# **Structure Formation in Polymeric Fibers**

**David R. Salem** 



# HANSER

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David R. Salem (Editor)

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To the memory of Dana

### Preface

This book is intended to provide a comprehensive and critical review of the science of fiber formation. It focuses on the evolution of microstructure (on the scale of nanometers to micrometers) in relation to forming conditions and molecular properties, and it surveys the connection between fiber structure and macroscopic properties. The book should also be of value to those interested in the general phenomena of polymer deformation, orientation, and structure formation.

Although the properties, processes and applications of polymeric fibers have become highly diverse, it was considered preferable to cover the subject in a single volume. The approach has been to review the key areas in depth, emphasizing fundamental principles and recent advances, while indicating sources for further reading on less central topics. Although each chapter is self-contained and can be read independently, they have been arranged in an order that would provide a sense of direction to the reader who is patient enough to start at the beginning and proceed to the end.

It will be clear from this book that there has been intense and highly productive research activity on the physics of fiber formation and polymer orientation over the last forty years, in both industrial and academic laboratories, and that there remains enormous potential for further advances. For those entering the field, this book should provide the foundation necessary to understand and contribute to the development of the subject in the 21st century. It will be of use to all scientists and engineers involved in the research and practice of fiber formation (as well as other polymer deformation processes) and to undergraduate and graduate students taking courses in polymer physics, polymer engineering, materials science and engineering, fiber science, and chemical engineering.

I wish to thank Professor Martin Sussman of Tufts University for suggesting this project to me. Due to personal circumstances Martin was unable to contribute to the book himself, but his belief in it was a constant source of encouragement. I would like to express my sincere appreciation to the contributors, for the quality of their work and for their enthusiasm and commitment. It is also important to acknowledge the thorough efforts of the reviewers of the draft manuscripts, including Peter Barham, Henry Chanzy, Dan Edie, John Hearle, Karl Jacob, Maurits Northolt, Ludwig Rebenfeld and Andrzej Ziabicki.

It would not be possible, or at least it would be very unwise, to take on a project of this type without the whole-hearted support of one's family, which I am fortunate to have had. And after the death of my wife, Dana, I could not have completed the book without the knowledge that she would strongly wish it to be published, or without the full backing of my daughter, Julia. I am deeply grateful to them both. I am also thankful to Betsy and Fred Levinton for their moral and practical support, in ways that freed-up my time for the book at some critical moments.

## 1 Variations on a Theme of Uniaxial Orientation: Introductory Remarks on the Past, Present and Future of Fiber Formation

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The formation of polymeric fibers through human invention (rather than natural processes) was achieved decades before the molecular structure of polymers was understood. Regenerated cellulose fibers were produced, albeit by a slow and polluting process, at the end of the 19th century. The strong resistance to Hermann Staudinger's idea, first put forward in the early 1920s, that small molecules could link together by covalent bonds into long polymer chains, and the eventual acceptance of this kind of molecular complexity about ten years later, is a well-known story. Wallace Carothers was an early proponent of Staudinger's view, and his experimental studies on polymer synthesis at DuPont furnished the proof that polymers are giant molecules and not, as previously supposed, colloidal aggregates of small molecules. It was this breakthrough in understanding that lead quite rapidly to the synthesis of polyamide (nylon) 66 and its formation into fibers of considerable commercial importance. Throughout the remainder of the 20th century numerous new polymers were synthesized that could be formed into fibers, covering an enormous range of properties.

It became increasingly evident in the 1950s and 60s that the properties of polymers are as strongly dependent on the physical organization of the macromolecules as on their chemical constitution. For example, a flexible-chain polymer of a given molecular weight and molecular weight distribution can exhibit a broad spectrum of mechanical properties (brittle, ductile, elastic, tough ...), mirroring the equally diverse arrangements that the molecules can assume. There emerged, therefore, a research imperative to understand how an assembly of macromolecules, each containing thousands of atoms, develops structure; how specific molecular arrangements can be induced; and how these structures are related to properties. This is the realm of polymer physics, where the fundamentals of fiber formation largely reside.

To form fibers from flexible-chain polymers, a randomly oriented (isotropic) melt or solution of the polymer must be converted into solid filaments having a high degree of preferred orientation along the fiber axis. This structural transformation, achieved through various spinning and drawing methods, entails a number of complex molecular processes. Some of the factors involved are time and temperature dependent molecular motions, crystallization and other phase transitions under high-stress, entanglement constraints, and various interchain interactions. Thus the final state of molecular order in a fiber from a given polymer is highly dependent on process variables such as stress, strain, temperature and time, and also on the length and length-distribution of the molecules.

Research on structure formation in polymeric fibers has both benefited from and contributed to the rapid advances in theoretical and experimental polymer physics over the last few decades – especially in the areas of rheology, network deformation, orientation phenomena, and crystallization. This has lead to a growing ability to control structure development in fiber and film forming processes, so that properties can be engineered to meet the specific demands of an ever-widening range of applications. Furthermore, the increasing precision with which the chemical constitution and conformational structure of macromolecules can be controlled has created an expanding array of molecular properties with which to explore the evolution of order during fiber formation, and to produce fibers that optimally reflect those properties.

The emergence of fibers with exceptional tensile modulus and strength, combined with their intrinsic low density, is one of the results of this research activity. For example: polymer scientists have designed and synthesized a variety of stiff, aromatic main-chain polymers exhibiting liquid-crystalline properties, and have learned how to orient them into highly ordered fiber structures with specific strength and modulus far exceeding that of steel: it has been discovered how to reorganize entangled, partially-crystalline assemblies of (flexible-chain) polyethylene molecules (previously used only for lowstrength fibers, plastic bags, inexpensive toys, etc.) into extended-chain 'high performance' fibers with specific modulus and strength similar or higher than those of liquidcrystalline polymer fibers: and methods have been found to convert polyacrylonitrile and mesophase-pitch fibers into carbon or graphite fibers that retain their outstanding mechanical properties at extremely high temperatures. Frequently, high strength/high modulus fibers are used as reinforcing materials in polymer composites, with diverse applications that include bone replacements and other biomedical implants, tennis rackets, bridges, automobiles, racing bikes, airplanes and space vehicles. Some examples of non-composite applications are heavy-duty ropes, satellite tethers, high-performance sails, and bullet-proof vests.

Research has brought about and enhanced numerous other remarkable fiber properties: chemical, oxidative, and UV resistance, electrical conductivity, biodegradability, nano-diameter fibers, etc. And the quest for new high-technology fibers is continuing unabated due to growing demands from the biomedical, construction, engineering, telecommunications, and electronics sectors. There have also been considerable improvements in the properties and functionality of fibers for the consumer textile market, such as high elastic recovery, high moisture absorption, bulk and texture, flame resistance and microfibers.

A number of these novel properties, for both specialty and commodity applications, have been realized by forming fibers from polymer blends and copolymers, taking advantage of the fact that properties of different polymers can be combined in a single material, sometimes with important synergistic effects. This has given rise to the concept of molecular (or *in situ*) composites, an example of which is the blending of flexible chain and liquid crystalline polymers to produce oriented fibers that combine high modulus with toughness.

Research and development efforts have also helped to provide major productivity gains. High quality textile fibers, with uniform and reproducible properties, are produced at throughput speeds of 100 m/s, making fiber manufacturing one of the most efficient and productive industries. These high throughput speeds have, in turn, revealed much fundamental information about the kinetics of polymer orientation and crystallization

processes. A current challenge is to further increase production rates without compromising fiber properties, or even while enhancing them.

Polymer physics and the study of fiber formation are no longer in their infancy, as they were forty years ago, but much remains to be learned. Some aspects of structure development have been clearly established through systematic experimental studies, but others remain stubbornly obscure due to the inability of characterization methods to provide the level of detail required. Theories of molecular motion, network deformation and crystallization have provided important conceptual insights and some useful predictive power, but they are unable to reliably quantify structure development during most fiber formation processes. It is arguable that this is because fiber formation usually occurs under conditions that are far from thermodynamic equilibrium.

Certainly, there are few substances more complex than polymers. In a polymer above its glass-transition temperature, different parts of a single molecule may be simultaneously in a mobile liquid-like state, a crystalline solid-state, and in various other states of order between these extremes. Moreover any event involving one part of the chain will influence the 'destiny' of neighboring parts, and will ultimately have repercussions at very long distances along the chain and along interacting chains. Of course, it is the complexity of polymers that provides their versatility, since the large range of (meta)stable states into which they can be driven provides a corresponding range of properties. But detailed characterization of these states and prediction of the conditions giving rise to them are areas of research that will occupy scientists for decades to come. It is likely that polymer physics, including the study of fiber formation, will benefit from and contribute to advances in theories of nonequilibrium thermodynamics and complex systems, and that these theories will become somewhat more tractable with the continuing gains in computational power. Continued developments in the sophistication and resolution of analytical instruments for characterizing polymer structure will also contribute to improved understanding of molecular organization in these materials.

Computational chemistry is now being used to design molecular structures suitable for fiber formation and it is possible to determine the intrinsic axial modulus and some other mechanical properties of real and 'virtual' molecules from quantum mechanical calculations. Molecular dynamics modeling of fiber formation processes, however, is very much in the preliminary stages. The intricacies involved in following the dynamics of about a million atoms over a period of half a second or more in the simulated forming process, requires enormous computing power (even with some significant approximations in the model). It is possible, however, that computer simulations will eventually be able to predict the evolution of fiber morphology under an almost limitless range of spinning and drawing conditions.

As mentioned earlier, one of the remarkable developments in fiber formation at the end of the previous century was the development of ultra-high modulus polyethethylene fiber via gel-spinning and ultra-drawing. Attempts to produce ultra-high modulus fibers from polymers with stronger (polar) chain interactions (e.g. polyesters and polyamides) have been unsuccessful, but the impetus to do so remains strong. A breakthrough may require approaches involving *in-situ* control of intermolecular interactions. Significant improvements in the mechanical properties of these fibers may also arise from further control of spinline dynamics, systematic studies of novel drawing sequences using the Incremental Drawing Process (IDP), in which temperature and strain-rate can be varied over a wide range *during* the deformation, and advances in computer simulations of spinning and drawing processes.

