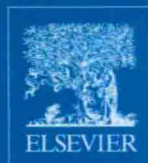


# **Beta Nucleation of Polypropylene**

Properties, Technology,  
and Applications

Philip Jacoby



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Philip Jacoby



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## Preface

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Polypropylene (PP) is one of the highest volume thermoplastics used today. PP applications include fibers, films, injection molding, extrusion, and blow molding. By 2010, worldwide consumption of PP exceeded 50 million tons. The combination of low cost, low density, excellent physical properties, and good processability has helped to spur this growth.

Over the past several decades, the technology to produce PP and broaden its property profile has also undergone dramatic changes. These developments include the introduction of new, high-activity catalysts, and new processes for producing both homopolymer and copolymer PP resins. The simultaneous development of a wide variety of functional and stabilizing additives has also broadened the application areas where PP could be used.

The performance properties of PP are intimately associated with its semicrystalline nature. Increases in crystallinity lead to improvements in stiffness, strength, and high-temperature performance. Various techniques can be used to alter the crystallinity of PP such as modifying the polymer molecular structure, changing the thermal conditions used to produce a part, and using crystal nucleating agents. Nucleating agents provide a very convenient and cost-effective way to improve both the mechanical and optical properties of PP. Nucleating agents can also dramatically effect the processing behavior of PP such as improving productivity and shortening cycle times.

One of the more interesting aspects of PP crystallinity is the fact that this polymer can crystallize into more than one crystal type. This property is known as polymorphism. An extreme example of polymorphism occurs for the element carbon where two different crystal forms (graphite or diamond) exist that have the most divergent set of properties that one can imagine, with graphite being one of the softest materials known, while diamond is the hardest.

In the case of PP, the only two crystal forms that have any significant commercial interest are the alpha and beta forms. The alpha form is the most common crystal type that typically develops when PP crystallizes from the molten state. A wide variety of nucleating agents are often added to PP to speed up the formation of the alpha crystals and to reduce the size of the crystal aggregates known as spherulites. Some

alpha nucleants can reduce the spherulite size to well below the wavelength of light, which causes a molded or an extruded PP part to become quite clear due to reduced light scattering from the alpha spherulites. This particular type of alpha nucleant is referred to as clarifier.

Other types of nucleating agents can cause the beta crystal form of PP to develop, and these additives are referred to as beta-nucleating agents. Although beta nucleants have been known for over 40 years, it is only in the last 25 years that beta-nucleating agents have been used in commercial applications. Since beta-nucleated PP products are typically used in small-volume niche applications, the incentives do not yet exist for most large PP resin companies to produce beta-nucleated PP grades. This means that the majority of beta-nucleated PP applications which exist today require either the use of beta-nucleant masterbatches or the compounding of pure beta nucleants into the PP resin.

I have been involved in the development and commercialization of beta-nucleated PP products since the 1980s, and I have developed products such as microporous PP films and improved thermoformable grades of PP using beta nucleation.

The purpose of this book is to familiarize the reader with the unique attributes of beta crystallinity and the conditions required to produce this crystal phase using commercial processing equipment. This text assumes that the reader has some familiarity with PP and commercial processing equipment, but it does not assume a detailed knowledge of either of these technologies.

The first part of this book deals with a basic discussion of the different crystal forms of PP and the unique attributes of the beta phase. Many illustrations and examples are used to explain the conditions required for the formation of beta crystals, and how both molecular and processing variables influence the beta crystal content of a fabricated article.

In the second part of this book, the different commercial applications of beta-nucleated PP are discussed. I have had a great deal of direct hands-on involvement with many of these applications, and I have also authored many papers and patents dealing with commercial applications of beta nucleation. Many of the examples discussed in this book come from my own work in this area, and other examples are taken from both the technical and patent literature. The benefits of using beta nucleation in the production of various commercial products are illustrated through the use of case study examples.

I would like to thank my current employer, Mayzo, and Ben Milazzo the owner of Mayzo, for the opportunity to pursue my passion in this

technology, and for the freedom to innovate and create an entire business based on the sale of beta-nucleant masterbatches. Without this support much of the work discussed in this book would never have been done. I am also indebted to my former employer, BP Amoco, for the opportunities that I was given to pursue applications of this technology. I also wish to acknowledge the many researchers throughout the world who did much of the ground-breaking work on the physics and chemistry of beta nucleation. It is my hope that this book will help to expand the awareness of this unique PP technology, and to also entice others to explore new applications for beta nucleation.

