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ORIGINAL CONTRIBUTION

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The physics of athermal nuclei in polymer crystallization

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Abstract The lower temperature limit for sporadic "thermal" nucleation, as estimated in a previous paper (Janeschitz-Kriegl (1997) *Colloid Polym Sci*), can be verified by a variety of earlier experiments which are compiled in this paper. Below the said limit only "athermal" nuclei are of importance in samples containing no large numbers of hetero-nuclei. The number of athermal nuclei increases tremendously (by many decades) with decreasing temperature. Why these nuclei are dormant and "awake" only at "their" temperature is explained in terms of their growth conditions, which depend on the length of the incorporated (helical) sequences. Also the sluggishness of molecular processes, occurring in the temperature range of metastable conditions, where sporadic nucleation can occur is demonstrated by some of the recalled experiments. Except for very fast industrial processes, where flow plays a dominant role, this sluggishness makes a noticeable influence of the sporadic nucleation on structure formation very improbable.

Key words Dormant nuclei – Growth mechanisms – Memory effects – Thermal histories – Flow histories

Introduction

Structure formation in crystallizable polymers under the influences of heat transfer and flow is a subject of major interest in polymer processing and in the development of "tailored resins". The first author of this paper observed in 1982 – to his own surprise – that no serious attempt had been made to understand the underlying processes. So it is also not surprising that the required mathematical tools had not been developed. For instance, the path was not paved for a description of the overall crystallization speed in terms of the increasing surface of the crystalline areas on which further growth takes place. In order to make use of the developments in mathematics, one needs several physical parameters, which – if one wants to avoid speculations – can only be determined by experiment. Traditionally, the rate of primary nucleation and the growth speed of spherulites, both as functions of temperature, were required in a wide range of temperatures for a description of structure development during solidification even for the simplest case of a quiescent melt.

The pertinent experimental difficulties, however, are tremendous, because of the fact that the relevant undercoolings are considerable. The experiments had to be extended over quite a large temperature range of undercooling. For i-PP a range of no less than 127 °C could be covered in our laboratory. In a recent review [1] the results of this extended research are compiled up to early 1995. Some more recent results were published afterwards in separate papers (growth speed measurements with four independent methods [2] and further findings in shear-induced crystallization [3, 4]).

The reader will understand that for all these experiments, in which heat transfer problems play a dominant role, some guidelines with respect to expected phenomena are rather desirable. In other words, a classification of the temperature range between the melting point and the glass-transition temperature is urgently needed. This is the reason why the first author of this paper has tried hard to do this on the basis of general principles by avoiding special model considerations. In fact, all model considerations known so far have only moved the problem from one unknown quantity to another unknown quantity (e.g. from an unknown characteristic temperature to an unknown height of a barrier). So he was extremely happy when he discovered that he could estimate at least one interesting parameter, viz the lower limit of the temperature range of metastability from the general behavior of the T(S) diagram (using only some plausible additional arguments). (T... absolute temperature, S... entropy.) In fact, the T(S) diagram can easily be obtained in the vicinity of the phase transition with the aid of the measurement of the latent heat and of some heat capacities. As the ordinate of such a graph is the temperature, one can almost "see" the possibilities for undercooling. The pertinent result has been published in a paper [5], of which the present paper is a sequel. As is well-known, only in the temperature range of metastability can "sporadic" or "thermal" nucleation be expected. The lower limit of this range can be estimated by the following equation:

$$T_m - T_u < (1/3)\Delta H_m / C_{p,1}, \qquad (1)$$

where T_m is the equilibrium thermodynamic melting point, T_u is the lower limit of undercooling until which the system is metastable, ΔH_m is the latent heat of melting and $C_{p,l}$ is the specific heat of the melt at the melting point. In principle, below that limit one has an unstable situation, which means that, in principle, one has to expect as a first stage of solidification the formation of less-ordered structures. This will certainly hold for "normal" materials, where below T_u any energy barrier g for the attachment of another molecule to the newly formed phase will obey the relation $g < k_B T$, whereas $g > k_B T$ holds for the metastable states. In fact, from the use of model considerations one only knows that such a barrier g must decrease faster than the decreasing crystallization temperature. However, the crucial temperature T_u, where the transition from $g > k_B T$ to $g < k_B T$ takes place (condition $g \cong k_B T$!), could not be evaluated from the models proposed so far.

