Polymer Microscopy

Third Edition

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Springer

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Preface to the Third Edition

The major objective of this text is to provide information on the microscopy techniques and specimen preparation methods applicable to polymers. The aim is to provide enough detail for the methods described to be applied by the reader, while providing appropriate references for those who need more detail than can be provided in a single text.

We recognize that scientists from a wide range of backgrounds may be interested in polymer microscopy. Some may be experienced in the field, and this text should provide a reference source and a resource whenever a new material or a new problem comes to their attention. The scientist, engineer or graduate student new to the field needs more explanation and help. The focus here is on the needs of the industrial scientist and the graduate student. Some may need to know more about the intrinsic capabilities of microscopes of all types, so there is a description of basic imaging principles and of instruments, both classical and those more recently invented. Others may know all about microscopes and little about polymers, so there is a discussion of polymer structure and properties to put the microscopy into context. A brief section on processing of polymers has also been added.

As the text has been designed to cater to this wide range of backgrounds, some of these more introductory sections will not be for every reader. However, the organization of chapter and section headings should lead the reader to the information needed, and an extensive index is provided for the same purpose.

The first edition of this book was published twenty years ago, in 1987, and a second edition was published in 1996. There were many changes between those two editions, but the advances in microscopy and polymers in the last decade have been even more significant, requiring major revision. We were pleased when Springer invited us to provide this third edition allowing us to bring "*Polymer Microscopy*" up to date once again. This edition follows the same basic principles as the first two, with significant editing of older work and inclusion of new material. The rapid development of Scanning Probe Microscopy (SPM) and complete conversion to digital imaging has most affected the image capabilities used for polymers. Additionally, new polymer materials such as nanocomposites have been developed that require the use of microscopy. Overall it has been an exciting decade for polymer microscopy and our goal is to provide a window to view these new technologies.

Chapter 1 provides a brief introduction to polymer materials, processes, morphology and characterization. Chapter 2 is a concise review of the fundamentals of microscopy, where many important terms are defined. Chapter 3 reviews imaging theory for the reader who wants to understand the nature of image formation in the various types of microscopes, with particular reference to imaging polymers and how instrumental parameters affect results. These chapters are summaries of large fields of science, to make this text complete, and they contain many references to more specialized texts and reviews.

Chapters 4 and 5 contain the major thrust of the book. Chapter 4 covers specimen preparation, organized by method with enough detail given to allow a reader to conduct such preparations.* Many new methods have been added, especially those developed for use with the SPM and those relating to improvements in cryo-TEM. The references are chosen to provide the best detail and support. Chapter 5 describes the application of these methods to the study of specific types of polymers. The organization is by the form of the material, as fibers, films, membranes, engineering resins and plastics, composites (including a new section on nanocomposites), emulsions, coatings and adhesives, and high performance polymers. The emphasis in this chapter is on applications, particularly where more than one specimen preparation method or microscopy technique is used.

Chapter 6 is newly named for this edition, "Emerging techniques in polymer microscopy." The change is to indicate that the chapter includes both techniques that have been recently developed and those which are not new but which have not yet been regularly applied to polymer materials. These techniques include optical, electron and scanning probe microscopy techniques. In many of these fields the techniques are still developing very rapidly and thus future improvement in practice and understanding is likely over the coming years. Chapter 7 describes how the various microscopies and other analytical techniques for investigating polymer structure should be considered together as a system for problem solving.

The selection of the authors for this text came from a desire for a comprehensive review of polymer microscopy with emphasis on methods and techniques rather than on the results obtained. The synergism provided by three authors with very different backgrounds is important. One author (LCS) has an industrial focus and a background in chemistry, while another author (DTG) is in an academic environment with a background in polymer physics. A third author (GFM), added for this edition, is a chemist with an industrial focus, and a specialist in SPM. The major contribution of David Grubb and Greg Meyers has been in Chapters 2, 3 and 6. Linda Sawyer has been responsible for Chapters 1, 4, 5 and 7, with input from her coauthors.

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*The specimen preparation methods used for microscopy of polymers involve the use of many hazardous and toxic chemicals as well as the use of instruments which can be radiation hazards. It is well beyond the scope of this text to provide the information required for the proper and safe handling of such chemicals and instruments. The researcher is strongly encouraged to obtain the required safety information from the chemicals and instrumental manufacturers before their use.

Kübel (Fraunhofer Institute), Ishi Talmon (Technion), David A. Zumbrunnen (Clemson University), G. Julius Vancso (University of Twente, the Netherlands), Javier González Benito (Universidad Carlos III de Madrid, Spain), Scot Gould (The Claremont Colleges), Gary Stevens (University of Surrey, UK), Inga Musselman (University of Texas, Dallas), Steven M. Kurtz (Drexel University), Vernon E. Robertson (JEOL, USA), Barbara Petti (Celgard LLC), Viatcheslav Freger (Ben-Gurion University of the Negev), Ron Anderson (Materials Today), Anne Hiltner (Case Western Reserve University), Francis M. Mirabella (Lyondell Chemical), Eduardo Radovanovic (Universidade Estadual de Maringa′). Greg Meyers would also like to thank Georg Bar of the Dow Chemical Company who provided technical advice on SPM content. We would also like to thank the many colleagues who supplied copies of their papers, advice and input on the content of this text. Special thanks go to Prof. James P. Oberhauser, Dept. of Chemical Engineering, University of Virginia, who enabled Linda Sawyer to have access to the UVA on-line library and obtain the electronic files needed for this new edition.

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Color plates appear between pages 306 and 307.

Chapter 1

Introduction to Polymer Morphology

1.1 POLYMER MATERIALS

1.1.1 Introduction

Organic polymers are materials that are widely used in many important emerging technologies of the 21st century. Feedstocks for synthetic polymers are petroleum, coal, and natural gas, which are sources of ethylene, methane, alkenes, and aromatics. Polymers are used in a wide range of everyday applications, such as in clothing, housing materials, medical applications, appliances, automotive and aerospace parts, and in communication. *Materials science*, the study of the structure and properties of materials, is applied to polymers in much the same way as it is to metals and ceramics: to understand the relationships among the manufacturing process, the structures produced, and the resulting physical and mechanical properties. This chapter is an introduction to *polymer morphology*, which must be understood in order to develop relations between the structure and properties of these materials. An introduction by Young [1], a recent book on microstructure and engineering applications of plastics by Mills [2], and a book by Elias [3] all provide a good starting point in any study of polymers. Subsequent sections and chapters of this book have many hundreds of references cited as an aid to the interested reader. The emphasis in this text is on the elucidation of polymer morphology by microscopy techniques. This first chapter provides a foundation for the chapters that follow.

Polymers have advantages over other types of materials, such as metals and ceramics, because their low processing costs, low weight, and properties such as transparency and toughness form unique combinations. Many polymers have useful characteristics, such as tensile strength, modulus, elongation, and impact strength, which make them more cost effective than metals and ceramics. Plastics and engineering resins are processed into a wide range of fabricated forms, such as fibers, films, membranes and filters, moldings, and extrudates. Recently, new technologies have emerged resulting in novel polymers with highly oriented structures. These include polymers that exhibit liquid crystallinity in the melt or in solution, some of which can be processed into materials with ultrahigh performance characteristics. Applications of polymers are wide ranging and varied and include the examples shown in Table 1.1. A listing of the names and abbreviations of some common polymers is shown in Appendix I for reference. Appendix II is a list of acronyms commonly used for analytical techniques. Appendix III provides a listing of common fibers, and Appendix IV is a listing of common plastics and a few applications. Finally, general suppliers of accessories, microscopes, and x-ray microanalysis equipment are found in Appendices V–VII.

