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From the melt via mesomorphic and granular crystalline layers to lamellar crystallites: A major route followed in polymer crystallization?

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Abstract. Based on broad and detailed evidence from a large variety of experiments on several polymer systems carried out by other authors and ourselves, a novel concept for understanding the crystallization of polymers from the melt is developed. The experiments generally indicate that the formation and growth of the lamellar crystallites is a multi-step process passing over intermediate states. We suggest a specific route which is compatible with the observations. It is proposed that the initial step is always the creation of a mesomorphic layer which spontaneously thickens, up to a critical value, where it solidifies through a cooperative structural transition. The transition produces a granular crystalline layer, which transforms in the last step into homogeneous lamellar crystallites. The model leads to predictions about the temperature dependencies of the crystal thickness and the growth rate which are at variance with conventional views but in agreement with findings in recent experiments.

PACS. 61.41.+e Polymers, elastomers, and plastics – 64.70.-p Specific phase transitions – 64.60.My Metastable phases

1 Introduction

Crystallization in polymer systems which transfers the entangled melt into a semi-crystalline state is a process of primary importance and has been studied since long time. Different from low molar mass compounds polymer systems never turn into perfect crystals but always end up in a metastable state which is only crystalline in parts. A semi-crystalline polymer is usually composed of lamellar crystallites which are separated by amorphous layers. Structure parameters like the volume fraction of the crystallites or their thickness are kinetically controlled and change with the crystallization conditions. Usually crystallites get thicker when the temperature of crystallization is increased. This is always accompanied by a decrease in the rate of crystallization described by an exponential law. Studies of polymer crystallization ask for an understanding of these dependencies based on a knowledge of the molecular processes controlling the transformation [1].

Over the years various conceptual models have been proposed and worked out. One became dominant and is now widely used in the evaluation of data, that developed by Hoffman and Lauritzen [2,3]. The model interprets the characteristic exponential law for the variation of the crystallization time with the crystallization temperature as originating from an increase in an activation barrier, namely that which has to be surmounted when placing a nucleating first stem onto the growth face. This "secondary nucleation" then presents the decisive step which determines the crystal growth rate. The longitudinal extension of the nucleus fixes also the crystallite thickness. The structure which evolves is, as always in kinetically controlled transformation processes, the one which develops with the highest rate. In the Hoffman-Lauritzen model this maximum is reached for a crystal thickness just above the stability limit of the crystallites as determined by the Gibbs-Thomson equation.

The Hoffman-Lauritzen approach encountered in spite of its success also always criticism, and it became quite substantial in publications of Point [4] and Sadler [5]. Sadler constructed an alternative model which works for rough growth faces, introducing as elementary steps a reversible detachment and attachment of short-chain sequences. Calculations within the framework of the model show that the growth face explores many configurations, of which only a minority allows the face to progress. One thus meets a high entropic activation barrier which controls the rate of growth.

In spite of the large differences in many aspects, atomically smooth or rough growth faces, nucleation or reversible attachment-detachment processes, short-chain sequences or whole stems as elements, the two approaches have one basic feature in common: It is assumed that the lamellar crystallites grow directly into the entangled melt. The growth face sets the border between the crystal and

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the melt, and crystallization proceeds by a movement of the face. In a general view the assumed mechanisms agree with those found for single crystals of low molar mass compounds. When crystallized from the melt one there can also find layer-for-layer growth if the growth face is atomically smooth, beginning for each new layer with a nucleation step, or "normal growth", if the growth face is rough, being determined by the balance between the rates of attachment and detachment of single molecules.

There is a field where crystallization occurs in quite different manner. Two-dimensional systems, with mono-layers of colloids or amphiphilic molecules on a liquid substrate as typical representatives, have a liquid-like disordered and a crystal-like ordered phase. Transitions can be induced by changes of the temperature or the interaction forces. Whereas for three-dimensional systems crystallization always starts with a nucleation step which is then followed by a growth of the crystallite, it occurs in two dimensions often in a continuous manner, as a cooperative process taking place in the whole layer at once. A typical phenomenon is a formation of a pattern with a characteristic length. Two examples from recent time are particularly illuminating. Zahn, Lenke and Maret [6] investigated by direct observation the order-disorder transition for paramagnetic colloidal particles dispersed on a liquid surface. The interaction potential could be continuously varied with an applied magnetic field. By changing the field, the system was brought from the crystalline to the liquid state. The transition occurs without a nucleation cooperatively in the whole mono-layer in two successive steps, with a hexatic phase as an intermediate. Hexatic phases are generally composed of domaines with a preferential common orientation, separated by disordered boundary regions. The behavior was found to be in perfect agreement with the theory of Kosterlitz and Thouless [7] dealing with this situation.

The second experiment was carried out by Chi *et al.* [8]. It deals with Langmuir-Blodgett films of stearic acids on a liquid surface and the way of change from the disorder ("liquid expanded") into the ordered ("liquid condensed") phase. Here the changes were observed with an atomic force microscope. The phase transition was induced by increasing the lateral pressure. Again it did not proceed by nucleation and growth of isolated ordered particles, but occurred in a cooperative way associated with the formation of characteristic patterns.

There might be more observations in the literature we are not aware of. But already these two examples demonstrate that ordering transitions in two-dimensional systems may proceed in a way quite different from the better known three-dimensional case, in a cooperative manner via intermediate states, rather than by a nucleation and growth. It is the intention of this paper to suggest that polymer crystallization from an entangled melt, although taking place in three dimensions, might resemble in central parts more the ordering processes in two-dimensional systems than the general scheme of nucleation and growth in the bulk. In fact, there is an accumulating amount of experimental observations which indicate that the lamellar crystallites do not form and grow directly from and into the isotropic melt, but via transient intermediate states. The growth front of a spherulite may well have a composite structure, being built up of several consecutive parts which are in different states.

We were led to a first revision of views away from conventional wisdom by the results of time- and temperature-dependent small-angle X-ray scattering (SAXS) experiments and observations in the atomic force microscope (AFM) carried out at the beginning on syndiotactic polypropylene (s-PP) [9] and then on polyethylene (PE), poly(ϵ-caprolactone) (PCL) [10] and isotactic polypropylene (i-PP) [11]. They provide clear indications for the occurrence of two structural states, an initial one to be described as "granular crystalline layer", being composed of crystal blocks with nm-edge lengths in planar assemblies, and the well-known lamellar crystallite into which they transform as the final one. Particularly instructive, because providing direct insight, are works of Kanig [12,13]. Early stages of the crystallization of PE could be fixed by applying a staining technique at the crystallization temperature. One observes in the transmission electron microscope (TEM) mesomorphic layers prior to the formation of the lamellar crystallites. The results of time-dependent FTIR studies during the crystallization of PE carried out by Tashiro *et al.* [14] confirm Kanig's observations: Bands attributed to the mesomorphic ("hexagonal") phase show up prior to the appearance of crystal bands. Rastogi *et al.* [15] observed under the special conditions of high pressure and temperature directly in an optical microscope a two-step process in the formation of the PE crystallites, beginning with the formation of the crystallites in the mesomorphic (hexagonal) phase which then spontaneously turn into the orthorhombic form. Okada, Saito and Inoue [16] studied the crystallization of i-PP in a light scattering experiment. They detected a weak but measurable densification of the melt, again setting in prior to the appearance of the first crystallites. The experiment was repeated and the observations confirmed by Pogodina *et al.* [17] and it was found that already the preceding densification produces a gelation of the melt. A preceding scattering of light as well as of X-rays in the small angle range was also reported by Imai *et al.* [18] and Matsuba *et al.* [19] for poly(ethyleneterephthalate) (PET) and polystyrene (PS), and by Terrill *et al.* in experiments on i-PP [20]. There are also changes in the molecular dynamics of the melt before crystallization. They showed up in measurements of the dielectric relaxation in PET, conducted by Fukao and Miyamoto [21].

Hence, there are quite a few experiments indicating that the formation and growth of the crystallites is not a one-step process proceeding directly into the melt but follows a route over intermediate states. We consider the experimental basis as reliable and broad enough to now propose a novel model for treating polymer crystallization.

To make the difference to the convential views as clear as possible, we start with an introduction of the concept in form of a thesis. Then follows a presentation of the experiments which motivated our considerations and speak

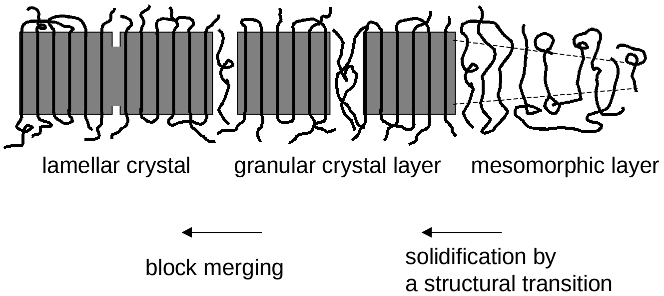

Fig. 1. Sketch of the route proposed for the formation of polymer crystallites. Stages passed through as reflected in the structural states found along a layer.

in support of the new model. The addressed experiments, carried out by other workers and ourselves, are all already published. We present them here in their context, only briefly, restricted to the main findings. The suggested new conception has consequences for the growth rate which contradict common opinions and these will be explained and discussed in the last section.

2 The route to polymer crystallites. A conjecture

We propose for the growth of the lamellar crystallites in an entangled polymer melt a mechanism as sketched in Figure 1. It schematically indicates the sequence of states which are passed through in the transformation of the melt into the final lamellar crystallite, as they would show up consecutively along a layer in a snapshot.

The process starts with the attachment of chain sequences from the melt onto the lateral growth face of a layer with a mesomorphic inner structure. The layer is composed of stretched sequences in a liquid-like cylinder packing. The stretching is not perfect, *i.e.* the chains, although basically helical, include many conformational defects. The density in the layer is slightly above that of the isotropic melt, away from the value in the crystal; the anisotropy following from the chain stretching is low, comparable to that in the L_α-phase of mono-layers of amphiphiles or of lyotropic liquid crystals. There exists a minimum thickness for the layer in order to be stable in the surrounding melt, and it is found at the boundary, *i.e.* the lateral surfaces in contact with the melt. As the inner mobility is high, the layer thickens with time and correspondingly with the distance from the moving boundary. The thickening process requires a continuous rearrangement of the chain sequences in the zone composed of folds and loops near to the layer surface. The mobility is not constant. The highest value is found at the growth face, and then it decreases with increasing layer thickness. It is this continuous lowering of the inner mobility, which finally brings the thickening to an end. When a critical thickness is reached a transition into a higher-ordered structure occurs, leading to a solidification of the layer and a stop of the thickening. The resulting structure can be described as a "granular crystal layer", being set up of crystal blocks in a planar assembly. The transition takes place in an easy manner, without meeting higher activation barriers, and cooperatively over a larger area. It is of "weakly first order". On approching the transition local density fluctuations in the system amplify and form a pattern. At the transition the densified regions, having lateral extensions similar to the layer thickness, turn into crystal blocks.

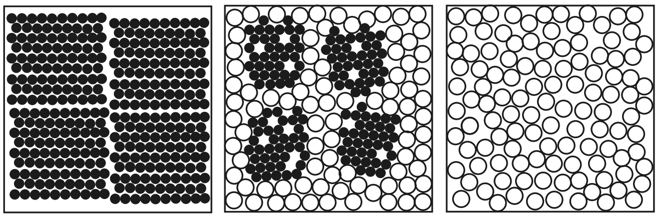

Fig. 2. Sketch of the changes in the internal layer structure: liquid-like packing in the mesomorphic state (right), pattern of crystal blocks after the transition in the granular state (center), lamellar crystals with mosaic block structure (left).

The envisaged transition shows similarities with the fluid-hexatic phase transition addressed in the first section, which also takes place cooperatively and produces an assembly of domains. It is a characteristic property of hexatic phases that the domains have a common preferred orientation. There exists also a common orientational distribution of the crystal blocks. A direction fixed in the system is the gradient of the thickness of the mesomorphic layers and it provides an orientation effect. The transition into the hexatic phase can be induced by a decrease in temperature, an increase in the lateral pressure or an increase in the interaction forces, here, in the mesomorphic layer, it is induced by the mobility decrease associated with the increase of the layer thickness. The fluid-hexatic phase transition covers the whole sample, the transformation in our case is induced locally, at the point where the mesomorphic layer has reached the critical thickness.

