

Chapter 8. Conclusions

The crystallization and melting behaviors as well as the morphology of a series of ethylene/ α -olefin copolymers with different types of branches and with varying degrees of branching were investigated. This was achieved by using a combination of techniques including Differential Scanning Calorimetry (DSC), Atomic Force Microscopy (AFM) and Fourier Transform Infrared Spectroscopy (FTIR). The results obtained from the three techniques were discussed in Chapters 5, 6 and 7 of this dissertation, respectively. It was also demonstrated from the results of Nuclear Magnetic Resonance (NMR) Spectroscopy experiments that the copolymers closely follow statistical random copolymerization statistics.

The thermal analysis studies discussed in Chapter 5 clearly indicate the existence of two distinct regions of crystallinity dependence on temperature, above and below a temperature, T^* . Furthermore, the crystallinities obtained during cooling and subsequently re-heating exhibit a transition from a hysteretic behavior ($> T^*$) to a reversible one ($< T^*$) at this temperature. The cooling rate dependence as well as the hysteresis observed in the high temperature region are reminiscent of the nucleation-controlled lamellar crystallization process observed in linear polyethylene. It further suggests that the crystals formed in this region are associated with a chain-folded lamellar morphology. The low temperature cooling rate independent region that also exhibits reversibility between heating and cooling cycles points to the involvement of thin and not very stable crystals. This was the first indication of the possibility of two different morphological forms in the copolymers.

Isothermal crystallization studies of the copolymers at different crystallization temperatures (T_x) below T^* revealed the presence of two endotherms. The higher melting endotherm that remains invariant with crystallization time (t_x) is associated with crystals that are formed during primary crystallization. In contrast, both the positions as well as the magnitude of the lower melting peak are found to increase with $\log(t_x)$. The relative positions ($T_m^{\text{low}} - T_x$) of the low endotherm for all three branch types were found to vary linearly with $\log t_x$. Furthermore, the data from all three branch types were

represented by a single line (of slope B), suggesting that the crystallization process examined is independent of branch type for the ethyl, propyl and butyl branches examined. Based on this observation and the argument that the lengthy butyl branch (in the ethylene-hexene copolymers) is not likely to be accommodated in the crystal, it was concluded that all three branch types are predominantly excluded from the crystal structure.

The slopes, B, of the lines from the $(T_m^{\text{low}} - T_x)$ vs $\log t_x$ plots described above were close to a value of 3 for $T_x < T^*$, while at higher crystallization temperatures, a dramatic decrease in the values, tending towards those of LPE, was observed. It was also noted (for $T_x < T^*$) that the extrapolation of T_m^{low} to very short crystallization times consistently yields the crystallization temperature, T_x . This is in sharp contrast to the melting behavior of the lamellar crystals of linear polyethylene that melt ~ 5 to 10°C higher than their temperatures of crystallization. This result indicates that the crystals associated with the melting of the low endotherm (secondary crystallization) formed at $T_x < T^*$ are less stable than those formed during the primary crystallization.

The areas of the low endotherm were deconvoluted from the rest of the heating scan using mathematical curve fitting. The variation in the areas of the low endotherm with t_x was represented by an Avrami type plot. The slope of the initial linear region, i.e., the Avrami exponent, n , was found to be equal to 0.5 for $T_x < T^*$. From the definition of n in the derivation of the Avrami equation, this value is suggestive of a one-dimensional diffusion controlled growth mechanism. However, as the crystallization temperature was increased beyond T^* , the value of the exponent progressively increased, approaching the value for linear polyethylene.

Therefore, the temperature, T^* , below which the crystallinity was found to be cooling rate independent as well as reversible, was also identified as the temperature below which the kinetic parameters (such as n and B) remain independent of crystallization temperature. At temperatures higher than T^* , these parameters began to display a marked dependence on T_x . These results further support the earlier suggestion that a dramatic change in the crystallization mechanism and resulting morphology occur at the temperature, T^* .

Based on the above results, a qualitative model for the crystallization mechanism in these copolymers was proposed. This model differs from the previous models in the literature in the fact that the formation of crystals during the primary and secondary crystallization are redefined in terms of the ability of the sequences to participate in the chain-folding process leading to lamellar growth. This model was described in detail in Chapter 4 of this dissertation. According to this model, the longest sequences in a copolymer form chain-folded lamellar crystals during primary crystallization. This process pins down the remaining portion of those sequences and other crystallizable sequences at the surfaces of the lamellae, thereby imposing severe constraints on their mobility and transport. Such highly constrained sequences are unable to form chain-folded crystals. However, they simply aggregate with neighboring sequences from the same chain or from different chains to form bundles that may be viewed as resembling the "fringed-micelles" associated with poorly crystallizable polymers such as PVC. The bundled crystals are expected to be much thinner and of smaller lateral dimensions compared to the lamellar crystals formed at higher temperatures. Then, an increase in branch concentration and/or a decrease in crystallization temperature tend to increase the proportion of crystals formed from the short, constrained sequences. Furthermore, the degradation in thickness, lateral dimensions and perfection of the crystals leading to the morphological transformation from chain-folded lamellar crystals to fringed-micellar crystals is gradual with increasing comonomer content and decreasing temperatures.

This prediction was experimentally confirmed from the Atomic Force Micrographs of the copolymers with varying degrees of branching. A gradual deterioration in the thickness and perfection of the lamellae with increasing branch concentrations was consistent with the ideas of the proposed model. In addition, the presence of bridge-like structures between the lamellae and approximately perpendicular to their surfaces was also discerned from the micrographs. These structures were associated with the bundled crystals co-existing with the chain-folded lamellar crystals, in the copolymers. The observation of such inter-lamellar bridge-like species in these copolymers has not been reported in the existing literature, to our knowledge.

The results from thermal analysis and AFM were correlated with those obtained from the infrared studies. The presence of another crystalline structure, in addition to the

usual orthorhombic crystal form expected for linear polyethylene, was also established from the results of the FTIR studies. The relative proportions of the various crystal forms in the copolymers as a function of branch content and temperature were estimated via mathematical deconvolution and curve-fitting processes. Comparing the results to those of the hexagonal rotator phase of *n*-paraffins, it was proposed that the non-orthorhombic crystal structure in the copolymers can be assigned to a hexagonal type unit cell structure.

The long-time dependence of the relative positions of the low endotherms was explained on the basis of a decrease in the configurational entropy of the remaining amorphous fraction, subsequent to the formation of the bundled crystals. This conclusion was based on the concept of secondary crystallization (at $T_x < T^*$) acting as an effective cross-linking process, where the bundled crystals serve as physical cross-links in the amorphous matrix. These fringe-like crystals are visualized as being comparable to the cross-link points in a network polymer. An increase in the number of such cross-links decreases the entropy of the amorphous phase, thereby causing its free energy to increase, and the melting temperature of the crystals concerned to shift to higher temperatures.

The results discussed above for the ethylene/ α -olefin copolymers were compared to those obtained from other semicrystalline polymers such as PET, PEEK, PBT, PVC, *i*-PS and polycarbonate, and it was established that the crystallization model proposed can be extended to these materials. This model further provides a means of correlating the temporal evolution of secondary crystallization to the time and temperature dependence of the physical properties of semicrystalline polymers.