Finally, I wish to thank my wife, Helene, for all of her support, and for putting up with some of my quirks such as stopping to examine the bottom of plastic packaging in the supermarket to see what polymer has been used, and whether the package was injection molded or thermoformed.

**Philip Jacoby**  
Marietta, GA  
September, 2013



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# **Part One**

## **Fundamentals of Nucleation**



# 1 The Semicrystalline Morphology of Polypropylene

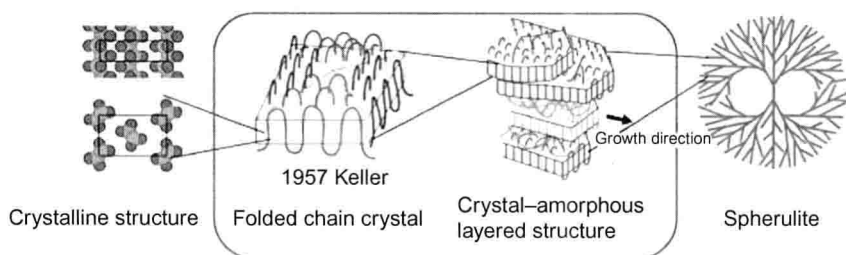
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## 1.1 Introduction: The Hierarchical Crystal Structure of Polypropylene

Polypropylene (PP) is a semicrystalline polymer. The most important factor influencing the properties of PP is its crystallinity and crystal structure. When molten PP is cooled to temperatures below the melting point, the molecules begin to form crystals when some degree of supercooling is achieved. The temperature at which this occurs is referred to as the crystallization temperature, or  $T_c$ . At this crystallization temperature the molecules begin to arrange themselves into ordered regions covering various size scales.

There are four different scales at which we can examine the crystalline morphology of PP. At the smallest size level we have the crystal unit cell, which exhibits geometric symmetry based on regular repeating units with dimensions on the order of 5–20 Å. These unit cells have parallel sides representing individual atoms or groups of atoms in the polymer chain, and their symmetry is described in crystallographic terms such as monoclinic, hexagonal, etc. These unit cells represent the subunits of the lamella crystals that form when the long-chain polymer molecules fold over on themselves to form flat plate-like structures known as lamella. The thickness of these lamellae is on the order of 50–100 Å, and the center-to-center separation between the lamellae, also known as the long spacing, is on the order of 100–300 Å. The lateral dimensions of lamellae can be on the order of microns in size. The regions between the lamellae contain tie molecules that are arranged in a mainly random manner, and this region contains the amorphous component of the solidified polymer.

The crystals and lamellae typically grow from the surface of heterogeneous particles in the melt, known as nuclei, and these lamellae grow radially outward in all directions from the nucleus to form spherical macrostructures known as spherulites. During crystallization, individual spherulites grow until they impinge on one another, and the typical spherulite size is in the range of 1–50 μm. The different scales of crystal structure that develop during melt crystallization are illustrated in Figure 1.1.



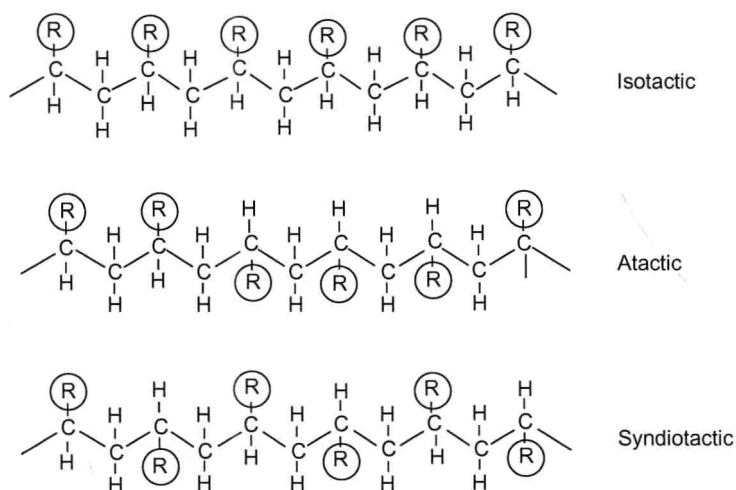
**Figure 1.1** Microstructures that form during polymer crystallization. (see color plate)