The last step on the route is a merging of the blocks, together with an improvement of their inner perfection. The resulting homogeneous lamellar crystallite has the same thickness as the constituent blocks. It still keeps some memory on the development history in having a mosaic block structure, but this with only thin grain boundaries and now exactly equal orientations of the component blocks.

The merging provides a stabilization, *i.e.* results in a decrease of the Gibbs free energy. The degree of stabilization, however, is not uniform through the sample; it may vary with the location. Some regions in the sample may even remain in the granular crystal state.

Figure 2 gives another sketch of the processes along the route, in a view along the surface normal of the layers. The three pictures show once again the mesomorphic layer, the transition into the granular crystalline layer and, on the left-hand side, the homogeneous lamellar crystallites with an inner mosaic block structure. The picture of the granular stage is meant in particular to visualize a situation

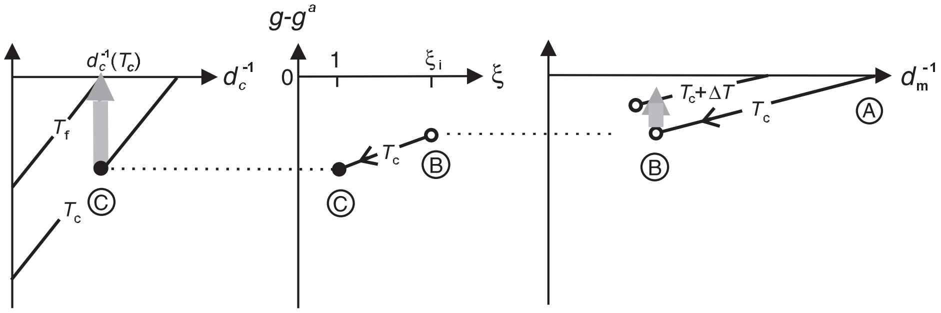

Fig. 3. Variations of the chemical potential difference per monomer $g - g^{\mathrm{a}}$ (g^{a}: chemical potential in the melt) along the route for a crystallization at T_{c}. Decrease due to the thickening of the mesomorphic layer, beginning with a minimum thickness at A, ending with the transition at B leading to a solidification (right). Decrease due to the perfectioning of the granular crystalline layer, described by a change of a global order parameter ξ from an initial ξ_i at B to unity at C (center). Chemical potential of homogeneous lamellar crystallites with the end point C being indicated (left). Grey arrows: Paths for the disaggregation of the blocks (right) and the melting of the lamellar crystallites (left).

where small imperfect crystallites develop in a cooperative manner associated with the formation of a pattern, rather than being created by a statistical nucleation followed by growth.

The mechanism proposed here concerns the growth of existing lamellae, rather than the primary nucleation of a spherulite, but has an obvious consequence for the latter: It implies that the primary nucleus formed in the isotropic melt is of mesomorphic nature and that spherulites in their earliest stages are composed of mesomorphic layers only.

Figure 3 represents in three related plots the route from the viewpoint of the corresponding changes in the chemical potential. The plots give the chemical potential per monomer, g, referred to that in the isotropic liquid, g^{a}. One has first to recognize that the chemical potential in layers is affected by their thickness. The dependence can be described by the Gibbs-Thomson equation, for both the lamellar crystallite and the mesomorphic layer. We write for the crystal layer

$$g - g^{\mathrm{a}} = (g^{\mathrm{c}} - g^{\mathrm{a}}) + \frac{a_{\mathrm{ac}}}{d_{\mathrm{c}}} \tag{1}$$

and for the mesomorphic layer

$$g - g^{\mathrm{a}} = (g^{\mathrm{m}} - g^{\mathrm{a}}) + \frac{a_{\mathrm{am}}}{d_{\mathrm{m}}}; \tag{2}$$

g^{m} and g^{c} describe the chemical potentials per monomer in the bulk of the mesomorphic and crystalline phases, respectively, the coefficients a_{ac} and a_{am} are proportional to the surface free energies associated with the two layers. We assume for the temperature range of crystallization

$$g^{\mathrm{a}} > g^{\mathrm{m}} > g^{\mathrm{c}} \tag{3}$$

and

$$a_{\mathrm{am}} < a_{\mathrm{ac}}. \tag{4}$$

Equation (3) implies that not only the crystal phase is stable against the isotropic melt, but the mesomorphic phase as well, although the latter is only metastable. Figure 3 refers to a certain crystallization temperature T_{c}. The lines in the plot on the left give the chemical potential in the lamellar crystals, in dependence on their (reciprocal) thickness d_{c}^{-1}. The lines with the lower slope in the right plot describe the same property for the monomers in mesomorphic layers with thickness d_{m}. The thickness at point A is the minimum thickness of the mesomorphic layer necessary to remain stable in the isotropic melt. Here the process starts and then continues along the path associated with the thickening. Thickening continues until point B is reached, where the layer solidifies. The transition occurs at a well-defined, critical layer thickness d_{m}, and results in a granular crystalline layer composed of blocks with an edge length $d_{\mathrm{c}} \neq d_{\mathrm{m}}$ in chain direction. The last step is the perfectioning and merging of the crystal blocks and this is formally described by the plot in the center. d_{c} remains unchanged, as the blocks just fuse together. The property varying along this section of the pathway is the degree of order within the layer. In order to formally describe this change we introduce a global "order parameter" ξ which plays the role of a reaction coordinate. It has an initial value ξ_i at the beginning of the prefectioning process at B, and ends up at unity when the perfect order of a homogeneous, laterally extended lamellar crystallite is reached. The chemical potential drops steadily along the path, down to its value at point C, which is the maximum gain in stability which can be acquired. The gain in stability along this section, *i.e.* from B to C, is much larger than that due to the mesomorphic layer thickening, *i.e.* from A to B; the drawing does not show the real relation. The initial order parameter ξ_i varies with T_{c}, going up with increasing crystallization temperatures. As a consequence, the gain in the Gibbs free enthalpy gets smaller with increasing T_{c}. Point C shows up again in the left part of the drawing, now plotted on the Gibbs-Thomson line of the crystallites, at the position d_{c}^{-1}, which was already fixed by the size of the blocks.

The route followed in the development of the lamellae thus is composed of both, sections with continuous structure changes and phase transitions, whereby the latter ones do not meet high barriers. Being selected by the kinetics out of a manifold of possible routes of transformation, the actual pathway represents the one with the maximum rate of decrease of the Gibbs free energy.

What happens if the sample is heated after the isothermal crystallization? There are two limiting cases, both indicated in the drawing. If there is no block merging at all, the solidifying transition will immediately go in the reverse direction. The drawing includes the line of the chemical potential in the mesomorphic layer for a slightly higher temperature $T_\mathrm{c} + \Delta T$ and shows that the layer indeed transforms back into the mesomorphic form. In the other limiting case, when the stabilization goes to the maximum reached at C, the crystallites can be heated up to the melting point T_f. The Gibbs-Thomson line related to T_f is included in the diagram. As is clear, crystals with a thickness $d_\mathrm{c}(T_\mathrm{c})$ will get unstable with regard to the isotropic melt and melt at T_f. As can also be seen, the difference between the crystallization temperature T_c and the final melting point T_f is proportional to the overall gain in the chemical potential achieved along the pathway from the begin at A to the end at C

$$T_\mathrm{f} - T_\mathrm{c} \sim g^\mathrm{a} - g^\mathrm{c}\big(d_\mathrm{c}^{-1}(T_\mathrm{c})\big). \tag{5}$$

As already mentioned, it is mostly due to the drop in the Gibbs free energy associated with the spontaneous transformation of the granular into the homogeneous crystal layer.

In summary, the model proposed for the development of the lamellae is based on the following main ingredients:

- The entrance step is the attachment of straightened chain sequences with a certain minimum length from the isotropic melt onto the moving boundary face of a mesomorphic layer.
- Each part of the mesomorphic layer thickens with time.
- When reaching a critical thickness the layer part solidifies by a structural transition. The result is a planar assembly of crystal blocks.
- The crystal blocks perfect and merge together, finally producing a homogeneous lamellar crystallite.

3 Experimental evidence

3.1 From granular to homogeneous crystal lamellae

We studied crystallization under isothermal conditions and the melting during a subsequent heating by carrying out time- and temperature-dependent SAXS experiments. The investigations concerned various polymer systems, at first s-PP [9], then PE, PCL [10] and i-PP [11]. In order to be free of disturbing solid-state thickening processes we chose polymers which included a low fraction of co-units or stereo-defects, PCL being the only exception. Evaluation of the SAXS data yields the (most probable) thickness of the crystallites d_c. The experiments therefore show if d_c changes with time or temperature. In addition, by evaluation of the intensities the experiments give the variation of the crystallinity during both crystallization and heating. There were two general observations:

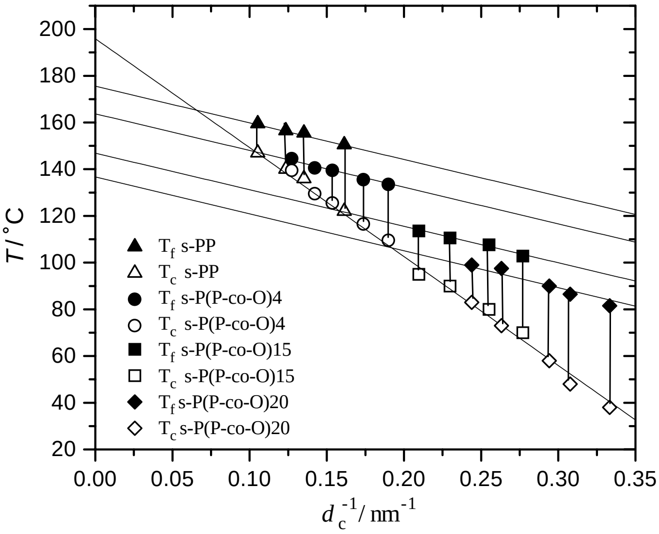

Fig. 4. s-PP and s-P(P-*co*-O)x: crystallization line T_c *versus* d_c^{-1} (open symbols) and Gibbs-Thomson melting lines T_f *versus* d_c^{-1} (filled symbols) as derived from time- and temperature-dependent SAXS experiments [9].

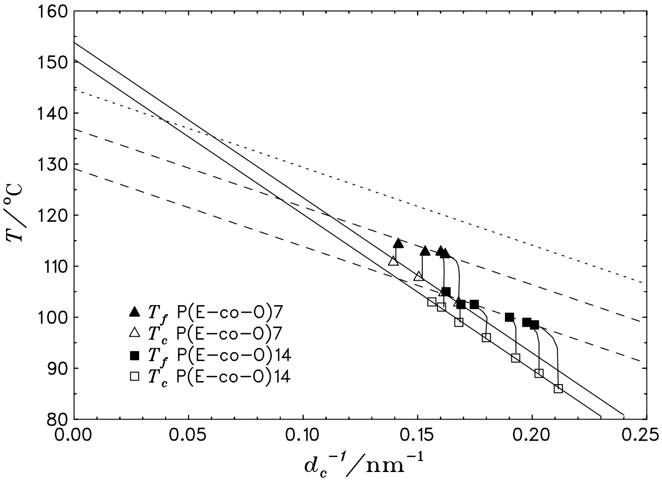

Fig. 5. P(E-*co*-O)x: crystallization lines T_c *versus* d_c^{-1} (open symbols) and melting lines T_f *versus* d_c^{-1} (filled symbols) as derived from time- and temperature-dependent SAXS experiments. The dotted line is the extrapolated melting line of linear polyethylene [10].

- Melting starts immediately above the crystallization temperature T_c and then extends up to the melting peak at T_f.
- The crystal thickness d_c does not change, neither during the isothermal crystallization nor the subsequent heating.

