yarn.

Although progress has been made in the mathematical analysis of the evolution of order in melt spinning,³⁻⁶ we are still far from quantitative predictions of measurable morphological parameters based on measurable polymer and process parameters. For this reason, the mathematical framework in the following will be restricted to those cases in which the results can be readily identified in relation to the trends in melt spinning processes.

The most comprehensive recent source of technical information on the fundamental aspects of melt spinning is the book by Ziabicki.¹ A simplified analysis of flow-induced orientation in melt spinning and the effects of process variables has been given by Hagler.⁷ (It is included in the present analysis with appropriate modifications.)

ZONES OF STRUCTURE FORMATION IN MELT SPINNING

A filament in a melt spinning threadline is shown in Figure 1. Flow-induced orientation of polymer chains occurs in the extensional and shear flow at the entrance to the spinneret capillary, in the shear flow inside the capillary, and in the essentially extensional flow of the deforming threadline. The data available in the literature^{1,8-15} show that the orientation in the capillary is almost completely lost by relaxation after the material exits the capillary, but the effects of the orientation introduced in the threadline, where simultaneous

*We use the terms "amorphous" and "noncrystalline" interchangeably in this presentation.

†We do not consider in this review polymers that may form liquid crystalline melts.

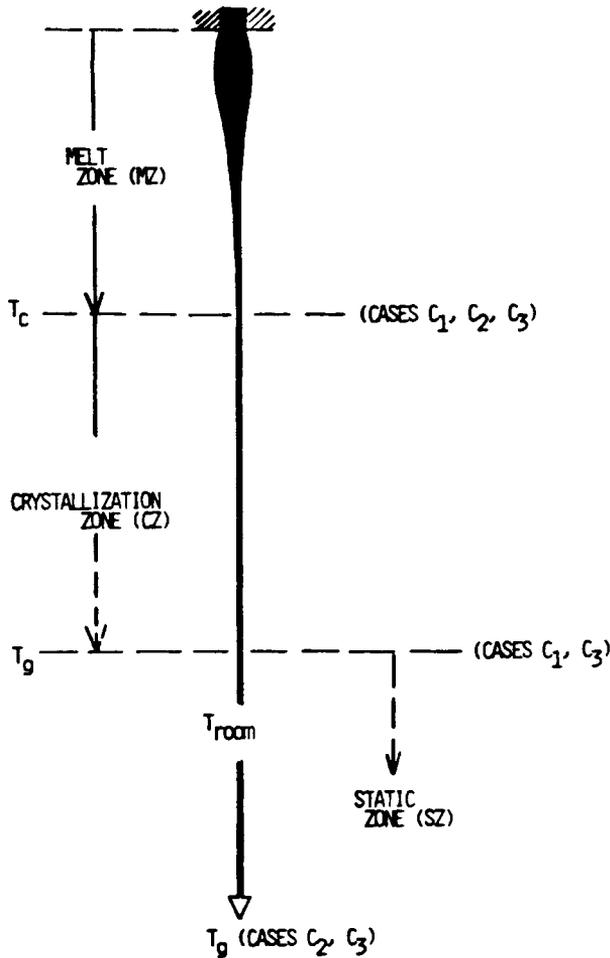


Fig. 1. Zones of structure development in a melt spinning threadline. C₁, crystallizable polymer with $T_g > T_{room}$; C₂, crystallizable polymer with $T_g < T_{room}$; C₃, crystallizable polymer with $T_g > T_{room}$ when dry but $T_g < T_{room}$ in the presence of moisture.

deformation and cooling occur, persists in the as-spun fiber. Essentially all the deformation in the threadline occurs prior to the onset of either glass transition, in the case of noncrystallizing polymers, or nucleation, in the case of crystallizing polymers. This deformation zone will be referred to as the *melt zone* (MZ) in this study. In the case of noncrystallizing polymers, the orientation introduced in the melt zone is "frozen in" with little change until subsequent processes. This zone will be referred to as the *static zone* (SZ). With crystallizable polymers, the melt zone is followed by the *crystallization zone* (CZ) where the oriented precursor leaving the melt zone can crystallize. Depending on whether the glass transition temperature T_g is lower or higher than the room temperature T_r , the material either stays in the CZ or enters the SZ. As we shall see in later sections, this classification can be used effectively in developing a generalized scheme for orientation development in melt spinning that can be applied to the study of different polymers. A

somewhat unique situation arises with such polymers as nylon 6, whose effective T_g when dry is higher than room temperature but is lowered to a temperature below it ($\sim 0^\circ\text{C}$) when equilibrated with the moisture under normal spinning room conditions. As we will see later, such cases can also be accommodated in the present framework.

