6.9. Multi-component crystallization and structure development in melt-crystallized systems

The morphology of a polyethylene blend – a homopolymer prepared from ethylene is a blend of species with different molar mass – after crystallization is dependent on the blend morphology of the molten system before crystallization and on the relative tendencies for the different molecular species to crystallize at different temperatures. The latter may lead to phase separation (segregation) of low molar mass species at a relatively fine scale within spherulites, and this is typical of linear polyethylene. Highly branched polyethylene may show segregation on a larger scale, so-called cellulation. Phase separation in the melt results in spherical domain structures on a large scale.

Hill and Barham (133) showed by transmission electron microscopy that blends of high and low molar mass polyethylene melts were homogeneous with no detectable phase separation. The blends were prepared by solution mixing to obtain an initially homogeneous blend before the thermal treatment in the melt. It should be realised that the mechanical mixing of high and low molar mass linear polyethylenes to obtain a homogeneous melt may require considerable work and time.

The melt morphology of blends of linear and branched polyethylene is another and more complicated story. Small-angle neutron scattering with one of the components being labelled (^{1}H being replaced with ^{2}H) provides direct information about the blend morphology of the molten systems: blends of linear polyethylene and branched polyethylene (low-pressure process using heterogeneous catalysts) are homogeneous provided that the branched polymer has less than 8 mol.% of branches (134,135). The same authors reported phase separation in blends where the branched polyethylene component had 16 mol.% branches. Barham et al. (136) developed an indirect method for the assessment of the blend morphology of the melt. This technique includes solution blending of the components, equilibration of the molten blend, rapid cooling to room temperature in order to minimize further phase separation and determination of the morphology of the semicrystalline polymer by transmission electron microscopy (linear and branched polyethylenes were expected to show different lamellar morphologies) and differential scanning calorimetry (bimodal melting was assumed to indicate phase separation in the molten state). The Bristol group has reported a great many studies suggesting that phase separation of linear and branched polyethylenes occurs in the molten state. Using this technique, phase separation was detected in binary blends with branched polyethylene with significantly lower degree of chain branching than was detected by the direct small-angle neutron scattering technique. Hill *et al.* (137) showed that the indirect methods could detect phase separation in blends with a branched polymer having less than 1 branch per 100 main chain carbon atoms. Similar results have been reported by Tanem and Stori (138, 139) using the indirect methods.

The main conclusions drawn from the studies of great many binary (in some cases ternary) blends were: phase separation was insensitive to the molar mass of the linear polyethylene (140,141) and to the branch type of the branched polyethylene (137,142) but dependent on the branch content (137,142-144). The typical diameter of the minority phase (supposedly enriched in linear polyethylene) was reported to be ~1 μm and this minority phase showed a coarsening with holding time – diameter $\propto t^{1/3}$, which suggested the occurrence of Ostwald ripening (145). The typical phase diagram constructed on the basis of results obtained by the indirect methods is a closed 'loop' (with both upper critical and lower critical solution temperatures) defining the two-phase region. The two-phase loop in the phase diagram is located near the 100% branched polyethylene, which typically extends in composition from 50-80% to 100% branched polyethylene and in temperature from ~120°C to ~170°C. Good examples of such phase diagrams are presented by Hill and Barham (136).

A recent paper from the Bristol group (146) provides a new perspective on the earlier findings obtained by the indirect methods. Micro-Raman imaging showed that phase-separated blends of linear and branched polyethylene remixed in the two-phase region of the phase diagram; the latter being mapped by the indirect methods. The authors concluded that the phase separation revealed by transmission electron microscopy does not occur on the basis of branch content. Morgan *et al.* (146) found evidence for regions of the same size as the domains observed by electron microscopy with either of the following two combinations: low crystallinity of the linear component and high crystallinity of the branched component or vice versa. The origin of this heterogeneity is not yet clear. Hence, the current view is that linear and branched polyethylenes do not phase-separate in the melt unless the branched polymer is very highly branched (>10 mol.% branching).