The experiments thus provided well-defined results for the relationships between the crystallization temperature, the crystal thickness and the location of the melting peak. As suggested by the Gibbs-Thomson equation, these relationships were represented in plots of T_c and T_f *versus* d_c^{-1}. Figures 4 and 5 show the results thus obtained for a series

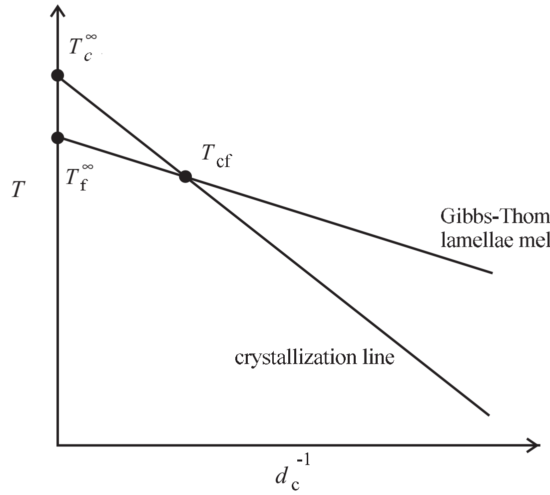

Fig. 6. General form of d_c^{-1}/T-diagram of crystallizing polymers, set-up of a crystallization and a melting line crossing each other at a finite d_c^{-1}.

of syndiotactic poly(propene-*co*-octene)s (s-P(P-*co*-O)x) and for two poly(ethylene-*co*-octene)s (P(E-*co*-O)x).

For each sample one finds two straight lines. The "melting line" describes the dependence of T_f on d_i^{-1}. It is in agreement with the Gibbs-Thomson equation; the equilibrium melting point T_f^∞ follows from the extrapolation $d_c^{-1} \rightarrow 0$. The novel feature is the "crystallization line", giving the relationship between T_c and d_c^{-1}. The crystallization line has a higher slope than the melting line and intersects the latter at a finite value of d_c^{-1}. Formally this is due to the fact that the limiting temperatures of the two lines T_c^∞ and T_f^∞ are different, whereby always $T_c^\infty \geq T_f^\infty$. The other investigated polymers showed the same behavior, and Figure 6 presents the relationships in their general form.

What is the meaning of this state diagram? The melting line describes the thickness dependence of a phase transition, that which leads from the crystalline to the isotropic amorphous state. Obviously the crystallization line has to be interpreted in an analogous way: It also represents the d_c dependence of a structural transition, but since $T_c^\infty \neq T_f^\infty$, certainly not another one between the crystalline and the amorphous state. Those parts of the structure which melt immediately above T_c experience exactly this transition. The state diagram Figure 6 is therefore indication for a crystal development in two steps: Crystallites first appear in an initial form which then transforms into the final lamellar crystallites. The latter process provides the stabilization expressed by the temperature difference $T_f - T_c$ and it occurs without a change in d_c. The initial crystalline state has an unusual property: The related crystal thicknesses do not (s-P(P-*co*-O)x) or only slightly (P(E-*co*-O)x) vary with the co-unit content. This is demonstrated by Figure 4, which shows only one common crystallization line, and Figure 5, where two crystallization lines appear, but with a shift which is much smaller than the displacement of the melting lines.

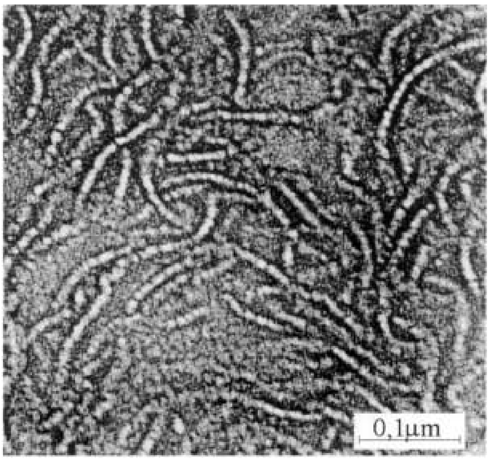

Fig. 7. Low density PE: TEM micrographs of a stained sample. From Michler [22].

Knowing about the existence of an initial crystal form the question about its structural characteristics arises. Literature gives a first answer. Differential scanning calorimetry (DSC) employed by various authors on many different copolymerized polymers usually shows two peaks in the thermogram, a "low-temperature endotherm", located directly above T_c and the melting peak at T_f. The relative weights of the two peaks change with the co-unit fraction, from the main peak to the low-temperature endotherm when increasing the number of co-units. In our view this indicates that a larger part of the crystals in the sample remains in the initial form when increasing the co-unit fraction. On the other hand, it is well-known from TEM-observations that for higher co-units contents the lamellar crystals split into an array of blocks. Figure 7 presents as one from many examples an image obtained by Michler [22] for branched PE. The division into blocks is clearly seen.

Recent studies with the AFM show a granular substructure also for lamellae of homopolymers. Figure 8 presents images obtained for s-PP, directly after the crystallization and after an annealing at a temperature near to the melting peak [23]. For the non-annealed sample, one observes a granular substructure of the lamellae. The substructure disappears with the annealing process. Similar observations on PE, i-PP, poly(vinylidenefluoride) and poly(ethyleneoxide) were reported by Magonov [24] and, with high resolution again on PE, in a recent work of Loos *et al.* [25]. The image obtained by Loos giving directly the size of single granules is reproduced in Figure 9. Hence, there are good reasons to identify the initial structure with a granular crystal layer.

The change into the final homogeneous lamellar crystallite is accomplished as indicated by the AFM images in Figure 8, obviously by a merging process. This is possible if sufficient time is given and/or additional thermal energy is provided by heating. The merging is apparently hindered if the non-crystalline regions within the layers contain too much co-units. Then, as indicated by the

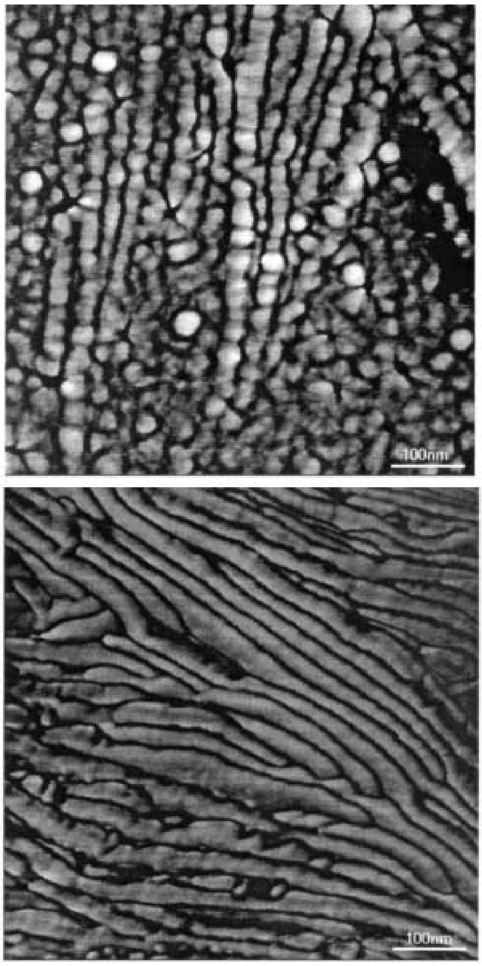

Fig. 8. s-PP, isothermally crystallized at 135 °C (top) and subsequently annealed at 150 °C (bottom). Tapping mode AFM phase image obtained at ambient temperature [23].

experiments, systems remain to a larger part in the granular form.

Having thus identified this initial crystalline structure the next questions come up: How is the granular crystal layer created? Out of which structure does it evolve, directly from the isotropic melt or out of another intermediate state? Which mechanism determines the thickness of the blocks and thus of the lamellae, and why does not d_c change with the content of co-units? Our answer, as stated in the introduction of the model is: the granular crystal layers evolve from a preceding mesomorphic monolayer. In the next chapter we collect the experimental evidence in favor of the occurrence of such structures.

3.2 A transient mesomorphic phase prior to the appearance of crystallites

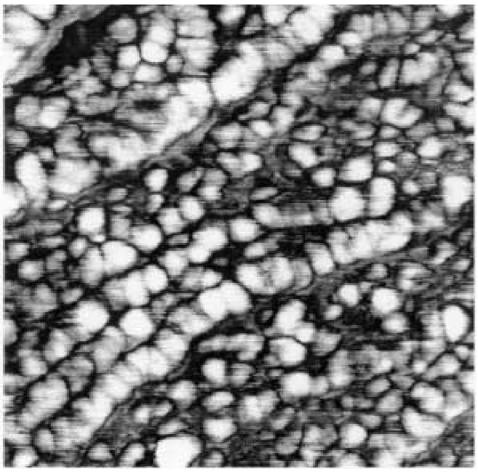

Fig. 9. PE: AFM image of the surface of a thin film obtained by Loos *et al.* (phase contrast; scan range $400 \times 400\,\mathrm{nm}^2$) [25].

Going through the literature one finds quite a few observations showing that when cooling a melt into the crystallization range, some ordering processes are activated prior to the appearance of the first crystallites. There are observations in different experiments, transmission electron microscopy, infrared vibrational spectroscopy, dielectric relaxation spectroscopy, scattering of light, or optical microscopy, always applied in time-dependent investigations, and in many cases they are accompanied by standard measurements of the kinetics of crystallization by DSC or wide-angle X-ray scattering (WAXS). Investigations concerned various polymer systems, in particular PE, i-PP and PET, and they were studied in different situations, cooling directly from the melt, or first quenching to the glassy state and annealing at the crystallization temperature, or under conditions of high pressure and high temperature. Taken as isolated observations, one could doubt the generality and relevance of one or the other observation and have the meaning that the observed effects could be particular ones without wider importance. However, considering all the observations together, they become convincing. According to our SAXS and AFM experiments, occurrence of the granular crystal layers is a general phenomenon. One therefore could expect that there exists also in general a preceding ordering process, as a characteristic phenomenon always found when polymer melts are cooled into the temperature range of crystallization. We present in the following a selection of results which we consider as particularly instructive and enlightening.

An especially sensitive tool are light scattering experiments, as they detect also very small density fluctuations. Applying this technique in a study of the crystallization of i-PP, Okada, Saito and Inoue [16] report that isotropic light scattering sets in prior to the development of crystallites. The phenomenon shows up when comparing the time-dependencies of the polarized and depolarized light scattering. The depolarized light scattering relates to the formation of crystallites and thus directly probes the crystallization as the standard techniques. The important result is the finding that the polarized scattering begins earlier than the depolarized scattering. It passes over a maximum, then when the densified parts in the sample, which produce the isotropic scattering, reach a volume fraction

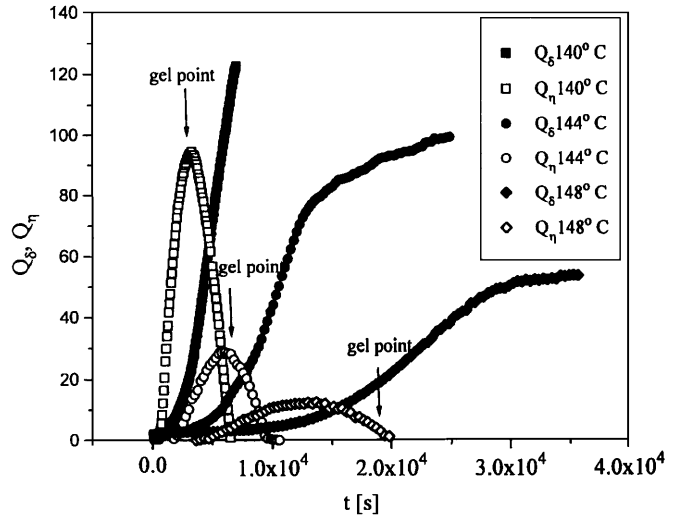

Fig. 10. Light scattering of i-PP after a cooling to different temperatures in the crystallization range: Time dependence of the intensity of the light scattered without (Q_η) and with a change of the polarization direction (Q_δ). Locations of the gel points determined by rheological measurements. From Pogodina *et al.* [17].

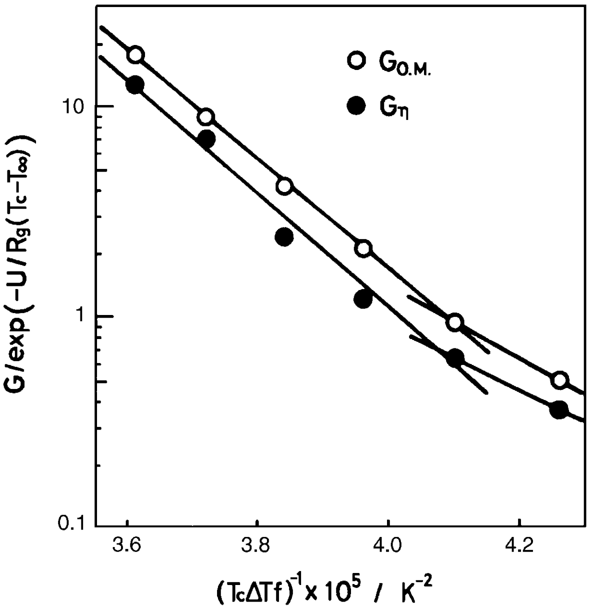

Fig. 11. Light scattering of i-PP after cooling to different temperatures in the crystallization range. Growth rate G_η of the densified domains appearing prior to crystal formation, in a comparison with the growth rate $G_{\mathrm{O.M.}}$ of the birefringent spherulites observed in a polarizing microscope. Plot as suggested by the Hoffman-Lauritzen theory ($\Delta T = T_{\mathrm{f}}^{\infty} - T_{\mathrm{c}}$). From Okada, Saito and Inoue [16].