ORIENTATION IN THE MELT ZONE

In the region between the capillary exit* and the position of final diameter, the bulk fiber is stretched and this stretching tends to give the chain molecules a degree of orientation in the direction of the fiber axis. The molecules that are consequently displaced from their preferred coiled state tend to relax, and this can be characterized by an average orientational relaxation time τ . A very viscous material, for example, would have a large τ and a very freely flowing one would have a small τ . In the stretching portion of the spinline, the molecules are thus oriented to an equilibrium level dictated by the two opposing forces caused by the rates of deformation and relaxation. As the spinning material travels downward toward the position of final diameter, the viscosity and relaxation time become larger and the rate of deformation becomes smaller. With the transition from the melt zone to either the static zone or the crystallization zone, the relaxation time becomes essentially infinite and the orientation introduced in the melt zone is either "frozen" into the fiber or altered through crystallization, essentially without relaxation.

The orientation developed in the MZ is only weakly related to the spin draw ratio, i.e., V_l/V_0 where V_l is the take-up speed and V_0 is the extrusion velocity. Rather, the orientation is related to how rapidly one stretches the fiber and how rapidly one cools the fiber while the molecules are in their oriented state. Ziabicki and Kedzierska^{16,17} found that the orientation of nylon 6, PET, and polystyrene increased with the difference $V_l - V_0$. It has been found by various authors that spinline orientation increases with polymer molecular weight and decreases with extrusion temperature (see references in Ref. 18). Sippel,¹⁹ in the early 1940s, postulated that the factor responsible for spinning orientation is the longitudinal velocity gradient dV/dx , where V is the spinline velocity at any position.

A very important unifying relation was found by Ziabicki and Kedzierska^{16,17} and others.^{12,13,20-22} These authors found for a wide range of spinning conditions that the orientation of spun fibers could be directly related to the spinline stress existing at the position of final diameter.

Ziabicki¹ derived for a simple case an expression for the ultimate orientation factor f_l at the take-up point.

$$f_l = \text{const} \frac{F_{\text{ext}}}{W} (V_l - V_0 e^{(1-\alpha)W/\rho b F_{\text{ext}} V_l}) \quad (1)$$

where F_{ext} = force at position of final diameter, W = mass flow rate, V_l =

*To be more precise, one should consider the position of maximum fiber diameter due to die swell slightly downstream of the exit.

take-up velocity, V_0 = extrusion velocity, α = spin-draw ratio V_l/V_0 , ρ = density, $b = \tau/\eta$, and η = extrusion viscosity and τ = relaxation time.

In other terms,

$$f_l \cong \text{const}(hR)\eta W^{-1}(\ln L)(V_l - V_0 e^{\text{const} W(1-L)/\alpha R \eta V_l(\ln L)}) \quad (2)$$

where h = heat transfer coefficient, R = final fiber radius, and L = length of spinline.

The orientation factor is defined as

$$\frac{3\langle \cos^2 \theta \rangle - 1}{2}$$

where $\langle \cos^2 \theta \rangle$ is the average of $\cos^2 \theta$ and θ is the inclination of chain segments with respect to the fiber direction.

These equations were used to make qualitative predictions of the effect of changes in the spinning parameters on the orientation of spun fibers. It is predicted that the orientation of fibers increases with heat transfer coefficient, take-up velocity, extrusion viscosity, and reciprocal flow rate, the effect of spin-draw ratio α being of only secondary importance. Since this analysis considers only the deformation-induced orientation and ignores the changes that might occur with possible crystallization of this oriented precursor in the threadline, the conclusions should be regarded as applicable only to the orientation of the material leaving the melt zone.

A much simpler equation may be obtained that will qualitatively predict the effects of changes of all the variables involved in the spinning process. The equation relates certain spinning parameters to the spinline stress existing at the position of final filament diameter. If one considers the simple elongation of a rod, the rate of elongation at any time is given in terms of the instantaneous length l as

$$\dot{\epsilon} = \frac{1}{l} \frac{dl}{dt} \quad (3)$$

If the rod is a Newtonian fluid, the axial stress is given by

$$\sigma_{xx} = 3\mu \frac{1}{l} \frac{dl}{dt} \quad (4)$$

where μ = Newtonian viscosity. For the case of isothermal stretching of a Newtonian spinline, in which the diameter varies,

$$\sigma_{xx}(x) = 3\mu \frac{dv}{dx} = 3\mu \dot{\epsilon}(x) \quad (5)$$

For non-Newtonian melts and for nonisothermal processes, eq. (5) has to be changed to

$$\sigma_{xx}(x) = \eta \dot{\epsilon}(x) \quad (6)$$

The apparent elongational viscosity η is not a constant and is not a function only of the instantaneous values of $\dot{\epsilon}$ and temperature, but depends on the entire history of deformation. We may define for a spinning process an average elongational rate

$$\bar{\dot{\epsilon}} = \int_0^{L_m} \frac{dv}{dx} dx \approx \frac{V_L - V_0}{L_m} \quad (7)$$

where L_m = length over which the spinline deforms. It may then be postulated that the spinline stress is directly related to $\bar{\dot{\epsilon}}$ and an average apparent elongational viscosity $\bar{\eta}$.

