

Kinetics of polymer crystallization under processing conditions: transformation of dormant nuclei by the action of flow

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Received 17 August 2004; received in revised form 20 January 2005; accepted 10 February 2005

Dedicated to Dr Wolfgang Neißl for having supported this work mentally and financially for 20 years on behalf of Petrochemie Danubia, now Borealis, in cooperation with the Austrian Funds for Research and Development and with the Austrian Science Foundation

Abstract

In previous papers [Janeschitz-Kriegl H, Ratajski E, Stadlbauer M. Flow as an effective promotor of nucleation in polymer melts: a quantitative evaluation. *Rheol Acta* 42 (2003) 355–364; Stadlbauer M, Janeschitz-Kriegl H, Eder G, Ratajski E. New extensional rheometer for creep flow at high tensile stress. Part II. Flow induced nucleation for the crystallization of iPP, *J Rheol* 48 (2004) 631–639. [1,2]] two types of experiments were carried out: (a) rapid quenches of quiescent melts of i-PP from their state of equilibrium to a series of rather low temperatures and (b) short term shearing or extension of melts at only mild degrees of undercooling. Strong undercooling as well as high mechanical loads cause similar tremendous increases in the number densities of nuclei by many decades. Unexpectedly, an extremely non-linear dependence of the said number densities on the loading times has been found.

In the present paper an explanation for this non-linear relation is tried. The assumption is made that in a quiescent melt there is a huge reservoir of badly organized aggregates (local alignments) of chain molecules, which as such can become effective nuclei only at rather low temperatures. These aggregates are assumed to grow by the action of flow after being oriented in the flow direction. In this way a large amount of low quality dormant nuclei can be transformed into nuclei of a better quality, which are active at higher temperatures. Starting at individual aggregates this growth can lead to thread-like precursors initiating shish-kebab structures.

Instead of the flow time the specific mechanical work has been found to be a useful universal parameter. Some measurements of the optical retardation are quoted, which strongly support the basic assumption.

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Keywords: Polymer processing; Flow induced crystallization; Model calculation

1. Introduction

The reader will become aware of the fact that some uncommon extraordinary ideas are put forward in the present paper. This means that the authors must show that such new ideas are unavoidable for an understanding of their experimental results, as obtained during recent years. In this connection two types of experiments were carried out on undercooled melts of an industrial i-PP. In one type the melt was rapidly quenched in thin layers down to considerably low temperatures—down to 80 °C, which

corresponds to a degree of undercooling of as much as 130 °C. In the second type only mild degrees of undercooling could be realized. Instead, deformation rates up to 1000 s⁻¹ could be applied in short term experiments with a duration down to 0.05 s. For the purpose a sandwich type of apparatus was developed for shearing [1] and a special extensional rheometer was constructed for stretching [2]. Shearing appeared to be particularly effective. Total shears up to 50 shear units could be achieved in fractions of a second in a unit, which created a uniform shear rate over its cross-section. (Contrast to duct flow.) Previously, nobody has ever tried to apply this type of experimental conditions, which permit an investigation of material's behavior under realistic processing conditions.

With respect to the first type of experiments, as mentioned above, the classical theory of nucleation, as put

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forward at the time by Lauritzen and Hoffman [3], had to be revised in order to allow for the presence of dormant nuclei (see the title of the present paper). With respect to the second type of experiments it must be said that a number of previous studies of other authors were carried out in ordinary rotational rheometers of the plate-and-plate type. In these commercial rheometers the achievable shear rates were too low and also their range too narrow for being of interest for the present purpose. An augmentation of the number density of nuclei could only marginally be indicated by these studies. On the other hand, there were the duct flow experiments, which were initiated at the time in our laboratory [4]. In these experiments we used a rather long duct of rectangular cross-section of large aspect ratio, which was mounted to the head of a screw extruder. We shall return to pertinent results, as obtained not only in our laboratory, in due course, when the outcome of the present investigation will be discussed. For the moment it suffices if we stress that in those ducts highly oriented crystalline surface layers are created, which remind us of those obtained in injection-molded strips. High shear rates can be achieved in these experiments close to the duct wall. The drawback of these experiments is the non-uniform flow pattern which makes it sometimes difficult to ascribe the various layers, which are obtained, exactly to certain shear rates and shearing times.

In our recent experiments, as carried out in our sandwich type of machine, this difficulty could be overcome because of the uniform flow pattern. With these experiments we were able to close a considerable experimental gap in the shear rates between the low shear rates of ordinary rotational rheometers and the high shear rates accessible near the duct wall. In this connection we should not forget that in this high shear rate range an enormous amount of ‘point-like’ nuclei, as occurring in the background, was masked by the shish-kebab structures.

In the middle range of shear rates, which became accessible in our recent sandwich apparatus, the increase in the number density of ‘point-like’ nuclei with shearing time could undoubtedly be ascertained. This number density increases with the shearing time, but also with the applied specific mechanical work, by many decades according to a strongly non-linear law. Such a law cannot be explained with the aid of the traditional nucleation theories. The present paper is concerned with an alternative interpretation.

On account of this situation the reader must not be surprised, if a section on the development of new ideas is interposed. In fact, circumstances, which forced us to ponder on the traditional view points, must convincingly be scrutinized.

2. Relevant experimental results

Fig. 1 shows a three-dimensional plot, in which the

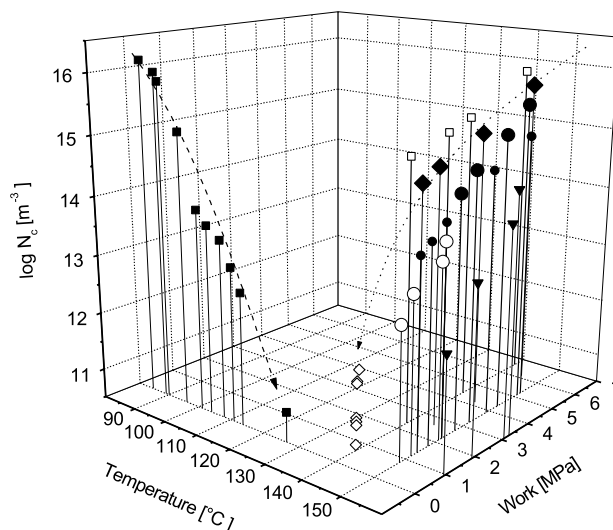


Fig. 1. Three-dimensional plot of the logarithm of the number density of nuclei (m^{-3}) vs. crystallization temperature and specific mechanical work (MPa), as obtained for an industrial PP (specified by $M_w=370,000$ and $M_n=74,000$). The points for zero work are from rapid quenches. All points for non-zero work are obtained between 140 and 160 °C. Except for the points at low specific work (open squares), which are obtained in short term elongational flow [2] at 145 °C, all other results are obtained in short term shear flow [1]. Courtesy of Springer Verlag.

logarithm of the number density of nuclei is plotted as a function of the temperature and of the specific work for an industrial PP (with $M_w=370,000$, $M_n=74,000$) [1,2]. The specific mechanical work, as applied during the period of flow, is used here instead of the time of deformation. At constant external stress the specific work is proportional to the shearing or stretching time. But it remains useful also, if the external stress is varied. The influence of the specific work could be investigated only at higher temperatures because of the fact that rapid quenches, which are necessary for the lower temperatures, cannot be carried out with more involved machines. But those machines are needed for the application of considerable external stresses. They always have too high a thermal inertia and, thus, can be cooled only slowly. Fortunately, the still quiescent polymer melt shows an extremely sluggish crystallization kinetics in the temperature range passed during this slow cooling process, which ends at a relatively high final temperature. This means that one has no problems with premature crystallization phenomena. Only after the onset of flow the frequency of the appearance of nuclei is enhanced considerably in this higher range of temperatures.

The machines, which were applied for shear and extension, have been described in Refs. [1,2,5], respectively. After the cessation of flow the samples were kept at unchanged temperatures in the machines until solidification was complete. Thereupon the number of spherulites was counted in cross-sections of the meanwhile solidified samples. Photographs were taken in a microscope at proper magnifications. The number of spherulites cut per unit

surface was raised to the power 3/2 in order to obtain an estimate of the number density per unit volume. There seems to be no alternative to this method. The unavoidable inaccuracy, however, does not seem of importance in view of the enormous effects.

It probably should be emphasized that very short term rapid shearing is almost the same as planar stretching. In fact, molecules do not get much chance for a steady state equilibration of their conformations during this treatment.

