

Chapter 7 General Conclusions and Future Work

7.1 General Conclusions

Investigations of the crystallization and melting behavior of linear polyethylene and of a series of ethylene/styrene random copolymers with styrene content ranging from 0.35 mol% to 11.7 mol% were discussed in chapters 3, 4 and 5 using the techniques of DSC and temperature modulated calorimetry. The focus of these studies was placed on the correlations between the temporal evolution of the degree of crystallinity, melting behavior and excess heat capacity during isothermal crystallization. The results suggest that: 1) The mechanism for the formation of low melting crystals varies with the crystallization temperature and comonomer content. With decreasing crystallization temperature and increasing styrene content, low melting crystals evolve from chain-folded lamellae to fringed-micelle type crystals; 2) The mechanism for the generation of excess heat capacity during quasi-isothermal crystallization also depends on the crystallization temperature and comonomer content. At high temperatures or in low styrene content copolymers, the generation of the excess heat capacity is most likely associated with the reversible segmental exchange on the fold surface. However, at low temperatures or in high comonomer content copolymers, the excess heat capacity is more likely to originate from a reversible attachment and detachment of segments on the lateral surface of crystals. Therefore a connection was established between the mechanism of secondary crystallization and that of reversible crystallization and melting.

In chapter 6, the chain length dependence of the spherulitic growth rate is discussed in the case poly(ethylene oxide) fractions. A regime I/II transition is observed in fractions with molecular weight ranging from 11 to 157 kg/mol while no obvious regime transition was detected for fractions of higher molar mass. The equilibrium melting temperature was estimated by assuming that the regime I/II transition occurs at a fixed undercooling. It is found that the ratio of nucleation constants in regimes I and II is, in general, not equal to 2, as predicted by the LH theory, but increases with increasing chain length. In addition, the exponential prefactor, G^0 , inferred from the LH analysis does not follow the power law predicted by Hoffman and Miller. All of these results cast some doubts on the nucleation-based regime concept and the incorporation of a simple

reptation idea in the LH theory. In the present work, we proposed that the regime transition in the crystal growth rate is associated with a transition in the velocity dependence of the friction coefficient, which is predicted by Brochard-de Gennes slippage model. Therefore a new interpretation of the regime I/II transition behavior, of the chain length dependence of nucleation constant and G^0 in regime I is provided. The proposed mechanism is also shown to be consistent with recent calculations by Toda who showed that the rates of both surface nucleation and substrate completion exhibit a strong temperature dependence.

7.2 Future Work

7.2.1 On the Lateral Surface Model

In the present work, the decay behavior of the excess heat capacity during quasi-isothermal crystallization is interpreted using the KWW analysis. In the case of linear polyethylene and low styrene content copolymers, this decay has been correlated with the lamellar thickening process, which tends to eliminate some of the available sites for reversible segmental exchange on the fold surface, therefore decreases the excess heat capacity. This conclusion is strongly supported by the similar activation energy values obtained from $B(T_x)$, $1/\tau(T_x)$ and those for α_c relaxation in the crystalline region. However, for the high styrene content copolymers, the mechanism underlying the decay behavior of the excess heat capacity is still an open question. Why should the apparent activation energy first decrease with increasing styrene content and subsequently increase with styrene content? In addition, a good linearity in the Arrhenius plot was observed for low styrene content copolymers while this plot shows non-linearity for high styrene content copolymers. A physical meaning for the characteristic time inferred from the KWW analysis and for the activation energy obtained from the Arrhenius plot has not been provided by our study and should be studied to obtain a better understanding of the correlations between the generation of excess heat capacity and the formation of secondary crystals in high styrene content copolymers.

In this case, the generation of excess heat capacity at low crystallization temperature for high styrene content copolymers was explained by the lateral surface model. One would like to understand how the reversible segmental attachment and

detachment process on the crystal lateral surface is controlled by the crystallization temperature, the level of topological constraints, the characteristics of chain segments (stiffness, length, etc...) and, any other factors. To achieve a comprehensive understanding of this mechanism, it would be interesting to study other polymer systems. For example, syndiotactic polypropylene (s-PP) may be a good candidate since this polymer does not show an α_c relaxation which would eliminate the possibility that segmental exchange occurs on the fold surface. The evolution of excess heat capacity at high temperature, where both primary and secondary crystallization can be observed, should provide valuable information regarding the correlation between the evolution of crystallinity, the excess heat capacity and the melting behavior.

7.2.2 On the Regime Transition Behavior

It is imperative to further test the LH theory using other polymer systems. Possible candidate are poly(ϵ -caprolactone) (PCL) and poly(L-lactic acid) (PLLA). A study of the molecular weight dependence of growth rate for a series of PCL fractions has been given by Chen et al.¹ A plot of the growth rate as a function of chain length shows a bell shape which is similar to that demonstrated by PEO in the present study. In addition, the temperature range in which the spherulitic growth can be observed is close to that characteristic of PEO. However, the growth rate data in Chen's study is insufficient for a reliable analysis. More detailed growth rate data as a function of crystallization temperature and chain length are needed. PLLA is also a very interesting candidate as, like PEO, it exhibits a regime I/II transition behavior.

It should be noted that the LH model is expected to work well in the flexible, linear homopolymer systems where regular chain-folding structure can be achieved. Therefore, testing of the LH model should be limited to these polymers. For other polymer systems, such as PS, PEEK, alternative kinetic model should be constructed to explain their crystallization behaviors.

7.2.3 On the Morphologies of Crystals in Different Regimes

Although distinct morphological differences can be observed in the three regimes for the case of polyethylene, such an observation is still absent for other polymer crystals.

Even for polyethylene, no consensus has been reached as to why different morphologies are observed in different regimes. One should note that the morphology study would benefit the kinetics study since the morphology of semi-crystalline polymer is kinetically determined. With the development of some new techniques such as hot-stage AFM, it would become feasible to monitor the morphology of crystals during isothermal crystallization. The information thus obtained is expected to further help investigators to understand the kinetics of crystallization in different regimes.

Besides temperature, the effect of molecular weight on the morphology is also an important topic. Recently, a transition from spherulitic to disklike hedritic morphology has been observed for isotactic poly(1-butene) (iPB) samples.^{2,3} It was also found that the transition temperature increases with molecular weight. It is noted that three regimes in the crystal growth of iPB were observed by Monasse and Haudin⁴ although the validity of their growth rate analysis is dubious in view of a lack of reliable estimate of the equilibrium melting temperature. One would like to measure spherulitic growth rates for a series of iPB narrow fractions to examine the possible correspondence between regime and morphological transitions. Such study would particularly interesting as we showed in our study that the regime I/II transition temperature also increases with molecular weight in the case of PEO.

7.3 Reference

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