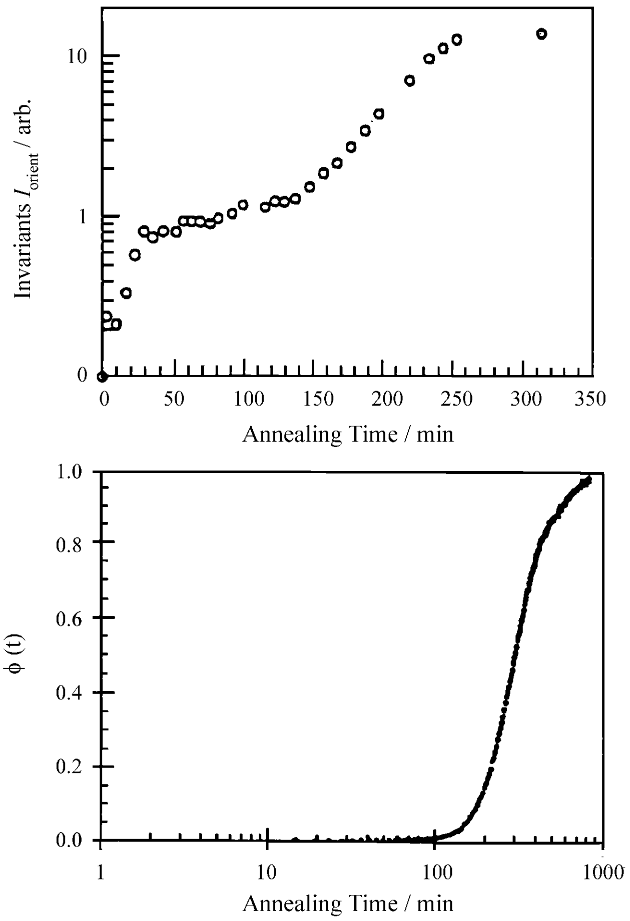

Fig. 12. PET annealed at 80 °C coming from the glassy state. Crystallization isotherm determined by wide-angle X-ray scattering (bottom) and time dependence of the depolarized component of scattered light (top). From Imai *et al.* [18].

of 50%. The experiment was recently repeated by Pogodina *et al.* [17] with an even clearer result, as the shifts in the onset times of the polarized and depolarized scattering are even larger. Figure 10 reproduces the data of the latter work. They demonstrate that at the point of the maximum of the polarized scattering the depolarized scattering is still on a very low level, in the order of some percent of the final value. Okada *et al.* derived from the scattering pattern of the polarized light a characteristic length of the densified structure. At low volume fractions, *i.e.* away from the maximum of the scattering, it increases linearly with time. From the time-dependence of the characteristic length a growth rate may be derived. It is found that this growth rate is very similar and strictly proportional to the growth rate of the crystalline spherulites which could be directly measured in an optical microscope. Figure 11 presents this result.

Another technique which is highly sensitive for even smallest changes in the melt is rheology, then when the changes have the character of association phenomena. In the work of Pogodina *et al.* the light scattering experiments were accompanied by rheological measurements, *i.e.* determinations of the frequency dependence of the compliance. As it turned out, the densification showing up in the isotropic light scattering leads to a gelation, and the gel-point is just reached at the scattering maximum, *i.e.* at a volume fraction of 50% of the densified regions. The observations indicate that a perculating network of associates is built up. In principle, it could also be due to

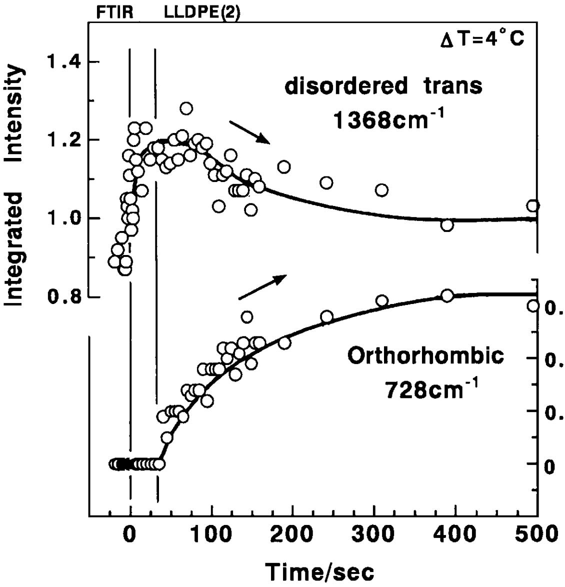

Fig. 13. Isothermal crystallization of (linear low density) PE analysed by time-resolved FTIR spectroscopy: Variation with time of the intensity of a band characteristic for the hexagonal phase (1368 cm^{-1}) and a band associated with orthorhombic crystallites (728 cm^{-1}). From Tashiro *et al.* [14].

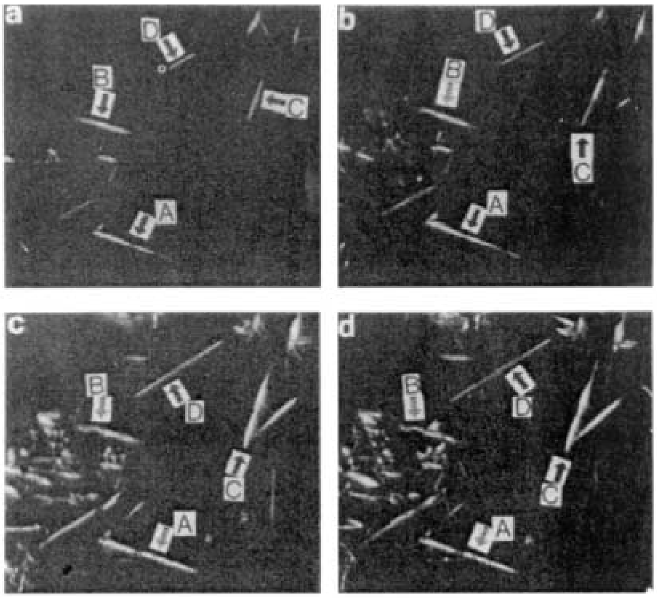

Fig. 14. PE, isothermal crystallization under an applied pressure of 2.82 kbar observed in a polarizing microscope: Different stages of crystal development. Initiation and growth in the hexagonal phase and transition to the orthorhombic phase which leads to a stop of growth. Transitions are indicated by a change in the appearance of the crystallites (crystal B: transition between (a) and (b); A: between (b) and (c); C, D: no transition). From Rastogi *et al.* [15].

the few crystallites, however, the location of the gel-point exactly at the maximum of the isotropic scattering suggests to associate it with the structures showing up in the polarized scattering.

In a light scattering experiment on PET carried out by Imai *et al.* [18] with a particularly high sensitivity, effects are also observed in the depolarized scattering. Experiments were conducted by annealing a sample coming from the amorphous glassy state. Figure 12 gives a typical result. The scattering of depolarized light increases in two-steps, whereby the second one is that associated with the development of the crystals. The first one is clearly separated from this time region and may therefore be understood as reflecting an ordering process prior to the crystallization. Infrared spectroscopy can be used to detect conformational changes occurring in the course of the crystallization process. A particularly clear result was obtained by Tashiro *et al.* [14] in a study of crystallizing PE. Figure 13 presents a typical set of data. They show the time dependence of two specific bands, one assigned to the orthorhombic crystalline state and the other known as being characteristic for the mesomorphic (hexagonal) phase which becomes stable under conditions of high temperature and pressure. Very clearly, after cooling at first the hexagonal phase forms and only afterwards the building up of crystals starts. Simultaneously with the increase of the intensity of the crystal band the intensity of the band from the hexagonal phase decreases.

Direct proof that polymer crystals can form out of a mesomorphic phase was obtained by optical microscopy in a study on PE carried out by Rastogi *et al.* [15]. Studies were conducted under peculiar conditions, namely at high pressures and temperatures where the development of large single crystals can be directly observed in the microscope. Figure 14 taken from the paper gives an example for this process. It is possible to discriminate between the mesomorphic (hexagonal) and the crystal phase from the external appearance. The homogeneous crystals with smooth boundaries without any substructures belong to the hexagonal phase, as was demonstrated by complementary X-ray scattering experiments. These expand with time in lateral directions, which is accompanied by a thickening. At a certain stage the appearance completely changes and the crystal growth stops. For the crystallite "B" this is already the case in Figure 14b, for the crystal "A" in Figure 14c; for the crystal "D" the phase transition does not occur. Even if these experiments have been carried out under peculiar conditions, at high pressure and temperature where crystals with μm-sizes observable in the microscope are obtained, they demonstrate that the route starting with a mesomorphic phase which then transforms into the final orthorhombic structure exists in principle. Authors put a more general meaning on these observations and suggested that the formation of polymer crystallites might always begin with a mesomorphic phase.

The same suggestion was brought up at about the same time by Kanig [13], based upon earlier TEM observations [12], which are indeed particularly instructive. Kanig studied the crystallization of PE using the staining technique invented by himself. It turned out as possible to fix initial stages of the crystallization by introducing the stain at the crystallization temperature. Figure 15 reproduces two

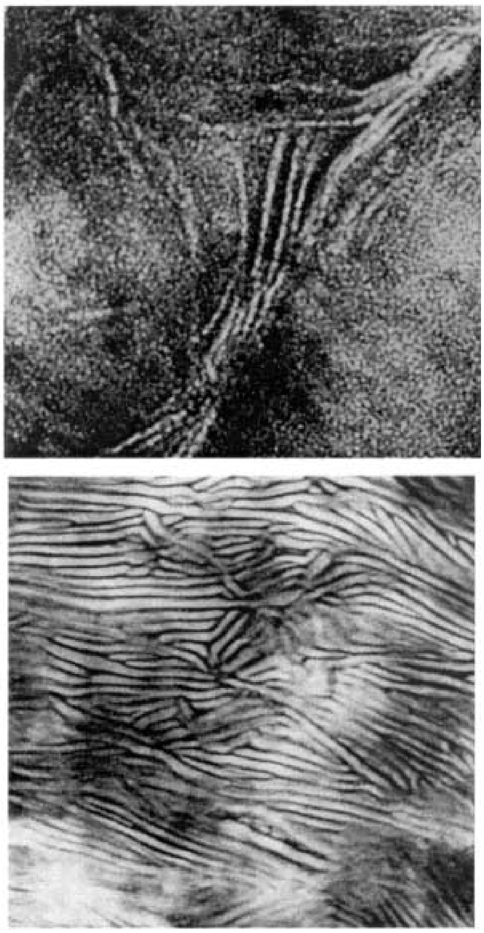

Fig. 15. TEM images of PE, cooled from the melt to 120 °C and stained by means of the chlorosulfonation technique after 2 min (top) and after 30 min (bottom). From Kanig [12].

typical results, in a comparison of structures found during the early stages, and after long times at the end of the crystallization process. The bottom image shows the well-known layer structure, the one on the top the structure at the beginning of the process. The difference in appearance is obvious. The image clearly demonstrates that the lamellar crystallites do not form by a direct growth into the melt but develop via intermediate stages. Kanig addressed the state of the layers at the beginning as "smectic", thus expressing that they might be built up of oriented chain sequences in a parallel liquid-like packing. He argues that the spotty structure of these early layers is a result of a micro-demixing of the staining agent as it always occurs for polymers in the fluid state. In fact, Kanig did not know about the general occurrence of granular crystal layers, and these, as shown by Figure 7, have a similar appearance. A discrimination between a mesomorphic and a granular crystal layer seems therefore difficult. Independent of this problem, Kanig's observations are especially important, because they demonstrate unambiguously the existence of intermediate stages during the formation of the lamellar crystallites.