1.1.2 Definitions

Polymers are macromolecules formed by joining a large number of small molecules, or monomers, in a chain. These *monomers*, small repeating units, react chemically to form long molecules. The repetition of monomer units can be linear, branched, or interconnected to form three dimensional networks. *Homopolymers*, composed of a single repeating monomer, and *heteropolymers*, composed of several repeating monomers, are two broad forms of polymers. Copolymers are the most common form of heteropolymers. They are often formed from a sequence of two types of monomer unit. Alternating copolymers can be simple alternating repeats of two monomers, e.g., –A–B–A–B– A–B–A–B–, or random repeats of two monomers, e.g., –A–A–A–B–B–A–B–B–A–A–B–, whereas block copolymers include long sequences of one repeat unit, e.g., –A–B–B–B–B–B–B–B–A–A–B–B–B–B–A–. There are several forms of block copolymers, including AB and ABA, where A and B each stand for a sequence of several hundred monomers. If monomer B is added while A chains are still growing, the result is a graded block copolymer. Additionally, each component of block copolymers can be amorphous or crystalline. Amorphous block copolymers generally form characteristic domain structures, such as those in styrene-butadiene-styrene block copolymers. Crystalline block copolymers, such as polystyrene-poly(ethylene

TABLE 1.1. Polymer applications

Fibers	Polyethylene, polyester, nylon, acetate, polyacrylonitrile, polybenzobisthiazole, polypropylene, acrylic, aramid
Films, packaging	Polyethylene, polyester, polypropylene, polycarbonate, polyimide, fluoropolymers, polyurethanes, poly(vinyl chloride)
Membranes	Cellulose acetate, polysulfone, polyamide, polypropylene, polycarbonate, polyimide, polyacrylonitrile, fluoropolymers
Engineering resins	Polyoxymethylene, polyester, nylon, polyethersulfone, poly(phenylene sulfide), acrylonitrile-butadiene-styrene, polystyrene
Biomedical uses	Acrylics, polyethylene, ultrahigh molecular weight polyethylene (UHMWPE), polyester, silicone, nylon
Adhesives	Poly(vinyl acetate), epoxies, polyimides
Emulsions	Styrene-butadiene-styrene, poly(vinyl acetate)
Coatings	Epoxies, polyimides, poly(vinyl alcohol)
Elastomers	Styrene-butadiene rubber, urethanes, polyisobutylene, ethylene-propylene rubber

oxide), typically form structures that are characteristic of the crystallizable component. Block copolymers that have the second component grafted onto the backbone chain are termed *graft copolymers*. Graft copolymers of industrial significance, high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS), have rubber inclusions in a glassy matrix. Many common homopolymers can also be found as repeat units in heteropolymers, such as polyethylene, as in polyethylene-polypropylene copolymer. Modified polymers, copolymers, and polymer blends can be tailored for specific end uses, which will be discussed.

There are three major polymer classes: thermoplastics, thermosets, and rubbers or elastomers. Polymers that are typical of each of these classes are listed in Table 1.2. *Thermoplastics* are among the most common polymers, and these materials are commonly termed "plastics". Linear or branched thermoplastics can be reversibly melted or can be dissolved in a suitable solvent. In some cases, thermoplastics are crosslinked in processing to provide heat stability and limit flow and melting during use. In *thermosets*, there is a three dimensional network structure, a single highly connected molecule, which imparts rigidity and intractability. Thermosets are heated to form rigid structures, but once set they do not melt upon prolonged heating nor do they dissolve in solvents. Thermosets generally have only short chains between crosslinks and exhibit glassy brittle behavior. Thermosets are used as high performance adhesives (e.g., epoxies).

TABLE 1.2. Major classes of polymers

Crystallizable thermoplastics	*Glassy thermoplastics*
Polyacetal	Polystyrene
Polyamide	Poly(methyl methacrylate)
Polycarbonate	Poly(vinyl chloride)
Poly(ethylene terephthalate)	Poly(vinyl acetate)
Polyethylene	
Polypropylene	
Thermosets	*Elastomers*
Epoxy	Polybutadiene
Phenolic	Ethylene-propylene copolymers
Polyester (unsaturated)	Styrene-butadiene rubber
	Ethylene-vinyl acetate
	Styrene-butadiene copolymers

Polymers with long flexible chains between crosslinks are *rubbers* and *elastomers*, which, like thermosets, cannot be melted. Elastomers are characterized by a three dimensional crosslinked network that has the well known property of being stretchable and springing back to its original form. Crosslinks are chemical bonds between molecules. An example of a crosslinking reaction is the vulcanization of rubber, where the sulfur molecules react with the double bonded carbon atoms creating the structure. Multiphase polymers, combinations of thermoplastics and elastomers, take advantage of the ease of fabrication of thermoplastics and the increased toughness of elastomers, providing engineering resins with enhanced impact strength.

The chemical composition of macromolecules is important in determination of properties. Variations in the stereochemistry, the spatial arrangement, also result in very different materials. Three forms of spatial arrangement are isotactic, syndiotactic, and atactic. The *isotactic* (i) forms have pendant group placement on the same side of the chain, whereas in *syndiotactic* (s) polymers there is a regular, alternating placement of pendant groups with respect to the chain. *Atactic* (a) polymers have disordered sequences or a random arrangement of side groups. Isotactic polypropylene (iPP) crystallizes and has major uses, whereas atactic polypropylene (aPP) cannot crystallize, is sticky (has a low thermal transition) and finds little application.

1.2 POLYMER MORPHOLOGY

In polymer science, the term *morphology* generally refers to form and organization on a size scale above the atomic arrangement but smaller than the size and shape of the whole sample. The term *structure* refers to the local atomic and molecular details. The characterization techniques used to determine structure differ somewhat from those used to determine morphology, although there is some overlap. Examples of polymer morphology include the size and shape of fillers and additives, and the size, distribution, and association of the structural units within the macrostructure. However, as is probably clear from the overlapping definitions, the terms "structure" and "morphology" are commonly used interchangeably. The characterization techniques are complementary to each another, and both are needed to fully determine the morphology and microstructure and to develop structure-property-process relationships.

X-ray, electron, and optical scattering techniques and a range of other analytical tools are commonly applied to determine the structure of polymers. X-ray diffraction, for example, permits the determination of interatomic ordering and chain packing. The morphology of polymers is determined by a wide range of optical, electron and scanning probe microscopy techniques, which are the major subject of this text. Finally, there are many other analytical techniques that provide important information regarding polymer structure, such as neutron scattering, infrared spectroscopy, thermal analysis, mass spectroscopy, nuclear magnetic resonance, and so forth, which are beyond the scope of this text but which are summarized in Chapter 7.

Polymers are considered to be either *amorphous* or *crystalline* although they may not be completely one or the other. Crystalline polymers are more correctly termed *semicrystalline* as their measured densities differ from those obtained for perfect materials. The degree of crystallinity, measured by x-ray scattering, also shows these polymers are less than completely crystalline. There is no measurable order by x-ray scattering techniques and an absence of crystallographic reflections in noncrystalline or amorphous polymers. Characterization of semicrystalline polymer morphology can require an understanding of the entire texture. This extends from the interatomic structures and individual crystallites to the macroscopic details and the relative arrangement of the crystallites in the macrostructure. The units of organization in polymers are *lamellae* or crystals and *spherulites* [4]. Bulk polymers are composed of lamellar crystals that are typically arranged as spherulites when cooled from the melt.

The general morphology of crystalline polymers is now well known and understood and was described by Geil [5], Keller [6], Wunderlich [7], Grubb [8], Uhlmann and Kolbeck [9], Bassett [10, 11], and Seymour [12]. The work of Keller and his group has been reviewed by Bassett [13]. More recent edited books by Bassett [14], Ciferri [15], and Ward [16, 17], among others, provide excellent updates on current knowledge in the area of polymer morphology.

1.2.1 Amorphous Polymers

Amorphous polymers of commercial importance include polymers that are glassy or rubbery at room temperature. Many amorphous thermoplastics, such as atactic polystyrene and poly(methyl methacrylate), form brittle glasses when cooled from the melt. The glass transition temperature, T_g, or glass rubber transition, is the temperature above which the polymer is rubbery and can be elongated and below which the polymer behaves as a glass. Thermal analysis of amorphous polymers shows only a glass transition temperature, whereas crystalline polymers also exhibit a crystalline melting temperature.

Commercially important glassy polymers include polymers that are crystallizable but that may form as amorphous materials. These noncrystalline polymers are formed by rapid cooling of a polymer from above the melting transition temperature. They yield by forming a necked zone where the molecules are highly oriented and aligned in the draw direction. Other important polymers amorphous at room temperature include natural rubber (polyisoprene) and other elastomers. These exhibit a high degree of elasticity, stretching considerably in the elastic region and then fracturing with no plastic deformation.