Crystallization of most polymers is accompanied by the separation of different molecular species, a process referred to as molecular fractionation. Bank and Krimm (147) provided the first direct evidence of molecular fractionation in polyethylene. The first extensive study performed by Wunderlich and Mehta (148) indicated that, at each crystallization temperature, there exists a critical molar mass (M_{crit}) such that the molecules of molar mass greater than M_{crit} are able to crystallize at this temperature, whereas molecules of molar mass less than M_{crit} are unable to crystallize. Fractionation was found to be relatively sharp in terms of molar mass. Fig. 4.26 shows that M_{crit} increases with increasing crystallization temperature. The lower limit of segregation is set by the hypothetical equilibrium of crystallization. It is assumed that dynamic equilibrium is achieved between fully extended-chain crystals and the surrounding melt. At equilibrium, the molecular length of the crystallizable species corresponds sharply to the lamellar thickness, and molecules that are shorter or longer than the fold length increase the free energy and are rejected from the crystal. The equilibrium melting point of a given molecular species is dependent not only on its molar mass but also on the molar masses of the other species present in the blended melt:

$$\frac{1}{T_{\mathrm{m}}} - \frac{1}{T_{\mathrm{m}}^{0}(M)} = \frac{R}{\Delta H}\left[-\ln v_{\mathrm{p}} + (\bar{x}-1)(1-v_{\mathrm{p}}) - \bar{x}\chi(1-v_{\mathrm{p}})^{2}\right] \tag{6.5}$$

where T_{m} is the melting temperature of the crystallizing species in the mixture of different species, T_{m}^{0} is the equilibrium melting-crystallization temperature of the pure species of the molar mass considered, v_{p} is the volume fraction in the melt of the crystallizing species, ΔH is the molar heat of fusion, χ is the Flory-Huggins interaction parameter and $\bar{x}$ is the volume fraction of crystallizing species with respect to all species in the blend. It is thus possible using Eq. (6.5) to calculate an equilibrium critical molar mass for each temperature of crystallization considering the molar mass distribution data of the polymer. Wunderlich and Mehta (149) showed that the experimental values were in accordance with the theoretical prediction at high degrees of supercooling. At low degrees of supercooling, the experimental data was significantly higher than the critical molar mass predicted by the equilibrium theory (Eq. (6.5). This led Wunderlich to suggest that each molecule undergoes a *molecular nucleation* before crystallization. Wunderlich claimed that fractionation is governed not by equilibrium considerations but rather by the size of the molecular nucleus under the given conditions. The free energy change on folded-chain crystallization of a molecule on a crystal substrate is given by:

$$\Delta G = \nu abL_{\mathrm{c}}\Delta g + 2bL_{\mathrm{c}}\sigma_{\mathrm{L}} + 2\nu ab\sigma + 2ab\sigma_{\mathrm{ce}} \tag{6.6}$$

where ν is the number of crystallizing stems of a given molecule and σ_{ce} is the extra free energy associated with each chain end. Zachmann (150,151) suggested that the major part of σ_{ce} is due to the entropy reduction of the non-crystallized cilia. The size of the critical nucleus (L_{crit}) can be calculated from Eq. (6.6) to be:

$$L_{\mathrm{crit}} = \frac{4\sigma\sigma_{\mathrm{L}}b\left(T_{m}^{o}\right)^{2}}{\left(\Delta h^{0}\right)^{2}\Delta T^{2}} + \frac{2\sigma_{\mathrm{ce}}T_{\mathrm{m}}^{0}}{\Delta h^{0}\Delta T} + \frac{2kT_{c}T_{\mathrm{m}}^{0}}{ab\Delta h^{0}\Delta T} \tag{6.7}$$

The first term of Eq. (6.7) dominates at low degrees of supercooling (ΔT), whereas the second and third terms predominate at higher ΔT. Eq. (6.7) was fitted to experimental data of Wunderlich and Mehta (148), where the adjustable parameter σ_{ce} was given a value of 100 mJ m^{-2}.

