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Invited Review

A Thermodynamic Frame for the Kinetics of Polymer Crystallization under Processing Conditions

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Summary. A retrospective view is given on work, which has been carried out at the Johannes Kepler University during the last two decades on the structure formation in crystallizable polymers during their processing. Emphasis is laid on some useful principles lend from basic physical chemistry: use of the *T,S*-diagram and of the temperature dependent courses of (effective) surface tensions along coexistence lines of phases. These considerations should be helpful in creating an overview, where a deficiency of direct experimental crystallization kinetics data exists. For a series of industrially important, mostly fast crystallizing, polymers data are given in the present paper for the quiescent melt (temperature dependences of number densities of nuclei and of growth speeds). Critical minimum cooling speeds for bypassing crystallization are given on the basis of the given data. These critical cooling speeds vary by almost six decades from *HDPE* to *i-PS*. These results are also helpful in the formulation of a viable classification of materials in the light of their processing conditions. This classification includes metals and glass forming minerals as limiting cases for extremely fast and extremely slowly crystallizing materials.

Keywords. Phase transitions; Kinetics; Thermodynamics; Crystallization; Materials' classification.

Introduction

As is well known, during processing the solidification of crystallizing polymers like polyethylene, polypropylene, or polyamides always occurs under the influences of heat transfer and momentum transfer (cooling and flow). For an understanding (or simulation) of the underlying processes one needs crystallization

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kinetics data in a wide range of temperatures and conditions of flow. Notwithstanding the fact that our research group has been engaged in pertinent measurements for more than twenty years [1–3], there is still a considerable shortage of data. One of the reasons for this shortage is the required experimental expenditure. Thus, only few research groups in the world seriously decided to join our ranks [4–7]. In fact, commercial instruments are mostly useless for our purposes. So, one has to construct special equipment, which requires a workshop and a good instrument maker. And it also goes without saying that such an endeavor is quite time consuming.

As a consequence, the aim of the present review must be a juxtaposition of already obtained experimental results in order to create a feeling for significant assumptions, where concrete data do not yet exist. It goes without saying that this intention can be supported effectively by the application of general principles, where possible. Such an approach is indicated by the title of this paper. In this respect principles, as borrowed from physical chemistry, are particularly useful.

Indeed, polymer crystallization forms a strong link between polymer chemistry and physical properties like stiffness, toughness, thermal and electrical insulation properties, thermal expansion, and optics (transparency, gloss). These properties can be tailored for particular application requirements by synthesising appropriate polymer structures and selecting additives serving as stabilizers, crystallization nucleating agents, and processing aids. Consequently, understanding the role of molecular structure and additives in polymer crystallization under processing conditions is essential for the successful polymer chemist in achieving target properties of the final product. But, returning to physical chemistry one should observe that certain diagrams like the *P*,*V*-diagram for real gases, or surface tension and conditions of nucleation, as paving the way for all kinds of phase separation, form normal subjects in a course of physical chemistry.

The *T*,*S*-Diagram

Figure 1 contains the *T*,*S*-diagram for isotactic polypropylene (*i-PP*) as a ground pattern, *T* being the absolute temperature and *S* the entropy per repeating unit of the polymer. For practical reasons also the Celsius-scale is given in the graph. The equilibrium melting point $T_m^* = 212°\mathrm{C}$ is taken from a paper by *Marand et al.* [8]. These authors used a clever extrapolation method for obtaining the melting point of ideal polymer crystals consisting of stretched macromolecules in their helical conformation. The pertinent value of $\Delta S_m = \Delta H_m / T_m$, however, is only estimated, as will be shown below. In principle, this diagram holds for constant pressure. The lines drawn are isobars. As already mentioned in previous papers [9, 10], one of the advantages of the *T*,*S*-diagram is that its ordinate axis is the temperature axis. So one can read possible degrees of undercooling and other characteristic temperatures directly from the graph. Entropy *S* is plotted as the independent variable, which requires some mental training.

In the classical *P*,*V*-diagram for real gases, however, the lines are isotherms. With the aid of usual constitutive equations for real gases one can construct the well known meanders characteristic for the gas–liquid transition. For a certain chosen temperature the corresponding equilibrium pressure of this transition is found by drawing a horizontal line through the meander, so that the surfaces between the

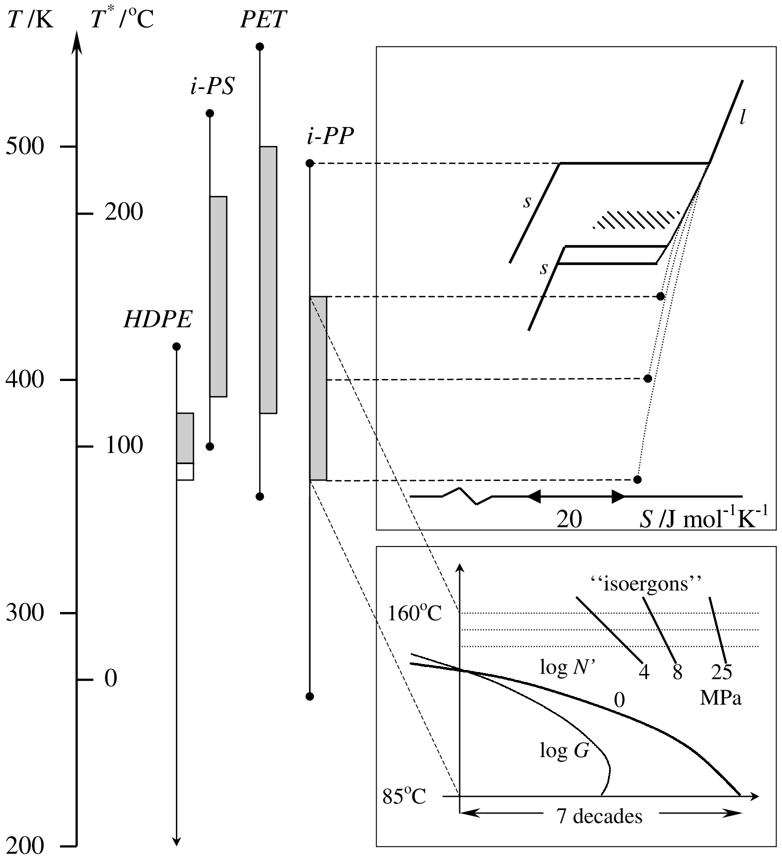

Fig. 1. An extended *T,S*-diagram; all curves are for *i-PP*; details are explained in the text; thick shaded vertical bars indicate the temperature ranges, where kinetic data are obtained experimentally for several polymers; thin vertical lines connect the equilibrium melting points with the corresponding glass transition temperatures; some data for *i-PP* are shifted to the lower right corner; lines connecting points, as obtained with equal amounts of specific work, are called "isoergons"

lower part of the meander and this line and between the upper part of the meander and this line become equal. In fact, because of the well known *Maxwell* relation $(\partial F/\partial V)_T = -P$, with F being the *Helmholtz* free energy, the integral $\int P\,\mathrm{d}V = -\int(\partial F/\partial V)\mathrm{d}V = -\Delta F$ must be independent of the integration path chosen, F being a function of state. Up to this point this consideration is a rehearsal of fundamental physical chemistry.