In Fig. 1 linear scales were chosen for temperature and work. Only in such a plot the situation at zero undercooling and zero work could be included. In contrast, Fig. 2 will show a double logarithmic plot of the number density of nuclei vs. specific work, as obtained more recently in still unpublished shearing experiments on the same PP at 150 °C. The approximate slope of such a line is very useful for a discrimination of the type of dependence of the said number density on the applied work. One clearly can make out a slope of more than three, but certainly not a slope of one. This figure is also important because of showing results, as obtained at very different shear stresses. If from the applied shear stress and the total deformation the specific work is calculated, points nicely fall on one line. In a previous publication [2] it could be shown for a lower temperature of 145 °C that the results, which were obtained in this way with another polypropylene of a higher molar mass, fall on a single line with those obtained on our polypropylene. A double logarithmic plot of number densities vs. specific works is given in Fig. 3 for temperatures between 140 and 160 °C. This figure has been published previously [1,6]. The results depicted in this figure were, in contrast to Fig. 2, mostly obtained by varying the deformation times at constant stresses. Remarkably, the slope shown in Fig. 2 for 150 °C is exactly the same as the one found in Fig. 3 for this temperature of 150 °C. Fig. 3 is taken over from the

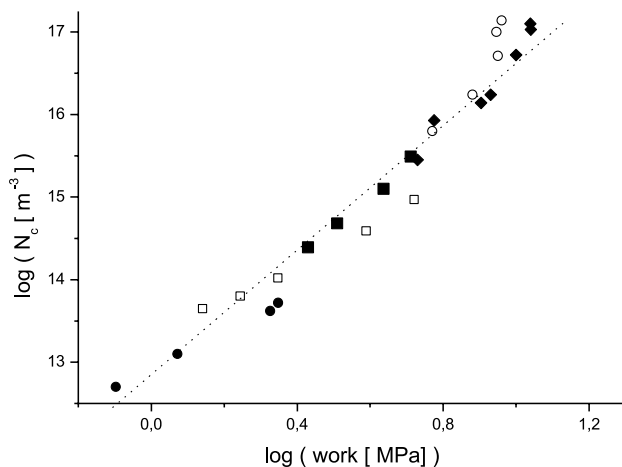


Fig. 2. Double logarithmic plot of the number density of nuclei vs. the applied specific work for the industrial polypropylene of Fig. 1 at 150 °C. A variety of shear stresses was applied: full circles 25 kPa, full squares 51 kPa, open squares 85 kPa, open circles 127–250 kPa, full diamonds 106–250 kPa.

previous publication because of forming the main basis for our present evaluations. On this graph one can also see the temperature dependence of the slopes. By the way, in this figure the points obtained with the extensional rheometer cover an unrealistically large range because of the expansion of the logarithmic work scale to negative values, as characteristic for low amounts of work. In Fig. 1 the pertinent points mark the steep descent to zero work. In Fig. 3 one finds two points at the upper end of the lines for 145 and 150 °C (open triangles). These points are taken over from our earlier work with duct flow [7]. Between these two points the transition to a highly oriented structure took place in the surface layers. On the linear scale of Fig. 1 these two points would lie very far to the right.

Because of the remark, which was made at the end of the abstract with respect to a temporary optical anisotropy, two new Figs. 4 and 5 are introduced. These figures describe a phenomenon, which is found regularly some time after cessation of flow. Fig. 4 consists of two parts. In the upper part the time dependent shear deformation is plotted for our PP, applied at 150 °C. A total shear of 50 is reached within two tenths of a second (sample thickness about 1 mm). For the case that the whole mechanical work is dissipated, which is not the case, and the sample is adiabatic, a temperature increase in about 4 °C is calculated for 8 MPa. This fact is ignored. An adequate correction would only increase the slope in Fig. 2. In the lower part of Fig. 4 the occurrence of the temporary optical retardation is shown. For the purpose, the reduced intensities, as obtained between parallel and crossed polars are given as functions of time. The curve, which starts at the value one, gives the reduced intensity for parallel polars. The one starting at zero gives the reduced intensity for crossed polars. Both intensities are reduced by dividing their measured values by the total intensity passing the sample. One has to look at the time scale. One notices a cross-over of the curves at a little less than 400 s. A slight maximum in the intensity with crossed polars and a corresponding minimum in the intensity with parallel polars indicates an optical retardation of half a wavelength. This occurs at almost 500 s. Total depolarization is reached after about 600 s. (This total depolarization is characterized by a value of one half of both reduced intensities.) One has 400 s of waiting time vs. 0.2 s of shearing time!

The importance of a micrograph, as taken with crossed polars and reproduced in Fig. 5, is that no traces of anisotropy were found in the spherulitic structure, which was obtained after cessation of flow and completed crystallization in a cross-section parallel to the previous flow direction. This is particularly remarkable for the extreme flow condition of this experiment characteristic for the upper end of the curve in Fig. 2. Also, when looking at Fig. 5 one observes only spherulites of low internal optical anisotropy. This type of spherulites is characteristic for the α -modification, as defined by Turner-Jones et al. [8]. Interestingly enough, with our experiments we never found another type of spherulites.

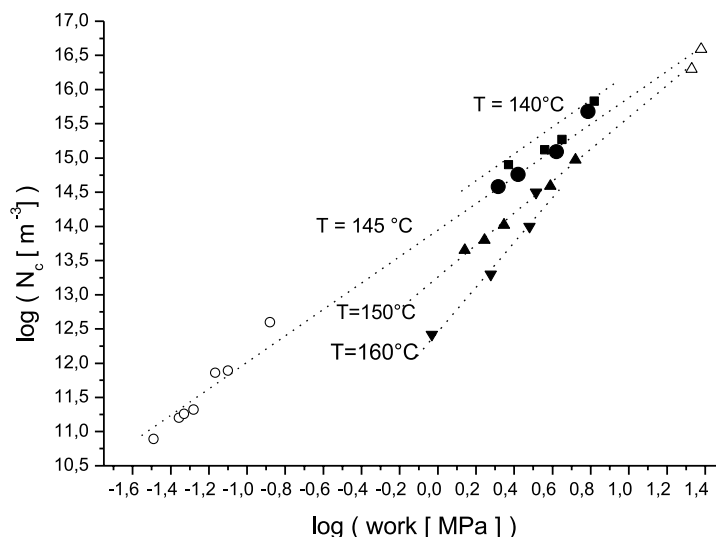


Fig. 3. Double logarithmic plot of number density of nuclei vs. applied specific work for various temperatures [1]. Data mostly taken from Fig. 1. The points obtained in short term extensional flow cover an unrealistically broad range of $\log w$, whereas the points, as obtained in duct flow experiments [7] (open triangles), seem to come too close to the other points. This is because of the logarithmic scale. Between the latter points near 25 MPa the transition to oriented structures was found. Courtesy of Springer Verlag.

3. The nature of the dormant nuclei

Before a beginning can be made with an interpretation of the flow experiments of the previous section, the nature of our dormant nuclei must be elucidated. For solutions Lauritzen and Hoffman [3] introduced a slender temporary nucleus with a large ratio of length to diameter. For such a nucleus two different effective surface tensions are required, one for the sides and one for the end surfaces. The surface tension at the end surfaces must be chosen much larger than that at the sides. Both surface tensions were considered as constant parameters. In this way one can explain the process of sporadic nucleation in a restricted temperature range at the lower side of the melting point. If in the course of Brownian motion such a nucleus surpasses a critical size, a lamella can grow by lateral association of other macromolecules. This process is in accordance with the concepts of the classical nucleation theory. The thickness of the lamella formed is predicted to be nearly equal to the length of the original slender nucleus.

This concept is softened for polymer melts by the fact that, as it were, two melting points are found. The higher one is the real equilibrium melting point holding for ideal crystals formed of completely stretched molecules. This equilibrium melting point was obtained for i-PP by Marand et al. [9] by the use of a clever extrapolation method. In this method the continuous thickening of the lamellae, as occurring during a sufficiently slow increase in the temperature, is taken into account. The other, somewhat blurred lower melting point can better be characterized as a melting range of the spherulites. For i-PP one has 212 °C vs. 165–170 °C. This corresponds to a melting point depression of more than 40°. Strobl [10] ascribed this melting point depression to the relatively high surface tension, as assumed

at the rather rough surfaces of the lamellae. This surface tension of the lamellae has been identified with the surface tension at the end surfaces of the slender nuclei. As is well known, the said roughness is a consequence of the fact that macromolecules are oriented nearly perpendicular in these lamellae [11]. However, which melting point is relevant for Lauritzen and Hoffman, if their considerations are applied to the melt?