Authors interpret their observations in various ways, as the existence of an "isotropic embryo" (Okada *et al.*), the growth of "clusters" with a very low inner crystallinity and anisotropy (Pogodina *et al.*), a spinodal assisted isotropic-nematic transition (Imai *et al.*) or, referring to a study of Ryan *et al.* [20] comparing the time dependence of density fluctuations registered by SAXS and the intensity growth of crystal reflections observed by WAXS, as "spinodal-assisted nucleation" [26]. Our preference is the interpretation put forward by Kanig and Rastogi *et al.* who both suggested that nucleation and growth of mesomorphic layers might be the general entrance step in the crystallization of polymers, being activated prior to the formation of crystallites. As we see it, all observations, while interpreted quite differently by the respective authors, can also be explained as originating from mesomorphic layers. We prefer this view because it yields a natural explanation for the formation of the observed granular crystal layer. That mesomorphic layers thicken is demonstrated by Rastogi's observations. Our model assumes that when reaching a critical thickness, the mesomorphic layer transforms into the granular crystalline form. The characteristic length linearly increasing with time deduced by Okada *et al.* from their light scattering data could be assigned to the diameter of a spherulite built up by mesomorphic layers. Their transformation into granular and homogeneous crystal layers would then take place and proceed within this first partially mesomorphic spherulite.

It is well known that the filling of a spherulite with the constituent lamellae is a sequential process (compare, for example, a recent work of Akpolu *et al.* on P(E-*co*-O) [27]), beginning with an open construction set-up by "dominant lamellae" which is then followed by a filling-in of "subsidiary lamellae" (the expressions were introduced by Bassett after corresponding TEM observations [28]). As SAXS experiments show that all the lamellae have the same thickness, the subsidiary crystallites obviously follow the same path over intermediate states as the dominant lamellae.

Even if the crystallization within the first spherulites set up by mesomorphic layers is a rapid process, one would still expect that the spherulite surface shows at least in a limited zone the initial mesomorphic structure. If the zone is very narrow it is difficult to detect it, but there might also exist favorable systems. i-PP could represent such a case. Figure 16 taken from a work of Olley and Bassett [29] shows in two perpendicular directions the appearance of an isolated spherulite which first developed under isothermal conditions and then was quenched into the glassy state. One observes a zone at the surface with different properties, as probed by the quenching process. Authors address this phenomenon as "quench-halo" and indeed understand it as an indication for a pre-ordering in front of the spherulite surface.

The mesomorphic layers of our model possess at the growth front a minimum thickness which keeps them just stable, and they extend laterally by an attachment of straightened chain sequences. The process may be

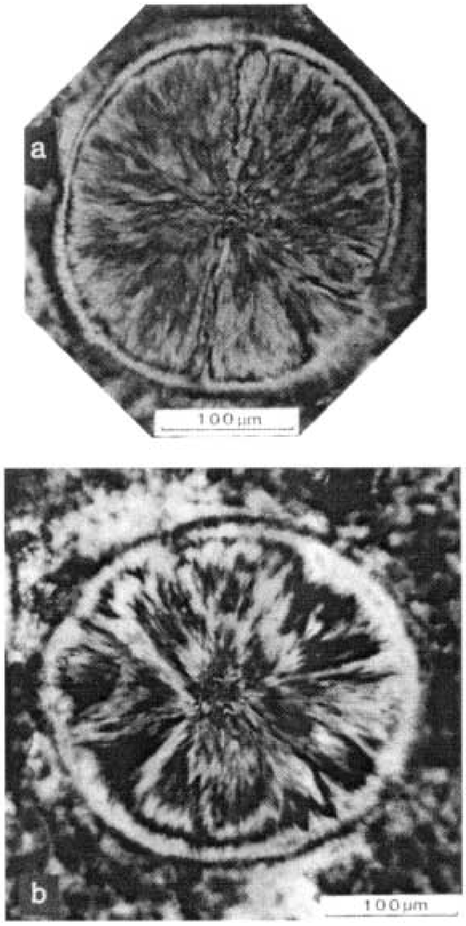

Fig. 16. Sections in perpendicular directions of a spherulite of i-PP grown at 155 °C, viewed in a polarizing microscope after quenching to the glassy state. Appearance of "quench halos" at the spherulite surface. From Olley and Bassett [29].

facilitated by the presence of bundle-like associates in the quiescent melt. This is a structural idea which is quite old, playing a dominant role in particular in the work of Pechold [30]. For long years the majority of workers considered it as pure speculation, without convincing experimental support. This may change now in view of results recently obtained by Graf, Heuer and Spiess [31] applying the novel double quantum NMR technique for a melt of 1, 4-polybutadiene. Using this method it is possible to measure the decay of orientational correlation functions of vectors connecting neighboring units along the chain. One generally observes a decay of the correlation function in two steps, a rapid and a much retarded one, with an intermediate plateau in between. The plateau value yields an orientational order parameter similar to that used for nematic liquid crystals. Here it describes a transient local ordering phenomenon. The surprise is its astonishingly high value, being in the order of $S = 0.2$. Considering that the Maier-Saupe theory yields for the nematic phase near to the clearing point a value $S = 0.45$, this is indeed high. Authors consider the finding as an indication for the existence of bundle-like clusters, which stabilize for a certain time the orientation of chain sequences. In a general sense the result demonstrates that quiescent equilibrated polymer melts are not normal liquids. One has a pronounced short-range ordering, so that polymer melts resemble associated liquids. In discussions of the crystallization process one should be aware of these peculiarities, which add to the entanglement effects.

3.3 Transition from mesomorphic to granular crystalline layers

The "crystallization line" T_c *versus* d_c^{-1} in the general diagram of Figure 6 describes the thickness dependence of the temperature of a certain structural transition. According to the SAXS experiments, AFM- and TEM studies discussed above, the transition has the following characteristic properties:

- the transition temperature changes linearly with the inverse crystal thickness
$$T_\mathrm{c} = T_\mathrm{c}^\infty - \mathrm{const}\ d_\mathrm{c}^{-1}; \qquad (6)$$
- the extrapolated limiting temperature T_c^∞, always located outside the range of the observable phase transitions, is above the equilibrium melting point T_c^∞,
$$T_\mathrm{c}^\infty > T_\mathrm{f}^\infty;$$
- the crystallization line is not (s-P(P-*co*-O)s in Figure 4) or only weakly (P(E-*co*-O)s in Figure 5) dependent on the fraction of co-units;
- the transition leads to "granular crystalline layers" composed of blocks with similar size in planar arrangements.

As will be seen, the observations are conceivable on the basis of the proposed model.

As already mentioned, the location of T_c^∞ above T_f^∞ demonstrates that this is not a transition between the isotropic melt and the crystal. The data for two P(E-*co*-O)s yield limiting temperatures T_c^∞ in the range 150–154 °C. Extrapolation to a zero number of co-units gives for the homopolymer a value $T_\mathrm{c}^\infty \approx 158°$. Interesting to note, this essentially agrees with the temperature of the transition from the crystalline into the mesomorphic (hexagonal) phase [32], to be observed if constraints are imposed during melting of a fiber, by keeping their ends fixed. For the assumed transition of a mesomorphic into a granular crystalline layer one would indeed expect this agreement.

Considering about the simple linear dependence expressed by equation (6) we are not aware of a strictly analogous situation in another field, however, one more loose connection can be found. Metal clusters with sizes in the nm-range also show pronounced melting point depressions. Over a certain range of sizes the depression is, as in our case, inversely proportional to the diameter [33,34]. For the clusters there are indications from experiments and computer simulations that melting here could represent an intrinsic breakdown rather than a process which proceeds from the surface [35,36]. Of course, the formation processes for the polymer blocks which develop together in a cooperative process and of the individually prepared metal clusters are incomparable, but the reverse processes of melting and transforming back into the mesomorphic phase may be comparable in some way. In a previous paper we correspondingly interpreted the crystallization line as the "limit of intrinsic stability of the blocks".

What could be the explanation for the observed independence of the crystallization line on the co-unit fraction? The model allows for various answers. First, the co-units may already be excluded when the mesomorphic layer forms. Whether or not this occurs would depend on the system. Here i-PP and s-PP, where it is known that co-units introduce a bend into a helical sequence, and PE, where this is not the case and, depending on their size, co-units are also partially incorporated into the crystal lattice, may behave differently. There are other possible answers. We assume that the transition occurs when the inner mobility in the mesomorphic layer reaches a critical limit. If the co-units do not affect the inner mobility, there is no effect. Considering the transition in the reverse direction, as induced by heating, one could think that blocks disaggregate when they reach their limit of intrinsic stability. As this is a property of the blocks only the presence of co-units in the surrounding liquid phase would again have no influence. To decide between the different explanations is difficult, and it might also be that all are partially correct. In any case, in the framework of the model one has ways to understand the observed invariance.

Support for an at least partially continuous character of the transition, as it is typical for a weakly first order transformation, comes from temperature-modulated DSC (TMDSC) experiments. They are sensitive for processes associated with a continuous and reversible change in the enthalpy. Wurm, Merzlyakov and Schick [37] report the results of measurements carried out during the isothermal crystallization of poly(ϵ-caprolactone) and poly(etheretherketone) (PEEK), and main findings are reproduced in Figure 17. TMDSC experiments measure the heat flow response to a sinusoidally varying programmed temperature. While irreversible first order crystallization or melting transitions give no stationary signal, a continuous solidification process would do it, and indeed signals are observed. Figure 17 shows the variations with time of the dynamic heat capacity c_p deducible from the heat flow response. It basically decreases during crystallization because crystals have a lower phononic heat capacity than the melt. However, for PCL the decay is much smaller than expected, and for PEEK it even turns into an uprise. The excesses indicated in the figures have to be due to fully reversible structural changes. In the model put forward here, some of the crystals remain in the granular state, namely those which melt immediately above T_c. An oscillating temperature then would reversibly change their inner order.

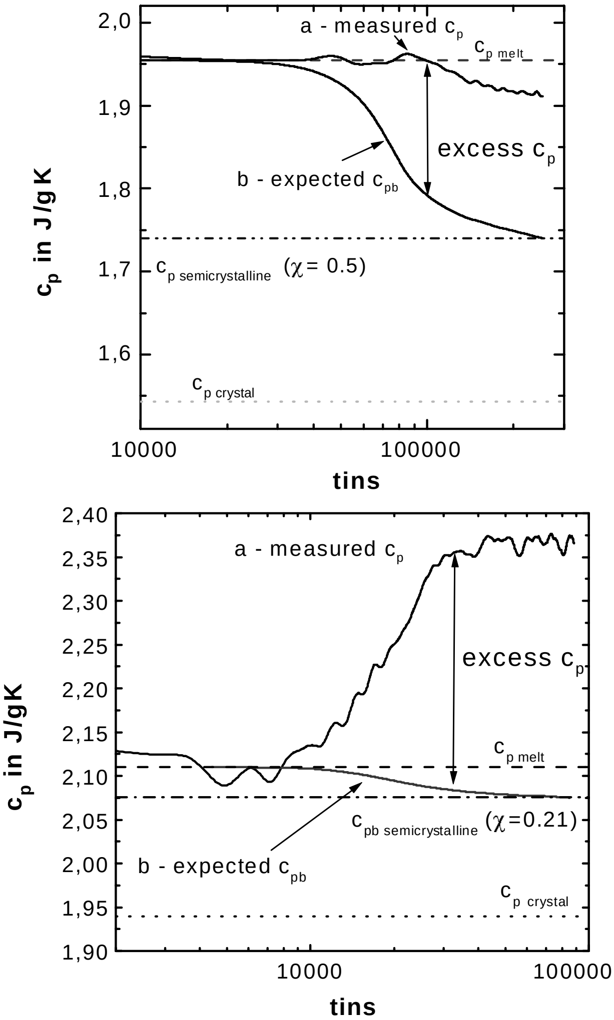

Fig. 17. Isothermal crystallization of PCL at 55 °C (top) and PEEK at 333 °C (bottom): Variation with time of the dynamic heat capacity determined by TMDSC measurements. Comparison with the changes expected on the basis of the phononic heat capacities and determination of the excess contributions originating from reversible structural changes. From Wurm, Merzlyakov and Schick [37].

