7 Crystallization Behavior [58–75]

7.1 Polymer Crystals and Growth Forms

Single polymer crystals were first recognized in 1953 (Schlesinger and Leeper). Such crystals grow preferably from dilute solution to form rhombic platelets several μm in diameter and approx. 10 nm thick.

Figure 72 shows single polyethylene crystals, grown from a dilute solution, in which spiral, layered structures can be interpreted. Since the layers have a maximum thickness of several dozen nm and the polymer chains are several hundred nm long and orientated normal to the layer surfaces, it is obvious that chain folding must take place during crystallization. An acceptance of the principle of chain folding for which up to now, no satisfactory, thermodynamic theory exists, requires a modification of the Fransen micelle model for partially crystalline polymer solids (Fig. 73).

![Fig. 72. Electron micrograph of single PE crystals (from [58])](image)
According to Wunderlich there are three possible macroconformations for the molecules in a polymeric solid (see Fig. 74).

The morphology of a partially crystalline polymer is usually composed of all three types of macroconformation. For the chain folds in a single lamella various models can be put forward (see Fig. 75).

When crystallization occurs from a melt under increased pressure, the individual fold-lamellae become thicker and the chains approach a stretched form to give extended chain crystals. For polyethylene it has been shown that the lamella-thickness also increases with increasing temperature. Lamella-crystals are obvious-

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Fig. 73. Fransen micelle model for partially crystalline polymer solids

Fig. 74. Sketch showing the three possible macroconformations for the molecules in a polymeric solid (from [59])

Fig. 75. Models of crystal-lamellae
a. Acute folds, adjacent reentry; b. loose folding; c. meander model according to Pechhold