As we shall see, however, polymers form an extraordinary class of materials because of the long, flexible molecules of which these materials are built up. As a consequence we shall be confronted with a second barrier. Actually, for polymers ΔH_m of Eq. (1) is meant as the heat of fusion of an ideal crystal, in which the macromolecules form a stack of helices laterally attached to each other in a parallel arrangement with no serious distortions at their ends. As a consequence it is the barrier g_{lat} for undisturbed lateral attachment which becomes equal to $k_B T$ at T_u of Eq. (1). For temperatures below T_u, however, a considerably higher barrier g_{end} will become of importance for the control of the growth of spherulites. This barrier g_{end} is felt by the ends of (helical) sequences of finite lengths, as soon as they are incorporated into existing crystal lamellae of finite thickness. In fact, the tangling ends of these sequences need more room in directions parallel to the extension of the lamella than the parts aligned inside the lamella, which causes an extra strain in the said ends. Why, nevertheless, Eq. (1) remains of importance, can only be explained a little later together with a more detailed discussion of the reasons for the said extra strains. In fact, this discussion will form the central point of the present consideration.

With respect to the use of Eq. (1) it should be observed that the values of ΔH_m, which are found in tables, are certainly too low for the present purpose. In fact, these values were not obtained on ideal crystals: they were obtained on samples which had undergone a not too slow crystallization process. We can see in Ref. [5] that even ΔH_m values which are 20% too low will not bother us too much: any uncertainty in T_u can never be so large that the total picture is challenged. Moreover, as Eq. (1) gives an overestimate anyway, as can be seen from its derivation, one may use this equation without too much hesitation. For i-PP a range of metastable undercooling from 30 to 40 °C can be estimated from Eq. (1). Looking at the tables given by Van Krevelen [6] one may conclude that for many other polymers a similar range of metastable undercooling can also be expected. Industrial crystallization, however, normally takes place far below this range. In contrast, the range of the relatively mild metastable undercooling has always been preferred by the experimentalists in the field of crystallization kinetics of polymers, so that, sorry to say, their results may not be too useful for the purpose of predicting structure formation during processing.

After what has just been said about the nature of T_m, it is not surprising that the determination of T_m is not easy. Monasse [7] has obtained T_m for i-PP by a tedious extrapolation process where, in principle, he plotted the differential scanning calorimetry (DSC) peak temperatures, as obtained for ever-decreasing cooling rates versus the DSC peak temperatures for ever-decreasing heating rates. Where this line cuts the diagonal of a "quadratic" plot, "T versus T", the required value of T_m must be localized. For i-PP this was 208 °C.

Under usual cooling conditions one mostly obtains spherulitic structures, in which the spherulites are built up of lamellae of finite thickness, in which according to Keller [8] the axes of the incorporated helical sequences are at a large angle with respect to the plane of extension of the lamellae. Because of the fact that during the crystallization process the macromolecules do not have time for a thorough reorganization, which would end in the incorporation of completely stretched helices, only shorter helical sequences have a chance of being incorporated into the said lamellae. These lamellae come into existence for kinetic reasons. As a consequence of this process one finds so-called tangling ends on either side of the lamellae. These tangling ends, however, which still show statistical conformations in the remaining polymer melt, need more space in directions parallel to the plane of extension of the lamellae when compared with the helical sequences incorporated into the lamellae themselves. This fact causes the gradual build-up of an extra stress (an extra free energy) at the ends of the incorporated helical sequences when the lamella grows. The word "gradual" must be emphasized in this case. (As is well-known, at least in a solution, this extra stress is attenuated by back-folding of the chain molecules into the lamella [8].) In our opinion this extra stress, which gives rise to the already mentioned barrier g_{end}, is the reason why one can find – instead of less-ordered structures – beautiful spherulites also at tremendous undercoolings, which are many times larger than the undercooling estimated from Eq. (1). For i-PP, however, one finds (fast-growing) α-spherulites after the proper quenching of ultrathin sheets down to 81 °C [2]. This is an undercooling of the melt for this stable α-modification (definition according to Turner-Jones et al. [9]) of no less than 127 °C! A more extended description of this complex behavior of polymers was tried in the previous paper [5]. In the present paper, however, a brief summary must suffice.

As pointed out in the previous paper, below the limiting temperature T_{u}, as given in Eq. (1), any incidental lateral attachment of only very few sequences of a certain length of proper (helical) conformation will have considerable stability (in contrast to what happens at temperatures above T_{u}). This is because of the fact that the barrier g_{end} is still practically absent in this stage of association. As already said, the few tangling ends can still go in any direction in the surrounding melt without causing extra strain! So, one can call such an associated bundle of properly conformed sequences an athermal nucleus. (Such a "nucleus" should not be considered as possessing all the characteristics of a crystal, as some of our previous critics have unjustly imputed!) According to the train of thoughts presented in the early paper by Fisher et al. [10], in which the term "athermal nucleation" was coined, the required pre-ordered neighborhood is a remnant of a local state of ordering, which was the consequence of a fluctuation typical for the melt in thermodynamic equilibrium (above T_{m}). Our "nucleus", however, will pass unnoticed in general. The reason for this fact is that the crucial conditions for the growth of a lamella out of such a nucleus is not given. These conditions depend strongly on the temperature chosen.