A valuable area for further fundamental and applied research is the electrospinning process, in which nanofibers are produced by application of an electric charge to a polymer melt or solution. An important objective of electrospinning studies is to increase throughput rates, since the current technology is too slow for most commercial applications.

The complexity of macromolecules that can be synthesized will increase dramatically over the next decade, as a result of research on molecular self-assembly and the production of polymers by genetically engineered enzymes. A number of current projects are specifically focused on producing novel polymers for fiber formation via biological systems that can synthesize proteins and polyesters. Organizing these molecules into fibers with properties that take proper advantage of the molecular design will require particular ingenuity. It may require, for example, a better understanding of how organization and self-assembly of complex macromolecules is achieved in biological systems.

Research on molecular machines (or nano-machines), based on very recent advances in the synthesis of 'discotic' molecules, is likely to impact fiber formation processes in the not-too-distant future. Current work in this area is too preliminary to justify a section in the book, but Karl Jacob and Malcolm Polk at the Georgia Institute of Technology have taken significant steps towards the synthesis of discotic molecules with rotational characteristics suitable for use in molecular machines for fiber production. The basic idea is that discotic molecular columns contained in a membrane are made to rotate in a magnetic field in a synchronized fashion. The rotation will pull down polymer molecules supplied at the top of the membrane, and organize and orient them as they pass through to the bottom surface, where they are released. The positioning of the discotics and the sequential interactions between the discotic end groups and molecular segments of the polymer must be precisely designed to pull segments of polymer in the prescribed sequence. It is clear that this approach would provide the potential for precise control over molecular ordering processes.

Examples of polymer fiber properties currently sought-after are ultra-high modulus and high strength *combined* with high compressive and shear strength/modulus, high strength combined with elastic recovery from very high deformations, high strength combined with high electrical conductivity and, for optical fiber applications, low-loss photon transmission. Development of nano-engineered 'smart' fibers that would change properties in response to environmental, mechanical or electrical stimuli is being pursued, and so is research on the formation of defect-free carbon nanotube fibers that would exhibit exceptional strength, flexural properties, electrical conductivity and transport properties.

As in any field of worthwhile endeavor, some concepts that look promising today will lead nowhere and others will emerge unexpectedly and succeed. There is no question, however, that the special properties arising from the geometry (e.g. high specific surface), low density, and structural versatility of polymeric fibers will continue to spur important discoveries in polymer science, fiber formation, and related areas, and will result in further growth of the range and sophistication of fiber applications.

# 2 Structure Formation During Melt Spinning

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#### 2.1 Concepts and Theories

#### 2.1.1 Introduction

The origin of the melt spinning process apparently dates to the 1845 English patent of R. A. Brooman [1] who conceived the basic concept as a method to produce filaments from gutta percha. But it was Carothers and Hill [2] who first described the process in the modern era. The work of Carothers and his associates [3] led to successful commercial application of melt spinning in 1939 as a process to produce polyamide 66 ("nylon") filaments and yarns.

The melt spinning process involves melting and extrusion of the material to be processed through a multihole capillary die, called a spinneret, followed by cooling and solidification to form filaments that can be wound on a bobbin or otherwise processed. A tensile force is usually applied to the molten extrudate in order to draw the filaments down to a desired diameter. This draw-down causes the filament velocity to increase along the spinning path until it reaches a final velocity, called the take-up velocity or spinning speed. The process is most commonly applied to polymer resins or inorganic glasses. In the present chapter, we will discuss only organic polymers.

A basic form of the melt spinning process is illustrated in Figure 2.1. Polymer, usually in the form of dried granules or pellets, is fed into an extruder where it is melted and conveyed to a positive displacement, metering pump. The metering pump controls and ensures a steady flow of polymer to the "spin pack" where the polymer is filtered and forced through the capillaries of a multifilament spinneret. The extruded filaments



Figure 2.1 The melt spinning process.

are drawn down to smaller diameters, i.e., finer deniers, by the action of a godet roll, while they are simultaneously being cooled (quenched) by air blowing across the filament bundle. The resulting filaments are either wound onto a bobbin or they are passed directly to another processing step such as "drawing" (see Chapter 4) or texturing (see Chapter 12).

Many modifications of the basic process have been developed in order to achieve specific new products. An example is the "spunbonding" process for producing non-woven webs, illustrated in Figure 2.2. In the particular process illustrated, the extruded filaments are cooled and drawn down by air that enters the enclosed chamber near the spinneret and which is sucked out of the chamber below a conveyor belt on which the filaments are deposited. A venturi increases the air speed in order to provide more air drag on the filaments and greater filament draw-down. The deposited filaments are conveyed to a bonding system, commonly a thermal bonding calender, whose purpose is to bond the fibers together at specific points so that the fibrous web becomes a non-woven fabric.

The earliest published papers dealing with the dynamics and structure development of filaments as a result of changes in melt spinning variables were those of Ziabicki and Kedzierska [4–8] published in 1959–1962. These authors gave the first quantitative description of the process and established the influence of various process and materials variables. A major review of available literature on the process that was available at the time it was published (1976) together with a further analysis of the process was provided in a classic book by Ziabicki [9].



Schematic of the Reicofil<sup>®</sup> Spunbonding Process.



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The major process variables for melt spinning are:

- (1) extrusion temperature,
- (2) mass flow rate of polymer through each spinneret hole,
- (3) take-up velocity of the wound-up or deposited filaments,
- (4) the spinline cooling conditions,
- (5) spinneret orifice shape, dimensions and spacing, and
- (6) the length of the spinline.

These variables are not entirely independent of each other. For example, the length of the spinline will generally be controlled by the efficiency of the cooling conditions along the spinline. More efficient cooling allows shorter spinlines. Spinline cooling is largely controlled by the velocity, temperature and distribution of the cooling air, but it is also affected by factors such as spinneret configuration, mass throughput and the specific design of the cooling system.

One of the most important variables of the melt spinning process is take-up velocity. For a given final filament diameter or linear density and a fixed number of holes in the spinneret, the take-up velocity controls the productivity of the spinline. It also has a marked effect on the structure and properties of the melt spun filaments and how the spun filaments behave in subsequent processing steps such as drawing and texturing. For about three decades after melt spinning was introduced as a commercial process, spinning speeds increased gradually to about 1500 m/min. Then, beginning in the 1970s, maximum commercial spinning speeds increased rapidly due to the development of winders capable of winding at higher speeds. The primary driving force for the development of these winders was increased productivity. Other important factors associated with the development of higher winding and spinning speeds included (1) the use of partially oriented feed yarns, produced in the range of 2750 to about 4000 m/min, for the draw texturing process, and (2) the desire to eliminate processing steps, such as drawing, by forming fully oriented yarns in a one step process [9, 10]. The study of the effects of "high speed spinning" attracted much attention in the 1970s and 1980s, as we shall see. Recent efforts in the 1990s include process changes such as the addition of "hot tube" spinning and/or "hydraulic drag" spinning. In the former case, the spinline is reheated, after the initial quench and before it reaches the first godet. The latter case passes the filaments through a liquid bath prior to the first godet that cools the filaments and allows higher spinline stresses to be achieved due to the hydraulic drag in the spinline. Both of these types of modifications influence the dynamics and thermal history of the treadline and can lead to improvements in the mechanical or dyeing properties of the yarns [11-13].

In addition to the process variables described above, there are a large number of materials variables that affect the spinnability and the structure and properties of melt spun filaments. Generally, the materials variables can be divided into two major categories: 1) variables that affect the rheology of the polymer melt, and 2) variables that affect the solidification behavior of the polymer. Variables of the former type include molecular weight, molecular weight distribution (MWD), chain stiffness, branching, additives, fillers, etc. which affect or control the resin's viscoelastic properties. Most fiber forming polymers are semicrystalline and solidification for these materials generally refers to crystallization. In this case, factors that affect the crystallization (and melting) temperature, crystallinity or crystallization kinetics are important. Such factors include composition and stereoregularity of the molecule (e.g., tacticity, comonomer content,

branching, etc.), molecular weight, and the influence of additives such as nucleating agents, antioxidants, pigments, etc. Of course, for fully amorphous polymers or polymers whose crystallization kinetics are too slow to allow crystallization during melt spinning, solidification refers to vitrification. In this case the glass transition temperature is an important parameter.

#### 2.1.2 An Engineering Analysis of the Process

A detailed engineering analysis of the melt spinning process involves a treatment of the dynamics of melt spinning, selection of an appropriate rheological constitutive equation for the melt being spun, application of material and energy balances, and a treatment of molecular orientation development and crystallization in the presence of molecular orientation. It is clear that any such analysis will contain numerous assumptions and approximations, as our understanding of several aspects of the problem is relatively poor. Nevertheless, even an imperfect analysis can be extremely valuable in helping us understand the influence of the many variables and the interactions among variables that occur in the melt spinning process. In the analysis that follows, we will limit ourselves to the description of a steady state spinning process. We will largely ignore radial variations within the spinning filament on the basis that (1) the filaments are thin and undergo a nearly pure extensional flow field and (2) thermal gradients across the radius of the filament are small. Other major assumptions will be described along the way.