In a previous paper [9] the proposal was made to introduce the *T,S*-diagram instead of the *P,V*-diagram because of the above mentioned advantages. Also with these diagrams one obtains meanders for the gas–liquid transition. These meanders, however, belong to the chosen pressures. The equilibrium temperatures are obtained on condition that the integral $\int(\partial H/\partial S)_P\,\mathrm{d}S = \int T\,\mathrm{d}S = \Delta H_m$ is independent of the path chosen (equality of the respective surfaces). In fact, the corresponding *Maxwell* relation is $(\partial H/\partial S)_P = T$, with H being the enthalpy per repeating unit. The distance between the equilibrium temperature of the gas–liquid-transition and the minimum of the lower part of the meander (which is on the right side of the *T,S*-diagram) should give the lower limit for metastable undercooling of the gas below the equilibrium boiling point of the fluid. This lower temperature also confines the temperature range for the sporadic formation of nuclei. In fact, below this limit the gas becomes unstable.

Unfortunately, it is not so easy to transfer this consideration without modification to the liquid–solid-transition, which is so important in our present context. In fact, the solid should be crystalline and there does not exist a pertinent constitutive equation, which is able to describe such a transition. From practical experience, however, we know that one can undercool a fluid in a similar way as a gas. As is well known, an effective surface tension between the new phase and the surrounding old phase causes a kinetic barrier [11–13]. Interestingly, one can quite easily calculate the course of the surface tension at the coexistence lines between gas and liquid and between liquid and solid for a normal fluid [9]. It turns out that the surface tension between gas and fluid at the boiling point cannot differ too much from the average surface tension between the liquid and the crystallographic surfaces at the melting point. But this would mean that the undercooled liquidus line should be very similar to the right branch of the gas–liquid meander. If this is true, one arrives for a normal fluid at a temperature range, of which the lower bordering is given by the shaded area in Fig. 1, marked as a parallelogram. A more detailed argumentation will be given below.

In first instance, however, the general character of Fig. 1 should be elucidated. In this connection it must be said that the fluid should be unstable below the marked shaded area or, to put it otherwise around, that nuclei, which survived the thermal prehistory, should be stable below this shaded area. For some reason, spinodal phase decomposition occurs only at much lower temperatures, probably below 85°C for *i-PP* (see the diagram).

However, when looking at Fig. 1, another interesting observation must be made. In fact, a second, lower and still quite orderly transition is sketched in this figure with the aid of a horizontal double line. The area between these two lines indicates the melting range of spherulitic structures in *i-PP*. The value of $\Delta S_{tr} = \Delta H_{tr}/T_{tr}$ is taken from *Van Krevelen*'s tables [14]. In fact, calorimetric data have been obtained only on spherulitic structures. As shown in the graph, the ΔS_m at the equilibrium melting point must be larger. So the drawing was carried out adequately. One can interpret this lower transition also as a somewhat blurred melting point depression, as caused by an additional surface tension developing at the surfaces of growing lamellae. The variation in the melting points of these lamellae seems to be caused mainly by the variation in their thicknesses. In fact, spherulites are built of those lamellae.

The nuclei, pertinent to these lamellae, can be considered as kind of fringe micelles, with a relatively low lateral surface tension, as responsible for a usual kinetic barrier in a normal fluid. The "fringes" (tangling ends) should not contribute too much to this kinetic barrier as long as the micelles are thin enough. In fact, in sufficiently thin micelles the fringes should enjoy considerable conformational freedom. Only when lamellae are formed by lateral growth on these micelles, this freedom must be constricted. As a consequence an additional surface tension is built up during this growth in the rough surfaces of the lamellae. This surface tension will level off as soon as the extension of the lamella is large enough. A nice equation for the corresponding melting point depression was derived by *Strobl* [15]. In fact, the thinner the lamella (the shorter the initial fringe micelle) the larger will be the melting point depression. This fact provides a wellcome selection rule for the capability of a nucleus to grow out into a lamella: the larger the effective length of the original fringe micelle is, the higher will be the temperature, where a lamella of corresponding thickness can grow. Apparently, such a growth does not occur at temperatures above the temperature of the indicated second transition, which is indicated by the double line in Fig. 1. Nuclei from higher temperatures can be considered as dormant because of their apparent longevity. In fact, one is reminded at this point of the mechanism of self-nucleation, as investigated by *Keller* and by *Alfonso et al.* [16, 17], where nuclei, which have been formed in the interior of a spherulite, survive the melting of this spherulite.

For the moment attention should be focused on other salient features of Fig. 1. Between 160 and 85°C one finds a range indicated for *i-PP* at the left side of the figure by a thick shaded vertical bar. Actually, in this temperature range almost all of our kinetic experiments were carried out. Above 160°C kinetics are too sluggish, below 85°C one finds the ‘‘conformational disordered phase’’, as defined by *Wunderlich* [18]. The corresponding temperature range of transition was determined for *i-PP* by *Piccarolo et al.* [19]. A schematic presentation of our own activities is transferred to the lower right side of Fig. 1 (see the oblique connecting lines). Details of these activities will be discussed in a later section. The corresponding measurement temperatures are reached by quenches from temperatures above the equilibrium melting point of 212°C. This melting point can be ascribed to the most stable α-crystal modification, as defined by *Turner-Jones et al.* [20]. The courses, which these quenches take on the *T,S*-diagram, are indicated by curved lines ending at encircled points. The curvatures are necessary, because of the fact that fluids will retain their internal equilibrium states even with high cooling speed over quite a distance along the undercooled liquidus line. Downwards deviations are expected to occur only at a relatively late stage of the quench, when the viscosity increases too much. Interestingly enough, after these quenches we had still to do in all cases with the formation of spherulites of the α-modification, recognizable from the low optical anisotropy of these spherulites. The glass-transition-temperature of *i-PP* is marked at -10°C [21].