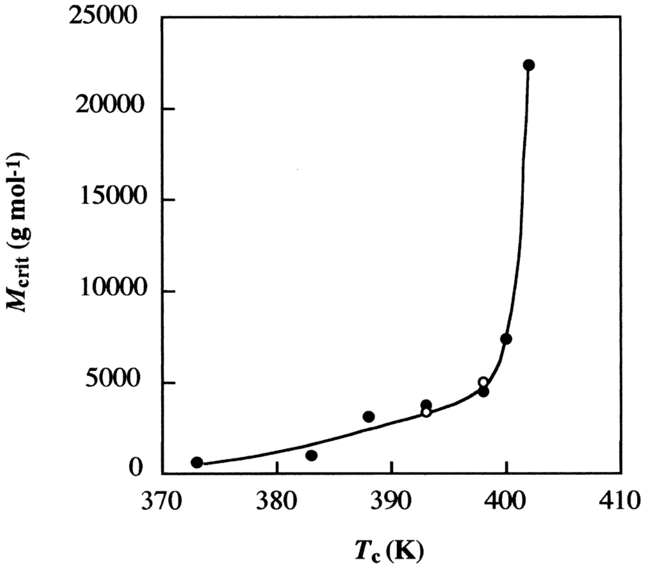


Fig. 6.26. Critical molar mass of melt-crystallized linear polyethylene as a function of crystallization temperature. Filled circles: data for a broad molar mass sample: $\overline{M}_n$ *= 8500 g mol*$^{-1}$*;* $\overline{M}_w$ *= 153 000 g mol*$^{-1}$ *of Mehta and Wunderlich (149). Open circles: data for a sample with* $\overline{M}_n$ *= 12 900 g mol*$^{-1}$*;* $\overline{M}_w$ *= 108000 g mol*$^{-1}$ *from Gedde et al. (152). From ref. (120) with permission from Kluwer, Doordrecht, Netherlands.*

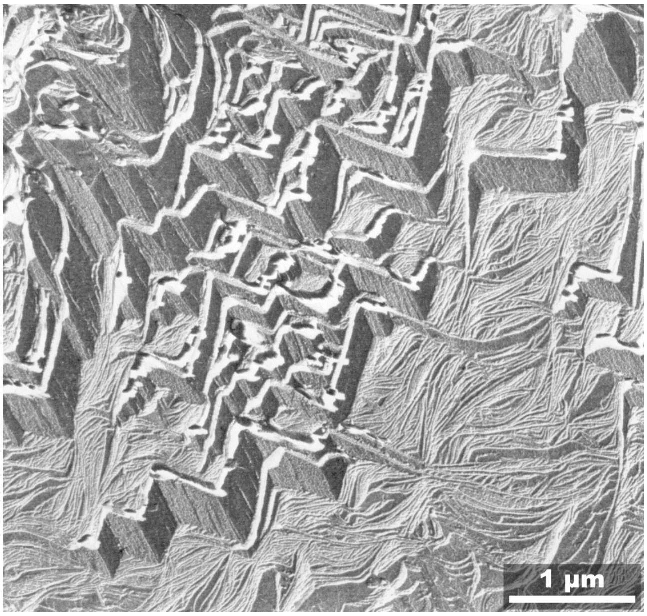


Fig. 6.27. Transmission electron micrograph of etched cut surface of a linear polyethylene after crystallization at 130.4 °C for 27 days followed by quenching. Etching was performed with permanganic acid. Note the continuity between dominant ridges and thinner S-shaped lamellae. From Bassett et al. (46) with permission from the Royal Society of London, UK.