This problem can be eliminated by the assumption that the surface tension at the end surfaces of a temporary nucleus is not a constant but is a function of the momentary thickness of the nucleus. In this picture the slenderness of the nucleus is no longer the consequence of the preponderance of the surface tension at the end surfaces. It must be, in contrast to the solution, the consequence of a necessary alignment of slender long molecules. In fact, such an alignment is unavoidable. The density of the melt is too close to that of the crystalline domains for a complete independence of the conformations of neighboring macromolecules. The lengths of those nuclei must show a statistical distribution. The characteristic rule for this distribution will be the length of the random link, expressing the persistence of a local direction along the macromolecule. An accidental length of a nucleus much larger than the length of the random link will be very improbable. On the other hand, much shorter effective lengths can characterize regions of lower ordering.

A nucleus of this kind can be considered as a fringe micelle. In fact, in a sufficiently slender fringe micelle the protruding fringes ('tangling ends'), which do not fit into the lattice of the body of the micelle, have still a considerable freedom in the choice of their conformations. As a consequence, the tension, which they cause at their root—at the end surface of a nucleus similar to the one by

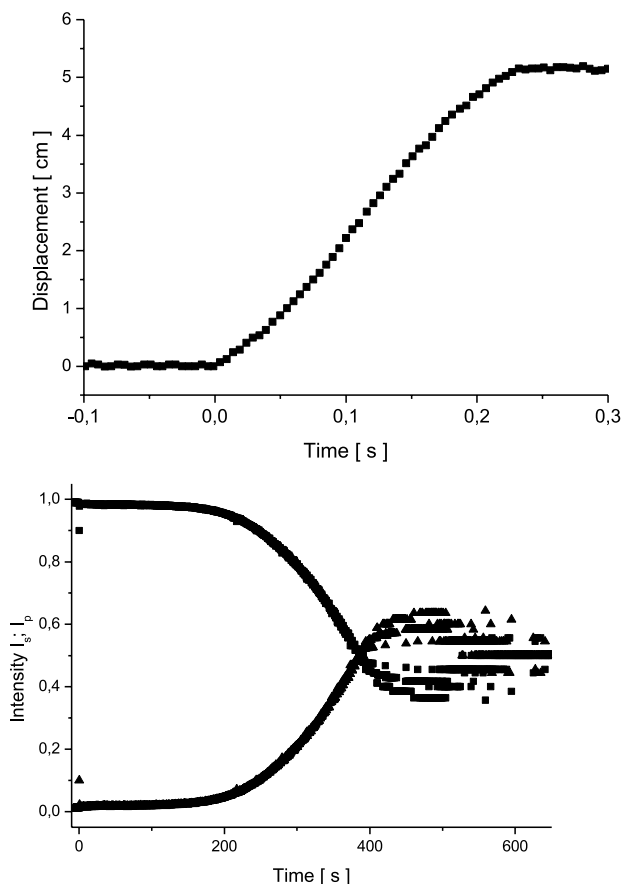


Fig. 4. Documentation of a special shear treatment on the above polypropylene at 150 °C and a shear stress of 106 kPa. Upper part: displacement of the upper glass plate of the sandwich type rheometer vs. shearing time [1]. A total shear of $\gamma = 50$ is reached within 0.2 s. Lower part: footprints of the temporary optical retardation, as recorded after cessation of flow. The curve starting at the value one on the ordinate axis gives the time dependence of the reduced intensity with parallel polars. The curve starting at zero gives the reduced intensity with crossed polars. A cross-over occurs after a waiting time of almost 400 s. The large scatter on the right side is because of the low absolute intensities achieved after long crystallization times.

Lauritzen and Hoffman—can only be mild. However, if the micelle grows thicker for some reason, these tangling ends must get into a squeeze. This is, because the space, which they need in the lateral direction, is larger than that inside the body of the micelle. During such a growth process the surface tension at both ends must grow considerably. If the growing lamella reaches a certain extension, this surface tension will level off in a plateau value. It goes without saying that also back-folding [12] can contribute to this plateau value.

Strobl's nice approximate equation for the melting point depression is the result of a balance between the said surface tension and the negative contribution of the free energy of the bulk, which is proportional to the thickness of the lamella—or to the length of the original nucleus. Formally this melting point depression goes to zero, if the surface tension is reduced to zero. This observation opens quite a

new aspect. In fact, as long as the surface tension at the ends of the temporary nuclei is nearly zero, a sporadic nucleation can be expected directly below the equilibrium melting point. Usually, the temperature range for any sporadic nucleation is restricted. But this means that one can expect stable nuclei already in the lower part of the temperature span between the equilibrium melting point and the melting range of spherulites. The extraordinary nature of these nuclei, however, is that they cannot grow. In fact, as soon as they start growing, the upcoming surface tension at their ends prohibits further growth. The well-known effect of self-nucleation, as found by Keller et al. [12], by Lotz et al. [13] and by Alfonso et al. [14] can be considered as a direct proof of this concept. Nuclei, as formed inside the spherulites during their crystallization, survive the melting of these spherulites. They appear to be stable at least in the lower part of the said temperature span between the equilibrium melting point and the melting range of the spherulites.

The essence is that there exist stable dormant nuclei at all temperatures below the equilibrium melting point. These nuclei cannot grow, if the melting temperature of a lamella, which has a thickness corresponding to the length of the nucleus, lies below the temperature, where this nucleus already exists. The consequence is: the thinner a lamella, or the shorter the body of the original nucleus, the lower will be the temperature, where such a nucleus can become effective. This is a welcome selection rule.

It goes without saying that the 'length' of the body of the nucleus can also be considered as a measure for its perfection. However, the lower this perfection is, the higher will be the frequency of its occurrence. This fact is clearly reflected by the left side of Fig. 1, where the increasing number density of nuclei, as found with decreasing temperatures in quiescent melts of i-PP, is shown. It should be clear that also catalyst residues can play in this game. But one should not forget the influence of local alignments, which are unavoidable in polymer melts.

As a final remark it should be emphasized that the possibility for the growth of nuclei was addressed only in connection with the proposed selection rule. In fact, the subject of this paper is only the nature of the nuclei. As a consequence, no particular mention is made of different growth regimes, as observed by several authors just in the range of temperatures close to the melting range of spherulites.

4. Development of a concept for the influence of flow

The point of departure is undoubtedly given by the experienced non-linear increase in the number density of nuclei with the duration of short term flow treatments [1,2]. The advantages of short term flow treatments were discussed quite a long time ago by our group [2,4,6,15]. The experience of the just mentioned non-linearity,

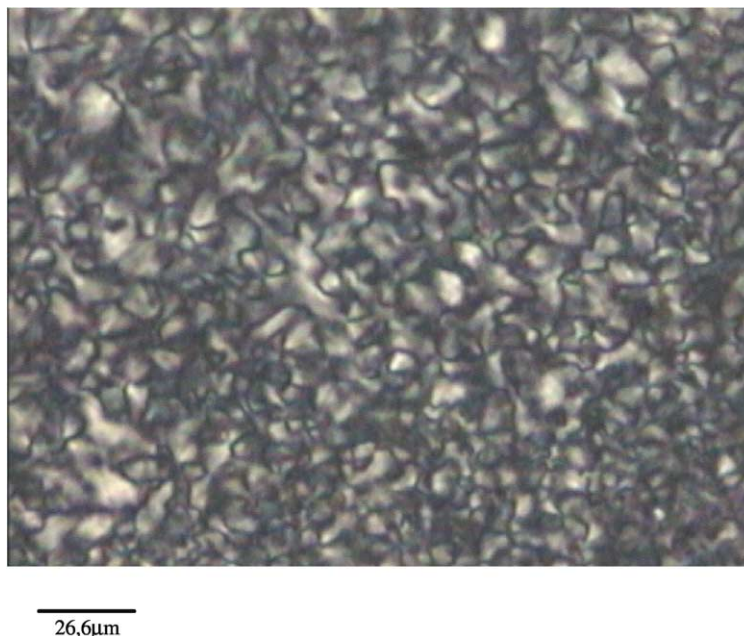


Fig. 5. A microphotograph taken from a cross-section of the solidified sample of Fig. 4. The direction of the cut was parallel to the previous flow direction. The magnification is indicated by the bar in the lower left corner. No anisotropic structures can be detected with crossed polars.

however, is not yet widely spread. As a consequence, nobody has tried so far to understand such a phenomenon. Usually one has assumed theoretically that nuclei are formed sporadically under conditions improved by the flow field. However, with this basic idea one can only expect a linear increase in the said number density with the time of the flow treatment.