For an eventual comparison with the behavior of other polymers additional characteristic temperature bars are inserted in Fig. 1 for high density polyethylene (*HDPE*), isotactic polystyrene (*i-PS*), and polyethylene terephthalate (*PET*) . Thin vertical lines indicate the total temperature ranges from the equilibrium melting points down to the glass transition temperatures. Thick shaded bars indicate the ranges, where kinetic measurements could be carried out. One can see that the total range of interesting temperatures is about the same with *i-PP* and with *HDPE* (having a glass transition temperature of -110°C [21]). For *HDPE* the boundaries are shifted by about 70 degrees to lower values. Unfortunately, measurements on *HDPE* are difficult because primary crystallization of this polymer is more than ten times as fast as that of *i-PP*. This will be shown below. The slowly crystallizing polymers *i-PS* and *PET* are of interest because their glass transition temperatures are much closer to their melting points. As a consequence, their crystallization speeds are many decades lower, as *Van Krevelen* has explained convincingly [22]. For the same reason these polymers do not show a conformational disordered phase. But this means that the growth speeds of their spherulites can be described by a complete bell shaped curve as a function of crystallization temperature from the melting point down to the glass transition temperature (see a later section). The same situation existed in the classical experiments by *Gandica* and *Magill* [23]. These authors restricted their measurements to polymers of slow growth rates. In fact, they preferred the use of a microscope – instead of quenches of a series of extremely thin samples in two steps, first to the chosen crystallization temperature, and second for fixation. But for the polymers, as chosen by *Magill*'s group, glass transition is always rather close to the equilibrium melting point.

In contrast, the corresponding curve for *i-PP* is interrupted at the transition to the conformational disordered phase at about 85°C. The situation with *HDPE* is still unclear. In fact, for this extremely fast crystallizing polymer, there must be "room" enough on the temperature axis for such a disordered phase. So far, however, it seems that nobody has ever observed this phase. A corresponding discussion will be tried below. This remark confines the preliminary discussion of Fig. 1.

The Role of Surface Tension

In the case of a gas–liquid transition one obtains a guess for the difference between the equilibrium boiling point T_b and the lower limiting temperature T_s for sporadic nucleation (Eq. (1)) [9] with $C_{p,b}$ being the heat capacity of the gas at the boiling point.

$$T_b - T_s \cong (1/3)\Delta H_b / C_{p,b} \tag{1}$$

With the data for nonadecane as a suitable model fluid (see Table 1 in Ref. [9]) one obtains 94 J mol^{-1} K^{-1} for $\Delta H_b/T_b = \Delta S_b$. This value is quite close to the value given by the rule of *Trouton*. So, this fluid, surely being apolar, is very normal. For the corresponding temperature difference one obtains $T_b - T_s \cong 25$ K from Eq. (1).

In this connection the value of the kinetic barrier Δg for the creation of a spherical nucleus is of interest. According to the classical theory [11] one has Eq. (2).

$$\Delta g = \frac{16\pi}{3} \frac{\sigma^3 M^2}{(\Delta\mu)^2 \rho^2} \tag{2}$$

In Eq. (2) σ is the said surface tension, M is the molar mass, ρ is the density of the liquid phase, and $\Delta\mu$ is the difference of the chemical potentials of the undercooled gas and the undercooled fluid. For an interpretation of this equation one needs a relation between $\Delta\mu$ and the degree of undercooling $\Delta T = T_b - T_s$. A first approximation in ΔT is given by Eq. (3) where T_b is now understood as the boiling point in K.

$$\Delta\mu = -\frac{\Delta H_b}{T_b}\Delta T \tag{3}$$

If one inserts this equation into Eq. (2), one notices that in this approximation Δg is inversely proportional to the square of ΔT.

Now the question arises of the lower temperature limit for the usefulness of these equations. Evidently, the barrier looses its effectiveness as soon as its value becomes commensurable with kT during the cooling process (T again in K).

Admittedly, also kT decreases with the temperature, but rather slowly. In comparison, however, the decrease of Δg is very fast, so that there is a cross-over temperature. By inserting kT_b instead of Δg on the left side of Eq. (2) and the expression for $\Delta\mu$ from Eq. (3) on the right side of Eq. (2) one obtains an equation, which can be solved for the surface tension σ. For the purpose one has only to know the value for ΔT, where the system becomes unstable. With the above mentioned value of ΔT, as obtained from Eq. (1), *i.e.* $\Delta T = 25\,\mathrm{K}$, one obtains with the tabulated thermal data of *n*-nonadecane [9] Eq. (4).

$$\sigma = 2.3\,\mathrm{mN\,m^{-1}} \tag{4}$$

This value is quite satisfying. Nevertheless, one of the present authors tried to get a value for this σ along an independent route. In Ref. [9] he described the way for a calculation of the course of the surface tension of *n*-nonadecane along the whole interesting parts of the coexistence lines between gas and fluid and between fluid and solid, incorporating the critical temperature and the triple point. The result of this calculation is shown in Fig. 2. For the purpose two influential assumptions had to be made. The surface tension between gas and fluid at 20°C was guessed to be 30 mN/m and the thickness ε of the zone of transition from gas to fluid was chosen to be just 1 nm. The latter quantity is important for the calculation of the slopes of the curve. For 20°C this slope is drawn in Fig. 2. It confirms the realistic choice of ε. All other required data were found in tables [9]. Densities are assumed to vary not too much within the separate phases.

