Chapter 1. Introduction

1. 1   Introduction

The last several decades in the history of mankind have been characterized by the recognition and an increasing concern for the limited abundance of the resources available on this planet. This has led to the search for newer substitutes that can replace the naturally occurring materials, without imposing unreasonable compromises on the applications involved. A wide spectrum of polymeric materials have been developed for this purpose, and are being extensively used in a variety of applications, ranging from containers and packaging materials to substances used in artificial organs and space shuttles. Although the structural principles of polymer synthesis were beginning to be developed in the mid-nineteenth century, it was not until the early twentieth century that the acceptance of polymers as true macromolecules began to emerge. Since then, tremendous advances have been made in the understanding of the synthesis as well as the nature of polymeric materials and of the relationship between their structure and properties.

Polyolefins are the most widely used class of polymers in the world, and are the simplest in terms of composition. Polyethylene is the simplest of the polyolefins; however it has been and remains the most extensively studied polymer. This can be realized from the fact that the term "polyethylene" can no longer be used to refer to a single polymer. Instead, it encompasses an array of ethylene-based materials that differ from each other in several respects, some of which include molecular weight and its distribution, chain length, presence /absence of branches etc. Furthermore, another sub-class of materials involving the copolymerization of ethylene and α-olefins has become increasingly important in the last two decades. These materials collectively termed ethylene/α-olefin copolymers have been synthesized with varying macro and microstructures using different types of catalysts and comonomers.

Polyethylene is a thermoplastic material and therefore deforms readily on heating and recovers its rigidity on cooling. This property makes it possible to fabricate the

polymer by means of a variety of techniques, including injection molding, calendering, extrusion/blown extrusion molding and thermoforming. Polyethylene is also extremely stable and inert towards most reagents, possesses excellent water resistance and insulating properties as well as biocompatibility. These properties render this polymer an easy choice for different applications such as wire and cable insulation, films and seal layers in multilayer films for packaging, soft tissue reconstruction, surgical implants, carpet backing and mattress construction fabric, bookbinding, civil engineering uses etc. According to the Society of Plastics Industry, commercial production of polyethylene in the United States alone was approximately ten million metric tons per year, in 1996.

It is important to realize that the applications mentioned above demand different specific properties from the same material. For instance, film and packaging applications require increased toughness, those involving resistance to detergents require increased solvent resistance, biomedical applications demand specific adhesion properties, wire and cable applications require increased resistance to heat and ultraviolet radiation etc. These properties are largely determined by the characteristics of the polymer such as molecular weight, molecular weight distribution and degree of branching. The average molecular weight has a significant influence on properties in the melt and those involving large deformations of the solid. The melt drawability (at moderately high molecular weights) and the coefficient of friction of the molten film decrease with increasing molecular weight; while the tensile, tear and impact strengths, low-temperature toughness, softening temperature and resistance to environmental stress cracking of the solid increase with increasing molecular weight. The breadth of the molecular weight distribution, M_w/M_n, also influences the above properties in addition to affecting the ease of processability of the polymer. The degree of short chain branching strongly influences variables such as crystallinity and density, which in turn determine the ultimate properties of the material. A decrease in the number of branches results in an increase in the density as well crystallinity of the sample. The increased density favors an increase in chemical resistance, hardness, stiffness, tear strength and yield point; however, it decreases the flex life of the polymer as well as its permeability to liquids and gases. Thus, it is evident that the variables discussed above strongly affect the end-use properties of the polymer in its applications. As a result, it is indispensable to completely understand the relationship

between the structure (as represented by these variables) and the properties of the polymer, in order to successfully manipulate the applicability of the polymer.

1.2   Goals and Justification

It is clear from the above discussion that polymers are used in a wide range of applications depending on their properties. The properties of the material, in turn are strongly influenced by its morphology. Parameters such as molecular weight, molecular weight distribution, chain length, concentration of branches as well as the processing conditions play a significant role in determining the morphology developed in the polymer. Among these parameters, processing conditions, more specifically, thermal history is a major factor. This is evident from the fact that a given material with specified molecular weight and its distribution, branch content, etc. can be made to exist with a different morphology, at say, two different temperatures or at different times. These variations in morphology are clearly associated with the differences in the crystallization processes involved. Therefore, a clear understanding of the nature of the crystallization process under a specified condition would allow for better control of the ultimate properties of the polymer.

The concepts discussed above are particularly relevant for polymers with moderate and low levels of crystallinities, such as the ethylene/α-olefin copolymers studied here. In these materials, the crystallinities continue to increase considerably with time, suggesting that the morphology and properties are also evolving with time. This process in which additional crystallinity develops with time is referred to as secondary crystallization (that which occurs after the primary crystallization). Several mechanisms including lamellar thickening, formation of new lamellae and crystal perfection have been suggested for this process. However, the exact mechanism of this process in polymers with low crystallinities is not well understood. Therefore, there is a need to investigate the effects of long term annealing on the crystallization behavior of these materials.