At first sight, only an interaction between already formed nuclei can give an explanation for the said non-linearity. However, such an interaction can safely be excluded because of the relatively low number of macromolecules which can reasonably be expected to take part in nuclei [6]. For instance, we found a number density of nuclei of 10^{10} m^{-3} in the quiescent melt of an industrial polypropylene at 145°C . After the most severe short term flow treatment, which we were able to apply in our sandwich construction (a shear treatment for 0.05 s at a shear rate of about 1000 s^{-1}), we found an increased density of 10^{16} m^{-3} . Admittedly, this increase is overwhelming. However, one has, at an average molar mass of industrial polypropylenes of—say—500,000, the tremendous number of 10^{24} macromolecules per m^{-3} . Even, if for a nucleus acting as a starting point for crystallization one thousand macromolecules are tolerated, one still has, at the beginning of the flow treatment, a factor of 11 decades between free and bound macromolecules. At the end of the said flow treatment one still would have a gap of five decades. But this means that for the great majority of arbitrarily chosen free macromolecules, the environment remains practically unchanged during the whole flow treatment.

All theoretical approaches, as known so far, predict the said linear increase in the number density of nuclei with the

duration of the flow treatment. In particular this result also holds, if the often-discussed decrease in the average specific entropy is invoked, as caused by the orientation of the molecules by the action of flow. Previously, we also believed in a linear law, even if we warned that the effect of the decrease in the entropy, as averaged over the volume, might be insufficient [16]. This conclusion was based on normal stress measurements. Those measurements were sometimes carried out even under severe flow conditions (employment of flow birefringence).

As an alternative, a growth mechanism is envisaged, as possibly occurring on the extremely frequent alignments (aggregates) of low internal orderliness. As such, these aggregates can become effective nuclei only at rather low temperatures. The improvement of their shape, as caused by the flow treatment, can make of them active nuclei at the higher temperature of that flow treatment. This mechanism would explain, why so many more nuclei should appear after such a flow treatment.

Fig. 1 is particularly suggestive in this respect. By quenches of increasing rapidity, as carried out on thin layers of a quiescent melt, one obtains number densities tremendously increasing with decreasing crystallization temperatures (see the left side of Fig. 1, zero work). At low crystallization temperatures these number densities appear to be of the same order of magnitude as the number densities, which are obtained at much higher temperatures after flow treatments of increasing strength (see the right side of Fig. 1). So one is tempted to assume that the same nuclei, which are dormant in a still quiescent melt at the temperature of the flow treatment, are transformed into active nuclei by this flow treatment.

The idea of such a growth mechanism is also supported by the occurrence of a temporary optical anisotropy, which is regularly developed some time after cessation of flow and is finally drowned during a prolonged period of waiting in the upcoming depolarization effect. (See Fig. 4 above.) This phenomenon was first studied painstakingly with the application of elongational flow [2]. In contrast, Fig. 4 refers to rapid shearing. The just described phenomenon is typical for all of our short term flow treatments: in our experiments flow takes times between fractions of a second and a few seconds. At the chosen higher temperatures of the flow treatments the temporary optical anisotropy appears always in the quieted down melt after a considerable waiting time, sometimes after a quarter of an hour. Complete depolarization occurs even later. Obviously, the explanation for this retardation is given by the fact that secondary growth occurs on the formed elongated nuclei on a slow pace characteristic for the quieted down melt. Secondary growth must be responsible as, apparently, the oriented primary particles are so tiny that they themselves do not cause a measurable optical retardation.

In contrast to the found evidence for the occurrence of elongated nuclei, very often one gets the impression that an increased number of ‘point-like’ nuclei has come up. In fact, this kind of nuclei seems responsible for the spherulites showing up in the finally solidified samples. At a closer approach, however, one must conclude that the only condition for the appearance of spherulites is that, at the end of the flow period, the lengths of the oriented tiny particles still remain smaller than the final diameters of the obtained spherulites. It goes without saying that these latter diameters are determined by the room left for the spherulites to grow after cessation of flow. And with growing number densities of nuclei, as caused by more intensive shearing or stretching, this room becomes smaller.

Interestingly enough, one almost always finds traces of a few thread-like precursors (‘shish’) interspersed between the said spherulites. Apparently, during flow these interspersed thread-like nuclei grew on ‘better’ original nuclei, so that their length could surpass the diameter of the said spherulites. With increasing flow times a decreasing room for spherulites and an increasing average length of nuclei can lead to a break-through to a thoroughly oriented structure, as found in the surface layers of injection molded parts.

By the way, an ‘improvement’ of nuclei of some kind can also be documented along other routes. Boon, Challa and Van Krevelen [17] carried out experiments at the extremely slow crystallizing isotactic polystyrene. They cooled samples of a melt of this polymer down to the glass transition temperature and reheated these samples to certain crystallization temperatures. They found that the number densities of nuclei increased by this treatment by a factor as large as 100,000, when compared with number densities measured directly at the said crystallization temperatures. Apparently, during the cooling process nuclei, which

normally become active only close to the glass transition temperature, have grown there a little bit. This process made them suitable for higher temperatures. Also, some preliminary experiments in our laboratory have shown that slightly undercooled melts of polypropylene contain an increased number of nuclei after a temporary pressurization.

5. A preliminary mathematical model for the influence of flow

An alternative presentation of the data contained in Fig. 3 is given in Fig. 6. In this figure the logarithm of the number density of nuclei is plotted against the logarithm of the degree of undercooling $\Delta T = T_m - T_k$, where T_m is the equilibrium melting point and T_k is the temperature of the crystallization. In obtaining this plot, vertical lines are drawn in Fig. 3 at various values of the specific work. The points of intersection of these lines with the experimental curves for constant temperatures are transferred into Fig. 6.

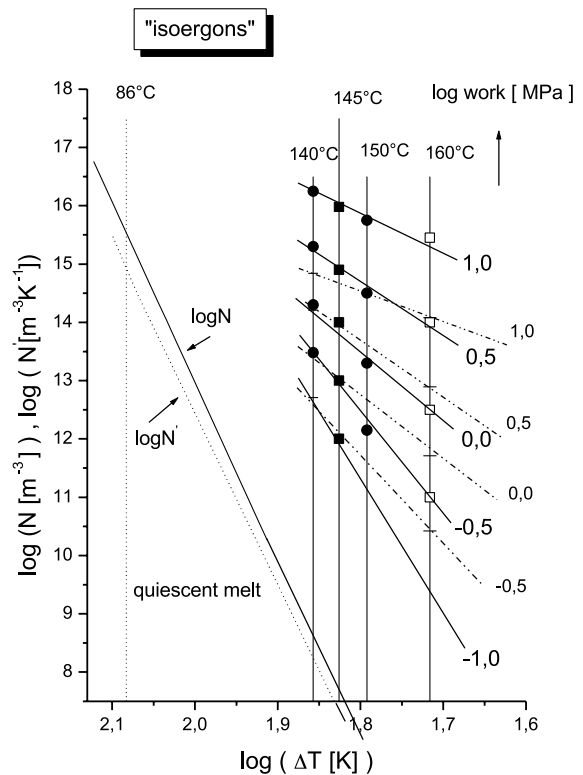


Fig. 6. Double logarithmic plots of the number density N (m^{-3}) and the differential number density N' ($\text{m}^{-3} \text{K}^{-1}$) vs. the degrees of undercooling $\Delta T = T_m - T_k$ for various amounts of specific work applied. Our proposal is to call these lines ‘isoergons’. ΔT is plotted in the inverse direction according to decreasing crystallizing temperatures T_k . These temperatures are indicated at the upper ends of the pertinent vertical lines. The isoergons indicating the courses of N are given as full lines. Those for the differential number densities N' are given as dotted lines. The logarithms of the specific works are given by bigger ciphers for N and by smaller ciphers for N' . The inserted points are no measuring points. They are obtained from interpolations on Fig. 3.

For each of the chosen values of the specific work these points are simply connected in Fig. 6 by full (straight) lines. We called these lines ‘isoergons’. The isoergon for zero work is also introduced. It represents the course of the points of the left side of Fig. 1. In Fig. 6 this special isoergon is a straight line of the enormous slope 30. The direction of increasing undercooling is chosen in the negative direction in order to emphasize the decrease in the corresponding crystallization temperatures, which for convenience are indicated at the upper ends of corresponding vertical lines. N is given per m^{-3} and ΔT in $^{\circ}\text{C}$.