A look on Fig. 2 shows that the surface tensions between gas and fluid at the boiling point and between fluid and solid at the melting point cannot differ essentially. If for the surfaces between the fluid and the crystal a smaller ε is assumed,

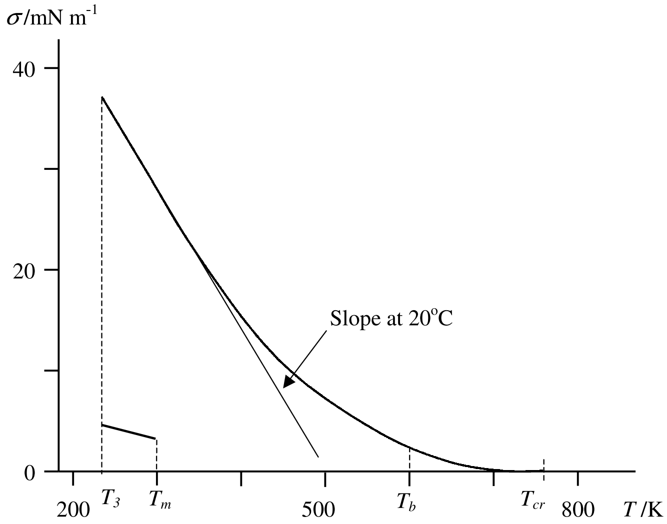

Fig. 2. Interface tension of *n*-nonadecane against equilibrium temperature along the co-existence lines of the *P*,*T*-diagram; on the temperature scale one finds from left to right: triple point, melting point, boiling point, and critical point; the conclusion, which can be drawn from the surface tension values at T_b and T_m, is that kinetic barriers for gas-liquid and liquid-solid transitions must be of the same order

which seems reasonable, the latter surface tension (fluid-solid) should even be lower. A number of values for other surface tensions in condensed matter are quoted in Ref. [9]. So, the order of magnitude of Eq. (4) is very realistic.

Let us now switch to the situation with *i-PP*, and in particular, to the temperature range between the equilibrium melting point and the melting zone of spherulites. For this range we provisionally assumed the possibility for a sporadic formation of very slender lengthy nuclei represented by the bodies of fringe micelles. For convenience we call these nuclei truncated nuclei. In fact, we assumed that the tensions caused by the fringes are negligible, as long as the micelles are thin enough. However, according to the classical point of view an increasing number of thinner nuclei of this type must come up with decreasing temperature. For these nuclei the square of the lateral surface tension σ_l shows up instead of the third power in the numerator of an equation analogous to the above Eq. (2). The square of $\Delta\mu$ and, as a consequence, also the square of ΔT remains in the denominator. But this means that for practically the same value of Δg (kT is only slightly changed by ΔT) a doubled value of the undercooling ΔT also means a doubled critical surface tension σ_l. However, this would mean a surface tension characteristic for a polar fluid at its boiling point. This arguing shows that, in principle, one cannot arbitrarily extend to lower temperatures the temperature range for sporadic nucleation, which has been estimated for normal fluids by Eq. (1). As a consequence, the shaded area in Fig. 1, as shown just above the melting range of the spherulites, does not seem unrealistic as a lower bound for the metastable range of our truncated nuclei.

However, for the lower temperature range spreading from the melting zone of spherulites down to the transition into the conformational disordered phase, a new idea must be born. As a matter of fact, one observes the growth of nice spherulites also in this range. But this points to a sporadic secondary nucleation process linked to a barrier mechanism. Apparently, with further decreasing temperatures a new kinetic barrier is formed. As already mentioned in the introduction, a rather strong surface tension must develop with the growth of lamellae at their surfaces as a consequence of the increasing constriction of the fringes.

On the other hand, no sporadic primary nucleation has been observed in this lower temperature range. After rapid quenches these primary nuclei are there immediately. Their number density is just a function of the chosen crystallization temperature. In this lower temperature range nuclei always behave like so-called athermal nuclei [24]. Of course, the participation of real heterogeneous nuclei, as formed by catalyst residues or impurities cannot be excluded. However, the number densities of the athermal nuclei increases tremendously with decreasing temperature, by up to five decades (see the next section). So, it seems very improbable to ascribe this phenomenon only to impurities and the like.

In this connection it must be emphasized that also local alignments of molecules, which exist already in the melt above the melting point, can serve as athermal nuclei at lower temperatures. In fact, those alignments must exist in the melt because of the relatively large density of the melt, being of the same order of magnitude as the density of the crystalline domains. But this means that in the melt neighboring macromolecules can never have completely independent conformations, even if they appear arbitrary, when considered separately. In this connection the length of the random link of the polymer will play a role. Of course, also this quantity is of a statistical nature, but seems to be quite instructive. In fact, local alignments stretching over lengths greater than the length of the random link, will become extremely rare. All these arguments help in explaining, why crystallization kinetics are extremely retarded in a temperature range close to the equilibrium melting point, where only very long fringe micelles can grow according to our selection rule.

Interestingly enough, fast shear flow can help to produce lengthy nuclei. We shall return to this subject in the next section. In the present context it is only worth mentioning that even close to the equilibrium melting point short term isothermal shearing can cause highly oriented crystalline structures. One can find these structures in the surface layers of duct flow, if a quench is applied immediately after cessation of flow. However, if this quench is postponed, one observes a relaxation phenomenon dependent on the waiting time. This has been found for *i-PP* and also for polybutene-1 (*PB-1*) [25–27]. But this would mean that close to the equilibrium melting point the thread-like precursors, which are formed during the flow, are destabilized in the quieted-down melt.

In fact, these thread-like precursors must be extremely thin. They do not contribute to the optical anisotropy to any extent. A considerable optical anisotropy arises only by the lateral growth of lamellae, which cannot directly occur in these high temperature shearing experiments. This growth only occurs after a quench to a lower temperature. Because of the fact that in a quieted-down melt only micelles of the approximate length of the random link seem available, one will get stacks clinging to the thread-like precursors, causing seeming row nucleation or kebab formation [28]. Are at the temperature of shearing the original thread-like precursors thinner than the critical thickness required in a quiescent melt?

As is well known, in the classical theory the pendant to the height of the barrier is the critical size of the nucleus. Only if this size is large enough, the free enthalpy of the new phase can show the required decrease during the growth of the phase. See the theory of the absolute reaction rate [29].

By the way, another puzzle is, why the relaxation time for the said precursors increases so dramatically with decreasing temperature. At the temperature of shearing this relaxation time is much smaller than the terminal relaxation time [30] for free or entangled molecules in the melt, as reflected by dynamic mechanical measurements. With decreasing temperatures, however, the relaxation time of the thread-like precursors increases much faster than the said terminal relaxation time. There must be a cross-over temperature also in this case. Below this cross-over temperature the thread-like precursors can be considered as practically stable. For a *PB-1 Alfonso et al.* [31] found relaxation times for these precursors at lower temperatures, which look astronomic compared with corresponding terminal relaxation times (see also Ref. [32]).