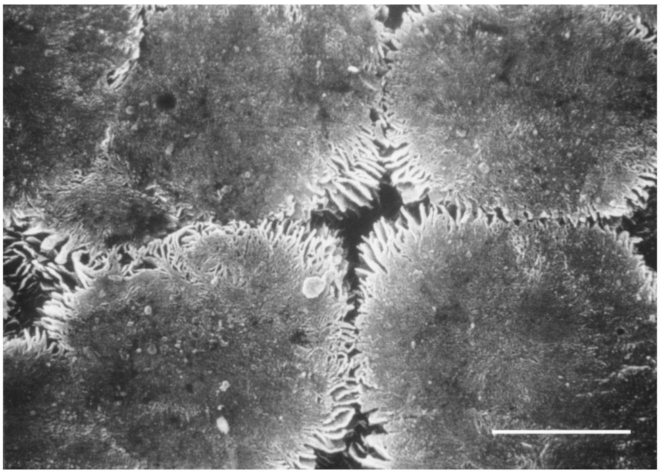


Fig. 6.28. Scanning electron micrograph of high density polyethylene first isothermally crystallized at 128 °C for and then rapidly cooled to room temperature. The sample have been etched with hot p-xylene to remove the material crystallizing in the cooling phase. Scale bar represents 20 µm. From Gedde and Jansson (154) with permission from Elsevier, UK.

Linear polyethylene shows fractionation of different molar mass species (148,149,152). The low molar mass material crystallizes at low temperatures in subsidiary lamellae located between the dominant lamellae and in the spherulite boundaries (46,118,153,154). Direct evidence for crystal continuity between dominant and subsidiary lamellae was presented by Bassett *et al.* (46). Fig. 6.27 shows dominant ridged sheets that are growing further and converting into much thinner and S-shaped subsidiary lamellae. Fig. 6.28 displays isothermally crystallized high-density polyethylene after solvent extraction to remove the segregated low molar mass species. This particular sample demonstrated a certain preference for segregation towards the spherulite boundaries.

Most of the early studies concerned with molecular fractionation dealt with samples having a broad molar mass distribution. The crystallization of binary mixtures of sharp fractions was studied to a lesser degree. The crystallization of binary mixtures of linear polyethylene sharp fractions in the molar mass range from 1000 to 20 000 g mol^{-1} depended upon the cooling rate, and two types of crystallization were observed (155): (i) Separate crystallization of the components occurred at low degrees of supercooling; (ii) Water-quenched mixtures crystallizing at very extensive degrees of supercooling displayed only one melting peak and one small-angle X-ray scattering peak, which was taken as evidence of co-crystallization of the components.

Later work on binary linear polyethylene blends reported by Rego Lopez and Gedde (114), Rego Lopez *et al.* (156) and Conde Braña *et al.* (157) provided a somewhat different view. The blends studied were based on the combination of a low molar mass linear polyethylene ($\overline{M}_w$= 2500 g mol^{-1}; $\overline{M}_w / \overline{M}_n$ =1.1) with one of a series of higher molar mass linear polyethylenes (11 000< $\overline{M}_w$ < 66 000 g mol^{-1}; $\overline{M}_w / \overline{M}_n$ =1.1). Different types of crystallization were observed in the binary linear polyethylene blends (156): (a) At high crystallization temperatures the high molar mass polymer crystallized alone. Data for the fold surface free energy obtained from linear growth rate data supported the view that the nature of the fold surface of the dominant lamellae was related only to the molar mass of the crystallizing component and was not affected by the composition of the melt; (b) At intermediate temperatures, i.e. at temperatures below the temperature corresponding to M_{crit} = 2 500 g mol^{-1}, both components crystallized but in separate crystal lamellae. Crystallization of the low molar mass component in the blend was promoted by the presence of crystals consisting of the high molar mass material. This finding was consistent with the crystal continuity between dominant and subsidiary crystals reported by Bassett et al. (46). (c) At low temperatures, partial co-crystallization was indicated by transmission electron microscopy and differential scanning calorimetry

(156,157). Both electron microscopy of stained sections and optical microscopy showed that the segregated low molar mass material was present as small domains between the stacks of dominant lamellae within the spherulites/axialites (114,157,158).