It must now be realized that the quoted number densities of nuclei, as found after sufficiently fast quenches to the respective crystallization temperatures, contain all nuclei, which are activated in the whole temperature range from the original temperature of the melt down to the intended temperature of crystallization, where the spherulites start growing. In order to obtain only the number of those nuclei, which are activated in a small temperature interval of—say— 1° near their temperature of activation T_a , the curves, which are drawn as solid lines in Fig. 6, have to be differentiated with respect to ΔT . By this differentiation one obtains a differential number density N' , as given in $\text{m}^{-3} \text{K}^{-1}$. Only these nuclei are activated in the small temperature interval around T_a . For the isoergons, which hold for non-zero values of the specific work, the same type of differentiation must be carried out. In fact, except for the differential number density of N' nuclei, all other nuclei located on the same isoergon can be activated already at higher temperatures by the same amount of specific work.

This differentiation has to be done in a correct way, which means that $N \propto (\Delta T)^n$ —with $n=30$ —has first to be transformed into a dimensionless expression, which is differentiated and transformed back. It is just for this operation that the plots of Fig. 6 are required. The lines for the differentiated values N' are inserted as dotted lines. The lower the slope of the original isoergon is, the larger becomes the influence of the differentiation. The logarithms of the specific works of the original isoergons are given in bigger ciphers than those for the isoergons, as obtained by the said differentiation. In spite of the low accuracy a tendency may be observed for all transformed lines to converge at some temperature below 86°C . The corresponding value of N' is about $10^{16} \text{m}^{-3} \text{K}^{-1}$. Interestingly, enough, the so-called smectic phase, which more correctly may be called the conformational disordered phase [18], has been found below 86°C [19] for polypropylene. It looks almost as if at this degree of undercooling dormant nuclei, which can be improved by flow, do no longer exist.

On the basis of N' Fig. 6 is now transformed back into a Fig. 7, a figure similar to Fig. 3. The only difference is that instead of the values of $\log N$ those of $\log N'$ are plotted against the specific mechanical works applied. When looking at this axis of $\log N'$, one discovers a new and interesting feature of this figure, namely a unique relation between $\log N'$ and the temperature of the activation T_a . In

Fig. 6 this inverse relation is given by the dependence of $\log N'$ on $\log \Delta T$ for zero work. Near $\log N'$ on the ordinate axis of Fig. 7 also the corresponding temperatures T_a of activation are given. One obtains for $T_a=90^{\circ}\text{C}$ a value $\log N'=15$, for $T_a=113^{\circ}\text{C}$ a smaller value $\log N'=12.5$ and for $T_a=130^{\circ}\text{C}$ only a value $\log N'=10$.

Because Fig. 7 is highly schematized, only the lines for the highest and the lowest working temperature T_w of the mechanical treatment, i.e. $T_w=160$ and 140°C , are drawn. The parameters T_w and T_a are to be distinguished strictly. The question now arises, how this figure can be interpreted. From the foregoing section it will be clear that a closer description of the assumed dormant nuclei does not exist. We only know numbers and values of the specific work applied. So we must try to lay open as many facts as possible with the aid of this scarce source of information. However, this source is certainly better than nothing, as we hope to show. Nevertheless, some bold assumptions have to be made. So, we decided to make reasonable assumptions for the effective lengths of two specific nuclei. Before doing so, we have to define the notation to be used.

Capital L stands for the effective length of a nucleus. A first subscript refers to the value of N' (actually of $\log N'$) and a second subscript indicates, whether a nucleus is meant, which is activated at the temperature T_a , belonging to N' , or is a product of work, applied to the unit volume of the fluid at T_w . In the first case a subscript ‘a’ is used, in the second case a subscript ‘w’ is used. Behind L (between brackets) one finds the temperature T_w , at which shearing or stretching has occurred. An indication of the activation temperature T_a between brackets is unnecessary, because T_a is uniquely linked to N' . Nevertheless, T_a is sometimes quoted between brackets in an effort to simplify reading. The following example will be explained: $L_{15,w}(160)$ means the effective length of a nucleus, which has gotten this effective length by a mechanical treatment at 160°C , but is active in a quiescent melt only at $T_a=90^{\circ}\text{C}$ ($\log N'=15$) with a length of $L_{15,a}$. The corresponding specific work $w_{15}(160)$ must be read from the graph given in Fig. 7.

Before presenting some model calculations in more detail we must emphasize that these calculations have been carried out only by way of example. They should help us in elucidating our train of thoughts. First we consider the line for $T_w=160^{\circ}\text{C}$ on Fig. 7. Our basic assumption is now that the effective length of any nucleus is the same along this line, irrespective of the process, by which it has been created. At zero specific work this length must be the one, corresponding to $T_w=T_a$. Before making an assumption about this length the value of $\log N'$ corresponding to $T_a=160^{\circ}\text{C}$ must be found. For this purpose one actually has to carry out an extrapolation in Fig. 6. In this figure two lines have to be lengthened toward lower values of $\log N'$: the vertical line at 160°C and the isoergon for zero specific work. In doing so one obtains a point of intersection. At this point, one has $\log N'=4.4$. This is the value of this quantity, which corresponds to the rather high activation temperature

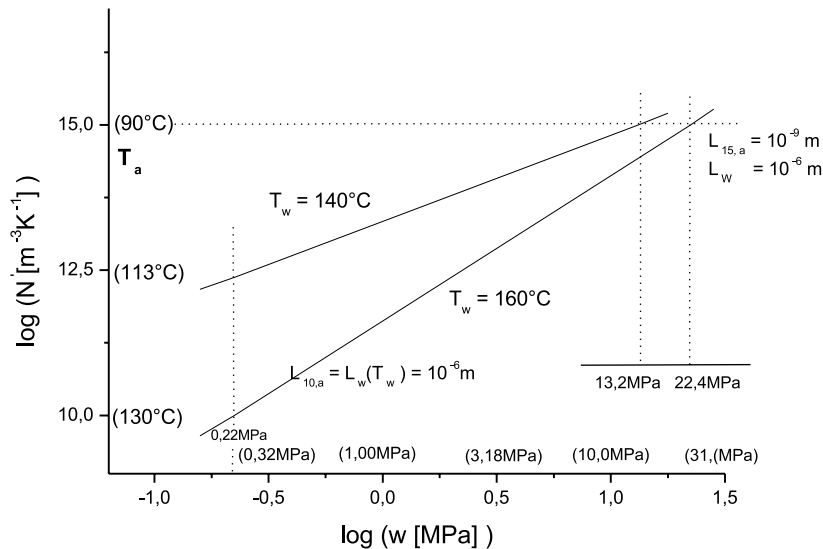


Fig. 7. This figure is related to Fig. 3: On the ordinate axis the differential number density N' ($\text{m}^{-3} \text{K}^{-1}$) is plotted instead of the cumulative number density N (m^{-3}). In this highly schematized figure, however, only the lines for the lowest and highest experimental working temperatures, i.e. 140 and 160 °C, are drawn. Because N' being uniquely related to the activation temperatures T_a , these temperatures are also indicated at the ordinate axis.

of $T_a = 160$ °C. At first sight such an extrapolation seems quite dared. However, the accuracy of this point does not matter too much because of the extremely low value of the specific work, amounting only to 0.22 MPa, necessary for arriving in Fig. 7 at the lower end of the line for $T_w = 160$ °C.

Now the announced bold assumptions are made, namely:

$$L_{4.4,a} = 10^{-6} \text{ m}, \quad L_{15,a} = 10^{-9} \text{ m} \quad (1)$$

As one can see, the effective length for $T_a = 160$ °C is chosen to be 10^{-6} m, a length, which just can be recognized under the microscope on condition that the little thread (fringe micelle) is thickened during the subsequent crystallization process by some lateral growth (see e.g. Fig. 4). At the activation temperature of $T_a = 90$ °C, corresponding to $\log N' = 15$, an effective length of only 10^{-9} m is chosen because of being the lowest effective length imaginable for a nucleus. This length reflects the length of a single low molar mass molecule. Decisive for the given choices, however, is the curiosity of finding out, how realistic the consequences of these assumptions will be. In this connection one should not forget that, in first instance, the whole consideration is brought about in order to give a tangible interpretation of the implications contained in the empirical results finally leading to Fig. 7.

When looking at Fig. 7 one should first consider the said lowest point for $T_w = 160$ °C. For this point one has $T_a = 130$ °C ($\log N' = 10$) and $w_{10}(160) = 0.22$ MPa ($\log w_{10}(160) = 0.34 - 1$). As we shall see in Table 1, for this activation temperature of $T_w = 130$ °C the effective length must be only a little lower than the one, which has been chosen for the higher activation temperature of $T_a = 160$ °C. In fact, the influence of $w_{10}(160)$ on the length of 10^{-6} m, as is assumed for an activation temperature $T_a =$

160 °C, can only be rather small: a value of $L_{10,a} = 0.94 \times 10^{-6}$ m is quoted in Table 1. (For calculations see below.) In the second place the other end of the line for 160 °C is considered. The pertinent point holds for $\log N' = 15$ and $w_{15}(160) = 22.4$ MPa, ($\log w_{15}(160) = 1.34$). For more data see Table 1.