#### 2.1.2.1 Force and Momentum Balance

A schematic illustrating the forces acting on a single filament in a spinline is shown in Figure 2.3. An overall force balance on a single filament of the spinline may be written as [9]

$$F_{\text{rheo}} = F_{\text{o}} + F_{\text{inert}} + F_{\text{drag}} - F_{\text{grav}} + F_{\text{surf}}$$
(2.1)

where  $F_{rheo}$  is the rheological force in the fiber at a distance z from the spinneret,  $F_o$  is the rheological force at the exit of the spinneret (z = 0),  $F_{inert}$  is the inertial force produced by the acceleration of the polymer mass along the spinline,  $F_{drag}$  is the the drag force caused by the fiber moving through the cooling medium (usually air),  $F_{grav}$  is the gravitional force acting on the spinline, and  $F_{surf}$  is the surface tension force at the fiber/air interface. Surface tension is usually small compared to other components of the force except for very low viscosity materials. Thus for most polymeric materials, we may neglect it. Assuming a circular filament cross section of diameter D, the other terms may be expressed by [9]

$$F_{\text{inert}} = W(V - V_0)$$

$$F_{\text{drag}} = \int_0^z \pi D\sigma_f \, dz \qquad (2.2)$$

$$F_{\text{grav}} = \int_0^z \rho g\left(\frac{\pi D^2}{4}\right) dz$$



Figure 2.3 Schematic illustration of the forces acting on a spinning filament.

where D and V are the diameter and velocity at a given point in the spinline; subscript zero refers to the exit of the spinneret at z = 0. Here,  $\sigma_f$  is the shear stress at the fiber/air interface due to aerodynamic drag,  $\rho$  is filament density, g is acceleration due to gravity, and W is the mass throughput rate per spinneret hole. Continuity (material balance) requires that

$$W = \rho A V = \rho \pi (D/2)^2 V$$
(2.3)

and we may write

$$\sigma_{\rm f} = \frac{1}{2} \rho_{\rm a} V_{\rm r}^2 C_{\rm d} \tag{2.4}$$

where  $\rho_a$  is the density of air,  $V_r$  is the relative axial velocity of the spinning filament and the cooling medium, and  $C_d$  is called the drag coefficient. If the cooling air has no component of velocity parallel to the spinning filament, then  $V_r$  is just the filament velocity V. Various methods of evaluating  $C_d$  have been described in the literature [14–21]; the interested reader is referred there for details. A common result correlates the air drag coefficient with the cooling air Reynolds number, Re:

$$C_d = K(Re)^{-n} \tag{2.5}$$

Values of K and n determined by various investigators have been tabulated and compared by Shimizu et al. [21, 22]. The exponent n typically lies in the range 0.6–0.8. With n fixed at 0.61, K ranges from 0.23 to >1, depending on the investigator and the method used to obtain the result.

With the above assumptions, the gradient of axial tension along the spinline can be written as,

$$\frac{dF_{rheo}}{dz} = W\frac{dV}{dz} + \frac{1}{2}\rho_a C_d V^2 \pi D - \frac{Wg}{V}$$
(2.6)

The rheological force is directly related to the axial spinline stress,  $\sigma_{zz}$ , by

$$\sigma_{zz} = F_{\rm rheo}/\pi (D/2)^2 \tag{2.7}$$

The value of spinline stress at the point in the spinline at which solidification is occurring is a very important quantity that, for a given material, largely determines the final structure and properties of the spun filaments. We can obtain the spinline stress at any point in the spinline using a modified version of the force balance of Eq. 2.1 which expresses  $F_{rheo}$  from the perspective of the measureable quantity  $F_L$ , the tension in the spinline at distance L from the spinneret (near the take-up device):

$$F_{rheo}(z) = F_{L} - \int_{z}^{L} \rho_{a} C_{d} V^{2} \pi D dz - W[V(L) - V(z)] + \int_{z}^{L} \rho g \pi (D/2)^{2} dz$$
(2.8)

A number of investigators [e.g., 9, 22–27] have discussed the relative magnitudes of the various force components of Eqs 2.1 and 2.2 as a function of spinning speed. As already mentioned the surface tension force is negligible except when spinning low molecular weight materials. Further, the gravity force is small compared to other forces except when spinning thick filaments at low speeds. Thus, under the usual spinning conditions for a high polymer, the inertial and air drag forces are the major components of the rheological force. The way the forces develop along the spinline is illustrated in Figure 2.4, which shows calculated values of the component forces as a function of distance from the spinneret. For these calculations, a mass throughput of 2.5 g/min per hole and a take-up velocity of 6600 m/min were assumed. The polymer density was taken as that of



Figure 2.4 Calculated rheological, air drag, inertial, and gravitational force profiles for polyamide 66 at a spinning speed of 6600 m/min.

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polyamide 66. This figure shows that at high take-up speeds, the inertial force increases in the upper part of the spinline and then levels out as the filament freezes and its diameter stops drawing down. The air drag component develops later, increasing with increase in fiber velocity, and continues to increase, after the velocity (and diameter) levels out, due to the increase in length of the spinline contributing to the drag. As first noted by Shimizu et al. [21], this suggests that the inertial force plays the dominant role in the determination of the structure of the filaments. It is the dominant force in the region of the spinline in which the structure is being developed, just prior to the leveling out of diameter, velocity and the inertial force.

#### 2.1.2.2 Constitutive Equation

Molten polymers are viscoelastic fluids and exhibit both elastic and viscous response to applied forces. Several authors [e.g., 28–32,22] have examined the use of viscoelastic constitutive equations to describe the melt spinning process. The influence of elastic effects become more important as spinning speed increases due to the increase in the rate of elongation of the filament. Polymers with high molecular weight, broad molecular weight distribution and branched chains, e.g. certain polyolefins, are also more viscoelastic and require a viscoelastic constitutive equation. In spite of this, it is known that the omission of elastic effects still provides a reasonable approximation to the actual behavior in many spinning processes and materials such as polyesters, polyamides, and spinning grade polypropylene [25–27,33,34]. Possible reasons for this are (1) the polymers used for spinning are often chosen to have modest molecular weight and, hence, elasticity, and (2) the rapid decrease in temperature of the spinning filaments and consequent rapid increase in viscosity may overshadow the effect of elasticity. Thus, it is common to use a purely viscous constitutive equation to describe behavior during melt spinning. We define a uniaxial "apparent elongational viscosity,"  $\eta$ , as

$$\eta(\mathbf{T}, \dot{\boldsymbol{\varepsilon}}) = \left\{\sigma\right\}_{zz} \left/ \left(\frac{\mathrm{d}V}{\mathrm{d}z}\right) \right.$$
(2.9)

Here,  $\eta$  may be a function of temperature, T, and strain rate,  $\dot{\epsilon}$ . If  $\eta$  is assumed independent of strain rate, then Equation 2.9 describes the constitutive equation for a Newtonian fluid. On the other hand, a generalized power law equation of the Cross/Carreau [35, 36] type has been used [37] to describe the viscous behavior in elongation for a material whose viscosity decreases with strain rate. In this case the viscosity is described by an equation of the form

$$\eta(\mathbf{T}, \dot{\boldsymbol{\varepsilon}}) = \frac{\eta_{o}}{1 + (a\eta_{o}\dot{\boldsymbol{\varepsilon}})^{b}}$$
(2.10)

where  $\eta_o$  is the zero strain rate viscosity and a and b are empirical constants. The viscosity is usually assumed to follow Arrhenius temperature dependence in the high temperature range well above the melting point:

$$\eta_{o} = A \exp(B/T) \tag{2.11}$$

As temperature approaches the glass transition temperature, the temperature dependence of amorphous polymers no longer follows Equation 2.11 well, and it is advisable to shift to the Williams-Landell-Ferry (WLF) equation [38] to describe the temperature dependence of viscosity.

A major problem in the treatment of melt spinning is the influence of crystallization on the rheology (i.e. the viscosity) of the spinliine. It was recognized early that the viscosity increases rapidly as crystallization sets in. To account for this effect Shimizu et al. [22] introduced an empirical expression:

$$\eta(\mathbf{T}, \dot{\boldsymbol{\varepsilon}}, \boldsymbol{\theta}) = \eta(\mathbf{T}, \dot{\boldsymbol{\varepsilon}}) \exp(\boldsymbol{\varepsilon} \boldsymbol{\theta}^{\mathrm{d}}) \tag{2.12}$$

where c and d are appropriately chosen constants and  $\theta$  is the relative crystallinity.

Ziabicki [39] later introduced the idea that, due to crystallization, the long chains in a polymer melt become gradually interconnected, small crystals acting as 'physical crosslinks.' He suggested that, when the number of these physical crosslinks reaches some critical value, the system loses fluidity and converts into an elastic solid. With further increase in crystallinity (i.e. crosslinking) the solid becomes rigid. This led him to propose the following equation to describe the temperature and crystallinity dependent viscosity:

$$\eta(\mathbf{T},\boldsymbol{\theta}) = \mathbf{f}(\mathbf{T}) / \left[ 1 - \frac{\boldsymbol{\theta}}{\boldsymbol{\theta}_{cr}} \right]^{\alpha}$$
(2.13)

where f(T) is a function of temperature only and  $\theta_{cr}$  is the critical crystallinity needed for sufficient 'crosslinking' of the melt that  $\eta \to \infty$ . Experimental evidence has recently been published [40] that suggests that the level of crystallinity corresponding to  $\theta_{cr}$  may be quite low, of order 2–3%.

Clearly, the effect of even small amounts of crystallinity will drastically change the dynamics of melt spinning. Therefore, it is very important that further studies be performed to develop a better understanding of the interaction of crystallization and rheology.

#### 2.1.2.3 Energy Balance

The variation of fiber temperature as a function of distance from the spinneret is determined from an energy balance on the spinline. Heat is transferred from the filaments by convection, radiation, and conduction along the fiber to cooler sections of fiber and to objects in contact with the fiber such as the take-up godet. Conduction is easily shown to be negligible in comparison to other mechanisms. Radiation is very dependent on the temperature of the filament; it can be very important for spinning of inorganic glasses or metals where spinline temperature can be quite high. But, because spinline temperatures for organic polymers rarely exceed 300  $^{\circ}$ C, radiation is often neglected or is incorporated into the convective contribution through the value of the heat transfer coefficient chosen [9,22,23,26,27,34,41–43].