Short Description of Previously Achieved Results of Kinetic Measurements

The reader is asked to pay attention to the lower right corner of Fig. 1. The presentation of these data for *i-PP* is highly schematized. For a closer inspection

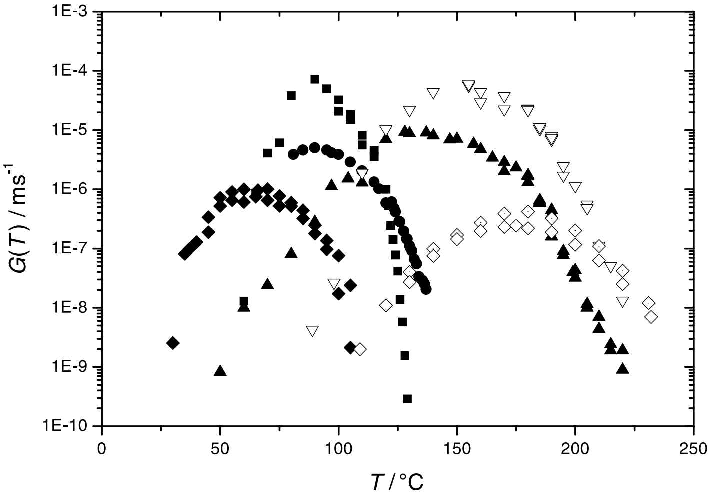

Fig. 3. Growth speeds of several industrial polymers as functions of temperature: full squares... *HDPE*, full circles... *i-PP* [1, 33], full diamonds... *PB-1* [39] (two grades), full and open triangles... two polyketons of different comonomer contents [38], open diamonds... PET of two molar masses [37]

the original papers should be consulted [1–3, 33, 34]. On the vertical axis temperatures between 85 and 160°C are plotted. On the horizontal axis one finds the scales for $\log N'$ and $\log G$, where N' is the number density of nuclei activated at the indicated temperature within a temperature range of one degree (with $[N'] = \mathrm{m}^{-3}\,\mathrm{K}^{-1}$) and G is the growth speed of spherulites at the indicated temperature (with $[G] = \mathrm{m\,s}^{-1}$). In avoiding overcrowding the scales are not indicated. This omission is repaired in Figs. 3 and 6. For the investigated *i-PP* the growth speeds increase from 2×10^{-10} to 0.7×10^{-5} $\mathrm{m\,s}^{-1}$ in a temperature interval from 160 to 90°C. Pertinent measurements could be carried out only on quiescent melts. For the same quiescent polymer melts values for the number densities N' vary from 10^8 to 10^{15} $\mathrm{m}^{-3}\,\mathrm{K}^{-1}$ in a temperature interval between 140 and 85°C. As a measure for the influence of flow the specific mechanical work, as applied to the sample during the periods of shearing or extensional flow, was introduced. Pertinent experiments could be carried out in a temperature range between 160 and 140°C. The logarithms of the number densities of nuclei, as found after various mechanical treatments, are connected by – what we call – "isoergons" [10] for equal values of specific work. One notes that there is a tremendous influence of flow on the number densities. Zero MPa stands for the quiescent melts. At a specific work of about 24 MPa thread-like precursors occurred. Interestingly enough, the influence of temperature decreases with increasing specific work. In a recent publication [34] two of the present authors have tried to understand these phenomena. However, in the present paper this subject will not be treated.

Instead, we present a series of results as obtained on the quiescent melts of other polymers of industrial interest. Figure 3 shows growth speeds of spherulites of several polymers as functions of temperature. The corresponding references are given in the caption to the figure. One notes that the growth speed of *HDPE* near its maximum is more than ten times as high as the corresponding growth speed of *i-PP*. Relatively large growth speeds are also found for two industrial polyketones and for a *PB-1*. At a close inspection of these curves one observes that they are somewhat asymmetric: the decrease of growth speeds with temperatures below the temperature of the maximum seems too fast. In fact, the corresponding glass transitions are still far away at much lower temperatures. An almost abrupt decrease is found with *HDPE*. The question arises, whether this is an indication for a transition into the conformational disordered phase. In fact, with *i-PP*, where this transition is quite conspicuous, the degree of crystallinity is much lower in the disordered phase, when compared with the spherulitic phase [19]. But this means that such a disordered phase does not at all represent a state of equilibrium. So, it may be that, on account of the greater mobility of the macromolecules in all crystalline phases of *HDPE*, a disordered phase of the latter polymer does not have too long a time of survival after the quench. Meanwhile, however, this phase may hamper the growth of spherulites in our short time experiments.

At this point we have to say a little more about the techniques, which have been applied in our laboratory to *HDPE*. Ultra thin layers of the polymer (down to 0.85 μm) were prepared on thin microscopy cover glasses by evaporation of dilute solutions. Second cover glasses were put on top of the layers. The obtained sandwiches were first heated by infrared radiation, in order to destroy residues of previous crystallization, and than quenched in a stream of a heat transfer fluid (mostly water) of proper temperature. The idea of using extremely thin layers has been brought forward by *Chew et al.* [40]. With those layers the number of spherulites (actually of thin discs) is considerably reduced compared with the number found in thin slices of the same thickness, as cut from the bulk. In fact, in the latter slices one finds also cross-sections of spherulites, of which the centers lie outside the body of the slice. Figure 4 shows a microscopic picture obtained on a 0.85 μm layer of a *HDPE* sample after a quench to 100°C. Any influence of the glass surface on the nucleation can be excluded because thicker layers showed a proportionate increase of the number of those "spherulites". The growth speed of the spherulites was obtained from the slope of a line connecting radii, as obtained after various crystallization times, being the intervals between the first and the second quench, as mentioned above. This is shown in Fig. 5 for quench temperatures between 85 and 110°C.

Also the number of spherulites could be counted per unit surface of the samples. With the aid of the measured final thickness of the solidified sample, the corresponding number of nuclei per unit volume could be calculated. This was possible because the measured spherulite radii were between 10 and 45 μm, which means that there was always only a single layer of (disc like) spherulites in a sample of a thickness of about 0.85 μm. Because of the fact that the boundary angles between glass and the melt and between glass and the semi-crystalline domains cannot differ too much, the growth speed of a real spherulite cannot differ too much from that of a disc expanding between glasses. For the number densities of spherulites see Fig. 6.