There are more arguments in favour of a partially continuous "weakly first order" nature of the transformation. Principally, a mesomorphic layer could turn into a lamellar crystallite at any value of d_m, by a first order transition, forming a nucleus of thickness $d_c > d_m$ which then expands. Hence, there exists a manifold of pathways for a first order transition, but the nucleation barriers are obviously too high. The system follows an easy route with minimum activation barriers and according to the SAXS experiments, which show a well-defined dependence $d_c(T_c)$, this route is unique. It leads to a certain patterned ordered phase. A weakly first order transition, *i.e.* one which gets support from critical fluctuations and is still sharp, has these properties.

Also the pattern formation looks conceivable. In some phospholipid bilayers the transition from the liquid- expanded to the ordered dense phase passes over a patterned "ripple" phase as an intermediate state [38]. Theories associate it with a release of the stress which would follow from a direct homogeneous densification due to the different sizes of the headgroups and the alkyl chains [39]. The same effect could be induced by the folds of the basal surfaces of the mesomorphic layers. Forming a granular crystalline layer in a first step would localize and thus facilitate the necessary surface rearrangement, and relax the stress.

A central feature in the crystallization of polymers is the systematic linear increase of the temperature difference $T_f - T_c$ with decreasing T_c. Our model explains this stabilization as being caused by the spontaneous transformation of the granular crystalline layer into the final homogeneous crystal lamellae. A direct transition of the mesomorphic into a homogeneous crystal layer by a first order transition, without the detour over the granular phase, would not provide the stabilization. There is an instructive example in the literature, demonstrating this particular effect of a pathway over an intermediate state. In a study of the crystallization of even-numbered short chain n-alkanes, Sirota and Herhold [40] observed a well-defined supercooling, *i.e.* a fixed difference between the onset of crystallization at T_c and the equilibrium melting point T_f. Time-resolved X-ray scattering experiments proved that the triclinic crystals do not form directly in the melt but via a detour over a metastable transient rotator phase. T_c represents the temperature of an equilibrium between the melt and the metastable rotator phase. Immediately below T_c the melt nucleates into the rotator phase; the second step from the rotator into the triclinic phase then follows spontaneously. The analogy between this pathway, melt - (distinct temperature decrease, equilibrium phase transition) → rotator phase - (irreversible transformation) → triclinic crystal and the route in our model mesomorphic layer - (distinct d_m-increase, equilibrium phase transition) → granular crystalline layer - (irreversible transformation) → homogeneous crystal lamellae is obvious. Both produce in the second step a well-defined drop in the free energy, *i.e.* a certain temperature difference $T_f - T_c$.

That the blocks in the granular layers do not yet have the perfect order of the final crystallite, is also indicated by measurements of Bragg reflection intensities in WAXS experiments on i-PP. The contributions of the granular crystalline layers to the intensity of the Bragg-reflections are apparently smaller than expected from their volume fraction [11].

3.4 Cross-over from the route via intermediate states to direct growth of lamellar crystallites

The general form of the relationships between the crystallization temperature, the crystal thickness and the melting point of the lamellae as represented by Figure 6 immediately leads to a question. Lamellar crystallites, and these represent the final state in the crystallization process, can exist only at temperatures below the melting line. One must consequently expect that the route via transient states which produces crystals with thicknesses as given by the crystallization line ends when approaching the temperature at the intersection point T_{cf}. This is indeed confirmed by an experiment. SAXS results in the interesting temperature range were obtained for s-P(P-*co*-O)20 (20% per weight of octene co-units) [41] and they are shown in Figure 18. The expected cross-over shows up. The change begins already before reaching the cross-over temperature T_{cf} so that the crystallization curve keeps a finite distance to the melting line, which is necessary to have a thermodynamic driving force. In the experiment crystallization was conducted by employing a special procedure known in the literature as "self-seeding". Rather than inducing crystallization by a cooling from the melt it was carried out as a recrystallization, *i.e.* by heating an already crystallized sample to a temperature just above its melting point. Crystallization times are much reduced when using this technique, while, as checks prove [10], one ends up at the same crystal thickness as in the usual procedure of cooling a melt. As a matter of fact, for crystallization studies near T_{cf} there is no other way to achieve a crystal formation. When using the normal procedure, crystallization times become inacceptably high.

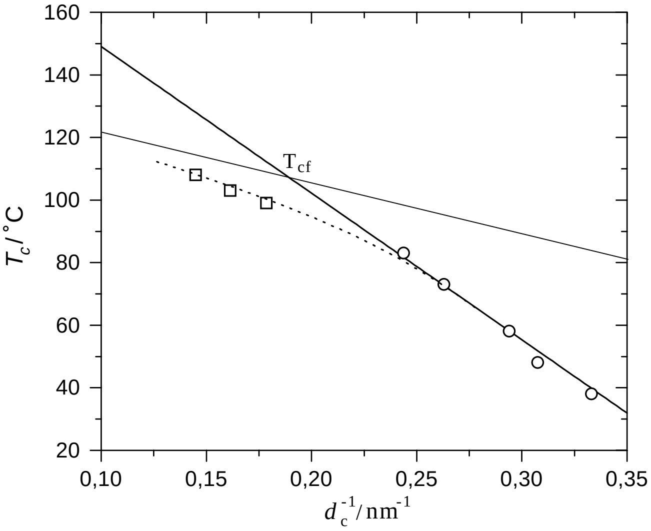

Fig. 18. s-P(P-*co*-O)20: Relationship between crystallization temperature and crystal thickness in the range around T_{cf}. Isothermal crystallizations were carried out with the aid of the self-seeding technique [41].

In the literature the self-seeding effect is usually associated with the persistence of nuclei after the melting. There is also another reason. Crystallization produces entanglement free regions in the sample and these are preserved for some time after the melting. Clear evidence comes again from Kanig's work [13] showing that after a temperature jump into the melting range lamellae do not disappear abruptly but fade away gradually. The redistribution of the entanglements and the re-establishment of the original topology of the equilibrium melt obviously requires a finite and, for some systems, also very long time.

The cross-over can be described in the framework of the thermodynamic scheme introduced in Figure 3. Figure 19 depicts the thickness dependencies of the chemical potentials per monomer in the mesomorphic and

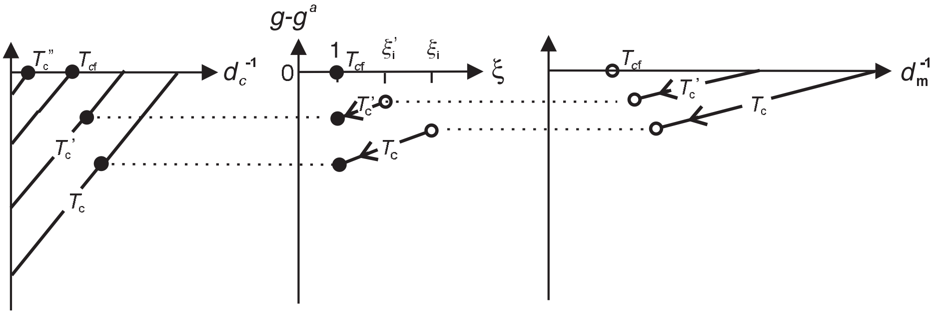

Fig. 19. Schematic representation of the thickness dependence of the monomeric chemical potentials in the crystal lamellae (left) and in the mesomorphic layers (right), where the points of transition into the granular crystal layer are indicated. Decrease of the chemical potential due to perfectioning processes (center). Situation for the cross-over temperature T_{cf}, two lower crystallization temperatures (T_{c} and T_{c}') and a higher temperature (T_{c}'').

crystalline layers for two temperatures below T_{cf} and one temperature above it. The situation at T_{cf} is peculiar. At this temperature the chemical potentials of the monomers in all four involved structural states, in the isotropic melt and in the layers —they may be mesomorphic, granular crystalline or homogeneously crystalline— coincide whereby the layers have the finite thicknesses $d_{\mathrm{m}}, d_{\mathrm{c}}$ associated with this peculiar point. As to be noted in particular, at T_{cf} the extent of thickening of the mesomorphic layer until solidification vanishes and the drop in the Gibbs free energy associated with the formation of homogeneous crystal lamellae too. This implies that above T_{cf} homogeneous lamellar crystallites must form immediately, without the path over intermediate states. Until T_{f}^{∞} the situation does not change any more. Mesomorphic layers can no longer temporarily exist. Even if they would be created at a higher Gibbs free energy by some external measure, the solidification would prevent them to achieve a thickness which would stabilize them against the surrounding isotropic melt. Therefore, the route which uses the mesomorphic phase as a simple entrance step for the crystallization is no longer available.

Is there the possibility of a direct formation and growth of crystallites out of the isotropic melt? As it very much appears, looking, for example, at the experiments of Rastogi *et al.* and also our general experience that it is practically impossible to crystallize polymers above T_{cf}, this is not a route which practically works. Hence, the approach chosen in the conventional theories, which all assume a direct growth, refer to a process which, although principally existing, has no practical relevance.

4 The rate of crystallization

Many of the discussions of polymer crystallization focus on the temperature dependence of the half-time of crystallization τ, thereby starting from an equation like

$$\tau(T_{\mathrm{c}}) \sim \exp\left(\frac{T_{\mathrm{A}}}{T_{\mathrm{c}} - T_{\mathrm{V}}}\right) \cdot \exp\left(\frac{C(T_{\mathrm{c}})}{T_{\mathrm{f}}^{\infty} - T_{\mathrm{c}}}\right). \tag{7}$$

The equation implies that the zero growth rate limiting temperature coincides with the equilibrium melting point T_{f}^{∞} of the given system. The first factor describes the change of the monomer mobility as given by the Vogel-Fulcher equation (T_{A}: activation temperature, T_{V}: Vogel temperature). The mechanism of crystallization is reflected in the coefficient C which can also account for variations in the densities of primary nuclei. Re-written in logarithmic form the equation becomes

$$\log\tau = \frac{\log \mathrm{e} \cdot T_{\mathrm{A}}}{T_{\mathrm{c}} - T_{\mathrm{V}}} + \frac{\log \mathrm{e} \cdot C(T_{\mathrm{c}})}{T_{\mathrm{f}}^{\infty} - T_{\mathrm{c}}} + \mathrm{const}, \tag{8}$$

and this is the form widely used in the evaluation of kinetical data, usually obtained by time-dependent DSC, X-ray scattering or dilatometry.

Equation (8) is generally applicable when lamellar crystallites extend by direct growth into the isotropic melt. This, however, is not the route taken in all cases of practical interest. For the major route via intermediate states one expects another behavior. For this route, beginning with a mesomorphic layer, the growth rate of the latter becomes a primary controlling factor as it sets a limit to all subsequent developments of the crystallites. The subsequent developments are sequential in character, starting up with the creation of some dominant crystal lamellae and then continuing with the filling-in of subsidiary lamellae. The time-dependence of the development of the crystallinity is therefore in general an involved property, difficult to analyze in detail.

A simpler temperature dependence can only be anticipated if all the subsequent crystallization processes occur rapidly compared to the growth rate of the mesomorphic layer. Then the latter growth rate turns into the only decisive factor. The light scattering experiments on i-PP by Okada *et al.* indicate that this polymer might represent such a case. Figure 11 compares the rate of growth of the initial mesomorphic structure with that of the birefringent spherulites. The growth rate of the initial structure was thereby derived from the time variation of the characteristic length included in the Debye-Bueche function. If, as proposed, the mesomorphic layers build up a growing spherulite, its radius will be proportional but not equal to the Debye-Bueche length. The data are therefore also consistent with the assumption that the growth rates of the initial partially mesomorphic spherulites and the birefringent semi-crystalline spherulites are not only proportional to each other but coincide. This, however, would mean, that the rate of crystallization is indeed controlled by the rate of development of the preceding mesomorphic layers.

Support for a decisive role of the mesomorphic layers comes also from a consideration of the effect of co-units on growth rates. Figure 20 depicts the half-times of crystallization derived from the SAXS experiments carried out for the copolymerized s-PPs and PEs of Figures 4 and 5. One observes curves of constant shape (very clear for the sPPs, approximately true for the PEs) which are just shifted along the temperature axis on varying the co-unit content. One may understand this behavior as indicating that the variations of the Vogel-Fulcher factor and the coefficient C in the temperature range of the experiment are not important, as there would otherwise be a change in the shape of the curves or a vertical shift, in addition to the horizontal displacement. The horizontal displacements vary with the molar fraction of octene units x_{o} as follows:

- for the s-PPs: $\Delta T = 15\,^\circ\mathrm{C}$ ($x_{\mathrm{o}} = 0.017$), $53\,^\circ\mathrm{C}$ ($x_{\mathrm{o}} = 0.064$), $64\,^\circ\mathrm{C}$ ($x_{\mathrm{o}} = 0.085$);
- for the PEs: $\Delta T = 15\,^\circ\mathrm{C}$ ($x_{\mathrm{o}} = 0.02$).