Early investigators [23,26,41–43] also ignored the heat of crystallization which is converted to sensible heat when the polymer crystallizes. One reason for this is that these early treatments were aimed largely at analyzing the behavior of PET, which did not

crystallize in the spinline under spinning conditions available at the time the treatments were carried out. However, for spinning of polyolefins or for high-speed spinning of PET, other polyesters and polyamides, it is necessary to include this term in the analysis. Neglecting radial temperature variations within the filament and including the heat of crystallization, the differential energy balance is [22,27,34,44]

$$\frac{\mathrm{dT}}{\mathrm{dz}} = -\frac{\pi \mathrm{Dh}(\mathrm{T} - \mathrm{T}_{\mathrm{a}})}{\mathrm{WC}_{\mathrm{p}}} + \frac{\Delta \mathrm{H}_{\mathrm{f}}}{\mathrm{C}_{\mathrm{p}}} \frac{\mathrm{dX}}{\mathrm{dz}} \tag{2.14}$$

where T is fiber temperature,  $T_a$  is the temperature of the cooling medium,  $\Delta H_f$  is the heat of fusion, X is crystalline fraction, h is the heat transfer coefficient, and  $C_p$  is the polymer heat capacity.

The key parameter in Equation 2.14, that is required to compute temperature profiles along the spinline, is the heat transfer coefficient, h. Using both theory and empiricism, many authors, e.g. [23,45–47], have developed relationships describing h as a function of spinning conditions through use of dimensionless groups such as Nusselt (Nu), Reynolds (Re), Prandtl (Pr), and Grashof (Gr) numbers. Many of these expressions relating heat transfer coefficient to process variables were summarized by Ziabicki [9]. The correlation developed by Kase and Matsuo [23,45] is one of the most commonly used:

$$\frac{hD}{k_{a}} = 0.42 \left(\frac{\rho_{a} V_{r} D}{\mu_{a}}\right)^{1/3} \left[1 + \left(8\frac{u_{c}}{V_{r}}\right)^{2}\right]^{1/6}$$
(2.15)

where  $k_a$  is thermal conductivity of air,  $\mu_a$  is kinematic viscosity of air,  $u_c$  is the component of air velocity perpendicular to the filament (called "cross blow"), and all other quantities were previously defined.

It is, perhaps, worthy of note that some melt spinning is done into water baths or other cooling media. Water baths often are used in order to rapidly cool large diameter filaments which otherwise may require very long spinlines to achieve enough cooling for take-up.

#### 2.1.2.4 Multifilament Effects

The description of the dynamics and heat transfer given above applies to each filament of a multifilament melt spinning process, but it is important to recognize that the air flow velocities, air temperature and the boundary conditions, may vary from one filament to another in the multifilament bundle. In particular, the hot filaments on the cooling air inlet side of the bundle will heat the inlet cooling air as it passes through the bundle. The air velocities can also vary from one side of the bundle to the other. The axial velocity of the running filaments will impart an axial component to the incoming air stream and reduce the velocity component in the cross-blow direction. Due to changes in both the cooling air temperature and velocity, the quench conditions on the cooling air exit side of the bundle may be substantially different than on the inlet side. When this is the case, it leads to substantial differences in the dynamics as well as the heat transfer as a function of position within the multifilament bundle. Barovskii et al. [48] studied the temperature and velocity distributions within a 140 filament bundle of nylon 6 filaments with crossflow cooling. They observed that, near the spinneret, the air velocity was reduced by 60% while the air temperature increased by 200 °C on passing through the bundle. The reduction in air velocity and increase in temperature was less, further from the spinneret. Such differences in the dynamics and heat transfer can lead to significant differences in structure and properties of filaments from different parts of the multifilament bundle.

Several authors have discussed and/or attempted to model multifilament effects. Yasuda et al. [49] subdivided the space containing the fiber bundle into individual cells to which they applied mass and energy balances. Ishihara et al. [50], Dutta [51] and Schoene and Bruenig [52] gave later treatments, using a somewhat similar approach. The interested reader is referred to these original works for more detail. While multifilament effects raise an important industrial problem of how to reduce such effects, so that the filament structures and properties are uniform throughout the bundle, our interest will be focused on the structure developed with a given set of boundary conditions. Hence, we will consider a monofilament approach in subsequent analysis, but it is important for the reader to realize that, in an actual multifilament spinning processes, the boundary conditions may differ within the filament bundle.

#### 2.1.2.5 Development of Orientation and Birefringence

Molecular orientation is generated as a result of polymer deformation, whether the deformation is carried out in the melt or the solid state. The main requirement is that the molecular relaxation time of the deformed molecules is long compared to the experimental time allowed for relaxation. This means that the temperature range in which the orientation is developed, the cooling rate and the deformation rate are critical parameters.

Maxwell first noted development of birefringence due to molecular orientation in flowing polymer melts in 1873 [53]. By definition, birefringence in a fiber or filament,  $\Delta n$ , is equal to the difference between the index of refraction parallel and perpendicular to the fiber axis:  $\Delta n = n_z - n_r$ .

Several investigators [54–56] have noted that well above the glass transition temperature and at relatively low stress levels, the birefringence of a filament being spun from an amorphous polymer is proportional to the applied tensile stress:

$$\Delta n = C_{op} \sigma_{zz} \tag{2.16}$$

This is simply one form of the stress-optical law, and  $C_{op}$  is called the stress optical coefficient. According to the theory of rubber elasticity [57,58]

$$C_{\rm op} = \frac{2\pi}{45kT} \frac{(n^2 + 2)^2}{n} (\alpha_1 - \alpha_2)$$
(2.17)

Here, n is the average index of refraction of the polymer and  $(\alpha_1 - \alpha_2)$  is the difference in polarizability parallel and perpendicular to the chain segment. It is noteworthy that

Equation 2.17 indicates that  $C_{op}$  is inversely proportional to the absolute temperature. However, it is frequently found that  $C_{op}$  can be treated as a constant over the range of temperature where the birefringence of the spinning polymer is developing. Note also that  $C_{op}$  can be positive or negative depending on the relative values of the two components of polarizability.

Specification of uniaxial orientation is normally done in terms of orientation factors defined by Hermans and his coworkers [59,60]. They defined an orientation factor, f (also denoted  $\langle P_2(\cos\theta) \rangle$ ), for the molecular chains relative to a reference axis (the fiber axis) in terms of the anisotropy of the polarizability tensor. Assuming cylindrical symmetry and a one phase system:

$$f = \frac{\overline{\alpha_{zz} - \alpha_{rr}}}{\alpha_1 - \alpha_2} = \frac{3\overline{\cos^2\phi} - 1}{2}$$
(2.18)

where  $\overline{\alpha_{zz} - \alpha_{rr}}$  is the mean value of the difference between the components of the polarizability in the axial and radial directions in the fiber and  $\phi$  is the angle between the chain axis (the 1 direction) and the fiber axis. According to this definition, f=1 when all molecules are aligned parallel to the fiber axis, f=0 when they are randomly dispersed (isotropic system), and f=-0.5 if all molecules are perpendicular to the fiber axis. Based on this definition it is readily shown [61] that

$$f = \frac{\Delta n}{\Delta^{o}}$$
(2.19)

where  $\Delta^{\circ}$  is the *intrinsic birefringence* of the material. The intrinsic birefringence is the maximum possible birefringence corresponding to all molecules aligned parallel to the fiber axis (see also Section 13.3.2).

In semicrystalline polymers we must specify the orientation of both crystalline and amorphous phases. In this case Stein and Norris [62] have shown that

$$\Delta \mathbf{n} = (1 - \mathbf{X}_c) \mathbf{f}_a \Delta_a^o + \mathbf{X}_c \mathbf{f}_c \Delta_c^o + \Delta \mathbf{n}_{form}$$
(2.20)

where  $X_c$  is the crystalline fraction and the subscripts c and a refer to the crystalline and amorphous phases.  $\Delta n_{form}$  is a form birefringence due to interaction of the two phases with light. In semicrystalline, homopolymer fibers it is small and is usually neglected [62,63]. Generally, the intrinsic birefringences have been assumed to be constants independent of the level of orientation and crystallinity in the sample, though some recent work has suggested that this may not be entirely true.

For crystalline materials, the concept of the Hermans' orientation factor can also be extended to describe the orientation of each of the crystallographic axes, a, b, and c, with respect to the fiber axis as described by Stein and Norris [62]. Since the chain axis is usually parallel to the c-crystallographic axis by convention, the c-axis orientation factor is equivalent to the crystalline orientation factor  $f_c$  described above. The use of a- and b-axis orientation factors is useful for obtaining a better understanding of the detailed

morphology present in the fiber. The orientation factors for the three crystallographic axes are referred to as Hermans-Stein orientation factors.

#### 2.1.2.6 Crystallization in the Spinline

In general, crystallization is a nucleation and growth process. At low supercooling, i.e., near the melting point, the driving force for nucleation is low and the material crystallizes slowly. On the other hand, at temperatures near the glass transition temperature, the growth of crystals is slow due to lack of molecular mobility. These effects produce a maximum in the overall crystallization rate at an intermediate temperature. But even at the temperature of maximum crystallization rate, a finite amount of time is required for crystallization to be completed. During melt spinning the filament cools continuously through the temperature range where crystallization is possible, spending a limited amount of time at any given temperature. Increasing the cooling rate decreases the amount of time available for crystallization at any given temperature. Thus, increasing cooling rates tend to suppress the amount of crystallization that can occur. Ultimately, if we cool sufficiently fast, crystallization does not have time to occur, and the material simply vitrifies into a noncrystalline glass when cooled below its glass transition temperature. Thus, the nature of crystallization in the spinline depends on a balance between the various factors that affect the polymer's crystallization kinetics and those that control the cooling rate.