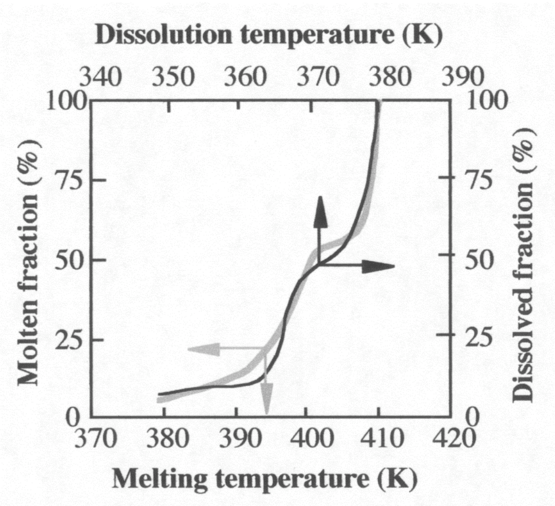
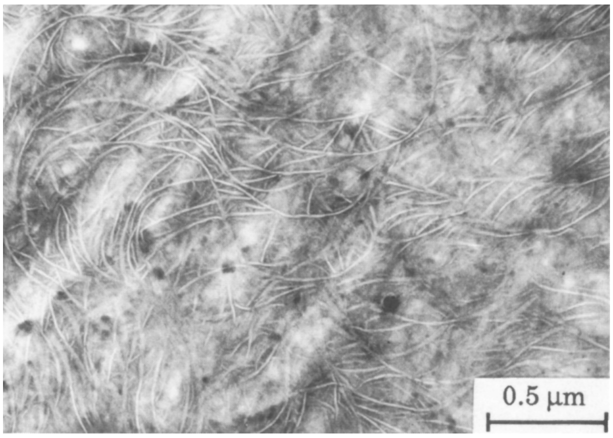


Fig. 6.29. Cumulative melting and dissolution (in p-xylene) curves of a linear polyethylene crystallised at 401 K to completeness and then rapidly cooled to room temperature. Drawn after data of Gedde et al. (158).

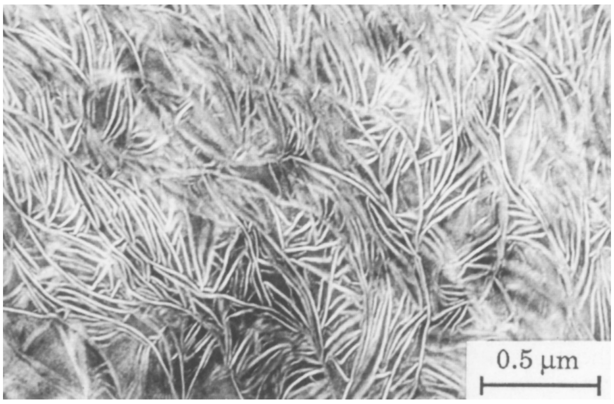
Branched polyethylene exhibits not only molar mass segregation but also fractionation due to structural irregularity. The crystallization temperature range is shifted towards lower temperatures with increasing degree of chain branching (159). The multi-component nature of branched polyethylene arises from the fact that the chain branches are randomly positioned on the polymer backbone chain. Segregation is thus never sharp, as in the case of linear polyethylene with differences in molar mass only. Linear polyethylene with a broad molar mass distribution which was melt-crystallized at constant temperature and then rapidly quenched to room temperature exhibited two crystal populations; one melting at high temperatures from the isothermally crystallized fraction and the second showing a low melting point associated with the material crystallized during quenching (148,160). In this particular case, it was possible to selectively remove the low melting point material by *p*-xylene extraction and, in fact , when the fraction dissolved at a given extraction temperature was plotted as a function of extraction temperature, the curve almost exactly resembled the cumulative melting curve shifted by 31°C towards lower temperatures (152). This finding, shown in Fig. 6.29, suggests that the different molar mass species of the linear polyethylene crystallize in different crystal lamellae. It is not possible to remove the low melting species to the same extent from branched polyethylenes, probably because of the statistical distribution of the branch points (152).