If a crystallization temperature below 85°C was chosen, the measurements became more difficult for *HDPE*, because on the pictures there was no interspace left between the spherulites. Also, these spherulites did no longer appear of equal size. Nevertheless, one could still draw straight lines through the radii of spherulites, which appeared as the biggest ones. Apparently, these spherulites grew steadily. Only, the said lines did no longer pass through the origin, as happened above 85°C (see Fig. 5). An "initial" spherulite radius showed up, which did not depend on the duration of the crystallization time. Apparently, it was determined by the reproducible cooling process. From the slopes of the latter lines lower growth speeds were derived for temperatures below 85°C, as shown in Fig. 3.

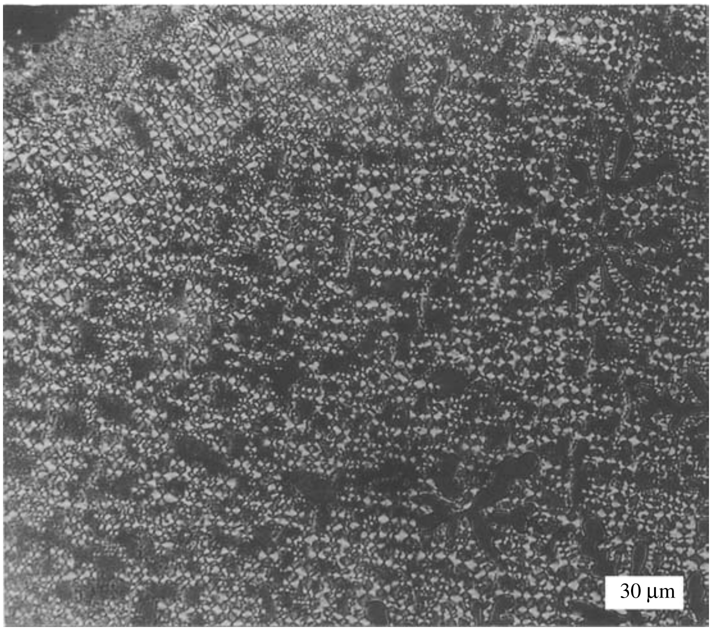

Fig. 4. A micrograph of a layer of *HDPE* of a thickness of 0.85 μm, as obtained after a quench from 180 to 100°C; the growth of the spherulites was stopped by a quench with ice water before coalescence of the (disk-like) "spherulites" occurred; a number of 300 of such spherulites were counted on an area of $7.13 * 10^{-8}$ m^2; knowing the thickness of the sample one arrives at $4.5 * 10^{16}$ nuclei per cubic meter

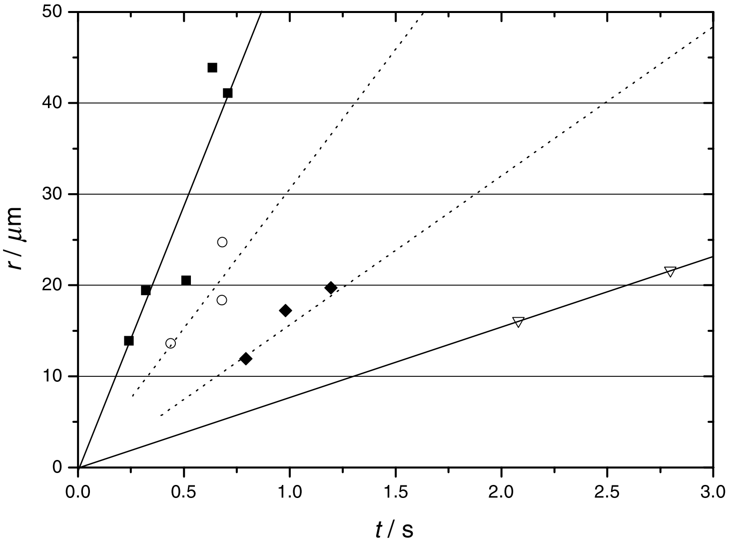

Fig. 5. Radii of disk-like "spherulites" of *HDPE* as functions of crystallization time for several crystallization temperatures, as reached after rapid quenches: open triangles . . . 110°C, closed diamonds . . . 100°C, open circles . . . 90°C, full squares . . . 85°C; for lower temperatures the lines do no longer go through the origin, but still show positive slopes

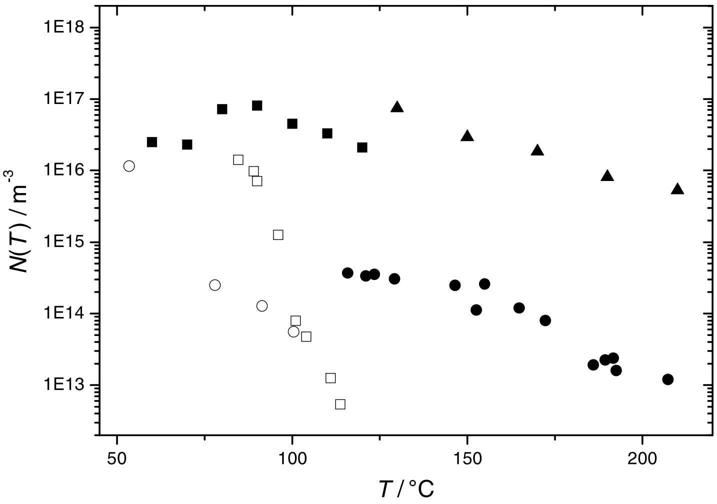

Fig. 6. Number densities of nuclei for several industrial polymers as functions of temperature: full squares . . . *HDPE*, open squares . . . *i-PP* [1, 32], open circles . . . *PB-1* [39], closed circles . . . polyketones [38], closed triangles . . . *PET* [37]

At this point, however, it should be emphasized, that the growth speeds of *HDPE*, as obtained above 85°C, are very reliable. Previously, they were determined in our laboratory in an indirect way by means of the delayed bursting out of light scattering on a quenched surface and of the so-called incubation time for the departure of a crystallization zone from a colder surface [1, 33]. The required calibration of the optical parameter was carried out by means of the measurements of *Chew et al.* [40], as carried out at higher temperatures.

In Fig. 6 the number densities of the polymers of Fig. 4 are shown as functions of crystallization temperature. In this figure one finds again deviations for *HDPE* at temperatures below 85°C. A decrease of the number density of nuclei with decreasing temperature really seems unthinkable for the state of an undercooled melt. However, as we only can count the number of spherulites, which have grown on nuclei, the question arises, whether the growth of some spherulites has been impeded completely. We do not dare to answer this question. We can only repeat that all counts were carried out on thin samples of a thickness considerably smaller than the radii of the observed spherulites. So it seems impossible that only part of the spherulites has been visible under the microscope.