The rate of crystallization and its temperature dependence varies greatly from one polymer to another. It is also well established that the rate of crystallization of polymers is greatly enhanced by the presence of molecular orientation. The reasons for this will be described in more detail below. Assuming that this is true, we can obtain a good qualitative understanding of the important relationships between cooling conditions and crystallization kinetics using the concept of a "continuous cooling transformation diagram" [64]. The concept is illustrated schematically in Figure 2.5. Here, cooling curves, numbered 1–5, are plotted for the material on temperature versus log time axes. The "c-



Figure 2.5 Schematic continuous cooling transformation diagram illustrating the influence of cooling rate and stress on crystallization behavior.

curve" on the right shows the start of crystallization under quiescent conditions as determined, for example, by cooling at different rates in a differential scanning calorimeter. It simply illustrates that faster cooling produces greater supercooling of the melt before crystallization occurs. The location and shape of this curve relative to the time and temperature axes is determined by the crystallization kinetics. A faster crystallizing material would have its "c-curve" displaced to shorter times and the c-curve for a slower crystallizing one would be shifted to longer times. Cooling at a rate that misses the "nose" of the curve will result in quenching the material to an amorphous, glassy state. Also, if stress in the spinline increases the crystallization rate, then there should be another curve, illustrated by the left-hand "c-curve" in Figure 2.5, which represents the start of crystallization under a given stress. Since the crystallization rate is expected to be a function of the level of molecular orientation in the melt, and orientation is a function of stress in the spinline, there is, in principle, a different "c-curve" for each stress level. According to this analysis, stress would also be expected to increase the temperature at which crystallization takes place for a given cooling rate as is illustrated by cooling curve 2. Figure 2.6 shows an actual continuous cooling transformation diagram for HDPE constructed by Spruiell and White [64] from the data of Dees and Spruiell [65] and other data from the literature [66-68]. It is obvious from this figure that crystallization on the spinline occurs orders of magnitude faster than under quiescent conditions, especially in the higher temperature range where the crystallization is under



Figure 2.6 Actual continuous cooling transformation diagram for HDPE comparing the effects of stress to quiescent crystallization behavior. Numbers in parentheses are the stress in dynes/cm<sup>2</sup> ×  $10^{-6}$ .

nucleation rate control. The melt spinning data are comparable to the data obtained by Haas and Maxwell [68] for melts crystallized under shear between two glass plates.

The quantitative treatment of crystallization in the spinline is fraught with difficulties due to the non-isothermal conditions and the influence of molecular orientation, i.e., stress-induced crystallization. The analysis of non-isothermal crystallization even in the absence of molecular orientation is not well established, and the situation is even worse for crystallization in the presence of molecular orientation. Other than direct measurements on the spinline, no experimental techniques are available for measurement of crystallization kinetics in the presence of molecular orientation and no reliable theory is available for guidance.

Most investigators [9,22,44,69–77] have started from the classical treatment of isothermal crystallization, and they have modified it in some way in an attempt to deal with these factors. Most authors have used an equation similar in form to the well-known Avrami equation to describe the progress of crystallization. For isothermal crystallization this equation is [78]

$$\theta = 1 - \exp(-kt^n) \tag{2.21}$$

where k is the crystallization rate constant and n is the Avrami index. Using the Avrami theory as a basis, Nakamura et al. [71] incorporated an "isokinetic approximation" and derived the following equation to describe the transformation process under non-isothermal conditions:

$$\theta = 1 - \exp\left[-\left(\int_0^t K(T)dt'\right)^n\right]$$
(2.22)

Here, n is the Avrami index derived from isothermal experiments, and K(T) is related to the isothermal crystallization rate through the relation

$$K(T) = [k(T)]^{l/n}$$
 (2.23)

For process modeling, a differential form of Equation 2.22 is often most useful [77]. It reads

$$\frac{d\theta}{dt} = nK(T)(1-\theta) \left[ ln\left(\frac{1}{1-\theta}\right) \right]^{\frac{n-1}{n}}$$
(2.24)

Several other mathematical descriptions of non-isothermal crystallization have been presented [69,73–75]. Patel and Spruiell [77] examined the various possibilities with the aim of choosing among them for process modeling. They concluded that the Nakamura et al. model described above was probably the best available at the time of their paper. In the case of melt spinning, we must interpret the value of K(T) to include the effects of molecular orientation. Thus it is no longer given by Equation 2.23, but must be written K(T,f) where f is a measure of molecular orientation in the melt such as the Hermans' orientation function [59,60].

Ziabicki [9] was the first to attempt a phenomenological analysis of the influence of molecular orientation. He proposed that K(T,f) could be written as a series expansion

$$\mathbf{K}(\mathbf{T},\mathbf{f}) = \mathbf{K}(\mathbf{T},0) + a_1\mathbf{f} + a_2\mathbf{f}^2 + a_3\mathbf{f}^3 + \dots$$
(2.25)

The linear term in the above equation drops out for symmetry reasons. For not too high orientations, we can obtain

$$\ln[K(T,f)/K(T,0)] = A(T)f^{2}$$
(2.26)

or

$$K(T,f) = K(T,0)exp(Af2)$$
 (2.27)

Since A(T) is assumed always positive, Equation 2.27 predicts a monotonic increase in K with increase in orientation. We can consider A(T) to be an empirical parameter to be determined from experimental data. Wasiak et al. [79] found the value of A(T) for PET to be 210 at 95°C and 940 at 115°C. Thus, crystallization of PET is extremely sensitive to even very small amounts of molecular orientation present in the melt. Ziabicki also suggested that the quiescent crystallization rate could be approximated by

$$K(T) = K_{max} exp\left[ (-4) \ln(2) \frac{(T - T_{max})}{D^2} \right]$$
(2.28)

where  $K_{max}$  is the value of the rate constant at the temperature of the maximum crystallization rate,  $T_{max}$ , and D is the half-width of the curve of K versus T. Substituting Equation 2.28 in Equation 2.27, we arrive at

$$K(T,f) = K_{max} exp\left[ (-4)\ln(2) \frac{(T - T_{max})}{D^2} + Af^2 \right]$$
(2.29)

A somewhat different approach was taken by Katayama and Yoon [44]. They and others have attempted to include the effect of orientation into the kinetic equation based on a combination of rubber elasticity theory and the quiescent crystallization theory of Hoffman et al. [80,81]. Following Kobayashi and Nagasawa [70] they argued that the change in crystallization rates was a result of the thermodynamic effects of deformation of the molecular entanglement network. If  $\Delta F_{iso}$  is the difference in free energy between the crystal and the amorphous melt for the isotropic (quiescent) state, and  $\Delta F_{or}$  is the free energy change on crystallization from the oriented melt, then the difference in the free energy change due to deformation and orientation of the melt,  $\Delta F_{def}$ , can be written

$$\Delta F_{def} = \Delta F_{or} - \Delta F_{iso} \tag{2.30}$$

Expressing the values of  $\Delta F_{iso}$  and  $\Delta F_{or}$  in terms of enthalpy and entropy differences and assuming that  $\Delta H_{iso} \cong \Delta H_{or}$ ,

$$\Delta F_{def} = -T(\Delta S_{or} - \Delta S_{iso}) = -T\Delta S_{def}$$
(2.31)

Here,  $\Delta S_{def}$  is interpreted as the entropy difference between the isotropic and oriented amorphous melt. According to rubber elasticity theory,  $\Delta S_{def}$  may be related to the molecular extension ratio,  $\lambda$ :

$$\Delta \mathbf{S}_{def} = \mathbf{k}_1 \left( \lambda^2 + \frac{2}{\lambda} - 3 \right) \tag{2.32}$$

and the birefringence,  $\Delta n$ , is given by

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$$\Delta n = k_2 \left(\lambda^2 - \frac{1}{\lambda}\right) \tag{2.33}$$

Thus for small extensions with  $\lambda \cong 1$ ,

$$\Delta S_{def} = k_3 (\Delta n)^2 \tag{2.34}$$

Since  $f = \Delta n / \Delta^o$  we obtain

$$\Delta F_{\rm or} = \Delta F_{\rm iso} + CTf^2 \tag{2.35}$$

Substituting  $\Delta F_{or}$  for  $\Delta F_{iso}$  in the classical nucleation and growth theories [80–82] and simplifying, we arrive at

$$\dot{N}(T,f) = \dot{N}_{o} exp \left[ -\frac{U^{*}}{R(T-T_{\infty})} \right] exp \left[ -\frac{C_{1}}{T\Delta T + CT^{2}f^{2}} \right]$$
(2.36)

and

$$G(T, f) = G_{o} exp\left[-\frac{U^{*}}{R(T - T_{\infty})}\right] exp\left[-\frac{C_{2}}{T\Delta T + CT^{2}f^{2}}\right]$$
(2.37)

where N(T,f) is the heterogeneous nucleation rate in the presence of orientation, G(T,f) is the linear growth rate in the presence of orientation. In the above equations, U\* is the activation energy for segmental jumping, R is the gas constant,  $T_{\infty} = T_g - 30(K)$ ,  $\Delta T = T_m^0 - T$  and C<sub>1</sub> and C<sub>2</sub> are grouped constants involving  $\Delta H_{iso}$ , R, surface energies and interchain distance. The values of C<sub>1</sub> and C<sub>2</sub> can be determined, in principle, from quiescent nucleation and growth rate data. Encouraged by the similarity of the above equations, Katayama and Yoon [44], and Patel and Spruiell [77] assumed that the overall crystallization rate constants have the same form. Thus

$$K(T, f) = K_{o} exp\left[-\frac{U^{*}}{R(T - T_{\infty})}\right] exp\left[-\frac{C_{3}}{T\Delta T + CT^{2}f^{2}}\right]$$
(2.38)

Again,  $K_o$  and  $C_3$  can be obtained from quiescent crystallization kinetics data. The value of C can only be determined by back calculation from data taken from the melt spinline. Thus, we may consider it an adjustable parameter required to bring the values of crystallization rate constant in the presence of molecular orientation into agreement with experiment.

As already noted, crystallization during melt spinning involves very high cooling rates (up to  $10^3-10^4$  deg/s). The isokinetic approximation of Nakamura et al. assumes that crystallization kinetics is a function of temperature alone and does not depend on cooling rate. There is now experimental evidence that at high cooling rates, crystallization kinetics become a function of cooling rate as well as temperature [83,84]. The reasons for this dependence are explained in a new model of crystallization kinetics in variable external conditions proposed by Ziabicki [85]. This model specifically deals with situations when temperature, pressure or stress change with time, and it includes transient and athermal effects associated with the change in external conditions. The athermal effects increase the

overall crystallization kinetics with increase in cooling rate. This is due to the fact that embryos (clusters) of molecules which are too small to be stable at high temperature may become stable crystal nuclei at lower temperature and greater supercooling, if the cooling rate is fast enough to prevent their relaxation before reaching the crystallization temperature. This new approach to crystallization kinetics under variable external conditions would appear to be ideally suited for application to the modeling of the melt spinning process. However, to date, it has only been applied to simple cases such as nonisothermal crystallization in the absence of stress and orientation [84,86].