## 1.2 Polymer Structure and Its Influence on Crystallinity

The ability of PP to crystallize depends fundamentally on the stereoregularity of the polymer chains. PP is produced using specific catalysts that direct the addition of propylene monomer units onto the growing polymer chain. These catalysts are typically based on transition metals and fall into one of two types, namely Zeigler–Natta and metallocene. The head-to-tail addition of the propylene monomer results in a carbon chain backbone with methyl groups attached to every other carbon backbone atom. If all of these methyl groups have the same orientation with respect to the backbone, then the PP is referred to as being isotactic. If the methyl groups have an alternating configuration, then the PP is referred to as being syndiotactic. If the orientation of the methyl groups is completely random, then the PP is referred to as being atactic. Since crystallization requires that the polymer chain contain some stereoregularity, a purely atactic PP would be completely amorphous. These different stereochemical forms are illustrated in Figure 1.2.

In this book, we will only discuss the isotactic form of PP, since this form represents the vast majority of all commercially produced PP. Commercially produced PP always contains some low level of stereo-defects in the polymer chain, so it is never 100% isotactic. The higher the level of tacticity, the higher the level of crystallinity that can be achieved when the molten polymer cools from the melt. As we shall see in later chapters, the total level of crystallinity in a molded part dramatically influences the physical properties of the part.

Another structural aspect of the polymer chain that influences its crystallizability is the presence of co-monomers used during the polymerization process. If small amounts of ethylene are co-polymerized



**Figure 1.2** Different tactic forms of PP.

with propylene in a single reactor, then the ethylene units will be randomly inserted along the polymer chain. These insertions will function as defects in the growing crystal phase, and will lower the overall level of crystallinity that is achieved in the final part, and also lower the melting point of the PP crystal phase. Significant changes in physical properties, such as reduced modulus and improved clarity, also occur in these random copolymers.

Another type of copolymer, known as an impact copolymer (ICP) or heterophasic block copolymer, can be produced if two reactors in series are used to make the PP, and large amounts of ethylene co-monomer are only introduced into the second reactor. In the first reactor, where only the propylene monomer is present, normal isotactic PP homopolymer is produced. In the second reactor, a largely amorphous copolymer of ethylene and propylene is made, which is also referred to as an ethylene-propylene rubber (EPR). The EPR material is incompatible with the isotactic PP, so that molded parts contain the EPR phase dispersed as discrete particles in the homopolymer PP matrix. These particles are generally in the micron size range, and they may contain very low levels of polyethylene crystals or PP crystals depending on the co-monomer ratios and catalysts that are used. The soft nature of these rubber particles and their low glass transition temperatures can dramatically boost the impact strength of molded parts made from this ICP resin, especially at low temperatures where homopolymer PP is quite brittle.



There is a trade-off with stiffness since the rubber phase lowers the modulus of the PP resin.

In addition to the effects of polymer chain structure on the crystallizability of PP, the processing conditions used to produce molded and extruded products have an enormous influence on the level of crystallinity, the type of crystallinity, and the crystal morphology of the final part. These structural and morphological changes in turn strongly influence the final properties of the part. The interaction between processing, structure, and properties will be discussed in more detail later in this book.

### 1.3 Spherulitic Structure of PP

The size of the spherulites that form during melt crystallization depends on the concentration of the nuclei that are present. If specific nucleating agents are not added to the PP resin, the spherulite size can be quite large, often exceeding 50  $\mu\text{m}$  in diameter. The spherulites contain both lamella crystals and the amorphous material between the lamellae. Also, polymer chains that have low molecular weight and more stereo defects are rejected from the spherulite growth and tend to concentrate in the interspherulitic regions.

The spherulites are birefringent, in that the refractive index of light is different in the radial versus the transverse direction. This means that the spherulites can easily be observed using a polarizing light microscope when viewed under crossed polars. The spherulites exhibit a Maltese cross pattern with dark wings that are parallel to the planes of the polarizer and the analyzer. Typical spherulite appearance is illustrated in Figure 1.3.

The size of the spherulites has a strong influence on the haze or clarity of a PP part. Since the spherulites are birefringent, they strongly scatter visible light. One technique for improving the clarity and reducing the haze of PP is to incorporate nucleating agents into the PP in order to dramatically reduce spherulite size, thereby reducing light scattering. Some nucleating agents can produce spherulites that are much smaller than the wavelength of light, and thereby produce very clear parts. A micrograph of a nucleated PP viewed under crossed polars is shown in Figure 1.4, where one can see the very fine-grained spherulitic structure that is produced. Nucleants that produce a very fine-grained spherulitic structure are also known as clarifiers. We will discuss the role of nucleating in more detail later in this book.