For that which follows one needs a law, relating L to w . An exponential law is chosen. Such a law means that the growth speed of a nucleus is proportional to its already achieved size and to the rate of specific work applied. From a physical point of view there does not seem a serious objection against such an assumption. In fact, in view of the fact that a particle disturbs the flow in its surrounding in relation to its size, its growth speed increases with its size. For a possible deviation from this law, in case the particle becomes rather lengthy, see below. For the moment one has:

$$L_{N',w}(T_w) = L_{N',a}(T_a) \exp(A(T_w)w_{N'}(T_w)) \quad (2)$$

In the special case of $\log N' = 15$ one has:

$$\begin{aligned} L_{15,w}(160) & (= L_{4.4,a}(160)) \\ & = L_{15,a}(90) \exp(A(160)w_{15}(160)) \end{aligned} \quad (3)$$

with $L_{4.4,a}$ and $L_{15,a}$ from Eq. (1) and $w_{15}(160) = 22.4$ MPa.

Table 1

Characteristics of activated nuclei, as calculated from specific works at 160 °C

$L_{N',a}$	$\log N'$	T_a	$\log w_{N'}$	$w_{N'}$
10^{-6}	4.4	160	$-\infty$	0
0.94×10^{-6}	10	130	0.34 - 1	2.2×10^{-1}
0.52×10^{-6}	12.5	113	0.33	2.14
10^{-9}	15	90	1.35	22.4

[$L_{N',a}$] = m, [N'] = $\text{m}^{-3} \text{K}^{-1}$, [T_a] = °C, [$w_{N'}$] = MPa.

In this way one obtains for the factor A , as valid at 160 °C:

$$A(160) = 0.308(\text{MPa})^{-1} \tag{4}$$

As this factor has to be the same as long as $T_w = 160$ °C is the same, we can now invert Eq. (2) in order to calculate intermediate values of $L_{N',a}$, heading that one has a constant $L_{N',w}(160) = L_{4.4,a} = 10^{-6}$ m. The corresponding values of $w_{N'}(160)$ can be read from the graph given in Fig. 7. The values of $L_{N',a}$ are plotted in the first graph contained in Fig. 8. If the low accuracy is allowed for, which is the consequence of several re-drawings, one can only say that reality is not too far from the linear relation between $L_{N',a}$ and $\log N'$, as indicated in the first graph of Fig. 8.

Obviously, these values of $L_{N',a}$ have nothing to do with any T_w . The corresponding values of T_a are uniquely related (in an inverse way) to $\log N'$. As a consequence, the same set of values of $L_{N',a}$ must form the basis for the calculation of parameters for $T_w = 140$ °C. So, one is no longer free in any choice of parameters for this second working temperature. For $T_a = 113$ °C one has $\log N' = 12.5$. The first graph in Fig. 8 shows that $L_{12.5,a}$ is equal to 5.2×10^{-7} m. This is about half the value of $L_{4.4,a}$, which has been used as a starting point for the calculations at $T_w = 160$ °C. The fact that at a lower working temperature $T_w = 140$ °C also a lower effective constant length $L_{N',w}$ will hold, really makes sense. But such an effective length must now be valid for all amounts of specific work applied at 140 °C. In other words, one has the condition:

$$L_{12.5,w}(140) = L_{15,w}(140) \tag{5}$$

With $w_{12.5}(140) = 0.234$ MPa and $w_{15}(140) = 13.50$ MPa the condition of Eq. (5) explicitly reads:

$$\begin{aligned} &0.52 \times 10^{-6} \exp(A(140) \times 0.23) \\ &= 10^{-9} \exp(A(140) \times 13.50) \end{aligned} \tag{6}$$

Solving this equation for $A(140)$ one obtains:

$$A(140) = 0.470(\text{MPa})^{-1} \tag{7}$$

One notices that this value is larger than the one given in Eq. (4). From a physical point of view, however, this fact is satisfying: the lower the working temperature is, the higher the sensitivity to the applied specific work will be. If $w_{15}(140) = 13.50$ MPa is now inserted together with the just obtained value of $A(140)$ into Eq. (2), one obtains:

$$L_{15,w}(140) = 0.55 \times 10^{-6} \text{ m} \tag{8}$$

This is a quite satisfying result, if one realizes that $L_{12.5,a}$ was chosen to be 0.52×10^{-6} m for $T_a = 113$ °C. With the low value of $w_{12.5}(140) = 0.22$ MPa the value of $L_{12.5,w}(140)$ cannot be very much higher. But this higher value must hold for all values of $\log N'$ and of $w_{N'}(140)$. For proof $L_{13.5,w}(140)$ with $w_{13.5}(140) = 1.2$ MPa was calculated. A value of 0.53×10^{-6} m was obtained, showing that the values of L_w are reasonably constant along the line for $T_w = 140$ °C, as it should be. (Looking at the first graph of Fig. 8 one realizes that the value $L_{15,a} = 10^{-9}$ m must remain unchanged.)

As a next step the fact should be considered that Fig. 7 clearly indicates increasing overshoots of work for nuclei with increasing values of T_a . (Overshot work means a surplus of work above the amount needed for an activation at T_w .) Again, one should look at the line for $T_w = 160$ °C in Fig. 7. Now an experiment is envisaged, in which at the said

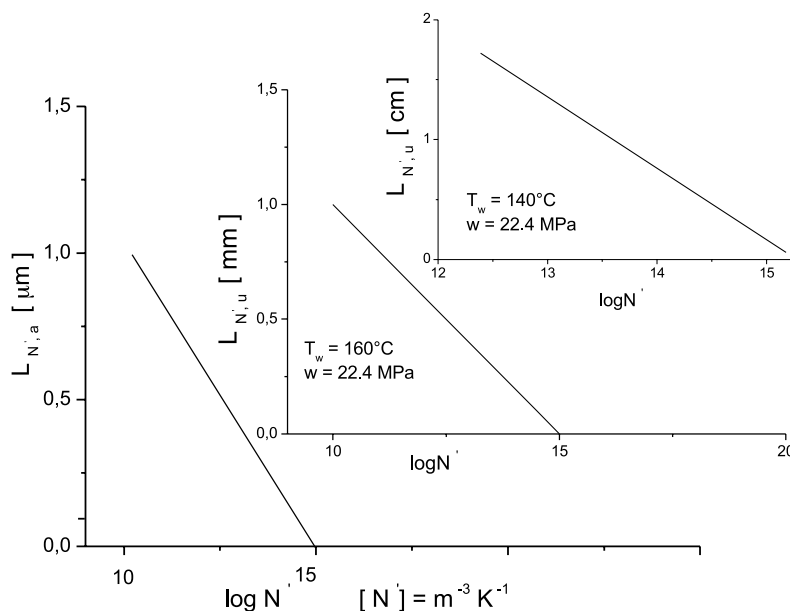


Fig. 8. Results of model calculations: effective lengths (of nuclei), as obtained after various imposed conditions and plotted against the differential number densities. First graph: effective lengths in the quiescent melt. Middle graph: effective lengths after a mechanical treatment at 160 °C. Upper graph: effective lengths after a mechanical treatment at 140 °C. In both latter cases a specific work of 22.4 MPa was applied.

temperature a total amount of 22.4 MPa is applied to a sample of our i-PP. Without flow these nuclei are activated only at the low activation temperature of $T_a = 90^\circ\text{C}$. But for ‘better’ nuclei, which are active without flow already at—say—an activation temperature of $T = 130^\circ\text{C}$, a specific work of only 0.22 MPa will suffice for activating them at 160°C . Consequently, they are getting an overshoot of specific work (22.4–0.22 MPa) with the mentioned experiment. The question is now, what the consequences are of this overshoot. As a working hypothesis one can assume that this overshoot leads to a further growth of the effective length of these nuclei. But such increasing lengths will soon be observable under the microscope. In fact, these lengths will become increasingly larger than 10^{-6} m, a value which was assumed to be critical for an observation under the microscope.