#### 2.1.2.7 Simulation of Dynamics and Structure Development

Using analyses similar to those discussed in preceding sections, a number of investigators [22,23,26–30,32,34,41–44] have mathematically simulated certain aspects of the melt spinning process. The reason for the great interest in simulating melt spinning is the large number of variables that affect the resulting filament properties, as discussed previously. Especially noteworthy among these efforts was the pioneering work of Kase and Matsuo [23,25,26] who first simulated the dynamics of both steady state spinning and time dependent phenomena.

Most of the early attempts to simulate spinning [23,25,26,28–30,41–44] omitted crystallization phenomena because of the difficulties of treating non-isothermal crystallization and the effects of molecular orientation. The omission of crystallization phenomena made it difficult to use the models to develop an understanding of the final structure and properties of the spun filaments. The models of Shimizu et al. [22] and Katayama and Yoon [44] were the first to simulate crystallization in the spinline, though Ziabicki [9] had previously laid the fundamental basis for such treatments. Later simulations emphasizing the treatment of crystallization and structure development include those of Spruiell and coworkers [27,34,37]. To date, simulations have been carried out for a variety of polymers, including PET [22,41–44], polyamide 66 [27], polyamide 6 [34] and polypropylene [37].

A typical example of simulated results is shown in Figure 2.7. These results were simulated using the working equations described in Table 2.1. The physical properties and crystallization kinetics used in the simulation were consistent with those of a polyamide 6 with a viscosity average molecular weight of 25,000. It was further assumed that the polymer was spun into ambient air without cross-blow. The mass throughput was taken to be 2.5 g/min per hole for these results. Because of its slow crystallization kinetics, the simulation predicts that polyamide 6 will not crystallize in the spinline at spinning speeds less than about 5000 m/min. This result is reasonably consistent with experimental data as described in the second section of this chapter. Similar results would be obtained for PET, which also exhibits slow quiescent crystallization kinetics.

Simulations carried out for polypropylene, a polymer that crystallizes faster than polyamide 6 or PET, are illustrated in Figures 2.8 through 2.11. These calculations were carried out using a somewhat more sophisticated model developed by Ding [37]. In this model Equation 2.10 is used to describe the effect of strain rate on viscosity and the differences resulting from differing molecular weight and MWD. A somewhat different method of dealing with crystallization kinetics was also used.



Figure 2.7 Simulated spinline profiles as a function of distance from the spinneret. (a) velocity; (b) temperature; (c) crystallinity; (d) birefringence. A mass flow rate of 2.5 g/min per hole and physical properties similar to those of polyamide 6 with a viscosity average molecular weight of 25,000 were assumed.

In Figure 2.8 is shown simulated diameter, temperature, birefringence and crystallinity profiles for a polypropylene homopolymer with  $M_w = 142,000$  and  $M_w/M_n = 2.8$ . The extrusion temperature is taken as 210 °C, mass throughput is 1.68 g/min per hole and the ambient air temperature is 30 °C. In Figure 2.8 the changes in the profiles are shown with change in take-up velocity. Figure 2.9 shows the effect of changing only the mass throughput of polymer at a constant spinning speed of 3500 m/min. Figure 2.10 shows the effect of changing the weight average molecular weight of the polymer at constant polydispersity, and Figure 2.11 shows the effect of changing the polydispersity at constant weight-average molecular weight. Note that all the calculations shown in Figures 2.8 through 2.11 relate to a fixed modest cooling condition corresponding to extrusion into stationary air (no cross-blow) at 30 °C, and that all results would change if we change the cooling condition. In particular, introducing cross blow will cause the crystallization and structure development to occur much closer to the spinneret.

The mathematical simulation makes it quite clear that crystallization in the spinline is controlled by a balance between factors that increase crystallization kinetics and the tendency for cooling rate to suppress crystallization, as previously discussed. The crystallization kinetics is determined, primarily, by the nature of the polymer and the level

(13)

(14)

Melt Spinning Process			
1. Continuity $W = (\pi D^2/4) \rho V$ $V(0) = V_0 \text{ with } D = D_0$	(1)		
2. Momentum balance $dF_{rheo} = dF_{inert} + \delta F_{drag} - \delta F_{grav}$ $F_{rheo}(0) = ? (Guess)$ $dF_{inert} = WdV$ $\delta F_{drag} = \pi \rho_a C_d V^2 Ddz$ $\delta F = (W \sigma/V) dz$	(2) (3) (4) (5) (6)		
3. Energy balance	(0)		
$\frac{dT}{dZ} = \frac{-h\pi D(T-T_a)}{WC_p} + \frac{\Delta H d\theta}{C_p dz}$	(7)		
$T(0) = T_0$ (Extrusion Temperature)			
4. Rheological equation			
$\frac{d\mathbf{V}}{dz} = \frac{\sigma}{\eta}$	(8)		
$\sigma = F_{\rm rheo} \ (\pi D^2/4)$	(9)		
For $T > T_m$			
$\eta = A(M_w)^{3.55} exp\left[\frac{B}{T+273}\right]$	(10)		
For $T < T_m$			
$\eta = A(M_w)^{3.55} exp\left[\frac{B}{T+273}\right] \left\{ a\left(\frac{\theta}{\theta\infty}\right)^b \right\}$	(11)		
5. Birefringence and orientation			
$\Delta n_{am} = C_{0p}\sigma$	(12)		

 Table 2.1 Working Equations for a Simple Mathematical Model of the

 Melt Spinning Process

6. Crystallization kinetics

 $f_a = \Delta n_a / \Delta^o_a$ 

 $\Delta n = (1 - \dot{\theta}) \Delta n_{am} + \theta f_c \Delta_c^0$ 

$$\frac{\mathrm{d}\theta}{\mathrm{d}z} = \frac{\mathrm{n}\theta\infty\mathrm{K}}{\mathrm{V}}\left[\int (\mathrm{K}/\mathrm{V})\mathrm{d}z'\right]^{\mathrm{n}-1} \exp\left[-\left(\int (\mathrm{K}/\mathrm{V})\mathrm{d}z\right)^{\mathrm{n}}\right]$$
(15)

$$\theta(0) = 0$$

$$k(T, f_a) = C_1 \exp\left[\frac{-C_2}{T + 71.6}\right] \exp\left[\frac{-C_3}{T\Delta T + CT^2 f_a^2}\right]$$
(16)

of molecular orientation developed. The major variables affecting the molecular orientation are those that have the greatest effect on spinline stress, namely polymer viscosity (i.e., molecular weight), spinning speed and mass throughput. Molecular



Figure 2.8 Simulated spinline profiles as a function of distance from the spinneret for a polypropylene homopolymer having an  $M_w = 142,000$ ,  $M_w/M_n = 2.8$ , melt temperature = 210 °C, mass troughput = 1.68 g/min per hole, ambient air temperature = 30°C. (a) diameter, (b) temperature, (c) birefringence and (d) crystallinity.

orientation is affected to a lesser extent by other spinning variables such as extrusion temperature and cooling air cross-blow velocity. The cooling rate is largely controlled by polymer mass flow rate, spinning speed and cooling air temperature and velocity. The balance of the competition between crystallization kinetics and cooling rate determines if crystallization occurs in the spinline and the temperature at which it occurs. Under appropriate conditions an increase in spinning speed can lead to either an increase or a decrease in the temperature at which crystallization occurs. Whenever the increase in spinning speed produces a major increase in the crystallization kinetics, we would expect the crystallization temperature to increase. But if the crystallization kinetics is saturated, an increase in take-up velocity will still increase the cooling rate and that will lower the crystallization temperature. Increasing the molecular weight increases the polymer viscosity



Figure 2.9 Simulated spinline profiles for same polypropylene as in Fig. 2.8 showing the effect of changing only the mass throughput. (a) temperature, (b) diameter, (c) birefringence, and (d) crystallinity.

and leads to a greater stress and molecular orientation in the spinline; this usually leads to higher crystallization temperature. Furthermore, the final orientation developed in as-spun fibers is strongly influenced by the orientation developed in the melt just prior to the onset of crystallization due to oriented nucleation and growth of crystals from the oriented melt.

We can rationalize many other experimental observations based on the results of such simulations. However, not all observations, especially the morphology and properties of the filaments, are predictable from such simulations, and it is necessary to examine carefully the experiments carried out for each polymer.

#### 2.1.2.8 Effects of Radial Temperature Distribution

In the analysis given above we have used the so-called thin filament approximation throughout, neglecting radial distributions in temperature, stress, viscosity, etc. While



Figure 2.10 Simulated spinline profiles for polypropylene showing the effect of changing the  $M_w$  of the resin at fixed  $M_w/M_n = 3.8$ . Take-up speed = 2000 m/min, melt temperature = 210 °C, mass throughput = 1.60 g/min per hole, ambient air temperature = 30 °C. (a) diameter, (b) temperature, (c) birefringence, and (d) crystallinity.

this is a reasonable approximation for most aspects of melt spinning, it must be noted that certain experimental observations, to be discussed later, indicate that radial distribution of temperature can produce significant radial variation of the structure of filaments under certain conditions. Analyses of radial temperature and velocity distributions were carried out by Matsuo and Kase [87], Shimizu et al. [22] and by Katayama and Yoon [44].

It was concluded that, under most conceivable spinning conditions, the velocity field within the filaments is essentially flat, and, for all practical purposes, purely extensional. However, the computed temperature profiles showed that there can be a significant temperature differential across the spinning filament. This temperature differential



Figure 2.11 Simulated spinline profiles for polypropylene showing the effect of changing  $M_w/M_n$  at constant  $M_w = 170,000$ . Other conditions are the same as for Fig. 2.10. (a) diameter, (b) temperature, and (c) birefringence.

reaches a maximum at a short distance below the spinneret and then decreases thereafter as the average filament temperature further decreases. The temperature distribution is approximately parabolic in shape and the differential may amount to as much as 10% of the difference between the temperatures of the fiber and the cooling air (e.g., about 10–15 degrees at the point of maximum differential for PET). This radial variation in temperature within the filament also implies that there is a radial variation in viscosity and stress across the filament. According to reference 44 the onset of crystallization perturbs the radial temperature distribution due to the heat of crystallization and vice versa, crystallization occurring first at the surface of the filament and gradually moving inward toward the center.