The goals of the present study may be summarized as follows:

1. To investigate the role of comonomer in the crystallization and melting behaviors of the ethylene/α-olefin copolymers, in comparison to linear polyethylene.
2. To follow quantitatively the temporal evolution of secondary crystallization in these copolymers, in view of the changes in morphology as well as structure.
3. Based on the results of 1 and 2 above, to propose a "universal" model for the secondary crystallization in a wide spectrum of similar semicrystalline materials. E.g., PET, PEEK, PC, PVC, PBT, PS and other ethylene/α-olefin copolymers.

1.3   Summary of Contents

The results of this investigation are presented and discussed in this dissertation. The organization of the chapters and their contents are summarized below.

Chapter 2 is a review of the fundamental aspects of polymer crystallization, including the various theories developed for modeling this phenomenon in homo- as well as copolymers of polyethylene. The significant differences between the two types of materials are pointed out. The history of the development of copolymers using metallocene-based single site catalysts is also revisited. This section provides a means of comparing the different types of copolymers available, including the ones based on Ziegler-Natta catalysts. An extensive review of the currently available literature related to the crystallization and melting behaviors of ethylene copolymers, similar to the ones employed in the current study is presented. The last section of this chapter is a discussion of the structural aspects of polyethylene, including the specific bands observed in the infrared spectrum as well as a summary of the pertinent literature.

Chapter 3 is the Experimental section of this dissertation. It includes a summary of the molecular characteristics of the copolymers. The experimental techniques [Nuclear Magnetic Resonance (NMR) Spectroscopy, Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Force Microscopy

(AFM)] as well as the specific conditions employed for each study are also explained in detail.

Chapter 4 is a detailed report of the characterization of the branch content and sequence distribution of the copolymers using Nuclear Magnetic Resonance (NMR) spectroscopy. The concentrations of branches in the samples are estimated from their NMR spectra and compared to the values provided by the supplier. In addition, a parameter related to random unit placement is also estimated for each copolymer, and it is demonstrated that the samples examined conform closely to the random statistics of copolymerization. The results from density gradient column measurements on the copolymers are also reported. The experimentally determined densities are compared to those of Hydrogenated Poly Butadienes (HPB) obtained in the literature. [The HPBs are often considered to be model random ethylene-butene copolymers].

Chapter 5 is focused on the calorimetric part of this investigation. The results from the cooling and isothermal crystallization studies are reported. It is shown by means of the cooling experiments that two distinct regions of crystallization - a lower temperature cooling rate independent and a higher temperature cooling rate dependent region - exist in these copolymers. The isothermal studies below a temperature, T*, reveal the presence of two melting peaks - a lower temperature endotherm that evolves with time, and a higher temperature melting peak that remains invariant with time. The temporal evolutions of the lower endotherm in the three types of copolymers are compared to each other. It is demonstrated that the crystallization and melting behaviors of the copolymers are independent of branch type, further implying that the branches are all excluded from the growing crystal. The lower temperature region is found to be comprised of thin and less stable crystals formed under a high degree of constraint. It is proposed that these crystals are formed by simple aggregation of short sequences in the interlamellar amorphous regions and may resemble the fringed-micelle type crystals present in poorly crystallizable polymers such as poly(vinyl chloride)[1,2].

The influence of branch content on the physical properties of the copolymers, as determined by the study, are clearly indicated in the discussion section of this chapter. A preliminary model representing the mechanism of crystallization in these copolymers is outlined.

Chapter 6 is a discussion of the results from the AFM experiments. The gradation in morphology of the copolymers from a lamellar-type to a bundled crystal-like form, as a function of branch content is seen from the micrographs. This morphological variation is also correlated with the crystallization mechanism proposed in the previous chapter.

Chapter 7 is devoted to the experiments using infrared spectroscopy. The results obtained from this technique are discussed in view of those derived from calorimetry. The co-existence of crystals with two different unit cell structures, namely orthorhombic and hexagonal, is demonstrated from the band intensities at 730 and 720 cm^{-1} of the infrared spectra of the copolymers. The effects of branch concentration and temperature on the relative proportions of these two crystal forms are also determined from the experiments. The presence of the two types of crystal structures is discussed in view of the cooling rate dependence/independence and the two melting peaks observed via thermal analysis. These observations are related to the idea of a dual morphology proposed in the previous chapters.

Chapter 8 is the concluding part of this dissertation. The results from Chapters 3-7 above are interpreted in terms of one another, in order to understand the nature of crystallization in the copolymers examined. These results are also compared to those obtained from similar studies on other semicrystalline polymers, performed in the same laboratory. Based on the comparison, the model proposed for the crystallization mechanism of the copolymers is extended to represent the crystallization mechanisms in semicrystalline polymers, in general. A few possible avenues to explore in the future are also pointed out.

[1] M. Gilbert, *J. Macromol. Sci. - Rev. Macromol. Chem. Phys.*, **C34(1)**, 77 (1994)
[2] W. M. D. Bryant, *J. Polym. Sci.*, **2**, 547 (1947)