A comparison with the corresponding changes of the equilibrium melting points T_{f}^{∞} as given in Figures 4 and 5 shows definitely no agreement; the shifts of the growth rate curves are much larger than the changes in T_{f}^{∞}. On the other hand, the shifts of the growth rate curves become conceivable when we identify the zero growth rate temperature with the equilibrium transition point between the mesomorphic phase and the isotropic melt. This temperature, denoted T_{am}^{∞}, is also affected by the co-units, if they are excluded from the mesomorphic layer, as is indicated by the x_{o}-invariance of the crystallization line. Flory's equation for the depression of the equilibrium melting point of a random copolymer may be directly transferred to the mesomorphic-isotropic liquid equilibrium and then reads

$$T_{\mathrm{am}}^{\infty,0} - T_{\mathrm{am}}^{\infty}(x_{\mathrm{o}}) = \frac{k(T_{\mathrm{am}}^{\infty,0})^2}{\Delta h_{\mathrm{am}}} x_{\mathrm{o}} \qquad (9)$$

(Δh_{am}: heat released during the transition from the melt to the mesomorphic phase). The temperatures of the phase equilibria $T_{\mathrm{am}}^{\infty,0}$ for the homopolymers s-PP and PE are unknown, but the relative displacements of the growth rate curves obtained for the different copolymers can be evaluated. Assuming that they just reflect the changes in the equilibrium transition temperatures $T_{\mathrm{am}}^{\infty}(x_{\mathrm{o}})$ equation (9) can be used for an approximate calculation of the heats of transition Δh_{am} (setting $T_{\mathrm{am}}^{\infty,0} \approx T_{\mathrm{f}}^{\infty,0}$). The shift values given above lead to $\Delta h_{\mathrm{am}} \approx 2.2\,\mathrm{kJ\ mol^{-1}}$ for the s-PPs and $\Delta h_{\mathrm{am}} \approx 2.4\,\mathrm{kJ\ mol^{-1}}$ for the PEs. This amounts in both cases to about 25% of the total heat of fusion, which looks quite reasonable. DSC measurements of the melting of constrained fibers of PE indeed indicate a value in this range [32].

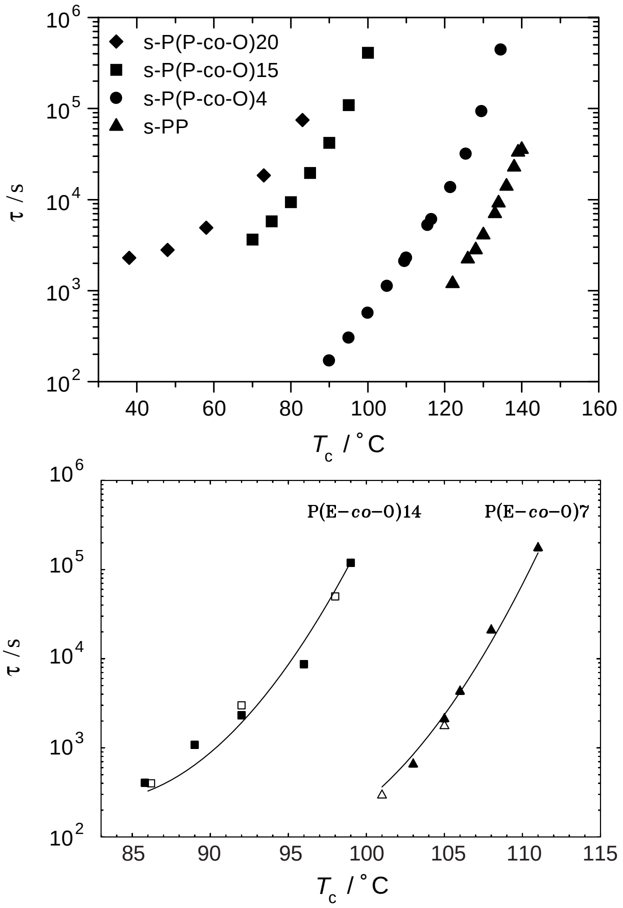

Fig. 20. s-P(P-*co*-O)x (top) and P(E-*co*-O)x (bottom): times of crystallization as a function of T_{c} determined by SAXS experiments (filled symbols) and dilatometry (open symbols) [9].

4.1 Modelling the growth rate of mesomorphic layers

Equation (7) holds for the majority of existing theoretical approaches, independent of the details. Considering about a possible transfer of formalisms to the new case, the growth of a mesomorphic layer, it surely would not be appropriate to use the Hoffman-Lauritzen approach. For the liquid structure of the mesomorphic layers, a layer-for-layer growth controlled by secondary nucleation is certainly not found. The situation is more favorable for other models, in particular those which assume a rough boundary, and we here pick up an approach developed by the author a couple of years ago [42,43].

To show that this approach can indeed be directly used after some obvious modifications we just cite the abstract: *Under the conditions of 'normal growth' on rough surfaces crystallization rates follow from the balance between the attachment and detachment of the chain sequences building up the layer-like crystallites. In the proposed model detachment rates are related to the change in the mean-field potential experienced in the crystal and the melt respectively; attachment rates are associated with the population number of straight sequences in the melt. Both rates show an exponential dependence on the sequence length.*

Combination of this picture with the basic kinetical criterion that the crystallite thickness found at a chosen crystallization temperature maximizes the growth rate yields equations which agree with the general observations.
The approach obviously can be transferred to the case of interest when replacing the "layer-like crystallites" by "mesomorphic layers", and the "straight sequences" by the more loose formulation "straightened sequences".

As it is unnecessary to repeat the developments of the work, we just explain the main variables and functions and then give the results. In order to describe the kinetics, two coefficients are introduced, j_- and j_+. These give the rates of detachment and attachment of chain sequences, respectively, referring to a single site with extension d_{m} on the lateral growth face. The growth velocity u is then given by

$$u \sim (j_+ - j_-). \tag{10}$$

The characteristic property governing the growth of macromolecular layers into a melt is a specific dependence of j_+ on the number of monomers in an attachable sequence, denoted n. The experimentally observed exponential change of the growth rate with temperature can be understood as originating from of an exponential dependence of j_+ on n:

$$j_+(n) = j_0 \exp(-\mu n), \tag{11}$$

whereby j_0 sets the basic time scale. The connection is easily seen. One only has to remind the general kinetical criterion which controls polymer crystallization: The thickness of the layer growing at a given temperature is that associated with the maximum growth rate. Use of this criterion yields this maximum growth rate and thus the crystallization rate. A short calculation gives

$$u \sim \frac{j_0(g^{\mathrm{a}} - g^{\mathrm{m}})}{\mu k T} \exp(-\mu n^*) \sim \frac{j_0(g^{\mathrm{a}} - g^{\mathrm{m}})}{\mu k T} \exp(-\mu' d_{\mathrm{m}}^*). \tag{12}$$

Here, n^* describes the number of monomers in the chain sequences building up the mesomorphic layer with thickness d_{m}^*, which is at T_{c} at the stability limit. Use of the Gibbs-Thomson equation, equation (2), for mesomorphous layers in an isotropic melt gives the relationship between d_{m}^* and T_{c}, as

$$d_{\mathrm{m}}^* = \frac{a_{\mathrm{am}} T_{\mathrm{am}}^{\infty}}{\Delta h_{\mathrm{am}}(T_{\mathrm{am}}^{\infty} - T_{\mathrm{c}})}. \tag{13}$$

For j_0 we may write on the basis of the Vogel-Fulcher law

$$u \sim j_0 \sim \exp\left(-\frac{T_{\mathrm{A}}}{T - T_{\mathrm{V}}}\right). \tag{14}$$

Introduction of equations (13) and (14) into equation (12) gives the final result

$$u(T) \sim \exp\left(-\frac{T_{\mathrm{A}}}{T - T_{\mathrm{V}}}\right) \cdot \exp\left(-\frac{C}{T_{\mathrm{am}}^{\infty} - T}\right). \tag{15}$$

It has the same form as equation (7) ($\tau \sim u^{-1}$), but the equilibrium melting temperature T_{f}^{∞} is replaced by the equilibrium transition temperature T_{am}^{∞} which now sets the zero growth rate point. Furthermore, the coefficient C, which determines the slope in the plots of τ *versus* T_{c}, is now dependent on Δh_{am} and a_{am}.

There remains only the question about the physical background of equation (11), and the answer is analogous to that given for the growing crystallites : Before a chain sequence which lies coiled in the melt can be incorporated into the mesomorphic layer, it has to be "activated" by transferring it into the straightened form required for an attachment. Obviously, the activation energy ΔG_{b} is proportional to the number of monomers in the straightened sequence n, $\Delta G_{\mathrm{b}} \sim n$. In thermal equilibrium chains reach this activated state with a frequency proportional to

$$\exp\left(-\frac{\Delta G_{\mathrm{b}}}{kT}\right) \sim \exp(-\mu \cdot n)$$

which agrees with equation (11).

5 Two main open issues: Crystallinities and crystallite textures in spherulites

So far, the focus was only on the route followed in the formation of the lamellar crystallites. This, however, is only one part of polymer crystallization. Its full understanding requires more and there are further main issues. Two of them are of first rank importance:

- How does the crystallinity arise and which controlling factors act on it?
- How does the characteristic spiral texture of the "banded spherulites" arise? The texture demonstrates that crystal orientations are exactly correlated over macroscopic distances.

In a general view, the existence of a well-determined crystallinity and of long-range orientational correlations gives evidence that the crystallites, blocks or lamellae, during the evolution have interacted over mesoscopic distances. The interaction forces control the distance between adjacent crystallites and thus determine the crystallinity, and they also establish the orientational correlations. The forces have to be transmitted by the amorphous regions. Their topology, *i.e.* the entanglements, surely plays a decisive role. Under normal conditions, for common molecular weights and crystallization rates, the crystallization process does not resolve the entanglements. They are just shifted and get accumulated in the amorphous regions. As opposing forces will arise from the increase in the entanglement density, it is basically conceivable that the crystallinity cannot reach unity. This, however, is just some qualitative statement. A theory describing the situation quantitatively, with a potential to predict crystallinities, does so far not exist.

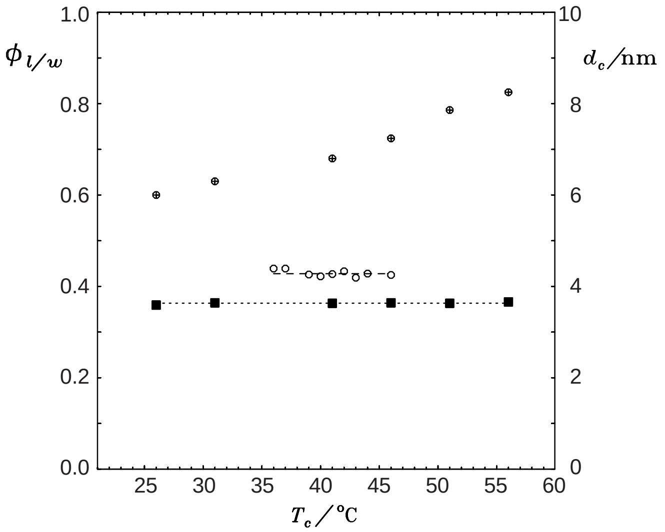

Fig. 21. Crystallinities of PCL after isothermal crystallizations at different T_c's: weight fraction crystallinity ϕ_w derived from the DSC signal (open symbols) and volume fraction crystallinity ϕ_l deduced from SAXS data (filled symbols). T_c-dependence of d_c (crossed symbols; right axis)[10].

In fact, there are some empirical laws of simple character which have to be explained:

- Crystallinities as determined at the end of isothermal crystallization processes are invariant over larger temperature ranges.
- The distance between neighboring lamellar crystallites, *i.e.* the "long spacing" L, increases with the molecular weight.