Blends of linear and branched polyethylene have received considerable attention (161-166). The two components in binary mixtures of linear polyethylene and branched polyethylene produced by the high-pressure process are unquestionably segregated in the solid state (161-163). The conclusions drawn from studies of blends of linear polyethylene and branched polyethylene produced by a low pressure process are diverse, although the studies were concerned with similar polymers of relatively high molar mass with medium to high polydispersity and with the branched polyethylene containing 1.4-1.8 mol% of ethyl groups (164-166). Hu *et al.* (164) and Edwards (165) presented evidence obtained by differential scanning calorimetry, X-ray diffraction and Raman spectroscopy supporting the hypothesis that co-crystallization of the components occurs in slowly cooled samples. In contrast to this view, Norton and Keller (166) reported data obtained by differential scanning calorimetry, polarized light microscopy and transmission electron microscopy, which established predominantly segregation of linear and branched polyethylene (1.4 mol% of ethyl groups) components in a 50/50 blend of commercial HDPE and LLDPE crystallized at different constant temperatures between 394 and 403 K. The linear polymer crystallized first under isothermal conditions to form thicker and less curved dominant lamellae, whereas the branched polymer crystallized at a later stage during the rapid cooling in finer, S-shaped lamellae located between the stacks of dominant lamellae. Some limited co-crystallization was however indicated in samples crystallized close to 394 K. According to differential scanning calorimetry, the quenched samples exhibited less pronounced segregation.

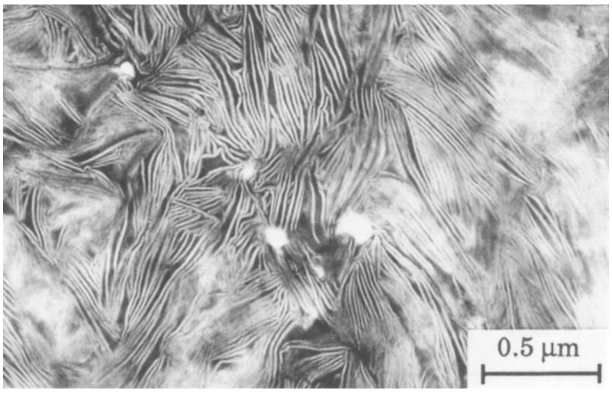
The morphology and crystallization behaviour of a series of binary blends based on a low molar mass linear polyethylene ($\overline{M}_{\mathrm{w}}$= 2500 g mol^{-1}; $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$ =1.1) and two higher molar mass branched polyethylenes [166 000 <$\overline{M}_{\mathrm{w}}$ < 290 000 g mol^{-1}; $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$ =6-15; 1.5 mol% ethyl branches (**BE1.5**) and 0.5 mol% butyl branches (**BB0.5**)] were reported by Gedde and co-workers (158,167-170).



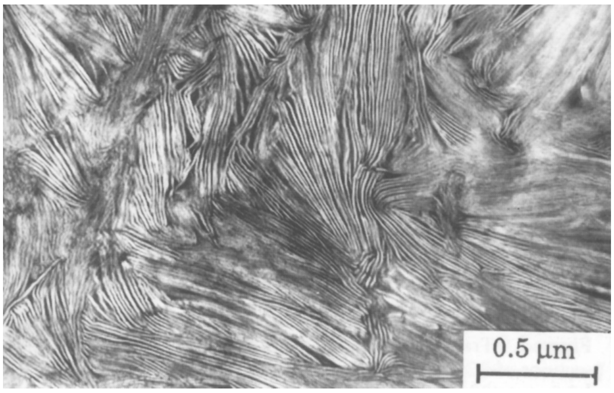
(a)