From the overshoots of specific work, which can be read for several values of $\log N'$ and a total work $w_{\text{tot}}(T_w)$ from Fig. 7, one can easily calculate these ‘over-lengths’ $L_{N',u}(T_w, w_{\text{tot}})$, using the equation:

$$L_{N',u}(T_w, w_{\text{tot}}) = L_w(T_w) \exp[A(T_w)(w_{\text{tot}}(T_w) - w_{N'}(T_w))] \quad (9)$$

where $L_w(T_w)$, $A(T_w)$ and the total specific work $w_{\text{tot}}(T_w)$ are constant along the line for T_w . The first goal was a calculation of the consequences of an activation of dormant nuclei of an equal number density of $\log N' = 15$ at two different temperatures of $T_w = 160$ and 140°C . The practical reason for this choice was the same point of departure, i.e. the same effective length $L_{15,a} = 10^{-9}$ m for the quiescent melt, at $T_a = 90^\circ\text{C}$. As a consequence different values of w_{15} had to be chosen, namely 22.4 MPa for 160°C and 13.5 MPa for 140°C (see Fig. 7).

In a next step, interest shifts to the effectiveness of one and the same specific work of 22.4 MPa at various working temperatures T_w . In this connection it does not matter, if for $\log N'$ a somewhat higher value than 15 must be chosen, when at 140°C a specific work of $w = 22.4$ MPa is to be applied, namely $\log N' = 15.3$. This can easily be seen, if in Fig. 7 the line for $T_w = 140^\circ\text{C}$ is lengthened until a point of intersection is obtained with the vertical dotted line drawn at $w = 22.4$ MPa. So one has for $T_w = 160^\circ\text{C}$:

$$L_w(160) = 10^{-6} \text{ m and } w_{\text{tot}}(160) = 22.4 \text{ MPa} \quad (10)$$

and for $T_w = 140^\circ\text{C}$:

$$L_w(140) = 0.53 \times 10^{-6} \text{ m and } w_{\text{tot}}(140) = 22.4 \text{ MPa} \quad (11)$$

In Fig. 8 the results of these calculations are given, and well in the middle graph for 160°C and in the upper graph for 140°C . In both cases one had $w_{\text{tot}} = 22.4$ MPa. Remarkably, notwithstanding the fact that for 140°C one has a smaller value for L_w than for 160°C , the over-lengths are much larger for the lower working temperature of

140°C . But also this result is satisfying from a physical point of view. It is related to the larger value of $A(140)$.

6. A possible improvement of the model

This section will be of interest mainly for readers, who remember our early work in duct flow [4,7,15,16,20]. In this respect one must say that the exponential growth, as assumed above for small nuclei, is certainly overdoing for the final growth phase of large ‘over-lengths’. A linear growth law seems more adequate for this end phase. In fact, if the particle becomes very long, the disturbance at the end of the particle is no longer influenced by the length of this particle. As a consequence, the growth speed will gradually become independent of this length.

It can also happen that the threads start to break in the middle, if a critical length is surpassed. In the average, the flow pattern around a growing thin filament will cause an increasing maximum stretching force near its middle. As a consequence, the effective lengths $L_{N',u}$ will not increase above a limiting value. In fact, one has to look at the unrealistically high lengths up to 1.7 cm, as calculated according to the exponential growth for the upper graph of Fig. 8 for $T_w = 140^\circ\text{C}$.

Such a perception will bring us also closer to the earlier experimental results, which have been obtained in our laboratory in duct flow experiments [4,7,15], where much higher mechanical loads could be achieved near the duct walls. In these experiments the influences of the shearing time and the shear stress were discussed separately. Instead of the shear stress very often the shear rate was envisaged. For instance, we found an approximate dependence on the forth power of the shear rate for the sum of the lengths (i.e. the total length) of all thread-like precursors, as observed in the unit volume.

Let us now assume that a shish starts growing just when the length of its priming nucleus becomes comparable with the average diameter of the spherulites appearing finally in its surroundings. (Section 4.) From this moment onwards a linear dependence of the length of shishes on the specific work can better be assumed in the present context. In the previous papers [4,15] it has—erroneously—been assumed that the ‘primary’ nuclei come up at a constant frequency proportional to the square of the shear rate. (In this connection the reader is reminded that a constant frequency means a linear increase with time.) And these primary nuclei would grow into shishes from the moment of their appearance with a speed again proportional to the square of the shear rate applied. In a simple way this combination explained the fourth power of the shear rate found in the experimental results. However, according to our present knowledge at least the first step of this process must be modified. In fact, the said frequency of the occurrence of primary nuclei is not a constant but seems to increase with the flow time.

In persecution of the just uttered ideas a quadratic dependence of N on the shearing time is now introduced into the said first step [4,15]. This quadratic dependence should be sufficiently representative for the results of Figs. 2 and 3. For the following growth of shishs on the obtained primary nuclei, however, a linear dependence on the shearing time is retained. This is in rough accordance with our assumption of a transition from an exponential to a linear growth law. By the way, in the early papers the square of the shear rate has been introduced merely because of the demand that the result must be independent of the direction of shearing and the square is the most simple even function. If with the just introduced procedure the square of the shear rate is retained for both steps, one obtains a sixths power for the dependence on the shear rate. Later, however, the specific work was introduced instead of the square of the shear rate, being also an even function. However, because of the fact that the viscosity, which is engaged in the work, strongly decreases with increasing shear rate, the model becomes less rigid and the power of the shear rate is reduced. In this way the legendary expression $(d\gamma/dt)^4 t^2$ (with γ being the total shear and t the shearing time), as found for the total length of shishs per unit volume, will approximately remain valid.

The only further condition is that at the temperature of the shearing experiments the relaxation time of the shishs, which is finite and shows a strong temperature dependence close to the equilibrium melting point [16,20,21], must be considerably larger than the shearing time. In fact, this relaxation time of the shishs is extremely small near the equilibrium melting point but increases enormously with decreasing temperature. Interestingly enough, this temperature dependence is much stronger than that of free or entangled molecules. This means that there is a cross-over temperature T_{cro} , where with cooling the relaxation time of the shishs becomes larger than the relaxation time relevant for the viscosity of the melt. (One can guess for i-PP a value of T_{cro} between 170 and 180 °C, cf. also Section 3 for the stability range of nuclei obtained by self-nucleation.) When determining the shish-kebab structure [4] in duct flow, we certainly worked below the said cross-over temperature.

7. Discussion of the equations of Section 5

It was explained directly at the outset that, in first instance, the presented calculations have to serve as a demonstration of the qualitative implications contained in the experiments leading to Fig. 7. Notwithstanding the fact that Fig. 9 is based on these simple calculations, it will give a qualitatively correct picture of the situation, at least for i-PP. In this figure a three-dimensional picture is presented. First, the axis of T_a for the activation temperatures, as valid for a quiescent melt of i-PP, is considered. It stretches from 90 to 130 °C, according to the range of activation temperatures presented in Fig. 7. On the vertical axis the

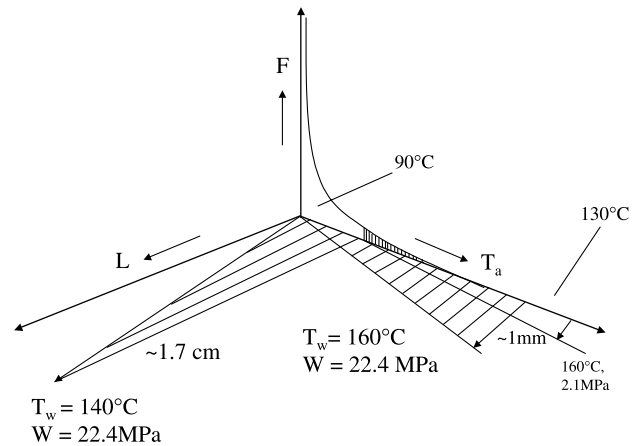


Fig. 9. A schematic three-dimensional plot indicating the interrelationships of frequency F ($=N'$) of occurrence, activation temperature T_a (in the quiescent melt) and effective lengths L for several conditions indicated in the graph. For an interpretation see Section 7.

frequency of the occurrence of diverse nuclei is plotted. This frequency decreases much more rapidly with increasing T_a , than can be shown on the figure. In fact, this frequency must be obtained by delogarithmizing the curve of $\log N'$ vs. $\log \Delta T$, which stretches over many decades. On the second horizontal axis the over-lengths of nuclei are plotted, as obtained for three working situations, of which two are given by Eqs. (10) and (11) as functions of T_a . The courses of these over-lengths as functions of $\log N'$ are shown in the middle and upper graphs of Fig. 8. One should not forget that T_a is uniquely related to the inverse of $\log N'$.