$$\text{Stress} = \sigma(\bar{\eta}, \bar{\dot{\epsilon}}) \quad (8)$$

and that as $\bar{\eta}$ or $\bar{\dot{\epsilon}}$ increases, so does stress and, therefore, orientation of the fiber at the end of the melt zone.

The overall orientation of the single phase material leaving the MZ can be conveniently measured with birefringence, ΔN_m , which will then be a function of $\bar{\eta}$ and $\bar{\dot{\epsilon}}$; i.e.,

$$\Delta N_m = \Delta N_m(\bar{\eta}, \bar{\dot{\epsilon}}) \quad (9)$$

Using these simple concepts, one can predict the influence of the various processing parameters on the birefringence of the material leaving the MZ (entering the CZ). The effects of some of the parameters are given in Table I.

THE CRYSTALLIZATION ZONE

When the oriented, uncrystallized material leaves the MZ, it can begin to crystallize. A simplified but useful model of the resulting morphology is that of a two-component morphology, consisting of crystalline and noncrystalline regions. It is necessary to know the extent and orientation of the two components in order to develop a rational link between the process and the properties of the resulting fibers.

TABLE I
Factors Governing Orientation in Melt Zone

$$\Delta N_m = \Delta N_m(\bar{\eta}, \bar{\dot{\epsilon}}) \quad \bar{\dot{\epsilon}} = \frac{V_L - V_0}{L_m} \approx \frac{V_L}{L_m}$$

Increase in	Effect on $\bar{\eta}$ or $\bar{\dot{\epsilon}}$	ΔN_m
Winding speed	$\dot{\epsilon} \uparrow$	$\uparrow\uparrow$
Molecular weight	$\eta \uparrow$	$\uparrow\uparrow$
Spinning temperature	$\eta \downarrow \dot{\epsilon} \downarrow$	$\downarrow\downarrow$
Cooling rate		
Water quench	$\dot{\epsilon} \uparrow$	$\uparrow\uparrow$
Quench airflow rate	$\dot{\epsilon} \uparrow$	$\uparrow\uparrow^a$
		\uparrow
Output	$\dot{\epsilon} \downarrow$	\downarrow
Spinneret hole size	$\dot{\epsilon} \uparrow$	\uparrow
Cross-sectional shape	$\dot{\epsilon} \uparrow$	\uparrow

^a Near the spinneret.

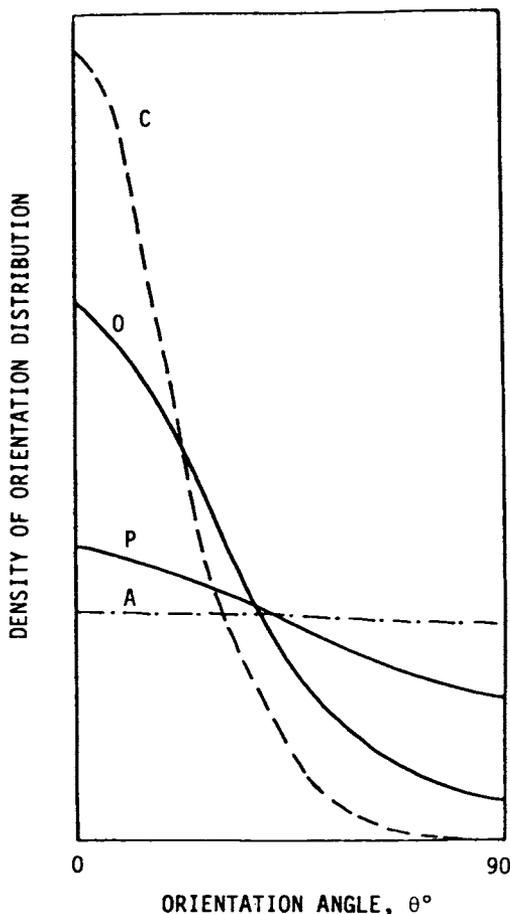


Fig. 2. Schematic representation of orientation distributions resulting from crystallization. Orientation distributions of all the segments prior to crystallization (P), crystallized segments (C), and uncrystallized segments (A); the weighted combination of C and A is the orientation distribution of all the segments following crystallization (O). (From Ref. 6.)