Plastic deformation in glassy polymers and in rubber toughened polymers is due to crazing and shear banding. *Crazing* is the formation of thin sheets perpendicular to the tensile stress direction that contain fibrils and voids. The fibrils and the molecular chains in them are aligned parallel to the tensile stress direction.

Crazes scatter light and can be seen by eye as whitened areas if there are many of them. Crazing is often enhanced by rubber inclusions, which impart increased toughness to the polymer and reduce brittle fracture by initiating or terminating crazes at the rubber particle surface. *Shear banding* is a local deformation, at about 45° to the stress direction, which results in a high degree of chain orientation. The material in the shear band is more highly oriented than in the adjacent regions. The topic of yielding and fracture will be further explored (see Section 4.8). Overall, the mechanical behavior of amorphous polymers depends upon the chemical composition, the distribution of chain lengths, molecular orientation, branching, and crosslinking.

1.2.2 Semicrystalline Polymers

Semicrystalline polymers exhibit a melting transition temperature (T_m), a glass transition temperature (T_g), and crystalline order, as shown by x-ray and electron scattering. The fraction of the crystalline material is determined by x-ray diffraction, heat of fusion, and density measurements. Major structural units of semicrystalline polymers are the platelet-like crystallites, or *lamellae*. The dominant feature of melt crystallized specimens is the *spherulite*. The formation of polymer crystals and the spherulitic morphology in bulk polymers has been fully described by Keith and Padden [18], Ward [16, 19], Bassett [10, 11, 20, 21], and many others. Bassett [21] points out that a knowledge of morphology is an essential part of the development of polymer materials and a complete understanding of their structure-property relationships. Single crystals can be formed by precipitation from dilute solution as shown later (see Fig. 4.1). These crystals can be found as faceted platelets of regular shape for regular polymers, but they have a less perfect shape when formed from polymers with a less perfect structure. The molecular chains are approximately normal to the basal plane of the lamellae, parallel to the short direction. Some chains fold and re-enter the same crystal. In polyethylene, the lamellae are on the order of several micrometers across and about 10–50 μm thick, independent of the length of the molecule. Bulk crystallized spherulites can range from about 1 to 100 μm or larger. Small angle x-ray scattering (SAXS) and electron diffraction data have confirmed the lamellar nature of single crystals in bulk material.

1.2.2.1 Crystallization Under Quiescent Conditions

When a polymer is melted and then cooled it can recrystallize, with process variables such as temperature, rate of cooling, pressure, and additives affecting the nature of the structures formed. Two types of microstructure observed for semicrystalline bulk polymers are spherulites and row nucleated textures. Bulk crystallized material is composed of microscopic units called *spherulites*, which are formed during crystallization under quiescent conditions. The structures exhibit radially symmetric growth of the lamellae from a central nucleus with the molecular chain direction perpendicular to the growth direction. The plates branch as they grow. The molecular chains therefore run perpendicular to the spherulite radius. The crystallite or lamellar thickness in the bulk polymer depends upon the molecular weight of the polymer, crystallization conditions, and thermal treatment. The size and number of spherulites is controlled by nucleation. Spherulites are smaller and more numerous if there are more growth nuclei and larger if slow cooled or isothermally crystallized. In commercial processes, additives are commonly used to control nucleation density. When crystallizing during cooling, the radial growth rate of the spherulites is an important factor in determining their size. The morphology of isothermally crystallized polyethylene (PE) melts has revealed the nature of the lamellae [22] by a sectioning and staining method for transmission electron microscopy (TEM) (see Fig. 4.15), which will be described later.

A schematic of the spherulite structure is shown in Fig. 1.1 [16]. The structure [16, 18, 20, 23] consists of radiating fibrils with amorphous material, additives, and impurities between the fibrils and between individual spherulites. Although the shape of the growing spherulite

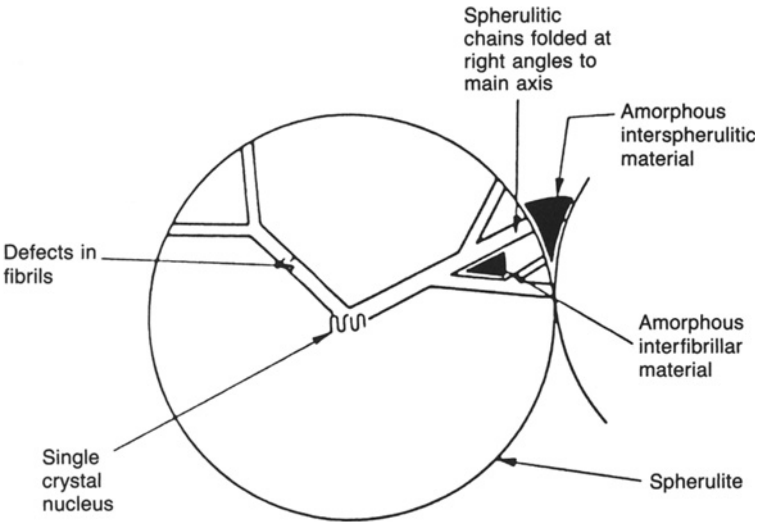

FIGURE 1.1. Schematic of spherulite structure. (From Ward [19]; used with permission.)

is round, as shown in a polarized light micrograph (Fig. 1.2), spherulites generally impinge upon one another during cooling, resulting in polyhedral shapes in the final product (Fig. 1.3). When thin melt quenched films or sections of a bulk polymer are viewed in crossed polarizers, the spherulites appear bright because they are anisotropic and crystalline in nature. Isotropic materials exhibit the same properties in all directions, whereas anisotropic materials exhibit a variation in properties with direction. Polarized light micrographs of a sectioned, bulk crystallized nylon (Fig. 1.3) show the size range of spherulites obtained by bulk crystallization. A more complete discussion of polarization optics will be found later (see Section 2.2.5 and Section 3.1.7), but for this discussion it is clear that the size of individual spherulites can be determined by analysis of polarized light micrographs. Average spherulite sizes are determined by small angle light scattering techniques.

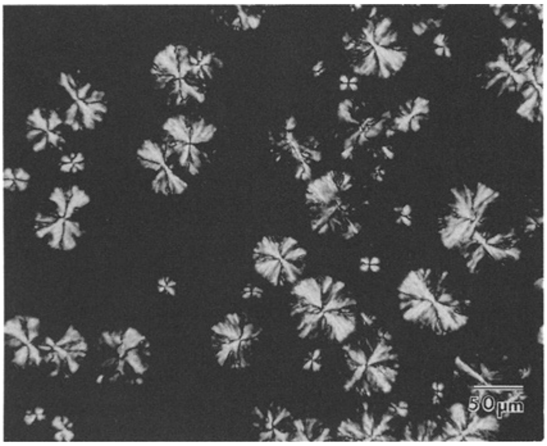

FIGURE 1.2. Polarized light micrograph of this polyoxymethylene film cooled from the melt shows recrystallization and formation of spherulites. The shape of the growing, birefringent spherulites is round.

1.2.2.2 Crystallization Under Flow

When a bulk polymer is crystallized under conditions of flow, a *row nucleated*, or "shish kebab," structure can be formed. Typically, the melt or solution is subjected to a highly elongational flow field at a temperature close to the melting or dissolution temperature. A nonspherulitic, crystalline microstructure forms from elongated crystals aligned in the flow direction and containing partially extended chains. At high flow rates, these *microfibers*, some 20 nm across, dominate the structure. At lower flow rates, the backbones are overgrown by folded chain platelets. This epitaxial growth on the surface of the extended chain produces folded chain lamellae oriented perpendicular to the strain or flow direction [23]. At still lower flow rates, the large lamellar overgrowths do not retain this orientation. Dilute solutions of polymers stirred during crystallization are known to form this

