

## Chapter 1 Introduction

There are two major objectives for this work. The first objective is to gain a better understanding of the mechanisms of secondary crystallization and reversible crystallization and melting for linear polyethylene and for a series of random ethylene/styrene copolymers. The second objective is to critically test the classical Lauritzen-Hoffman polymer crystallization theory using spherulitic growth rate data for a series of poly(ethylene oxide) fractions obtained at different temperatures.

In random ethylene copolymers, a continuous morphological shift from spherulites with stacked lamellae at very low branch content, to thin lamellae with reduced lateral dimensions at higher branch content, and to fringed-micellar type crystals at even higher branch contents has recently been observed in studies of ethylene/1-octene random copolymers.<sup>1,2</sup> The evolution of the morphology with comonomer content originates from the introduction of non-crystallizable comonomers into the chain backbone. Copolymerization of ethylene with styrene leads not only to a dramatic slowing down of the crystallization kinetics but also to a greatly reduced extent of primary crystallization. Secondary crystallization can therefore take two different forms depending primarily on the comonomer content and the temperature: 1) lamellar thickening, and 2) the formation of secondary crystals. To gain a better understanding of secondary crystallization processes, the technique of temperature modulated calorimetry (TMC) combined with traditional differential scanning calorimetry (DSC) will be used in this work. The excess heat capacity during quasi-isothermal process is detected by TMC and is believed to be associated with reversible crystallization and melting processes. However, the mechanism for the generation of the excess heat capacity is still under discussion. Two competing models, the lateral surface model by Wunderlich et al.<sup>3</sup> and the fold surface model by Strobl et al.,<sup>4,5,6</sup> have been in dispute for many years. Our strategy is to establish correlations between the secondary crystallization process and the generation of the excess heat capacity. On this basis, we will be able to achieve a better understanding of the mechanism of reversible crystallization and melting using the knowledge developed in the area of secondary crystallization.

In the second part of this thesis, we revive a fundamental discussion on the kinetic theory of polymer crystallization. As the only tractable kinetic model which is capable of

describing the main features of the polymer crystal growth process quantitatively, the Lauritzen-Hoffman (LH) theory has achieved great successes in the last 40 years. The core part of the LH theory has never been abandoned although some modifications and improvements have been made to accommodate new experimental findings and to answer some criticisms. However, a strict test of the LH theory is still absent. For example, whether the LH theory correctly accounts for chain transport has not been established. The work by Hoffman and coworkers<sup>7</sup> on the chain length dependence of growth rate for a number of polyethylene fractions did not give solid support for the incorporation of the reptation concept into the LH theory. In addition, testing of the LH theory regarding the chain length dependence of growth rate with other polymeric systems has been very limited. In the present work, we measured the growth rate of a series of poly(ethylene oxide) narrow molar mass fractions. The data were first analyzed using the classical LH formalism. Investigation of the chain length dependence of the crystallization regime transition behavior shows some inconsistencies with the predictions from the LH theory. Furthermore, while we found evidence of a regime I/II transition, we also discovered that this regime transition can be explained in terms of the rate dependence of the friction coefficient rather than on the basis of a change in secondary nucleation rate. On this basis, we begin to question the LH theory.

Apart from the literature review chapter, the dissertation consists of several manuscripts which are either published, in print or, in preparation. Therefore, the writing style is somewhat different from what may be expected for a Ph. D. dissertation.

This dissertation is organized in the following way. In Chapter 2, a literature review on polymer crystallization is given, focusing primarily on the morphology of semicrystalline polymers, on thermodynamic and kinetic aspects of polymer crystallization and, on the crystallization of copolymers. Special emphasis will be placed on the classical Lauritzen - Hoffman (LH) surface nucleation theory.

In Chapter 3<sup>\*</sup>, a lamellar thickening model is given, which explains the sigmoidal behavior of melting temperature evolution during isothermal crystallization. This model

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<sup>\*</sup> Chapter 3 is published in *Macromolecules*. Chapter 4 is accepted for publication in *Macromolecules*. Chapters 5 and 6 are also being prepared for submission to *Macromolecules*.

demonstrates for the first time that the evolution of both the degree of crystallinity and the melting temperature are correlated and can be characterized by a common parameter.

In Chapter 4\*, the crystallization and melting behaviors in a linear polyethylene and a low styrene content ethylene/styrene copolymer are investigated. The primary and secondary crystallization are correlated to the generation of excess heat capacity measured by temperature modulated calorimetry. Lamellar thickening, which is considered as the dominant mechanism for the secondary crystallization in these materials, is responsible for the decay of excess heat capacity under isothermal conditions. Our results favor the fold surface model as the basis for reversible crystallization and melting.

Chapter 5\* deals with the crystallization and melting behavior of a series of ethylene/styrene copolymers with high styrene content. This study focuses on the origin of the multiple melting behavior and on correlations between secondary crystallization and generation of excess heat capacity. The results support the idea that the reversible crystallization and melting in high styrene content copolymers at low temperature most likely occurs on the lateral surface of primary crystals. Combination of results obtained in Chapters 4 and 5 allow us to propose a full description for the mechanism of reversible crystallization and melting as a function of temperature and comonomer content.

In Chapter 6\*, the chain length dependence of spherulitic growth rates will be studied for a series of poly(ethylene oxide) narrow molar mass fractions. A new regime transition mechanism based on the Brochard-de Gennes slippage model is proposed, which casts some doubts on the regime concept in the classic Lauritzen-Hoffman (LH) theory.

Chapter 7 gives the general conclusions and suggestions for potential future work.

## Reference

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- (1) Bensason, S.; Minick, J.; Moet, A.; Chum, S.; Hiltner, A.; Baer, E. *J. Polym. Sc., Polym. Phys. Ed.* **1996**, *34*, 1301.
- (2) Mathot, V. B. F.; Scherrenberg, R. L.; Pijpers, T. F. J. *Polymer* **1998**, *39*, 4541.
- (3) Wunderlich, B. *Prog. Polym. Sci.* **2003**, *28*, 383.
- (4) Hu, W.; Albrecht, T.; Strobl, G. *Macromolecules* **1999**, *32*, 7548.
- (5) Albrecht, T.; Armbruster, S.; Keller, S.; Strobl, G. *Macromolecules* **2001**, *34*, 8456.
- (6) Albrecht, T.; Strobl, G., *Macromolecules* **1995**, *28*, 5827.
- (7) Hoffman, J. D.; Miller, R. L., *Macromolecules* **1988**, *21*, 3038.