Crystallization in Oriented Polymers

Before discussing the evolution of structure in the CZ of a melt spinning threadline, we examine the nature of crystallization in an initially amorphous precursor that exhibits a preferred orientation.

Figure 2 shows an arbitrary distribution of chain segments in different directions with respect to the preferred direction in the precursor, i.e., in the material that is about to undergo crystallization. Detectable crystallization can occur in polymers only between the glass transition temperature T_g , and the melting temperature T_m . In Figure 2, the orientation angle represents the inclination of chain segments with respect to the preferred direction (for example, the direction parallel to the fiber axis).

Crystallization involves forming a small but stable nucleus between a critical number of segments to which chain segments are added until the growth process terminates for one reason or another. Polymers would rarely crystallize completely. Such constraints as entanglements, which exist in the

mass of polymer chains, prevent a fully crystalline material from developing even when it is held for a long time in the crystallization range, i.e., between T_g and T_m . Formation of a stable nucleus in a given direction is an event dictated by the chance that the necessary critical number of molecular segments within a small volume are aligned essentially in the same direction.²³ This requirement increases the likelihood of forming a nucleus with the chain direction close to the preferred direction (Fig. 2).

So far we have shown that when an oriented precursor crystallizes, the crystals formed should have an even higher orientation than the precursor. In many instances, it is more important to know the orientation of the segments that have been left uncrystallized. If we consider two precursor segments around a growing crystal, the one that is less inclined with respect to the segments in the crystal is more likely to be incorporated in the crystal than the other. In a system in which an increasing number of crystals grow closer to the preferred direction, the inference is that those precursor segments that are closer to the preferred direction are more likely to crystallize when compared with segments at higher inclination to that direction. Thus the consequences of crystallization in an oriented precursor (Fig. 2) are that (1) the crystals formed are more oriented than the precursor and (2) the part left uncrystallized (amorphous) is less oriented than the precursor.

An interesting consequence of the high orientation of crystalline nuclei along the preferred direction and the preferential incorporation into crystals of precursor segments that are oriented close to this direction is that it may possibly lead to a distribution of uncrystallized segments with their preferred direction normal to the initial preferred direction. If primary nuclei appear subsequently, they would reflect this change in orientation distribution, and thus a bimodal orientation distribution of crystals may be generated (Fig. 3).

A quantitative framework for the kinetic process of formation of primary crystalline nuclei and the preferred incorporation of polymer segments into these during crystal growth is given in Reference 6. The results of this analysis are summarized in the following.

Let $f_p(\vec{\eta})$ be the orientation density function (ODF) of an oriented polymer in which crystallization is set to begin. $\vec{\eta}$ is the vector of orientation angles (θ, ϕ, λ) with respect to the coordinate axes.

Let $f_c(\vec{\eta})$ be the ODF of crystals growing in the polymer. With the assumption that the ODF of crystals is the same as that of the primary crystalline nuclei, $f_n(\vec{\eta})$, i.e.,

$$f_c(\vec{\eta}) = f_n(\vec{\eta}) = F_n(f_p(\vec{\eta}))$$

we can obtain $f_c(\vec{\eta})$ from such theories as those of Ziabicki and Jarecki.³ Let $g_a(\vec{\eta}, X_a/\vec{\eta}_c)$ be the ODF of amorphous segments resulting from the growth of a crystal with orientation vector $\vec{\eta}_c$. X_a is the mass fraction of amorphous segments. Then,

$$g_a(\vec{\eta}, X_a/\vec{\eta}_c) = [f_p(\vec{\eta})/X_a] e^{-K_\beta C}$$

where β is the angle between $\vec{\eta}$ and $\vec{\eta}_c$, K_β is the rate constant for relative incorporation of segments at different inclinations to the growing crystal, and