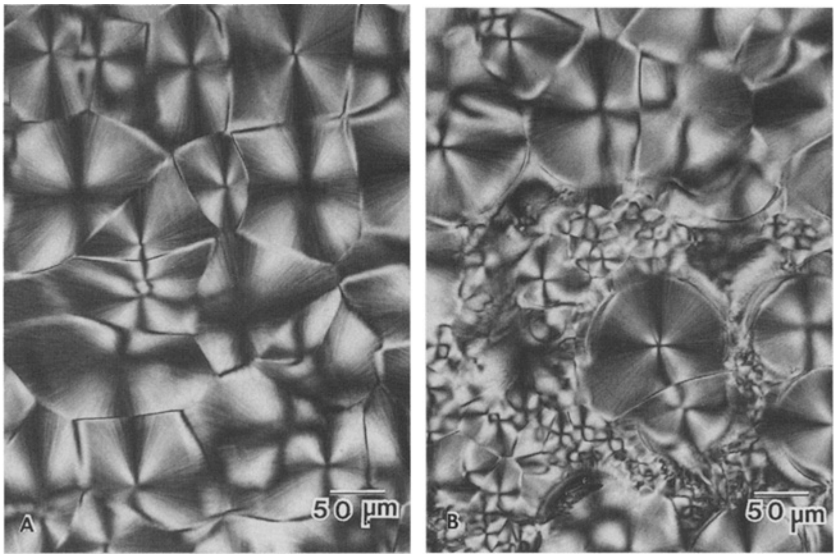

FIGURE 1.3. A thin section of bulk crystallized nylon, in polarized light, reveals a bright, birefringent and spherulitic texture. At high magnification, a classic Maltese cross pattern is seen, with black crossed arms aligned in the position of the crossed polarizers (A); the sample was isothermally crystallized, and exhibits large spherulites. The sample quenched during crystallization (B) yields large spherulites surrounded by smaller ones. (See color insert.)

shish kebab structure where the shish is the elongated crystals in the row structure and the kebabs are the overgrown epitaxial plates, as shown in the schematic in Fig. 1.4 [24].

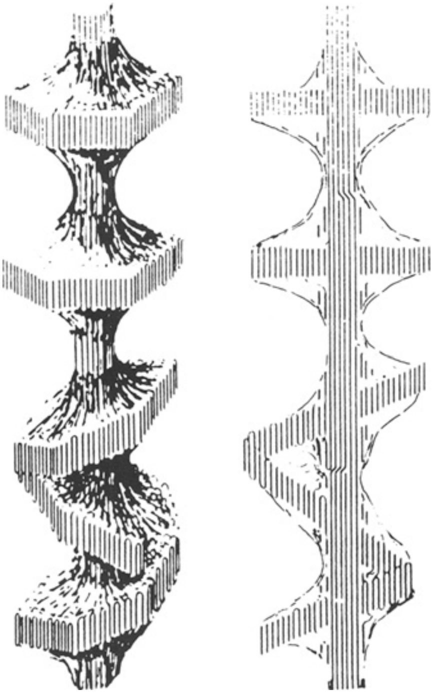

FIGURE 1.4. Schematic of a shish kebab structure. (From Pennings [24]; used with permission.)

High modulus fibers and films are produced from extended chain crystals in both conventional polymers, notably PE, and in liquid crystalline polymers (LCPs). The topic of high modulus organic fibers has been described and reviewed [15–17, 25] providing information on their preparation, structure, and properties. High modulus fibers are found in applications such as fiber reinforced composites for aerospace, military, and sporting applications. Industrial uses are for belts, ropes, and tire cords. Extended chain crystals can also form when polymers are crystallized very slowly near the melting temperature, but they are weak and brittle.

1.2.3 Liquid Crystalline Polymers

Rigid and semirigid polymer chains form *anisotropic* structures in the melt or in solution, which result in high orientation in the solid state without drawing. Liquid crystalline melts (*thermotropic*) or solutions (*lyotropic*) are composed of sequences of monomers with long rigid molecules. Aromatic polyamides and polyamide-hydrazides are examples of two polymers that form liquid crystal solutions. Aromatic copolyesters and polyazomethines form nematic liquid crystalline melts at elevated temperature. Melt or solution spinning processing of anisotropic LCPs results in an extended chain structure in the fiber or film. Heat treatment generally improves the orientation and the high modulus and tensile strength properties of these materials.

1.2.4 Multiphase Polymers

Many amorphous thermoplastics are brittle, limiting their range of applications. Toughening with rubber is well known to enhance fracture resistance and toughness. Many major chemical industries are based on *toughened plastics*, such as ABS, HIPS, and ionomers [26–30]. Important issues in the design of fracture resistant polymers are compatibility, deformation, toughening mechanisms, and characterization. Particle size distribution and adhesion to the matrix must be determined by microscopy to develop structure-property-process relationships.

Rubber toughened polymers are usually either copolymers or polymer blends. In random copolymers, a single rubber or matrix phase can be modified by the addition of the second component. Graft and block copolymers have modified properties due to the nature of the rubber-matrix interface. In graft copolymers, grafting provides a strong bond between the rubber and matrix in the branched structure where one monomer forms the backbone and the other monomer forms the branch. Graft copolymers are usually produced by dissolving the rubber in the plastic monomer and polymerizing it to form the graft. Typical block copolymers are polystyrene-polybutadiene and polyethylene-polypropylene. They have the monomers joined end-to-end along the main chain, which results in a bonding of the two phases. New processes have resulted in novel polymer blends that will be discussed in the process section of this chapter.

1.2.5 Composites

Polymer *composites* are engineering resins or plastics that contain particle and/or fibrous fillers. Specialty composites, such as those reinforced with carbon or ceramic fibers, are used in aerospace applications, and glass fiber reinforced resins are used in automobiles and many other applications requiring enhanced mechanical properties compared with the plastic. Composite properties depend upon the size, shape, agglomeration and distribution of the filler and its adhesion to the resin matrix. It is well known that long, well bonded fibers result in increased stiffness and strength, whereas poor adhesion of the fibers can result in poor reinforcement and poorer properties. Fillers for polymers include glass beads, minerals such as talc, clay, and silica, and inorganic fillers used to strengthen elastomers. Small particles (carbon blacks or silica) are added during manufacture to change color or specific properties, such as conductivity. Reinforcements that change mechanical properties include long and short carbon and glass fibers. The toughness and abrasion resistance imparted by fillers is very important in rubber applications such as tire cords.

The theory, processes, and characterization of short fiber reinforced thermoplastics have been reviewed by De and White [31], Friedrich et al. [32], Summerscales [33], in an introductory text by Hull and Clyne [34], and in a handbook by Harper [35]. Natural fibers and composites have been reviewed by Wallenberger and Weston [36]. The introduction of new composite materials, called *nanocomposites*, has resulted in new materials that are being applied to various industrial applications. These materials have in common the use of very fine, submicrometer sized fillers, generally at a very low concentration, which form novel materials with interesting morphology and properties. Nanocomposites have been discussed in a range of texts including two focused on polymer-clay nanocomposites by Pinnavaia and Beall [37] and Utracki [38].

1.3 POLYMER PROCESSES

The growing global market for plastics has resulted in manufacturers focusing on performance improvements and novel processing to improve efficiencies and lower costs. The major point of this section is to emphasize that the structure and properties of polymers are basically a function of their chemical composition and the *process* used to make the product. The polymer manufacturing processes are not discussed here, but rather the focus is on the processes used to take neat polymers and form them into useful products. There are many processes used to manufacture polymer materials but only the basic ones will be mentioned. Important commercial processes used to manufacture polymer materials fall into three major categories: continuous (i.e., fiber spinning, extrusion, pultrusion, and calendaring); semicontinuous (i.e., injection molding and blow molding); and batch (i.e., compression molding and thermoforming) [39]. Another approach is to consider processes based on the form of the final product (e.g., fibers, films, extrudates, moldings, etc.). Development of relationships between the chemical and physical structure and properties of the polymers requires an understanding of the specific process and its effect on the resulting morphology. The objective of this section is to outline the nature of some basic processes, the important process variables, and the relation of those variables to the structure of the final product. General references on the topic of polymer processes (e.g., [2, 16, 39–45]), equipment manufacturers' Web sites, and the Society of Plastics Engineers Web site and journals should be referred to for more specific detail.