The graphics of Fig. 8 suggest that the spectrum of frequencies of nuclei is simply shifted to the diverse working temperatures. In fact, the original abscissa in terms of T_a is no longer of direct use. In the original plot (first graph of Fig. 8) the values of $N'(T_a)$ give the frequencies of point-like nuclei, as activated in the quiescent melt at the respective values of T_a . At a working temperature T_w , which is higher than all available values of T_a , this T_a is no longer meaningful as a direct parameter. In this connection the reader can help himself by directly looking at the increasing over-lengths of the nuclei. In fact, these over-lengths are descending from nuclei, which are activated in the quiescent melt at the activation temperatures T_a , to which the right horizontal axis of the graph is related. So, the eye of the observer has to catch a certain over-length and look at the corresponding frequency. One can see from this Fig. 9 that, the longer the over-length of a nucleus is, the lower is its frequency of occurrence. At nearly zero length (point-like nuclei) one finds the highest frequency.

In obtaining the values of $N'(T_a)$ a differentiation of N with respect to ΔT was required. After the application of mechanical work the need for this differentiation becomes obvious in the fanning out of the respective over-lengths. The length of a certain nucleus is the length of the corresponding arrow drawn parallel to the horizontal axis for the over-lengths. The frequency of its occurrence is

given by the height of the ordinate of $N' (=F)$ at the nadir of this arrow. The consequences of three situations are depicted in Fig. 9. Two of them are characterized by the data given in Eqs. (10) and (11). In both cases the same amount of specific work was applied, but at different temperatures. This work was 22.4 MPa. However, also different amounts of specific work can be applied at the same temperature. For instance, one can apply only 2.14 MPa at $T_w=160^\circ\text{C}$. In this case only nuclei are raised from sleep, which have frequencies N' below $3.1 \times 10^{12} \text{ m}^{-3} \text{ K}^{-1}$, or activation temperatures T_a above 113°C . But this means that the nearly straight line for $T_w=160^\circ\text{C}$ and $w_{\text{tot}}(160)=2.14 \text{ MPa}$ starts only at $T_a=113^\circ\text{C}$ instead of $T_a=90^\circ\text{C}$. In this case only the shaded area of the (F, T_a) -plain will be of interest.

Looking at the relations between over-lengths $L_{N',w}$ and T_a , as caused by the same $w=22.4 \text{ MPa}$, one finds a much steeper course for $T_w=140^\circ\text{C}$ than for $T_w=160^\circ\text{C}$. On the other hand, the curve for 140°C seems to end at a lower value of T_a than the curve for 160°C . This is only because in Fig. 7 the line for 140°C starts at a higher value of $\log N'$ than for 160°C . Because of the limits of our experimental technique lower values of specific work (Fig. 7) than 0.22 MPa could not be applied so far. This fact does not influence, however, the conclusion that, with the same specific work of 22.4 MPa, the course of the over-lengths $L_{N',u}$ vs. T_a would be even steeper at a working temperature still lower than 140°C .

8. General discussion

First of all a possible influence of polydispersity should be discussed. The industrial PP, of which results have been presented in the present paper, is characterized by the following parameters: $M_w=370,000$, $M_n=74,000$ and $M_w/M_n=5.0$. In connection with polydispersity a very interesting investigation by Kornfield et al. [22] should be mentioned. These authors added small amounts of a very high molar mass PP to a standard PP. Homogenization was carefully done by dissolving the components, mixing the solutions and evaporating the solvent. The influence of the high molar mass component on the formation of oriented structures was enormous. But this fact is also in accordance with our model. The longest molecules will most effectively further the growth of dormant nuclei. The values of $A(T_w)$ will be effected by these molecules.

Another problem is given by the influence of nucleation agents. In one of the previous investigation, which were carried out in our laboratory, methyl-dibenzylidene-sorbitol was used as a nucleation agent for i-PP [23]. For the purpose, duct flow experiments were carried out. In samples, which did not contain this nucleation agent, one found highly oriented surface layers of limited lateral extension. With unchanged working conditions, however, the thickness of the highly oriented layers was terribly

augmented, when the nucleation agent was added. Practically the whole sample became highly oriented. This phenomenon also fits in our model. One has only to look at Fig. 9. The nucleation agent increases the frequency of nuclei at higher values of T_a . As the frequency of nuclei at those values of T_a is extremely low in the pure sample, the effect has to be tremendous.

For a next point we return to Fig. 6. When this figure was considered, the opinion was voiced that there were no improvable dormant nuclei with a number density higher than $10^{16} \text{ m}^{-3} \text{ K}^{-1}$. For a considerably lower number density of $10^{15} \text{ m}^{-3} \text{ K}^{-1}$ an effective length as short as 10^{-9} m was assumed above. If this assumption is correct, one arrives for $\log N' = 16$ at dimensions smaller than those of a single tiny molecule. At this scale no dormant nuclei can be expected. Only structural peculiarities can lie at those dimensions. What is the influence of the nature of chemical bonds adjacent to the catalyst residues? Can these bonds be particularly prone to peroxydic degradation in reducing the number of nuclei? In fact, polypropylenes, which have been degraded with peroxide, usually show a much lower number density of nuclei. Nobody seems to know at the moment, how sensitive the systems react to these modifications of chemical structure. But this is a promising field for future investigations in collaboration with industrial chemists.

Now we have also to discuss the contrast between the behavior of the two most important classes of polyolefins, i.e. PP and HDPE. Eder [24] has given an equation, which permits the calculation of the critical minimum cooling speed, which is required for bypassing crystallization in quiescent melts and thus obtaining amorphous samples. This speed is proportional to the growth speed of spherulites at the temperature of its maximum (occurring halfway between melting point and glass transition temperature), the cubic root of the number density of nuclei at this temperature and the width of the distribution of growth speeds over the said temperature interval. For i-PP a sufficient number of data exists [15,25] for the calculation of this critical cooling speed. One arrives at about 60 K s^{-1} . For HDPE the pertinent data are scarcer. In our review [15] one can find an approximate curve for the growth speed as a function of temperature almost down to the temperature of the maximum growth speed. Together with some still unpublished data of the number density of nuclei one arrives at the safe conclusion that primary crystallization in HDPE is at least a factor one hundred faster than in PP. From such a factor one learns that the aspects for an investigation of HDPE along the lines sketched here for PP are rather gloomy. Apparently, PP is rather slow because of the fact that the helical conformation, as occurring along stretched parts of the molecule can be left- or right-handed. So, chains do not fit under all circumstances. The zig-zag conformation of HDPE, however, seems to pose less problems in this respect. Under processing conditions another polyolefin, i.e. PB-1, behaves almost like iPP [21,26].

Finally, we arrive at the prospects for a successful

simulation of structure formation during practical polymer processing. One of our friends in this field complained that our model was too complicated for his purposes. However, sorry to say: this is the physics. Its rules are certainly not less complicated than our model. First, one should know about all possible details of a crystallization process. Only in a next step one can make responsible simplifications. Nowadays many computer people suck their assumption simply from their thumb. As the structures observed in sample cross-sections, always pose mathematically ill posed problems, one should know better: many assumed processes can lead to very similar structures. However, the corresponding calculations do not inform the chemist about necessary modification of the chemical structure and also do not guide the process engineer to optimum conditions of processing.

At the end of this story a utilizable remark should be made, however. From Fig. 9 one learns that the course of the over-lengths vs. the frequencies of their occurrence becomes steeper and steeper with decreasing working temperature T_w . Whereas with low steepness practically only point-like nuclei show a sufficient frequency, with higher steepnesses also long threads get their chance. With injection molding the highest amounts of specific work are applied close to the mold wall. At the same time, solidification occurs near the wall at the lowest possible temperatures. So, it should not surprise, if the transition from the highly oriented surface layer to the core of the sample is rather sharp. As mentioned above in Section 4, the sharpness of this transition is also promoted by the dwindling room for spherulite growth, as caused by the increasing number of activated nuclei.

9. Conclusions

In the present paper for the first time a realistic approach is given for the structure formation under the influence of flow. This was only possible by a modification of the classical nucleation model. The new approach enables an appreciation of the highly non-linear increase in the nucleation density with the mechanical loading time, as applied to the polymer melt. This approach also explains the occurrence of shish-kebabs interspersed between spherulites. A clever theoretician should be able to construct an unlabored theory embracing all of the compiled experiences.

Acknowledgements

The authors are very much indebted to Drs W. Neißl and M. Gahleitner of Borealis RCPR, Linz, for their benevolent agreement to the use, in this publication, of non-classified results of a decade long cooperation. They also remember gratefully the merits of Mr M. Lipp as an instrument maker,

who made the required equipment. Last not least, elucidating discussions with Prof G. Eder should be mentioned. Finally, two recent projects should be mentioned, on which the conclusions of the present paper are based: 5/802155/809 K ‘Modified Polyolefines’ of the FFF (Austrian Funds for Research and Development), together with Borealis, as well as P13123-TEC ‘Crystallization of Polymers in Fast Extensional Flow’ of the FWF (Austrian Science Foundation).

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