Evaluation of the Data

One of us [41] developed Eq. (5), which permits the calculation of the critical minimum cooling speed, which is required in order to bypass crystallization, ending up with an amorphous sample. In this calculation the heat transfer problem, which normally causes the mathematics to become cumbersome, is circumnavigated by simply introducing the cooling speeds. Such a procedure is permitted, if the sample is continuously cooled from a sufficiently high temperature and no

Table 1. Critical cooling rates for vitrification

Polymer	$G_{max}/\mathrm{m\,s^{-1}}$	k_G/K^{-1}	N_{max}/m^{-3}	$q_{crit}/\mathrm{K\,s^{-1}}$	grade
HDPE	$>8*10^{-4}$	~0.05	$>10^{17}$	>10000	Borealis
PK	$5.4*10^{-6}$	0.045	$6*10^{13}$	620	RDP-211 Shell
	$9.7*10^{-6}$	0.036	$3*10^{14}$	240	Carillon Shell
i-PP	$5*10^{-6}$	0.051	$1*10^{14}$	60	KS10 Borealis
PB-1	$1.6*10^{-6}$	0.072	$6*10^{14}$	25	0110 Shell
PET	$2.5*10^{-7}$	0.033	$1.5*10^{15}$	11.5	mPET Sinco
	$4*10^{-7}$	0.034	$1.5*10^{14}$	8.3	DMT Sinco
	$2*10^{-8}$	0.030	$\sim10^{15}$	~0.9	v. *Antwerpen* [37]
i-PS	$2.5*10^{-9}$	0.035	$\sim10^{13}$	~0.02	v. *Krevelen* [35, 36]

latent heat is evolved. But this latter condition is sufficiently realized, if a final crystallinity of only 1% is permitted as the goal of the calculation.

$$(\mathrm{d}T/\mathrm{d}t)_{crit} = 13.24\ G_{max}(N_{max})^{1/3}/k_G \tag{5}$$

In Eq. (5) G_{max} is the growth speed of spherulites at the temperature of the maximum, N_{max} is the number density of nuclei at this temperature, and $1/k_G$ is the width of the temperature range, in which crystallization occurs. It should now be clear to the reader that, in principle, Figs. 3 and 6 provide all data needed for a use in Eq. (5). However, we know that the left sides of the peaks in Fig. 3 are not fully developed for some polymers. Here one is at a parting of the ways. If one thinks that only the technique of the measurement is insufficient for the low temperature range, one can assume a mirror image of the right curve, departing from the glass transition temperature. If a parabola is used for the purpose (with $y = \log G$), its point of culmination will mostly lie a little higher than the highest point of the measurements. The second way of approach is just to take the highest point of the measurement (G_{max}, N_{max}). A width of the temperature range can only be guessed in this case. However, the error, which can be made in this case, does not change the order of magnitude of the result. In the latter way Table 1 could be prepared. It contains data for some of the most important industrial polymers. In this table the symbol q_{crit} stands for $(\mathrm{d}T/\mathrm{d}t)_{crit}$. One notes that the spectrum is extremely wide.

It seems to the authors that this table is extremely instructive for those, who develop processing or experimentation strategies. This table also shows that differential scanning calorimetry (DSC) has no chances for a characterization of the most important polymers. This method appears to be much to slow. In fact, with DSC cooling speeds are always given in K/min instead of K/s, as quoted in Table 1.

With the introduction of Table 1 a beginning is made with a survey of a more general nature, including metals on one side and glass forming minerals on the other side of the spectrum of materials.

A Viable Classification of Materials in the Light of Processing Conditions

For such a classification Table 2 is introduced. On top of this table one finds a time scale. At first sight one may be surprised that this time scale refers only to the time

Table 2. A viable classification of materials

10^{-10} — 10^{-5} — τ_{cr}/s — 10^{0} ⟶ 10^{5} — 10^{10}

Metals	Polymers	Glass forming minerals
Crystallization near T_m, subsequent cooling of the solid	Cooling and crystallization interfere	Serious undercooling of the melt, subsequent retarded crystallization
$\tau_{th}/\tau_{cr} \gg 1$	$\tau_{th}/\tau_{cr} \approx 1$	$\tau_{th}/\tau_{cr} \ll 1$
Heat diffusion controlled	Critical number $\frac{\tau_{th}}{\tau_{cr}} = Jk = \frac{1+Ste}{De}$ [47]	Crystallization kinetics controlled
Slow down in alloys by mass diffusion		
Classical *Stefan* problems	New mathematics required	*Cf.* crystallization in ancient glasses

needed for crystallization. This crystallization happens mostly at a pressure not too far from atmospheric pressure and always between the temperature of the molten state and the temperature, where the material is to be used as a solid. In this connection one should not forget that solidification not always occurs as a consequence of crystallization. Quite often practical solidification is a consequence of vitrification, notwithstanding the fact that, strictly speaking, the glassy state is never a state of equilibrium. One may also be surprised that no reference is made in Table 2 to the thermal properties of the materials, as there are heat conductivity, heat capacity, and density. However, these properties are of minor influence because of the predominance of the time scale of crystallization, which stretches over about 18 decades! In comparison, values of heat diffusivities vary less than 4 decades. To take two extreme cases: For silver one has $1.7 * 10^{-4}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ and, on the other side, for a polyethylene melt $1.3 * 10^{-7}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ has been found [42].

The first column of Table 2 holds for metals, the second for polymers, and the third for glass forming minerals. Below these entries one finds pertinent remarks, as there are: a) modes of solidification, and b) the approximative ratio of two characteristic times, namely the time τ_{th} for thermal equilibration and the time τ_{cr} needed for crystallization, both under conditions of processing. For the extreme limiting cases for metals and minerals a further specification of conditions is not necessary. c) In contrast, one is in need of a critical dimensionless number for the processing of polymers. In this number also the dimensions of the sample are contained (see below). d) Solidification processes in metals are, except for extremely thin samples, heat diffusion controlled. This means that heat diffusion is the slowest process, notwithstanding the relatively high heat conductivity. For glass forming minerals crystallization is always the slowest process. As a consequence, one always has crystallization kinetics controlled processes with these materials. In fact, nobody will be afraid that in a melt of quartz the process of crystallization will already occur during the period of cooling. After vitrification it can take thousands of years until crystallization becomes noticeable by the onset of turbidity and increasing brittleness. e) Most fascinating is a fact, which was discovered twenty years ago [1]: We have found that with the solidification of crystallizable polymers heat transfer and crystallization are strongly interacting (not to speak of the tremendous influence of flow, which is only touched in the present paper). In fact, with metals and with glass forming minerals the processes of heat transfer and crystallization are uncoupled: with pure metals one has a period of cooling of the melt, then very fast crystallization after a faint undercooling and, afterwards cooling of the solid. With glass forming minerals one has serious undercooling down to room temperature first and crystallization after extremely long times.