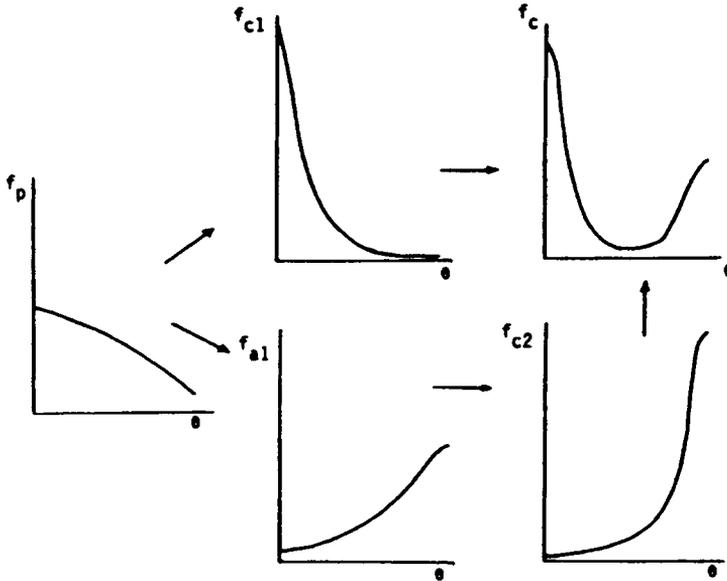


Fig. 3. Illustration of the development of two sets of crystals in melt spinning with preferred axial and lateral orientations; f_p , orientation distribution function (ODF) of precursor; f_{c1} , ODF of crystals appearing initially in the process; f_{a1} , ODF of segments remaining uncrystallized at an intermediate stage; f_{c2} , ODF of crystals appearing in the second stage; f_c , ODF of all crystals at the completion of the crystallization process. (From Ref. 6.)

C is given by

$$\int \frac{f_p(\vec{\eta})}{X_a} e^{-K_\beta C} d^3\vec{\eta} = 1$$

($d^3\vec{\eta}$ is the volume element in the space of orientation angles). The ODF of all the amorphous segments in the sample is then given by

$$f_a(\vec{\eta}, X_a) = \frac{f_p(\vec{\eta})}{X_a} \int F_n(f_p(\vec{\eta})) e^{-K_\beta C} d^3\vec{\eta}_c$$

Orientation in the Crystallization Zone

Figure 4 shows the development of orientation in the MZ and the consequences of crystallization in the CZ of the melt spinning threadline of a homopolymer. The low orientation of the uncrystallized segments is primarily the result of the higher rate at which the segments in the precursor with lower inclinations to the fiber axis are incorporated into the growing crystals. The overall orientation shows a sharp increase because of the higher average orientation of the crystals formed when compared with that of the precursor segments prior to their incorporation in crystals.

It is well known that the rate of crystallization at all temperatures between T_g and T_m increases significantly with precursor orientation and/or stress during crystallization. Thus, increased stress in the threadline should increase the likelihood of the crystallization-induced reordering discussed here. The

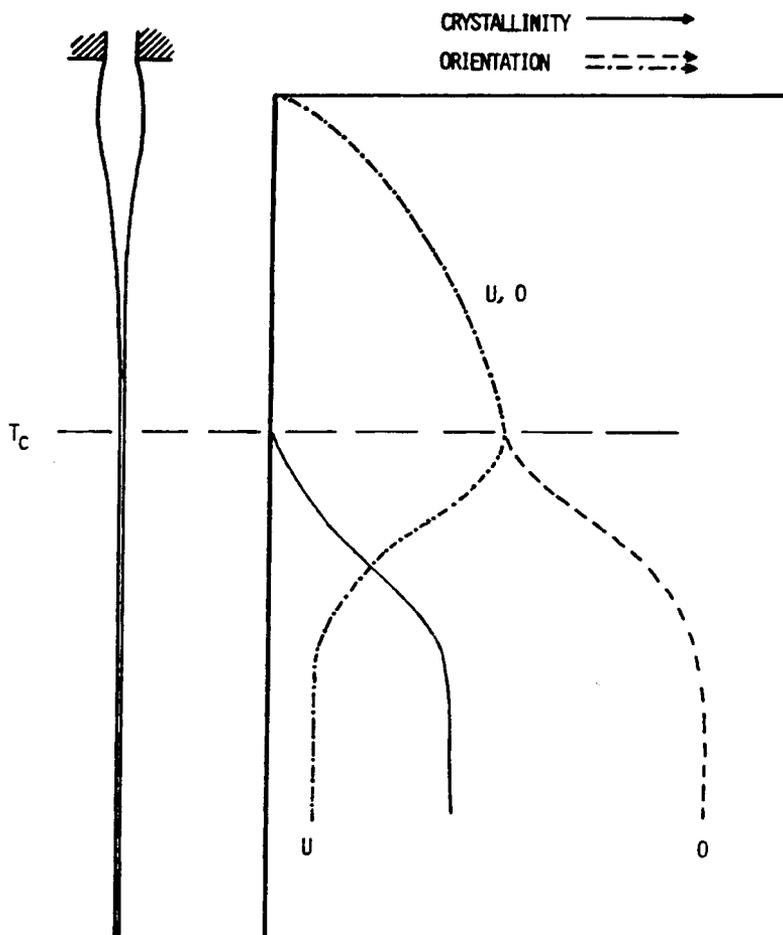


Fig. 4. Development of orientation in melt spinning of a crystallizable homopolymer. (T_c , temperature of initiation of crystallization; U , orientation of uncrystallized segments; O , overall orientation)

extent to which crystallization takes place in undrawn filaments and the orientations of the crystallized and uncrystallized segments depend on

1. Average axial stress in the melt zone
2. Stress in the crystallization zone
3. Crystallization time, i.e., the time between the temperature at which the material begins to crystallize and the glass transition temperature. Analysis of the trends in any melt spinning operation should consider all three structure formation factors.