1.3.1 Fiber and Film Formation

1.3.1.1 Fiber Processes

Polymer fibers are found in textile applications (Appendix III) for clothing and household items, such as sheeting and upholstery, and also for industrial uses, such as cords, ropes, belts, and tire cords. Polymer fibers can be either short in length (staple fibers) or continuous, very long filaments. Fibers are produced by a melt or solution spinning process, as shown in the schematic in Fig. 1.5 [46]. In either case, the polymer melt or solution is extruded through a *spinneret* (or jet) to form the fiber, which cools and crystallizes and is taken up on a bobbin and may be further oriented by drawing on-line or by a post-treatment process resulting in high tensile strength and modulus. Requirements for textile fibers are that the crystalline melting temperature must be above 200°C, so that the textile fabric can be ironed, and yet below 300°C, to permit conventional, melt spinning processing. Alternatively, the polymer is dissolved in a solvent from which it can be spun by such processes as wet and dry spinning.

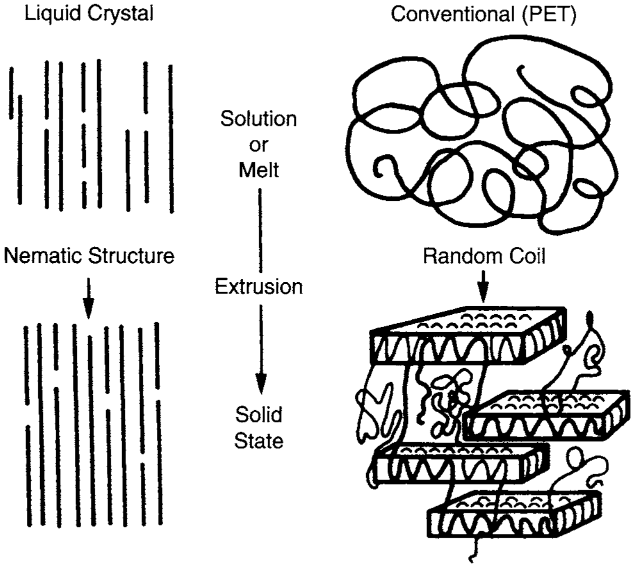

FIGURE 1.5. Schematic of fiber formation process for conventional and liquid crystalline polymers. (From Calundann and Jaffe [46]; Celanese Americas, formerly Hoechst Celanese; used with permission.)

Polymers that can be melted within this range are typically melt spun and include polyesters, polypropylene, and nylon. Polymers that are solution spun include some acetates and lyotropic LCPs. Schematic diagrams of the spinning apparatus are reviewed and shown, for example, by Griskey [39] and have been well known for decades.

In tensile drawing, stress is applied, resulting in thinning and elongation of the crystal and rotation of the molecules or bundles in the draw direction; increasing the draw ratio is known to increase the Young's modulus and the breaking strength by improving the degree of molecular alignment or extension. The diameter of the microfibrillar texture is also affected by the draw ratio with thinner microfibrils at higher draw ratios. The high speed spin-draw fiber process also yields fibers with high modulus and tensile strength when temperature, draw ratio, and speed of the process are well controlled. Heat treatments are often used to impart desired structures and properties in the fiber, and annealing of fiber forming thermoplastics yields a highly crystalline morphology. Uniaxially oriented fibers have a high degree of molecular symmetry and high cohesive energy associated with the high degree of crystallinity. Specific variables in the spinning process play an important role in the final fiber properties.

1.3.1.2 Orientation Methods

There are a variety of well known methods used to orient materials, generally by use of *tensile stress*, as reviewed by Holliday and Ward [47], Ciferri and Ward [48], and Gedde [49] and more recently by Ward [16, 50], Ciferri [15], and Chung [44]. Orientation takes place during the spinning process, as the polymer is first extruded through the spinneret, in the fiber skin and core as they solidify, and by postspinning processes. Ductile thermoplastics can be *cold drawn* near room temperature, whereas thermoplastics that are brittle at room temperature can only be drawn at elevated temperatures. Thermosets are oriented by drawing the precursor polymer prior to *crosslinking*, resulting in an irreversible orientation. Rubbers can be reversibly elongated at room temperature. The orientation in oriented rubbers is locked in place by cooling, whereas heating drawn thermoplastics causes recovery.

Cold drawing is a solid transformation process, conducted near room temperature and below the melting transition temperature of the polymer, if it is crystalline. The process yields a high degree of chain axis alignment by stretching or drawing the polymer with major deformation in the neck region. Deformation of the randomly oriented spherulitic structure in thermoplastics, such as in PE and nylon, results in a change from the stacked lamellae (ca. 20 nm thick and 1 μm long) to a highly oriented microfibrillar structure (microfibrils 10 nm wide and very long) with the molecular chains oriented along the draw direction, as shown in the schematic in Fig. 1.6 [51]. The molecules, links between the adjacent crystal plates in the spherulites, also appear to orient and yet still connect the stacked plates in the final fibrillar structure. Additionally, the drawing process

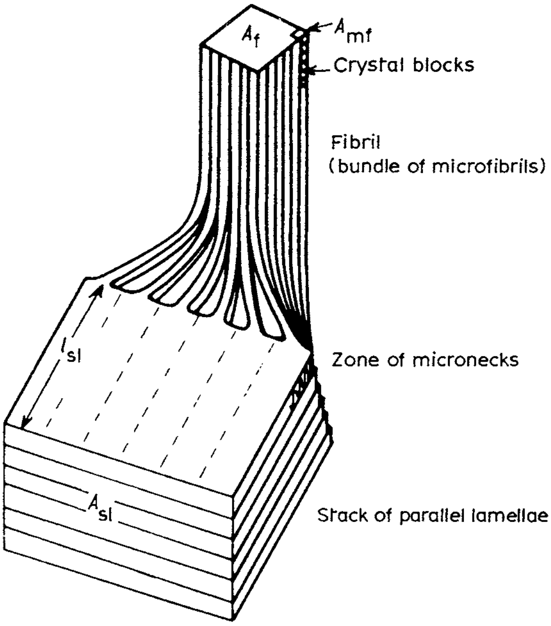

FIGURE 1.6. Schematic of cold drawing process with transformation of the lamellar texture into a microfibrillar structure. (From Peterlin [51]; used with permission.)

causes orientation in the noncrystalline amorphous component of the polymer. The degree of orientation of the crystalline component is characterized by wide angle x-ray scattering (WAXS) and birefringence. Clearly, the deformation process causes a major change in the microstructure of the polymer resulting in improved strength and tensile modulus.

1.3.1.3 Film Processes

Polymer films are used in many applications including packaging and electronic recording and in membranes for separations applications. Films are formed by similar uniaxial or biaxial processes used for fibers that impart high strength properties in either one or two directions, respectively. Processes include film extrusion, drawing, stretching, extrusion at high pressure through a die, and crystallization under flow. Extrusion is generally followed by stretching to orient the structure and also by blown film manufacture (see Section 1.3.2). Deformation processes that impart orientation to polymers can result in anisotropic mechanical properties. The increase in molecular alignment can result in increased stiffness and strength. The effects of orientation are dependent on the nature of the starting materials and on whether they are isotropic or anisotropic.

1.3.2 Extrudates and Moldings

Polymer morphology in extrudates and moldings is affected by process variables, such as melt and mold temperature, pressure, shear, and elongational flow. Process variables affect the morphology of the material thus affecting the fabricated product performance and mechanical properties. Pressure increases, for instance, can increase both the melting temperature and the glass transition temperature of a polymer, with the result that the polymer solidifies more quickly. In a crystalline polymer, the nucleation density can increase, resulting in a decrease in spherulite size with increased pressure in injection molding. In the special case of polymer blends, care must be taken to fully understand the effect of the process on the two or more polymers being used in the blend as even the size of the extruder or molding machine can cause major changes in the local orientation and stresses in the part and thus the morphology and the final properties. Many of the references cited [39, 43, 52, 53] cover this topic, but further references specific to polymer blends should be considered, for example, [26, 28, 54] and others found in Chapter 5 in the various relevant application sections.

1.3.2.1 Compounding

Many of the fabricated plastic products manufactured today include fillers and additives to modify and/or reinforce the final product properties. Fillers are blended with polymers to modify physical properties, enhance tensile strength or modulus or specific characteristics, such as wear resistance, flammability, electrical properties, color, and so forth [34, 55], or to reduce the polymer level in expensive materials. Reinforcements modify strength and modulus as the particles or fibers bear a fraction of the applied load. *Compounding* is the process of introducing fibers or particles into a resin prior to molding. Generally, the fillers or additives are added to the molten polymer and they are mixed together and extruded and cut into pellets that can be used in other processes such as molding. Process parameters, such as screw design, melt temperature and pressure, relate to the structure in the final material. High speed and pressure are known to result in a glossy surface finish, and high melt temperature is used to reduce viscosity and minimize fiber breakage. Fillers such as titanium dioxide and clay are used in paints and adhesives as pigments or toughening agents. A book edited by White, Coran, and Moet [30] examines the characteristics and methods of preparing polymer blends and compounds in batch and continuous mixing equipment.