(b)



(c)



(d)

Fig. 6.30 (on previous page). Transmission electron micrographs of chlorosulphonated sections of L2.5/BE1.5 crystallized at 114°C for 0.7 h and then cooled at a rate of 80 °C min^{-1} to room temperature: (a) 0% L2.5; (b) 20% L2.5; (c) 60% L2.5; (d) 80% L2.5. From Conde-Braña and Gedde (170) with permission from Elsevier, UK.

In these blends transmission electron microscopy (Fig. 6.30 shows a series of binary blends with **BE1.5** and the low molar mass linear polyethylene) showed a progressive change from curved to straight and occasionally roof-ridged lamellae and a strong decrease in average amorphous layer thickness with increasing content of the linear polyethylene (168,170). Data obtained by model calculations of the average amorphous thickness assuming complete co-crystallization of the linear and branched polymers show good correspondence with the experimental data obtained for the **BE1.5** blends, except for the blend consisting of 80% of linear polyethylene, but a pronounced deviation for **BB0.5** blends. For most of the **BE1.5** blends there was good agreement between the calorimetric crystallinity and the crystallinity determined by transmission electron microscopy, indicating co-crystallization of the components. There was however a significant deviation between the two crystallinity values for all the **BB0.5** blends, and for the **BE1.5** blend containing 80% linear polyethylene. This can be explained by partial segregation of the low molar mass linear polyethylene in these blends. The linear growth rate and the supermolecular structure were found to be highly sensitive to composition (169). The pronounced increase in linear growth rate with increasing content of the linear fraction may be explained by an increase in the rate of diffusion of crystallizable segments due to a reduction in chain entanglement. The introduction of the linear polyethylene fraction changed the originally spherulitic structure into a predominantly axialitic superstructure. When segregation of low molar mass component occurred in these blends, it was confined to domains within spherulites between stacks of dominant lamellae (168,170).

Segregation of highly branched species in finger-like cells within spherulites on a length scale visible in the optical microscope was more recently discovered by the Reading group (171,172). The descriptive term for this phenomenon is ‘cellulation’, which means ‘separation of fingers of crystalline polymer by regions containing poorly and non-crystalline material’ (172). A series of branched polyethylenes (13.8 to 37.4 branches per 1000 carbon atoms) showed cellulation at the later stages of spherulite growth together with a continuous decrease in the spherulite radius growth rate (171,172). The radial distance to the onset of cellulation and the width of the cells were independent of spherulite growth rate but they both decreased with increasing degree of chain branching (172). These parameters showed no scaling with the $\delta = D/G$ ratio (D=segregant diffusion coefficient, G=spherulite growth rate). It is important to point out that segregation of low molar mass species in linear polyethylene occurs without any continuous decrease in spherulite growth rate and without cellulation (156,173).

6.10. Conclusions and final comments

Chain folding in a particular way leading to an inclined fold surface determines the lateral habit with growth sectors and the shape of the crystals as viewed along the crystallographic **b** axis. The lamellar branching through screw dislocation, which leads to lamellar twisting and a new growth direction of daughter lamellae, is another consequence of the fold structure. The continuity of crystal lamellae in polyethylene spherulites is well established but the detailed morphology is not easily described for the modelling of transport and mechanical properties. It is a demanding task to describe the morphology in sufficient detail to be able to predict the geometrical impedance factor for diffusion. Adjacent regular chain folding is a dominant feature of solution-grown single crystals and it is also very important in melt-crystallized polyethylene. The memory of the chaotic molten state persists to some extent in the semi-crystalline polymer. The nature of the crystal interface with constrained chains leaving the crystal is less well understood, although it is very important for certain properties, e.g. diffusivity (174).

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