Figures 21 and 22 present as examples two typical results, obtained for PCL and PEEK. Measurements of the crystallinity of PCL after a crystallization at different T_cs, both by DSC and SAXS, show a constancy over the full temperature range of the measurements. On the other hand, the length scale of the structure as determined by the crystal thickness d_c changes quite remarkably [10]. The PEEK data in Figure 22 obtained by Fougnies *et al.* [44] demonstrate that while the crystal thickness does not depend on the molecular weight, the thickness of the amorphous intercrystalline layer, *i.e.* the distance of the crystal lamellae, varies. The data confirm a suggestion by Rault [45] that L is proportional to the chain diameter in the melt, $L \simeq R \sim \sqrt{M}$.

The invariant crystallinity for changing length scales of the structure means that the amorphous regions always end up at the same entanglement density, which intuitively makes sense. However, the molecular weight effect shows that the entanglement density does not act alone as controlling factor for the crystallinity. Quite generally speaking, the molecular weight dependence of L and, as a consequence, of the crystallinity indicates that a chain which has been included with one or more sequences in a crystallite will usually not be incorporated into another one. By this effect adjacent crystallites are kept at a distance in the order of the coil diameter.

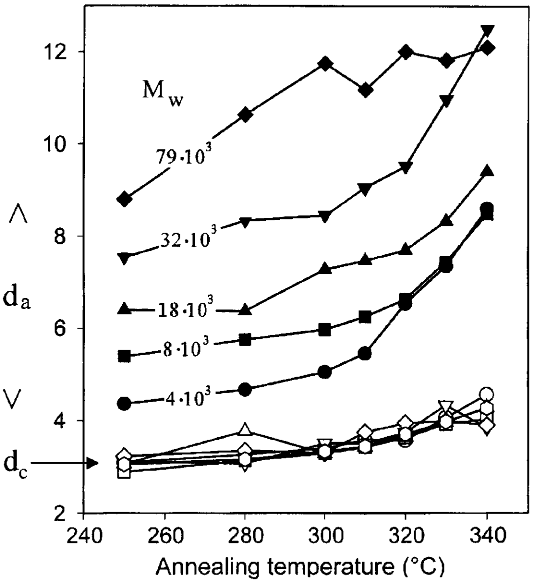

Fig. 22. Fractions of PEEK: Temperature variation of the thicknesses of crystallites and amorphous intercrystalline layers for different molecular weights. From Fougnies *et al.* [44].

Even more intriguing questions arise from the frequent observation of "banded spherulites". Within these objects there exist exact long-range orientational correlations, both in a radial and azimuthal directions. There is a regular periodic twist in the radial direction, and the angle of twist changes for all radius vectors in a strictly correlated manner. The twist period may be changed in a controlled way by the temperature or also by the addition of a non-crystallizing second polymer [46] (compare, for example, a work of Wang *et al.* [46]).

Both phenomena, the definiteness of the crystallinity and of the texture after isothermal crystallizations, give evidence that polymer crystallization includes as an essential feature a high degree of cooperativity which requires the action of mesoscopic forces between the evolving building elements. Simple rules are obeyed; however, more than a rather diffuse qualitative understanding, for part of the phenomena only, has not been reached so far. For the proposed route one has to ask at which stage of the development these mesoscopic ordering phenomena become effective. Probably this occurs already to a large part during the building up of the mesomorphic layers, as corrections are at this stage much easier than after the solidification. To give one example: The layer thickening will affect a range with extension R, as any change will be transmitted over the whole length of a chain. A decoupling of the thickening process of adjacent layers can therefore only be achieved if they remain at a distance $L \simeq R$.

6 Final remarks

Two items in the chosen title deserve some more explanations, the formulation "major route" and the question mark at the end. The term "major route" implies a limitation. The proposed model is thought to deal with the most common situation, the crystallization out of a quiescent melt of polymers with molecular weights above the entanglement limit, but there are several other cases where it cannot be applied, and we quote some of them explicitly. Not dealt with are:

- the crystallization of oligomers and low molar mass polymer fractions with the typical discrete number effect;
- the development of lowest crystallinity structures in copolymers with a high number of co-units, where quasi-crystalline aggregates ("fringed micelles") appear at random locations;
- the growth of "shishs" in oriented flowing melts; and
- the entire field of crystallizations from solution.

Expressed in structural terms, the proposed model concerns crystallization processes in an entangled polymer melt which result in homogeneous or granular crystal layers embedded in and coupled by the fluid matrix. Whether or not the growth of chain-extended crystallites, which is accompanied by a chain disentangling, follows the same or a similar route cannot be said at present. Chain disentangling necessarily sets in if the crystal thickness gets larger than the radius of gyration of the chains in the melt, and the consequence is, first of all, a change in the surface structure of the crystallites. As demonstrated by Rastogi's observations (Fig. 14), a transition from a mesomorphic to a crystalline layer does occur also in this case; whether or not the transition changes its character has to be investigated.

Why the question mark? We are convinced that the understanding of polymer crystallization needs new concepts. We see no way how the conventional approaches could explain the general state diagram Figure 6 or Kanig's observation Figure 15, picking up two particularly important observations out of all the presented experimental results. Furthermore, according to equation (5), polymer crystallization is associated with a drop in the Gibbs free energy which is well determined, varying linearly with the crystallization temperature. Every approach dealing with polymer crystallization has to give a convincing explanation for this characteristic property, but the conventional models treat it only as a side effect, if at all. On the other hand, we cannot expect that the proposed new conception is already perfect in all its parts. The main ingredients setting up the model do not all have the same degree of certainty when considering the experimental evidence. The existence of granular crystal layers as an intermediate state is in our view rather well demonstrated, by the finding of a distinct crystallization line different from the melting line and by the growing number of observations of lamellae with a blocky substructure. The evidence for the existence of mesomorphic layers prior to the appearance of the first crystallites looks also quite reliable, considering the clear experimental results obtained by Kanig and by Rastogi, Hikosaka, Kawabata and Keller. The view that polymer crystallization might generally begin with the formation of a mesomorphic layer was introduced by these authors and also further extended, in generalizing treatments together with Goldbeck-Wood [47] and Cheng [48]. However, it is not yet commonly accepted. Typically, other authors who detected ordering phenomena prior to crystallization present other interpretations. Therefore, the existence of pre-ordering processes appears to be sure, but one needs more experiments which can resolve the underlying structure. The lowest support has the assumed weakly first order character of the transition from the mesomorphic into the granular crystalline layer. This is indeed more a hypothesis than a proved fact, stimulated by the observations of the ordering processes in mono-layers and by the general expectation that, in order to be efficient, the route which transforms the entangled polymer melt into the semi-crystalline state is selected as a mostly continuous one, without higher barriers to be surmounted. Therefore, although arguments based on experimental observations could be given for all the steps along the route, they vary in quality and future experiments may well lead to modifications.

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References

1. G. Strobl, *The Physics of Polymers* (Springer, 1997) p. 143.
2. J.D. Hoffman, G.T. Davis, J.I. Lauritzen, in *Treatise on Solid State Chemistry*, edited by N.B. Hannay, Vol. **3** (Plenum Press, 1976) p. 497.
3. J.D. Hoffman, R.L. Miller, H. Marand, D.B. Roitman, Macromolecules **25**, 2221 (1992).
4. J.J. Point, M. Dosiére, Polymer **30**, 2292 (1989).
5. D.M. Sadler, Nature **326**, 174 (1987).
6. K. Zahn, R. Lenke, G. Maret, Phys. Rev. Lett. **82**, 2721 (1999).
7. J.M. Kosterlitz, D.J. Thouless, J. Phys. C **6**, 1181 (1973).
8. L.F. Chi, M. Anders, H. Fuchs, R.R. Johnston, H. Ringsdorf, Science **259**, 213 (1993).
9. G. Hauser, J. Schmidtke, G. Strobl, Macromolecules **31**, 6250 (1998).
10. B. Heck, T. Hugel, M. Iijima, E. Sadiku, G. Strobl, New J. Phys. **1**, 17 (1999).
11. M. Iijima, G. Strobl, Macromolecules **33**, 5204 (2000).
12. G. Kanig, Kolloid Z.u.Z. Polymere **261**, 373 (1983).
13. G. Kanig, Colloid Polym. Sci. **269**, 1118 (1991).
14. K. Tashiro, S. Sasaki, N. Gose, M. Kobayashi, Polymer J. **30**, 485 (1998).
15. S. Rastogi, M. Hikosaka, H. Kawabata, A. Keller, Macromolecules **24**, 6384 (1991).
16. T. Okada, H. Saito, T. Inoue, Macromolecules **25**, 1908 (1992).
17. N.V. Pogodina, S.K. Siddiquee, J.W. van Egmond, H.H. Winter, Macromolecules **32**, 1167 (1999).

18. M. Imai, K. Kaji, T. Kanaya, Y. Sakai, Phys. Rev. B **52**, 12696 (1995).
19. G. Matsuba, K. Kaji, K. Nishida, T. Kanaya, M. Imai, Polymer J. **31**, 722 (1999).
20. N.J. Terrill, P.A. Fairclough, E. Towns-Andrews, B.U. Komanschek, R.J. Young, A.J. Ryan, Polymer Commun. **39**, 2381 (1998).
21. K. Fukao, Y. Miyamoto, Phys. Rev. Lett. **79**, 4613 (1997).
22. G.H. Michler, *Kunststoff-Mikromechanik* (Carl Hanser Verlag, 1992) p. 187.
23. T. Hugel, G. Strobl, R. Thomann, Acta Polym. **50**, 214 (1999).
24. S. Magonov, Y. Godovsky, Amer. Lab. **31**, 55 (1999).
25. J. Loos, P.C. Thüne, P.J. Lemstra, J.W. Niemantsverdriet, Macromolecules **32**, 8910 (1999).
26. P.D. Olmsted, W.C.K. Poon, T.C.B. McLeish, T.C.B. Terrill, A.J. Ryan, Phys. Rev. Lett. **81**, 373 (1998).
27. Y. Akpalu, L. Kielhorn, B.S. Hsiao, R.S. Stein, T.P. Russell, J. van Egmond, M. Muthukumar, Macromolecules **32**, 765 (1999).
28. D.C. Bassett, D. Patel, Polymer **35**, 1855 (1994).
29. R.H. Olley, D.C. Bassett, Polymer **30**, 399 (1989).
30. W. Pechhold, W. Blasenbrey, Kolloid Z.u.Z. Polymere **241**, 955 (1970).
31. R. Graf, A. Heuer, H.W. Spiess, Phys. Rev. Lett. **80**, 5738 (1998).
32. S. Tsubakihara, A. Nakamura, M. Yasuniwa, Polymer J. **28**, 489 (1996).
33. Ph. Buffat, J.-P. Borel, Phys. Rev. A **13**, 287 (1976).
34. S.L. Lai, J.Y. Guo, V. Petrova, G. Ramanath, L.H. Allen, Phys. Rev. Lett. **77**, 99 (1996).
35. H.S. Lim, C.K. Ong, F. Ercolessi, Z. Phys. D. **26**, 45 (1993).
36. F. Ercolessi, W. Andreoni, E. Tosatti, Phys. Rev. Lett. **66**, 911 (1991).
37. A. Wurm, M. Merzlyakov, C. Schick, J. Macromol. Sci.-Phys. **38**, 693 (1999).
38. J.A.N. Zasadzinski, M.B. Schneider, J. Phys. (Paris) **48**, 2001 (1987).
39. J.M. Carlson, J.P. Sethna, Phys. Rev. A **36**, 3359 (1987).
40. E.B. Sirota, A.B. Herhold, Science **283**, 529 (1999).
41. T. Hugel, Diplomarbeit, Fakultät für Physik, Universität Freiburg (1999).
42. G. Strobl, Acta Polym. **48**, 562 (1997).
43. G. Strobl, *The Physics of Polymers* (Springer, 1997) p. 160.
44. C. Fougnies, M. Dosiére, M.H.J. Koch, J. Roovers, Macromolecules **18**, 6266 (1998).
45. E. Robelin-Souffache, J. Rault, Macromolecules **22**, 3582 (1989).
46. Z. Wang, X. Wang, D. Yu, B. Jiang, Polymer **38**, 5897 (1997).
47. A. Keller, G. Goldbeck-Wood, M. Hikosaka, Faraday Disc. **95**, 109 (1993).
48. S.Z.D. Cheng, A. Keller, Ann. Rev. Mater. Sci. **28**, 533 (1998).