Compounding of long fiber reinforced thermoplastics (LFRTs) is very different from compounding short fiber or particle filled composites. Long fibers enhance properties such as impact strength and are finding great utility in a number of applications in the automotive, industrial, and sports markets. Most of these products use PP or polyamide (PA), but poly(ethylene terephthalate) (PET) and other resins are also used.

Processes that are used for such compounding include an extrusion process termed *pultrusion*. The formed shapes are structural, pipes and tubing or long pellets used for molding parts. Continuous fibers, such as glass or carbon fibers, are drawn through a heated die in this process forming highly oriented extrudates. In-line or direct compounding of LFRTs can be done in which the compound with fibers and additives is formed into extrudates and directly injected into the molding process to form a part. Most of the pellets are used for injection molding but some are also used for compression molding generally for larger parts. The polymer viscosity and thermal properties are key factors in the process as are the standard process variables as noted above.

1.3.2.2 Extrusion Processes

Fundamental factors of extrusion technology have been widely reviewed, for example, in a Society of Plastics Engineers (SPE) Guide edited by Vlachopoulos and Wagner [56] and in books on polymer processing by Griskey [39], on polymer extrusion by Chung [44], and on polymer blends by Utracki [29]. As with all processing of polymers, extrusion involves the controlled melting and flow of the polymer and shaping of the material by forcing it through a die with an extruder. The goal is to form a homogeneous melt at a uniform and high rate and is part of the extrusion, blow molding, and injection molding process. Extruders are basically helical screw pumps that convert solid polymer particles to a melt delivered to a die or a mold [39]. These extruders are called single screw or twin screw devices depending on the actual number and type of screw used. Basically, the process is similar to fiber processing in that the polymer in the form of pellets is fed into a hopper and into the screw, which is driven by a motor. Heat is generated both by the heaters and by the molten polymer itself. The heated plastic is conveyed along the extruder until the pellets are melted and mixed well through a series of sections that control the melt temperature, mixing, and pressure, and thus the final product. The choices of single, twin, and multiple screws and the screw designs depend on the polymer used and the desired product. For instance, twin screws provide increased output and ability to handle materials compared with single screws. Twin screw extrusion is generally used for compounding polymers with fibers and fillers and also to fabricate nanocomposites. Process variables are used to control the mixing, uniformity, and the rate of production of extrudates.

Extruders are used in a wide range of processes to manufacture a range of products. In the simplest case, an extruded rod or pellet of material, with or without fillers, is produced and generally chopped to form pellets for various other processes such as injection molding. Extruders are also used to manufacture filaments, rod and pipe, sheet, wire coatings, blown film, and cast film. Polymer properties that influence the extrusion (and molding) process include molecular weight and molecular weight distribution, melt rheology, thermal and mechanical stability, bulk density, compressibility, and melt density. The thickness of the extrudates is important as is the extrusion speed, temperature, and viscosity, all of which affect the overall structure of the processed part. One of the key structures affected by the process variables is the size of the spherulites in the product, which in turn affects properties such as the impact strength, elongation, temperature resistance, among many others. Another structure of major importance is the *skin-core* morphology, which results from rapid cooling of the outside surface or skin of the extrudates versus the slower cooling of the central core region. This is a very simple description of a very complex process that should be well known to the engineers and scientists developing new materials and evaluating process-structure-property relations.

1.3.2.3 Injection Molding Processes

Injection molding is widely used to produce plastic parts for a broad range of industries, notably electrical and electronic, automotive, appliances, medical, and so forth, because of its flexibility to provide high rates of production on parts with tight tolerance. In injection molding, a mix of polymer and fibers, fillers and/or additives is injected into a mold at elevated temperature and pressure. These parts can be neat polymers or polymer blends, but they are more commonly chopped fiber reinforced thermoplastic composites. Molding is a semicontinuous process during which polymer pellets are fed into the heated barrel, melted or thermally softened, injected or forced into the nozzle, sprue, runner, and gate on the way to the mold cavity. Once pressure is achieved, the mold is cooled and the part is ejected. Many of the factors discussed for extrusion (in Section 1.3.2.2) are similarly important for molding, such as melt temperature, mold temperature, injection rate, and of course material properties, such as viscosity (molecular weight), chemistry, and melt temperature. The thermal and shear history, which varies with location in the mold, also affects the molecular orientation and the morphology and thus the mechanical properties of the molded article. Generally, the pellets used for molding are predried as moisture affects the viscosity and degradation of many polymers. Gates are important because they present a high resistance to flow and they allow the melt to reach the mold cavity quickly while minimizing energy and pressure losses. Mold design, especially for very fine parts, is critical to the dimensional stability of the part and to shrinkage, warpage, and thermal and chemical stability. Engineering details are found in the cited references and on the Web sites of machine manufacturers.

Macroscopic product problems that can result from poor control in injection molding include, but are not limited to: voids and sink holes on the surface generally due to poor mold filling or low pressure, incomplete mold filling, weld lines and flow marks, warping or distortion of parts, high shrinkage, and so forth.

Microstructures that are typically observed in molded parts and extrudates include anisotropic textures. The higher orientation in extrusion can result in highly oriented rods or strands, at high draw ratios and/or small diameters, or in structures with an oriented skin and a less oriented central core in thicker strands. This skin-core texture is due to a combination of temperature variations between the surface and the bulk and the flow field in both extrusion and molding processes. For instance, the flow fields in a molded part are shown schematically in Fig. 1.7 [46]. Extensional flow along the melt front causes orientation. Solidification of the polymer on the cold mold surface freezes in this orientation. Flow between the solid layers is affected by the temperature gradient in the mold, and the resulting flow effects [57, 58] result in a rapidly cooled and well oriented skin

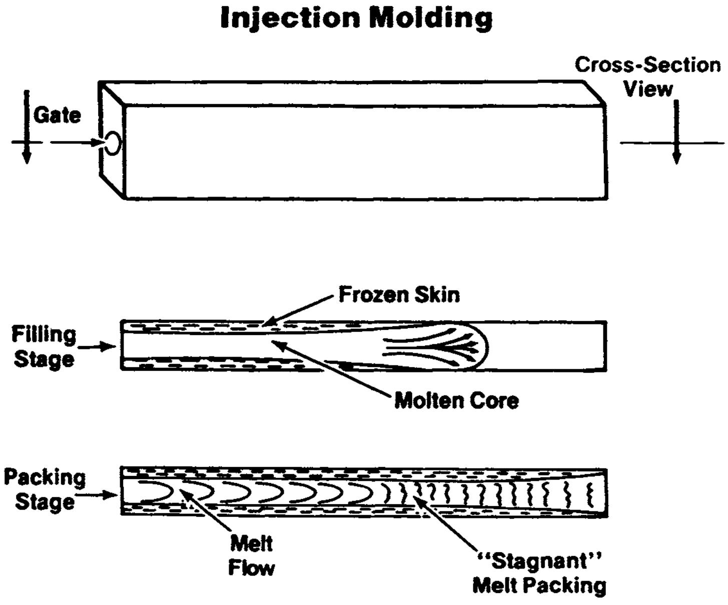

FIGURE 1.7. The pattern of the flow directions in the injection molding process is shown in the schematic diagram. (From Calundann and Jaffe [46]; Celanese Americas, formerly Hoechst Celanese; used with permission.)

structure and a slowly cooled, randomly oriented core. Extensional flow along the melt front results in molecular orientation parallel to the knit lines when two melt fronts meet. The resulting knit, or *weld line*, is a region of weakness in the molded part, and weld line fractures are commonly encountered. The local orientation is quite important as tensile strength and impact strength properties are known to be higher in the orientation direction.