#### 2.2 Experimental Observations and Discussion

#### 2.2.1 Polyolefins

#### 2.2.1.1 Early Observations of Structure Development in Polyolefins

As synthetic fiber forming materials, polyolefins developed much later than polyamides and polyesters. Materials that were sufficiently stereoregular to develop the properties demanded of fibers date to the Nobel Prize winning research and the development of coordination catalysts by Ziegler [88] and Natta [89] in the early to mid 1950s. The bulk of the work on polyolefins relates to polyethylene and polypropylene, with only a small amount of work being done on other polymers. Of the polyolefins, polypropylene has proven to be quite versatile as a melt spun fiber, finding uses in a variety of yarns, ropes, and in woven and non-woven fabrics covering such applications as garments, disposable diapers, hygiene products, and many others. For this reason there has been significantly more melt spinning research done on polypropylene than on any other polyolefin.

Although polyethylene is of limited commercial importance as a melt spun fiber, the studies of melt spinning of polyethylene are significant because of the role that this polymer has played in developing our understanding of the morphological structure of polymers. This is based on the pioneering work of Keller [90] and Till [91] on polymer single crystals in 1957, and in the later work of Keller and coworkers [92,93] and Pennings et al. [94-96] on crystallization in the presence of molecular orientation. This understanding of polymer morphology developed during and just before the period that much of the early work on polyolefin fiber formation from the melt was being done. As a consequence of this and the fact that polyethylene is one of the simplest polymers from the point of view of crystal and morphological structure, the early work on polyethylene and polypropylene incorporated these concepts of morphology into the description of the fiber forming process. This has contributed substantially to our current understanding of the structure of melt spun fibers. For this reason we begin our discussion of experimental work here. As an aside, we note that polyethylene has proved to be an important, high strength, high modulus fiber when prepared by the gel spinning technique. However, we will not deal with this process or fibers made from it in this chapter, but see Chapter 5.

The first major study dealing with structure development during melt spinning of polyolefins was carried out by Katayama, Amano and Nakamura [97]. They developed techniques for on-line measurement of filament surface temperature, diameter, birefringence, and both wide angle and small angle X-ray diffraction patterns as a function of distance from the spinneret on a running spinline. They applied these techniques to study the melt spinning of high-density polyethylene, polypropylene, and polybutene-1. An example of their results is shown in Figure 2.12 that shows a plot of filament diameter, birefringence and surface temperature as a function of distance from the spinneret for polypropylene. The experimental results are quite consistent with the overall appearance of the simulated profiles shown in Figure 2.8, bearing in mind that the process conditions are very different. The diameter draws down rapidly in the upper part of the spinline and levels out near its final diameter at a spinline position at which the



Figure 2.12 Experimentally measured changes in diameter, birefringence and temperature along the spinning way for iPP. (Data of reference [97]).

temperature profile exhibits a plateau and the birefringence rises rapidly. The on-line wide-angle X-ray patterns showed that crystallization is occurring in this part of the spinline, with crystalline reflections being first detected at the point marked "Crystallization point" in Figure 2.12. The plateau in the temperature profile is created by the heat of crystallization that is evolved during solidification of the polymer. The birefringence rises slightly before the start of crystallization, increases more rapidly during crystallization, and finally levels out near its final value as crystallization is completed. This sequence of events clearly shows that crystallization occurs in the presence of molecular orientation, but also suggests that oriented nucleation and growth of crystals contributes strongly to the development of the final orientation developed in the filament. The latter point was fully established by Oda, White and Clark [54].

Katayama et al. [97] also observed a two-point small angle X-ray pattern for polyethylene, after crystallization was largely completed, in agreement with off-line measurements made on as-spun filaments. Interestingly, they also observed a periodicity developing parallel to the fiber axis at a position in the spinline prior to that at which crystalline reflections could be detected in wide-angle diffraction patterns. The nature and significance of this observation is not yet fully resolved, but additional insight may be obtained from recent work carried out on polyvinylidene fluoride described in Section 2.2.4.1.

#### 2.2.1.2 Further Study of Polyethylene

Additional studies of structure development of melt spun high density polyethylene filaments were published by Fung and Carr [98], Abbot and White [99], White, Dharod and Clark [100], Nadkarni and Schultz [101] and Dees and Spruiell [65]. The latter authors studied a HDPE with a melt index of 5.0 and examined the influence of take-up velocity, mass throughput, and extrusion temperature. They also carried out on-line measurements similar to those of Katayama et al. They monitored the tension in the spinline and were able to compute the stress at any position in the filament. Figure 2.13



Figure 2.13 Measured fiber surface temperature profiles for HDPE spinning filaments. (After reference [65]).

shows the fiber surface temperature as a function of distance from the spinneret. From this figure it is clear that the crystallization temperature is a strong function of both takeup velocity and mass throughput. Under constant cooling air temperature and flow rate, these two factors have a major influence on the cooling rate of the polymer, as already discussed. Increasing the mass throughput at constant take-up velocity increases the filament diameter and the amount of material that must be cooled, resulting in a slower cooling rate. Increasing the take-up velocity at constant mass throughput reduces the filament diameter and increases the velocity of the filament running through the cooling air, resulting in an increase of cooling rate.

Dees and Spruiell computed crystallinity as a function of distance from the spinneret from on-line X-ray patterns and converted the distance scale to a time scale knowing the velocity profile. They found that the crystallization rate increased somewhat with take-up velocity, a fact that could be explained by the greater supercooling and lower crystallization temperature. However, they were able to show that the crystallization rate on the spinline was orders of magnitude faster than under quiescent conditions. This is best illustrated, as discussed previously, by the use of the "continuous cooling transformation diagram." This concept was illustrated schematically in Figure 2.5, and Figure 2.6 showed an actual continuous cooling transformation diagram for HDPE constructed by Spruiell and White from the data of Dees and Spruiell and other data from the literature [65–68].



Figure 2.14 Hermans-Stein crystalline orientation functions as a function of take-up velocity for as-spun HDPE filaments. (After reference [65]).



#### Crystallization During Melt Spinning of Linear Polyethylene

Figure 2.15 Model of the morphology developed in as-melt spun HDPE filaments. (After reference [65]).

Several investigators have studied the molecular orientation developed in melt spun polyethylene fibers [65,97,99–101]. Figure 2.14 shows Hermans-Stein orientation functions for as-spun polyethylene filaments as a function of take-up velocity as reported by Dees and Spruiell [65]. The polymer chains are parallel to the c-axis in the polyethylene unit cell; consequently, the gradual increase of the c-axis orientation function with increase of take-up velocity suggests that the chains are becoming more aligned with the fiber axis. The b-axis rapidly becomes nearly perpendicular to the fiber axis, while the a-axis orientation function first increases and then decreases.

Dees and Spruiell proposed the morphological model shown in Figure 2.15 to describe the structure of melt spun HDPE filaments. The model is based on a detailed interpretation of the orientation data of Figure 2.14, the observation of two-point small angle X-ray patterns (slightly modified at the lowest spinning speeds), and SEM photomicrographs showing lamellar texture perpendicular to the fiber axis. This model is based on the concept of row structure developed earlier by Keller and Machin [92] to describe the results from laboratory samples crystallized while stretching the melt. Ribbon-like, lamellar polyethylene crystals, similar to those that grow in the radial direction in spherulites, are nucleated by and grow epitaxially on, fibril nuclei generated by the elongational straining and molecular orientation of the melt. The fibril nuclei are not necessarily extended-chain crystals, but they may contain an appreciable number of chain-folds. Since the lamellar crystals can form all along the fibril nuclei, and the heat transfer from the filament is primarily in the radial direction, there is a tendency for them to grow perpendicular to the fibril and fiber axis. This results in the morphology referred to by Keller as a "row structure," but has also been called "cylindritic." The growth direction of the lamellar crystals is the b-axis of the polyethylene unit cell, which explains the rapid alignment of the b-axis in the direction perpendicular to the fiber axis in the melt spun fibers. If the stress is low the lamellae may exhibit twist, as they grow outward from the fibril nucleus, just as they do in 'banded' polyethylene spherulites grown from quiescent melts. If the lamellae twist about the b-axis, the a- and c-axes of the



Figure 2.16 Variation of birefringence across the diameter of a thick HDPE filament. (After reference [98]).

polyethylene unit cell will rotate about the b-axis, and the orientation of the a- and c-axes with respect to the fiber axis will be equal, as is approximately true at a spinning speed of about 50 m/min in Figure 2.14. In this case,  $f_b \cong -0.5$ ,  $f_a = f_c \cong 0.25^*$ . When the stress is higher there is less twisting of the lamellar crystals with the result that the c-axis becomes more aligned with the fiber axis while the a-axis tends to become more nearly perpendicular to it. In this case  $f_c$  increases while  $f_a \rightarrow -0.5$ .

A skin-core structure was found to exist under certain conditions of spinning, with higher orientation in the skin than in the core, as is illustrated in Figure 2.15. The experimental basis for this suggestion was a decrease of orientation with increased distance from the spinneret in the initial stages of crystallization, a behavior that was also observed by Katayama et al. [97]. Radial variations of birefringence in thick melt spun polyethylene filaments were observed by Fung and Carr [98], Figure 2.16. They suggested that the variations were the result of radial temperature gradients and crystallization under higher stress levels in the outer layer of the filament.