TRANSITION POINTS IN A MELT SPINNING THREADLINE

It is clear from the preceding discussion that the locations of the transition points in a melt spinning thread line, namely, the point of initiation of crystallization and the glass transition point, play an important role in determining the extent and the orientation of different morphological entities in the as-spun fiber. The different cases that can arise are shown in Figure 1.

The polymers one encounters in practice are classified according to the location of their physical state transition temperatures in relation to room temperature. N and C refer to noncrystallizable and crystallizable polymers, respectively. We ignore the case of $T_g < T_r$ in the case of noncrystallizable polymers because such a condition would result in a fluidlike polymer on the package. The noncrystallizable case N can be considered type C_1 behavior, where T_c and T_g merge into a single plane. C_3 is a special case in which the effective glass transition temperature changes with time owing to absorption by the fiber of a plasticizer. For example, glass transition in nylon 6 occurs around 40°C when it is dry but is reduced to approximately 0°C when the fiber absorbs moisture under the normal humidity conditions in winding rooms. Such a case would be described by C_3 in Figure 1, with the extruded polymer going through the sequence of melt zone, crystallization zone, and the static zone, as in case C_2 , but reverting back with time on the package to stay in the crystallization zone, as in case C_1 . The residence time in the static zone would be dictated by the nature of finish applied to the fiber before being wound on the package and by the ambient temperature and relative humidity.

Noncrystallizable Polymer (N)

As described earlier, this can be considered a special case of crystallizable polymer, with (1) $T_g > T_r$ and (2) either the rate of crystallization zero or the temperatures T_c and T_g merging into one. The orientation of the as-spun, single-phase fiber would be orientation introduced in the melt zone. The influence of different process variables on the orientation of this single-phase material has already been discussed and is summarized in Table I. The Hermans orientation factor f of the as-spun fiber can be estimated from a measurement of birefringence Δn as

$$f = \frac{\Delta n}{\Delta n_{\max}} \quad (10)$$

where Δn_{\max} = birefringence of a perfectly aligned uniaxially oriented material.

Case C_1 : Crystallizable Polymers, $T_g > T_r$

In the case of crystallizable polymers with $T_g > T_r$, the orientations in the as-spun fibers depend on the deformation-induced orientation in the melt zone and the extent of crystallization-induced rearrangements in the crystallization zone. The extent of crystallization depends on the rate of crystallization and the residence time in the crystallization zone. The significant increase that occurs in the rate of crystallization with increasing precursor molecular orientation has been amply demonstrated both theoretically and experimentally.²⁴ In polymers that crystallize slowly when the precursor orientation is low, e.g., polyethylene terephthalate, the extent to which crystallization occurs in the threadline can be expected to be strongly influenced by the orientation-introduced in the melt zone and the residence time in the crystallization zone.

If the extent to which crystallization occurs in the threadline remains unaltered by changes in the different process parameters, one can see clearly that the relative roles of these parameters in determining the orientation of the fiber in the melt zone remain the same with respect to the overall orientation of the crystallized fibers at an enhanced level, with the amorphous orientation greatly diminished by crystallization. Such is not necessarily the case, however, because the changes in the extent of crystallization can be independent of and, sometimes, opposite to that of the change in orientation introduced in the melt zone. An example of such effects can be seen in melt spinning of polyethylene terephthalate with an increase in spinning speed at constant output. Theoretical analyses and experimental observations^{25,26} show that at constant flow rate from a capillary, the heat transfer rate increases with the take-up velocity V of the threadline in such a way that the temperature profile as a function of position down the threadline is only slightly affected. This implies that (1) the positions of T_m and T_g in the threadline are changed little by a change in V , (2) the rate of deformation in the melt zone increases with V , and (3) the time of crystallization decreases with V . In excellent studies of the extent of crystallization in polyethylene terephthalate, Nakamura et al.,⁵ Ziabicki,⁴ and Shimizu et al.²⁷ have identified the relative effects of the increase in crystallization rate resulting from the increase in flow-induced orientation at higher speeds and the decrease in the duration of crystallization in the threadline resulting from the increased rate of cooling. In fiber formation at low speeds, the extent of crystallization is negligible owing to the extremely low rate of crystallization. At very high speeds, crystallization is limited by the extremely short residence time in the crystallization zone. In such a case, if spinning speed is increased at constant output, the extent of crystallization, and thus the overall orientation, would exhibit a maximum.