As a consequence, quite a new mathematics had to be developed for polymers. The difficulty with this mathematics lies in the fact that crystallization proceeds at the (internal) surface of already formed crystalline domains. The overall speed of momentary crystallization is not at all a unique function of temperature and of the already reached degree of crystallinity, as several authors [43, 44] have assumed erroneously. In fact, the area of this surface depends in a complicated way on the history experienced by the material during the cooling process. For instance: if at a certain temporary degree of crystallinity a few large crystals have been formed previously, the overall speed of further crystallization will be relatively low in comparison to a situation, where many small crystals have been formed. In fact, at the same degree of crystallinity the large number of small crystals has a much bigger surface than the few large spherulites. Knowing the number density of nuclei as a function of temperature, one can easily describe qualitatively a cooling process, in which relatively large crystalline domains (spherulites) are formed: one has to apply a slow cooling rate. Under this condition spherulites start growing on the few nuclei, which are active already at higher temperatures. During continued slow cooling these spherulites will become bigger and will cover part of the volume, where otherwise a larger number of nuclei is ready to become active after a fast quench to the reached lower temperature. The said erroneous theories [43, 44] are unable to predict a structure, the latter one in particular because of introducing the so-called isokinetic concept, according to which kinetics of nucleation and growth should follow the same temperature dependence (see Ref. [1]). In principle, the mathematical way out of this dilemma, which is engraved by heat transfer problems, has been sketched first by *W. Schneider* and his group [45, 46]. One of the present authors (*G.E.*) developed this theory for a series of important boundary conditions and for the influences of flow [1]. However, a description of this development will go beyond the scope of the present review.

When one of the present authors discovered the special behavior of polymers in engineering science, he defined the dimensionless number quoted in the second column of Table 2 [47]. In the beginning he was surprised that nobody else had previously proposed this number. After all, however, this omission is explainable. Except for polymer scientists nobody could be interested in such a number. In the definition of this critical number *Jk*, as reformulated by *Astarita et al.* [48], one finds two already known dimensionless numbers. The first one is the *Stefan* number

(Eq. (6)) where C_p is the (average) heat capacity, T_f is the original temperature of the fluid, and T_e is the temperature of the environment.

$$Ste = \Delta H_m / C_p (T_f - T_e) \tag{6}$$

The second one is the *Deborah* number (Eq. (7)) where a is the heat diffusivity and d is the thickness of the sample, if it is represented by a slab (by the way, the name *Janeschitz-Kriegl* number has been proposed by *Astarita* [48]).

$$De = \tau_{cr} a / d^2 \tag{7}$$

If the definition of *De* is inserted into the formulation given in Table 2, one has Eq. (8).

$$Jk = \frac{(1 + Ste) d^2}{\tau_{cr} a} \tag{8}$$

In Eq. (8) the expression $(1 + Ste)\ d^2/a$ is a good measure of the time needed for thermal equilibration (decrease of the temperature difference to a certain percentage of the original difference), if crystallization is to be completed during this process. In fact, *Ste* stands for the complete latent heat evolved. In the denominator of Eq. (8), however, one also finds the crystallization time τ_{cr}, for which we need an estimate as well, in order to obtain a useful picture of the situation.

For this purpose one can make use of the data of Table 1. One has only to take the reciprocal value of q_{crit} and multiply this value by the temperature difference applied during the cooling process $T_f - T_e$. In this way one obtains a measure for the upper bound of the crystallization time, *i.e.*, the time which is needed at the critical cooling rate to achieve a temperature decrease of $T_f - T_e$. In fact, if the thermal equilibration time is smaller than this upper bound of the crystallization time, one certainly has a crystallization kinetics controlled process.

The situation may be illustrated for *HDPE* and *i-PP*. With the aid of *Van Krevelen*'s tables [14] one obtains for the thermal equilibration times of sheets of $10\,\mu$m thickness $1.6 * 10^{-3}$ and $1.2 * 10^{-3}$ s. The corresponding upper bounds of the crystallization times are $1.2 * 10^{-2}$ and 3.1 s. For *HDPE* sheets of about $1\,\mu$m thickness were used, so that, theoretically, the cooling time should be even a factor 10^{-2} lower. But everyone knows, how uncertain quenching experiments are. What is the influence of the cover glasses? A much more detailed calculation will be necessary to decide over *HDPE*. For *i-PP*, however, one can safely conclude that the solidification process must be strongly influenced by the crystallization kinetics. Anyway, the ratios of the quoted values of the characteristic times clearly show that for both polymers *Jk* lies in the middle field of Table 2.

General Conclusions

In the present review it is shown that a general overview can be given over the behavior of crystallizing polymers under processing conditions. It could also be shown that the spectrum is rather broad, even if the crystallizable polymers cover in their speed of crystallization the middle range between metals and glass forming minerals. In fact, relatively thick samples of *HDPE* may show a solidification behavior, which is related to that of metals (diffusion controlled), whereas *PET* will mostly show the typical behavior of glass formers: if the chosen cooling rate is not too slow, one can cool the sample to environmental temperature without risking premature crystallization. In such a case the processes of cooling and (retarded) crystallization are uncoupled (see the well-known bottles for mineral water and the like). Only, if fast flow is applied, the situation with *PET* will drastically change. In fact, with fiber spinning one obtains highly crystalline samples. This is in accord with our findings with *i-PP*: See the insert in Fig. 1, where for the latter polymer the tremendous increase of the number density of nuclei is schematically shown for cases, where increasing amounts of specific mechanical work have been applied. In the original literature, which is cited in this review, we have been able to show clearly that the sensitivity for elongational flow is comparable to that for shear flow, if the specific mechanical work is used as a parameter.

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