#### 2.2.1.3 Further Investigations of Melt Spinning of Polypropylene

The early published studies of the melt spinning of polypropylene were those of Capuccio et al. [102], Compostella et al. [103], and Sheehan and Cole [104]. These authors established the basic characteristics of both as-melt spun filaments and filaments that had been drawn after spinning. In particular, Sheehan and Cole studied polypropylenes having weight average molecular weights that ranged from 245,000 to 470,000 (as estimated from correlation with intrinsic viscosity determined in decalin), and melt flow index (MFR) ranging from 9.37 to 0.61. The extrusion temperatures ranged from 235 °C to 280 °C. The filaments were spun into air at 25 °C or into water ranging in temperature between 10-90 °C. Their take-up speeds were very low, in the range 5-100 m/min, with consequently very low spin draw-down ratios (typically 3:1). They found that the high extrusion temperatures resulted in marked thermal-oxidative degradation of the polypropylenes, especially the higher molecular weight resins. The degradation was much worse in the presence of air than in its absence. Quenching into water, especially at the higher spinning temperature and lower water temperature, resulted in the formation of the paracrystalline form of polypropylene referred to as the "smectic" form by previous researchers [105,106]. Extrusion into air, under the conditions studied, resulted in the monoclinic  $\alpha$ -crystalline form. Higher molecular weight and lower extrusion temperature resulted in greater orientation in the spun filaments. The primary purpose of Sheehan and Cole's work was to develop filaments with tenacity's greater than 12 g/den. They were successful using high molecular weight resin that was spun to give the smectic phase and drawn to very high draw ratios.

Spruiell and White [64] showed that the development of orientation and morphology in polypropylene was fairly similar to that in polyethylene when spinning is carried out in air and the monoclinic  $\alpha$ -phase is formed. Figure 2.17 shows the crystalline orientation factors, for a polypropylene with a MFR of 6.6, for three different extrusion temperatures

<sup>\*</sup>Here, the symbols  $f_a$  and  $f_c$  do not refer to amorphous and crystalline orientation, but to the orientation of the crystallographic a and c axes with respect to the fiber axis.



Figure 2.17 Crystalline orientation functions versus take-up velocity for as-spun iPP with MFR = 6.6. (After reference [64]).

plotted versus take-up velocity. Note that lower extrusion temperature produces higher molecular orientation at a given spinning speed. The resemblance of Figure 2.17 to Figure 2.14 is quite striking; the major difference being that the a'-axis orientation factor does not reach as high a positive value at low spinning speeds as in the case of polyethylene. This was interpreted to mean that there is a lower tendency for lamellae to twist and rotate about their growth direction in polypropylene than in polyethylene.

Spruiell and White and Nadella et al. [107] showed that both the crystalline orientation and the total orientation as measured by birefringence could be correlated with the spinline stress. This is illustrated in Figure 2.18 for crystalline orientation. Here the orientation factors of Figure 2.17 are plotted versus spinline stress rather than take-up velocity. Nadella et al. showed that this sort of correlation also held when comparing resins with different MFR.

Using on-line measurements, Nadella et al. showed that crystallization of polypropylene in the spinline occurred at lower temperatures than for polyethylene, in spite of the higher melting point of polypropylene. They also showed that lower spinline stresses and higher cooling rates tend to enhance the formation of smectic phase. These features can be interpreted in terms of the schematic continuous cooling transformation diagram of Figure 2.19. Cooling rate 1 produces the expected result that polypropylene crystallizes at a higher temperature than polyethylene. For cooling rate 2 the faster crystallization kinetics of polyethylene results in a higher crystallization temperature for polyethylene than for polypropylene. Rapid cooling, as for cooling rate 3, completely misses the nose



Figure 2.18 Crystalline orientation functions versus spinline stress for as-spun iPP with MFR = 6.6. (After reference [64]).



Figure 2.19 Schematic CCT diagram illustrating the relative behavior in melt spinning of HDPE and iPP.

of the CCT curve for the formation of  $\alpha$ -monoclinic polypropylene, thus producing the smectic phase.

A number of investigators [97,103,107-110] observed that highly oriented polypropylene crystallized under stress frequently exhibits a "bimodal" crystal texture. This texture is characterized by one crystalline component, called the primary component, oriented with the c-axes of the crystals parallel to the fiber axis. Another component, called the secondary component, has the c-axes of the crystals nearly perpendicular to the fiber axis and the a- or a'-axis parallel to the fiber axis. (The a'-axis is a hypothetical one which is defined to be perpendicular to both the c- and b-axes, and is therefore at an angle of about 9.3° to the a-axis in the monoclinic unit cell). Estimates of the relative amount of the secondary component indicate that it typically composes 10-40% of the sample. According to Andersen and Carr [109], the secondary component exhibits broader X-ray diffraction peaks and cannot be easily imaged in dark field electron microscopy. This suggests that the crystals of the secondary component are smaller than the crystals making up the primary component. On-line X-ray patterns [97] showed that the reflections for the primary component appear first and the secondary component appears afterward at a somewhat lower position on the spinline. The evidence seems to indicate that crystallization occurs in three stages. In the first stage some form of fibril nuclei form. In the second stage crystal lamellae nucleate on the fibril nuclei and grow radially outward with their c-axes parallel to the fiber axis, creating a row or cylindritic type structure. Finally, in the third stage, the secondary component is nucleated by and grows epitaxially on the row nucleated lamellae to create the bimodal orientation. Based on these ideas, Clark and Spruiell [110] proposed the rough morphological model shown in Figure 2.20 for the structure of flow crystallized polypropylene. A similar model was suggested independently by Andersen and Carr. More recently, Lotz and Wittman [111] suggested that the source of the bimodal orientation in fibers is common to that which produces polypropylene lamellar branching and "quadrites" grown from solution [112] and is related to the extensive lamellar branching and unusual optical properties of melt grown spherulites [113,114]. They conclude that this effect is a natural consequence of a well-defined homoepitaxy on the structurally favorable lateral (010) faces of lamellar crystals of  $\alpha$ -phase.

Researchers at DuPont [115,116] and Celanese [117–119], motivated by the discovery that polypropylene filaments may be melt spun in such a way as to produce remarkably elastic filaments, reached rather similar conclusions about the structure of melt spun polypropylene filaments to those described above. The properties of these so-called 'hard elastic' filaments superficially resembled those of rubbery materials such as Spandex-type elastomers. Their studies also gave further insight into the nature of interlamellar tie molecules.

Typical curves for room temperature engineering stress versus strain are shown in Figure 2.21 for as-meltspun polypropylene filaments. The two examples illustrate the difference in behavior of a filament spun at low speed, with rather low molecular orientation ( $f_c = 0.18$ ), and one spun at a higher speed, with considerably higher



#### **Crystallization Stages**

Figure 2.20 Model of the bimodal texture that occurs in flow crystallized iPP. (After reference [110]).



Figure 2.21 Typical stress versus elongation curves for melt spun isotactic polypropylene filament.

orientation ( $f_c = 0.55$ ). The filament with low orientation exhibits a "yield point," filament necking and extension at essentially constant load to about 450% elongation (the so-called 'natural draw'), followed by a period of work hardening and high elongation to break. Because of its high ductility, this filament can be drawn to high draw ratios. The filament with higher orientation does not exhibit a marked yield point or neck down. It does have a higher yield strength, tenacity and lower elongation to break.

The elastic recovery after 100% extension of two filaments having similar properties to those in Figure 2.21 is illustrated in Figure 2.22. The more oriented sample with the welldeveloped row structure exhibits high elastic recovery, while the elastic recovery of the filament with low orientation is much smaller. The elastic recovery of the row structured filaments can be further improved by an annealing treatment, which increases the long period spacing as measured by SAXS and further perfects the row structure. The elastic filaments also exhibit a reversible decrease in density when stretched which is caused by the formation of numerous voids and surface connected pores. They also show a negative temperature coefficient of retractive force on stretching and high deformability with good elastic recovery at liquid nitrogen temperature. The latter behavior is not characteristic of true elastomers, as they generally become brittle below their glass transition temperature. These features suggest that the elastic recovery of these filaments is "energy driven" rather than "entropy driven," as in the case of true elastomers. Clark [116] and Sprague [119] suggested that this behavior could be explained by a structural model of the type illustrated schematically in Figure 2.23. The basic idea of the model is that a row structure exists in which lamellae are only connected to each other at certain tie points. When stretched, the lamellae bend elastically and voids are opened between lamellae. When the stress is released the lamellae regain their original shape, producing the elastic recovery and reduction in void volume. Electron microscopy observations of stretched, row-structured, elastic polypropylene films were shown to be generally consistent with this model [119].



Figure 2.22 Elastic recovery after 100% elongation of low and high orientation iPP filaments. (After reference [119]).

Studies described up to this point have dealt with spinning of polyolefins at relatively low spinning speeds, i.e., take-up velocities less than about 1000 m/min. The early studies were limited to these low take-up velocities for two reasons. First, winding devices were not commonly available for winding speeds much above 1000 m/min until the late 1960s and early 1970s. In fact, it was the late 1970s before Barmer Maschinenfabrik A. G. (BARMAG) began to market the first commercial high speed winder capable of reaching speeds approaching 6000 m/min [120]. Second, the early commercial polyolefin resins manufactured using Ziegler-Natta catalysts were highly viscoelastic due to high molecular weights and broad MWDs. These materials failed by cohesive fracture in the spinline when attempting to spin them at high speeds. In the 1970s patents began to appear, e.g. [121], for preparation of polypropylenes with "controlled rheology." These materials were and continue to be prepared primarily by "visbreaking" of reactor resins. The process of



Figure 2.23 Model illustrating reversible deformation of row structure present in highly oriented melt spun iPP. (After reference [99]).

visbreaking involves reducing the molecular weight and narrowing the MWD by chain scission due to addition of a peroxide initiator and extensive shearing and mixing in an extruder at elevated temperature.

The first studies of high speed spinning of polypropylene were carried out by Shimizu et al. [122–124]. They spun polypropylene at speeds ranging from 500 m/min to 6,000 m/min, but little information was given about the nature of the resin used in the study. It was found that both density and birefringence increased rapidly with increase in take-up velocity as shown in Figure 2.24. Higher spinning temperatures required higher take-up velocities to reach the same birefringence or density, but this dependence on extrusion temperature



Figure 2.24 Development of (a) density and (b) birefringence of iPP as a function of take-up velocity for three different extrusion temperatures. (Data of reference [123]).