



## CHAPTER I INTRODUCTION

It is a general knowledge that physical and mechanical properties of a semi-crystalline polymer are dictated by morphology, which, in turn, is influenced by crystallization behavior of the polymer. The kinetics of polymer crystallization and morphology are influenced by various factors such as molecular weight averages, molecular weight distribution, chain flexibility, chain defects, stereo-regularity of the polymer chain, etc. The crystallization process of a polymer product is also affected by the processing conditions such as temperature, pressure, addition of nucleating agent, shear stress, etc.

During the last decades, polymer crystallization has become a fascinating topic and a number of publications and experiments have been worked to investigate the effect of various factors on crystallization behavior of polymers and make an effort to the knowledge how these factors affect the crystallization kinetics which is very different to the crystallization of non-polymeric low molecular weight substances.

Firstly, in the next chapter, the crystal morphologies proposed by many researchers, the fundamental and the theoretical background based on thermodynamics and kinetics of polymer crystallization process were briefly reviewed. The several crystallization kinetics models which proposed to describe the crystallization process were presented here.

In chapter 4 and 5, the isothermal and non-isothermal melt-crystallization and subsequent melting behavior of syndiotactic polypropylene (sPP) were investigated by using sPP resins with different molecular characteristics (i.e. molecular weight average, stereo-regularity) to study the effect of chain properties on crystallization behavior. The crystallization kinetics were also described based on various kinetics models (i.e. Avrami, Malkin, Urbanovici-Segal, Ozawa, and Ziabicki models). An important thermodynamics parameter, the equilibrium melting temperature, was determined and studied how it is affected by the molecular characteristics of sPP chains. The differential scanning calorimetry (DSC) technique

is the main technique used to investigate and follow the crystallization and melting upon the temperature and time.

Furthermore, based on the knowledge that primary crystallization of semi-crystalline polymers comprises mainly the primary and the secondary nucleation mechanisms. A simple way for enhancing the overall crystallization rate of semi-crystalline polymers during processing is by the introduction of a heterogeneous substance that could induce the formation of nuclei. Substances that can induce the formation of nuclei very effectively are called clarifying and nucleating agents. Pigments are used to impart desirable colors to the final plastic products but, in many cases, they could have a large effect on the crystallization behavior of the plastic during processing. As reported by many authors (Sterzynki *et al.*, 1997; Broda, 2003; Broda, 2004), different types of pigments can effect the crystallization behavior and morphology of isotactic polypropylene iPP which exhibits several crystal modifications, such as the monoclinic  $\alpha$ , the hexagonal  $\beta$ , and the triclinic  $\gamma$  forms, the presence of some pigments, e.g. quinacridone, could promote the formation of the thermally less stable  $\beta$  rather than the thermally more stable  $\alpha$  form.

In chapter 6, the effect of three types of pigments, i.e. quinacridone, phthalocyanine, and diarylide, on non-isothermal melt-crystallization behavior of medium-density polyethylene (MDPE) was investigated by thermal analysis. The kinetics of the non-isothermal melt-crystallization process was analyzed based on the well-known Avrami macrokinetic model.

Finally, in the plastics and rubber industries, inorganic fillers have always played an important role. The main purpose of their use is confined not only to cost reduction, but also to improve physical and mechanical properties. Among the various mineral fillers,  $\text{TiO}_2$  is mainly used as a white pigment, due to its brightness. In addition,  $\text{TiO}_2$  can act as a flame retardant or antioxidant that could help improve the thermal stability of the final products (Allen *et al.*, 1998; Turton *et al.*, 2001; Titelman *et al.*, 2002).

Because of the high specific surface area, inorganic nanoparticles are interesting as a new class of inorganic fillers. So in chapter 7, the non-isothermal melt-crystallization of isotactic polypropylene (iPP) filled with neat,  $\text{SiO}_2$ -coated and

stearic acid-coated TiO<sub>2</sub> nanoparticles was investigated mainly by differential scanning calorimetry (DSC). The kinetics of the non-isothermal melt-crystallization process were analyzed based on the Avrami macrokinetic model. The mechanical properties (i.e. tensile strength, impact strength, and flexural strength) were also evaluated and reported.