Case C₂: Crystallizable Polymers, $T_g < T_r$

In crystallizable polymers with $T_g < T_r$, one usually finds little difference in the extent of crystallization in the as-spun fiber, given sufficient time on the package. Thus the influence of different process variables on the orientation developed in the melt zone in this case would be reflected similarly in the overall orientation of the as-spun fiber. The amorphous orientation would be low as a result of preferential crystallization of the more oriented precursor segments.

Process and Material Parameters in Crystallizing Polymers

The general consequence of higher precursor orientation and/or stress during crystallization is an increase in the rate of crystallization at any temperature in the crystallization zone. This zone is also widened by an increase in the temperature of initiation of crystallization T_c with precursor orientation. An obvious inference regarding the role of any process variable is that if any change in it causes an increase in orientation in the melt zone, it would also lead to an increase in the extent of crystallization with time in the crystallization zone until the equilibrium extent of crystallization is achieved. Difficulties arise, however, in many situations.

1. If winding speed is increased at constant output, it has been shown theoretically and observed experimentally,^{25,26} that the temperature profile as a function of position in the threadline remains essentially unchanged. As mentioned earlier, the combination of the resulting increase in crystallization rate and the decrease in the residence time in the crystallization zone can lead to a relative maximum in overall orientation and a relative maximum as well as a minimum in the orientation of the uncrystallized fraction as a function of winding speed.

2. Increasing output at constant winding speed, under conditions in which the extent of crystallization is significant but less than the saturation level, can also produce an effect in overall orientation opposite that of the orientation developed in the melt zone. Increasing output would invariably result in a decrease in the average extension rate in the melt zone and thus a lowering of the orientation developed in this zone. It also results in an increase in the time of crystallization, which can result in a higher extent of crystallization and thus a higher overall orientation from the crystallization-induced reordering.

3. Under conditions of rapid quenching in melt spinning, many polymers, e.g., polypropylene and nylon 6, develop a crystalline form of lower order, e.g., smectic or hexagonal order instead of the higher order crystalline structure that forms at lower stress levels. Experimental evidence suggests that the behavior of the filaments in subsequent deformation processes depends on the type of crystalline structure.²⁸

4. In the case of crystallizable polymers, with $T_g < T_r$, the fiber at room temperature is still above its glass transition temperature and it continues to undergo additional crystallization. Owing to the rather low mobility of the polymer segments at room temperature, the crystals formed in the undrawn package can be expected to be small but numerous. Even with little difference in measurable orientation, these fibers can behave differently depending on the length of "aging" of the package. Such an aging effect can also be seen over a long period of time in some polymers, e.g., polyethylene terephthalate spun at low speeds, whose glass transition temperatures are above the usual room temperatures.

5. Beyond the melt zone, the tension in a melt spinning threadline increases essentially linearly with distance from the spinneret.^{1,26,29,30} The framework proposed here in which the deformation is essentially confined to the melt zone is valid only when the maximum tension developed in the threadline is below the yield point of the "solidified" threadline. Otherwise, the total deformation in the threadline would be distributed into two zones, the melt zone and a subsequent "cold drawing" zone. Such a situation is especially likely to arise in long threadlines and in cases in which the temperature of the threadline is raised by external heating beyond the melt zone.

6. The high degree of reordering of polymer segments during oriented crystallization, preferentially along the fiber direction, can cause an extension of the fiber,³¹ leading to a reduction in the effective average extension rate in the melt zone. Although this phenomenon has been recognized in melt spinning of polymers that crystallize significantly on the package, no quantitative theory exists currently to account for the effect.

7. Generalized quantitative concepts regarding flow-induced orientation and crystallization as related to the physical nature of a polymer, namely, the

molecular weight distribution, degree of branching, copolymer composition, and sequence length distribution and distribution of stereoisomers, are yet to be developed. These factors can have a profound effect on structure development in melt spinning.³²

REMARKS

Obtaining a rational basis for the process-property relation in fiber formation from polymer melts involves two major steps: (1) identifying the relevant morphological parameters that govern the properties of interest in the product and (2) identifying the relevant process parameters that control the different morphological parameters. Although significant steps in this direction have been taken during the last two decades, we are still far from a full comprehension of fiber formation and other fabrication processes from polymer melts. Several aspects of our knowledge, especially those related to the nature of the polymer, remain empirical. This presentation is only an elementary effort in developing a simple model for one of the morphological aspects, the evolution of orientation in melt spinning. Many successful production operations have indeed been established with only a partial understanding of the processes involved. It is our belief, nevertheless, that these can be significantly improved and that new processes can be devised though improved comprehension even at an elementary level.