Typically, in a semicrystalline polymer there are three zones within the molded part: an oriented, nonspherulitic skin; a subsurface region with high shear orientation, or a transcrystalline region; and a randomly oriented spherulitic core. The thickness of the skin and shear zone is known to be an inverse function of the melt and mold temperature with decreased temperatures resulting in increased layer thickness. In the skin, the lamellae are oriented parallel to the injection direction and perpendicular to the surface of the mold. Amorphous polymers also show a thin surface oriented skin on injection molding. When amorphous polymers are heated to the glass transition temperature and then relaxed, they exhibit shrinkage in the orientation direction and swelling in the other directions.

1.3.2.4 Other Molding Processes

There are other molding processes that will be mentioned. *Compression molding* is a very old molding process generally used for thermosetting resins. Compression molding involves the introduction of a resin and a curing or crosslinking agent into a mold followed by heating and application of pressure to cause a reaction resulting in thermosetting the material in a specific shape (e.g., [39, 52]). An overview of this topic including the underlying theory and physics is found in a text on compression molding by Davis et al. [52]. Fillers and reinforcements are used similar to those used in injection molding. The morphology of the parts is complex due to the variation in thermal properties and stress with position in the part. The process is used for large parts that do not require good tolerance compared with injection molding.

Blow molding is a very common process that is used to produce hollow objects. Products as different as food and beverage products, fuel tanks, cylinders, and blown film are formed by three different processes: extrusion blow molding, injection blow molding, and stretch blow molding. In extrusion blow molding a hollow tube of molten or thermally softened polymer, termed a *parison*, is extruded into a split cavity mold and crimped at one end. Compressed air is blown into the parison to fit the mold shape, causing the polymer to solidify. In injection blow molding, molten or softened polymer is injected into a heated mold cavity around a core pin and then the mold is opened and moved using the core pin where it is blown open and then ejected. Stretch blow molding can be by either extrusion or injection molding and results in a biaxially oriented product. Variables that are important to the morphology include thermal properties and rheology of the polymer and the transfer of heat through the part during the process. Multilayer blow molding is also increasing in demand due to potentially improved barrier properties. These processes are quite complex and this brief section only introduces the topic, which is described elsewhere (e.g., [39, 43, 53, 59]).

Thermoforming is another process used for making polymer products, such as automotive panels, underhood and fuel tank applications, chemical tanks, and packaging materials for the medical and electronics industries. A sheet formed by another process, such as extrusion, is preheated and then placed in a heated mold under pressure to form it into a part. Variations on the method include simple heating and stretching, pressure forming, contact forming, and so forth [60]. The thermoforming process is viewed as an alternative to blow molding, and it can also handle multilayered sheets such as those needed for plastic fuel tanks. Whereas an entire tank is formed by blow molding, thermoforming can involve making two halves of a tank and welding them together after all components are placed in them. As with most other processes, the final product properties are a function of the material's thermal, rheological, and chemical properties, and these are affected by the process variables, which, in turn, affect the morphology of the part. One of the advantages of thermoforming is the production of high gloss surfaces without painting, key to some automotive applications as a metal replacement. Once again, this is a brief summary of a very complex engineering process that the polymer microscopist needs to be aware of in understanding process-structure-property relationships; for more details on the process, see the many Web sites and books on processing and properties (e.g., [16, 43, 60]).

Reaction injection molding (RIM) is generally used for thermoset polyurethane, nylon, polyesters, and epoxies [39]. This process generally uses two metered reactive streams that combine and mix and then are injected into the mold. In the case of urethanes, one stream contains a polyether backbone, a catalyst, and a crosslinking agent, and the other has an isocyanate. The use of a blowing agent expands the material after mixing to fill the mold.

1.3.2.5 Coating Processes

There is a wide variety of polymer coatings and of processes to apply them to other polymers, metals, electronic devices, and for many applications in the aircraft, chemical and petroleum, food, textiles, and transport industries [43, 61, 62]. For example, polymer based coatings are used to protect steel from corrosion and extruders used in food and medical applications from wear. Adhesion is important if good protection is sought. A text by Grainger and Blunt [61] describes the many methods used for formation of surface coatings and surface modification, generally used to delay degradation and prolong the life of engineering components. The mechanisms of wear and corrosion must be understood if the coating is to provide protection. Coatings are applied by spin casting, thermal spray, electrodeposition, physical and chemical vapor deposition, laser surfacing, and various powder methods.

Licari [62] in his book on materials and processes for electronics applications describes the proper application of coating materials for the protection of electronics from environmental factors such as humidity, temperature, and high space vacuum for military and commercial applications. The chemistry and properties of a broad range of polymer coatings are discussed, including acrylics, polyesters, polystyrenes, epoxies, polyurethanes, silicones, polyimides, benzocyclobutene, fluorocarbons, polyamides, phenolics, and polysulfides. Processes discussed are spray coating, aerosol spray, electrostatic spray, dip coatings, fluidized bed coating, electrocoating, vapor deposition, spin coating, extrusion coating, and many others. Clearly, the various coating methods are affected by the polymer chemistry, thermal stability, rheology, and other factors that affect the coating thickness, adhesion, and degradation. The polymer morphology is a direct result of the chemistry and properties of the polymer and the impact of the specific process used for its application.

1.3.2.6 Novel Processes

Several processes will be discussed in this section that are not as commonly applied to polymers but have found niches for new applications. The first to be discussed is the formation of novel composites by *hot compaction* of fibers, developed by Ward and his group at Leeds (e.g., [63–65]). In this process, highly oriented fibers, such as melt and gel spun PE, PET, and LCP fibers are compacted until selective surface melting of some of the fibers permits the formation of a fiber composite with high strength and stiffness [63]. Potential applications of these materials include automotive industry, sports protection equipment, and many others [64] requiring exceptional mechanical properties. Investigation of the various process parameters showed that the time spent at the compaction temperature, termed the *dwell time* [65], was critical to formation of the composite. Molecular weight measurements showed that hydrolytic degradation occurred rapidly at the temperatures required for successful compaction, leading to embrittlement of the materials with increasing dwell time; a dwell time of 2 min was found to be optimum to have enough melted material to bind the structure together while resulting in only a small decrease in molecular weight. These studies included evaluation of mechanical properties and morphology that resulted from variations in the process variables and the polymer, such as the use of high molecular weight materials, which resulted in high impact performance of the hot compacted sheets.

Layer multiplying coextrusion is a process that has been used to fabricate one dimensional polymer blends by forced assembly of two polymers into many alternating thin layers (e.g., [66]) even to the level of nanolayer films consisting of thousands of continuous layers of two polymers with layer thickness less than 10 nm. Multilayer films have potentially improved impact strength and may also have enhanced permeability useful for many industrial applications. A schematic of the process used for microlayer and nanolayer coextrusion in Fig. 1.8 [66] shows that the viscoelastic nature of polymer melts is to repeatedly split. The process permits two immiscible polymers to come into intimate contact, and the localized mixing creates an "interphase" region, key to the properties of polymer blends [28]. A critical process variable, in the case of an amorphous polyester and polystyrene, is the extruder temperature, which was adjusted to ensure that the viscosities matched when the melts were combined in the feed block. Once the melt exited the assembly, it was spread in a film die to further reduce the layer thickness and rapidly quenched on a chill roll equipped with an air knife to freeze the melt morphology. The number of layers is dependent on the number of die elements, and the film thickness ranged from more than 10 μm to a few nanometers [66]. The film properties were clearly a result of the morphology frozen in by the process and affected by the process variables used. An example of a film formed using this process will be described further in Section 5.2 (see Fig. 5.38).