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References

1. A. Ziabicki, *Fundamentals of Fiber Formation*, Wiley-Interscience, London, 1976.
2. R. J. Samuels, *Structured Polymer Properties*, Wiley-Interscience, New York, 1976.
3. A. Ziabicki and L. Jarecki, *Colloid Polym. Sci.*, **256**, 332 (1978).
4. A. Ziabicki, Fundamental scientific problems, in *High-Speed Fiber Spinning—Science and Engineering Aspects*, A. Ziabicki and H. Kawai, Eds., John Wiley and Sons, New York, 1985, Chapter 2.
5. K. Nakamura, T. Watanabe, K. Katayama, and T. Amano, *J. Appl. Polym. Sci.*, **16**, 1077 (1972).
6. A. S. Abhiraman, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 583 (1983).
7. G. E. Hagler, *Polym. Eng. Sci.*, **21**, 121 (1981).
8. I. Hamana, M. Matsui, and S. Kato, *Melliand Textilber.*, 382, 499 (1969).
9. K. Katayama, T. Amano, and K. Nakamura, *Appl. Polym. Symp.*, **20**, 237 (1973).
10. J. R. Dees and J. E. Spruiell, *J. Appl. Polym. Sci.*, **18**, 1050 (1974).
11. T. Katao, S. Ohya, J. Furukawa, and S. Yamashita, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1091 (1973).
12. J. E. Spruiell and J. L. White, *Polym. Eng. Sci.*, **15**, 660 (1975).
13. H. P. Nadella, H. M. Henson, J. E. Spruiell, and J. L. White, *J. Appl. Polym. Sci.*, **21**, 3002 (1977).
14. G. Vassilatos, B. H. Knox, and H. R. E. Frankfort, Dynamics, structure development, and fiber properties in high-speed spinning of polyethylene terephthalate, *High-Speed Fiber Spinning—Science and Engineering Aspects*, A. Ziabicki and H. Kawai, Eds., John Wiley and Sons, New York, 1985, Chapter 14.
15. G. Bragato and G. Gianotti, *Eur. Polym. J.*, **19**, 795 (1983).
16. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, **6**, 111 (1962).
17. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, **6**, 361 (1962).
18. A. Ziabicki, *Fundamentals of Fiber Formation*, Wiley, New York, 1976, p. 208.

19. A. Sippel, *Z. Electrochem.*, **50**, 256 (1944).
20. H. L. LaNieve, Polymer Engineering Seminar, University of Tennessee (1970).
21. K. Oda, J. L. White, and E. S. Clark, *Polym. Eng. Sci.*, **18**, 53 (1978).
22. J. Shimizu and N. Okui, *Sen-I Gakkaishi*, **39**, T445 (1983).
23. W. R. Krigbaum and R. J. Roe, *J. Polym. Sci., A*, **2**, 4391 (1964).
24. A. Ziabicki, Fundamental studies of fiber formation, in *Applied Fiber Science*, Vol. 3, Academic Press, New York, 1979, Chapter 6.
25. F. Fourne, *Chemifasern-textilindustrie*, **27 / 79**, E85 (1977).
26. J. Shimizu, N. Okui, and T. Kikutani, Simulation of dynamics and structure formation in high-speed melt spinning, in *High-Speed Fiber Spinning—Science and Engineering Aspects*, A. Ziabicki and H. Kawai, Eds., John Wiley and Sons, New York, 1985, Chapter 7.
27. J. Shimizu, N. Okui, and T. Kikutani, Fine structure and physical properties of fibers melt-spun at high speeds from various polymers, in *High-Speed Fiber Spinning—Science and Engineering Aspects*, A. Ziabicki and H. Kawai, Eds., John Wiley and Sons, New York, 1985, Chapter 15.
28. M. Compostella, A. Coen, and F. Bertinotti, *Angew. Chemie*, **74**, 618 (1962).
29. Y. D. Kwon and D. C. Prevorsek, *J. Appl. Polym. Sci.*, **23**, 3105 (1979).
30. A. Ziabicki and H. Kawai, Eds., *High-Speed Fiber Spinning—Science and Engineering Aspects*, John Wiley and Sons, New York, 1985.
31. P. Desai and A. S. Abhiraman, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 653 (1985).
32. G. Perez, Some effects of the rheological properties of polyethylene terephthalate on spinning line profile and structure developed in high-speed spinning, in *High-Speed Fiber Spinning—Science and Engineering Aspects*, A. Ziabicki and H. Kawai, Eds., John Wiley and Sons, New York, 1985, Chapter 12.

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