The development of *chaotic advection*, initiated more than two decades ago by Aref and reviewed by him more recently [67], has led to its application and development for materials processing of polymer blends and clay nanocomposites by Zumbrunnen and his group at Clemson University [68–72]. This process has the exciting result of providing significant improvements to the impact properties of blends by addition of low volumes of the second phase. In one case [68], a polystyrene matrix was improved by the addition of only 9% by volume of low density PE (LDPE). The polymers were combined in the molten state within a cylindrical cavity where a quiescent, three dimensional chaotic mixing process resulted in the formation of stretched and folded minor phase domains that were interconnected and stable upon solidification. The unique microstructures were due to the process used and differed from the normally observed fine domain textures that generally result when using low volumes of a second phase polymer. The process has also been used in continuous flow to form extruded films with many layers. A batch process study of polystyrene and LDPE was used as a model binary system so that thicker layers could be formed for evaluation [69]. Figure 1.9 [71] is a schematic of the continuous chaotic advection blender (CCAB). In this study, the unique CCAB was used to investigate the influence of the morphology formed on tensile and impact toughness properties of blends of polypropylene (PP) with LDPE. Process control of the melt flow, and the stir rods, as well as the specific machinery design is important to obtaining the unique morphology that is responsible for the unexpected property

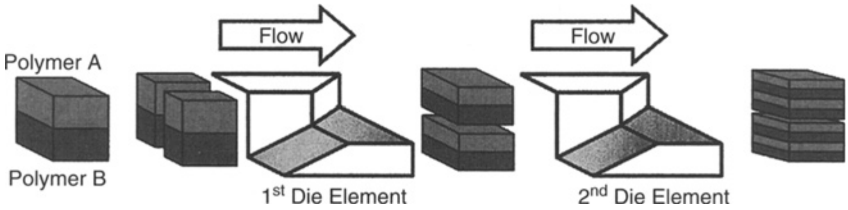

FIGURE 1.8. Schematic of layer multiplying coextrusion used for forced assembly of polymer nanolayers shows that two die elements multiply the number of layers from 2 to 8. (From Liu et al. [66], © (2004) American Chemical Society; used with permission.) (See color insert.)

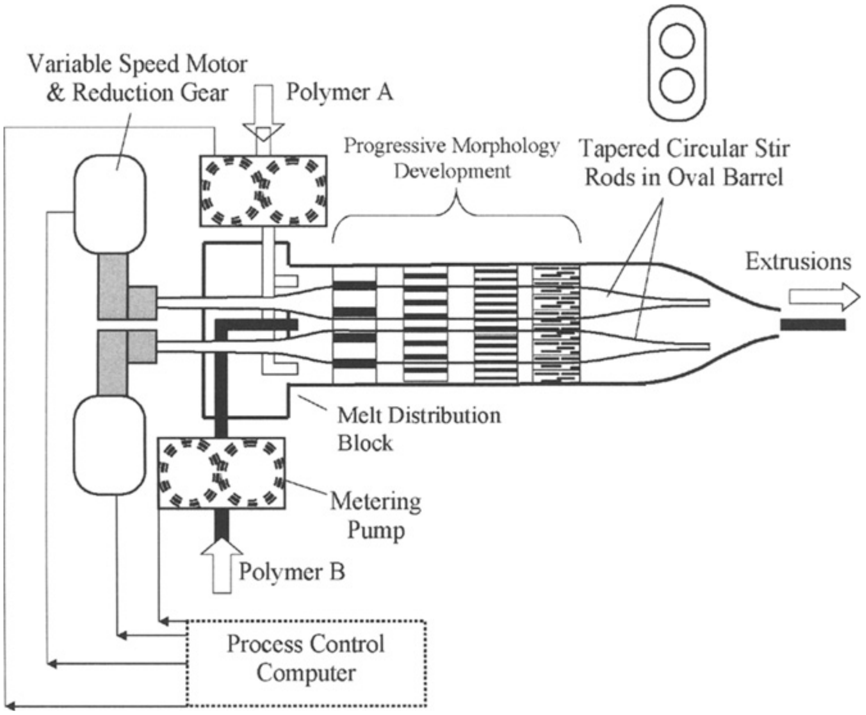

FIGURE 1.9. Schematic representation of the continuous chaotic advection blender. (From Zumbrunnen et al. [71], © (2005) Elsevier; used with permission.)

profiles. Further study currently under way involves the flow of the melt from this process into molds to maintain and control the morphology in molded parts [71]. Film formed using this process is described in Section 5.2 and an example shown in Fig. 5.39; an example of a nanocomposite formed by this process is described in Section 5.4 (see Fig. 5.109).

1.4 POLYMER CHARACTERIZATION

With the invention of scanning probe microscopes more than 25 years ago, the entire field of materials exploded into the realm of the nanoworld. The ease of imaging atoms and molecules has opened up the characterization of materials including polymers. The microscopes have changed and enabled materials to change as well, composites now include nanocomposites, and so on. Thus, the characterization of materials has changed dramatically in the past decade. Advances in many other microscopy and analytical techniques has also resulted in additional information being available about materials. The need for complementary techniques to fully understand materials continues to be required for full understanding of structure-property-process relationships.

1.4.1 General Techniques

A very wide range of analytical techniques are used to characterize polymer materials (e.g., see references on polymer physics [49], thermal analysis [73, 74], light microscopy [75, 76], Raman [77, 78], x-ray scattering [79], various spectroscopies [80, 81], and a wide range of microscopy techniques [82]). A text on polymer blends also describes many polymer characterization techniques [83]. Texts on microscopy with a focus on biological materials are often useful for the polymer microscopist (e.g., [84, 85]) as the materials have in common a tendency to be soft, to require contrast enhancement, and to suffer from radiation damage in electron beam instruments. The primary characterization of an organic material must be chemical. Elemental analysis by wet chemistry or spectroscopy may be useful in a few cases, for example to determine the degree of chlorination in chlorinated PE, but most chemical analysis is at the level of the functional group. Ultraviolet/visible spectroscopy and mass spectroscopy (MS) of fragments broken from the polymer chain are often used. Even more common spectroscopies are infrared (IR) absorption, Raman, and nuclear magnetic resonance (NMR), which is very important. All of these can distinguish specific chemical groups in a complex system. Raman may be used on small particles and inclusions much more easily than IR, but IR and in particular Fourier transform IR (FTIR) has advantages of sensitivity and precision. Nuclear magnetic resonance also gives local information, on a very fine scale, about the environment of the atoms investigated.

Once the chemistry of the molecule is known, the next important characteristic is the molecular weight distribution (unless the material is a thermoset or elastomer with infinite molecular weight). The molecular weight distribution is determined by a range of solution methods of physical chemistry, viscometry, osmometry, light scattering, and size exclusion chromatography. Chemical and physical characterization methods overlap in the polymer field, for NMR of solid samples can determine the mobility of atoms in various regions and the orientation of molecules. IR and Raman are also sensitive to orientation and crystallinity of the sample.

There are two further general types of physical characterization. They involve either scattering of light, neutrons, or x-rays or the formation of images of the polymer by microscopy, the subject of this text. Electron diffraction logically belongs in the first group but is always performed in an electron microscope, so it is associated with microscopy. This technique shares with microscopy the ability to determine the structure of a local region, whereas other scattering methods determine the average structure in a large sample volume. The impact of electron crystallography on the study of polymer materials has been reviewed by Voigt-Martin [86, 87].

The past decade has seen the emergence of analytical imaging, which is imaging using the signals from various analytical instruments, such as FTIR and Raman microscopy, x-ray microscopy, and imaging by surface analysis using secondary ion mass spectrometry (SIMS) and x-ray photon spectroscopy (XPS).

1.4.2 Microscopy Techniques

Microscopy is the study of the fine structure and morphology of objects with the use of a microscope. Resolution and contrast are key parameters in microscopy studies, which will be discussed further. The specimen and the preparation method also affect the actual information obtained as the contrast must permit structures to be distinguished. Optical bright field imaging of multiphase polymers, for instance, has the potential of resolving details less than 1 μm across; however, if the polymers are both transparent, they cannot be distinguished due to a lack of contrast. There are variations among microscopes in available resolution, magnification, contrast mechanisms, and the depth of focus and depth of field. Optical microscopes produce images with a small depth of focus, whereas scanning electron microscopes (SEMs) have both a large depth of focus and large depth of field.

There is a wide range of microscopy instruments available that can resolve details ranging from the millimeter to the subnanometer scale (Table 1.3). The size and distribution of

TABLE 1.3. Characterization techniques: Size ranges

Wide angle x-ray scattering (WAXS)	0.01–1.5 nm
Small angle x-ray scattering (SAXS)	1.5–100 nm
Transmission electron microscopy (TEM)	0.2 nm–0.2 mm
Scanning probe microscopy (SPM, AFM, STM, etc.)	0.2 nm–0.2 mm
Scanning electron microscopy (SEM)	4 nm–4 mm
Optical microscopy (OM)	200 nm–200 μm
Light scattering (LS)	200 nm–200 μm