In fact, with only a relatively small number of proper sequences attached to each other the cross-section of such a bundle is rather small. However, if more and more sequences become attached, problems start to arise because of the fact that the tangling ends require more and more space in the plane of the growing lamella than the well-ordered sequences incorporated into the lamella itself. (According to the experiences of Magill et al. [11] local rearrangements must be sufficient for the formation and attachment of new sequences. Otherwise the growth speed of spherulites should be strongly dependent on the molar mass, which is only the case with very short molecules [6].) The described increase in the tension in the ends of the sequences, is however, certainly limited. This tension must level off at a certain lateral extension of the lamella.

In connection with this the reader is reminded of the well-known fact that the surface tension of a liquid droplet is only constant if the droplet is large enough. It goes to zero with decreasing size of the droplet [12]. Along this line Rusli and Larson [13] could explain a very strange observation. Larson and his coworkers observed non-crystalline aggregates of more than a thousand sugar molecules (or even ionic species) in slightly supersaturated aqueous solutions. [Amongst others they found a Boltzmann ("barometric") distribution of concentration along the axis of a flat-bottomed glass cylinder of height only 40 cm!] Apparently, the size distribution of these aggregates was stable. Only by stirring were these aggregates made to coalesce. In this way they reached the critical size of effective nuclei, with crystallization and precipitation as a consequence. It goes without saying that a thousand molecules cannot get together spontaneously, as prescribed by the classical theory of nucleation [14]. The probability of such an event is virtually zero. However, Larson et al. have shown that the free energy of the newly formed phase shows a flat minimum close to zero radius before rising to the well-known maximum (equal to the height of the barrier), if the assumption is made that the surface tension goes to zero with decreasing size of the newly formed phase. The classical theory does not show this minimum because it operates with a constant surface tension. However, the said flat minimum enables the formation of subcritical clusters, presumably of a lower degree of ordering. For us it is important to state that the residence time of single molecules in each other's neighborhood must be large enough, so that large aggregates can be formed with time. There is no need for these molecules to form a crystal-like structure. Larson's observations occurred in the temperature range of the metastable states! So, one must assume that there is some exchange of molecules between the clusters. Later in this paper we shall see that in the temperature range of the metastable states, as defined by Eq. (1) for polymers, there is also some exchange, even if it is extremely slow. Below T_u, however, such an exchange appears to be virtually zero. In fact, if even small molecules can stay in their neighborhood for a considerable time, relatively long sequences of chain molecules, which have a much larger number of mutual contacts, will show very much longer residence times of interaction. So, it cannot be an absurd assumption if below T_u very slender "athermal nuclei", which contain only a few sequences, are bluntly considered as stable because there is no extra strain between their tangling ends. This dissolved strain is analogous to the surface tension going to zero together with the volume of the cluster. In our case it is the cross-section which approaches zero instead of the volume. We shall see later that with flow there are still more connections with Larson's clusters – *mutatis mutandis*.

Now we discuss the growth conditions of the athermal nuclei at temperatures below $T_{u.}$ Based on the assumption of a constant free energy at the ends of the sequences Strobl [15] developed an interesting theory for the growth speed of spherulites as a function of temperature. The result of this theory can be used as a criterion for the germinative power of our dormant nuclei. In fact, unhampered growth of a lamella only occurs if the ultimate energy barrier is overcome. (Interestingly enough, Strobl could disregard the much smaller barrier g_{lat} for the lateral attachment.) The existence of a (positive) free energy at the ends of the regular sequences causes a melting-point depression (cf. Thomson's rule), which becomes more and more pronounced the shorter the regular sequences incorporated in a lamella become. However this means that with decreasing crystallization temperature more and more and, at the same time ever-shorter athermal nuclei become active. This is, because the probability of the existence of properly aggregating neighborhoods must increase tremendously with the decreasing length of the required sequences. As the said probability is related to fluctuations in the melt existing before quenching, one has to arrive at the conclusion that the number of athermal nuclei must be a unique function of the crystallization temperature increasing rapidly (as experiments show – see next section) when this temperature decreases.

It should probably be mentioned that, in principle, Strobl's theory also indicates a lower limit for the temperature at which lamellae can grow. Unfortunately, there is a lack of useful physical data, so no pertinent quantitative prediction can be made, in contrast to Eq.(1). Nevertheless, it seems that, in principle, there are three characteristic temperature ranges between the thermodynamic melting point T_m of the polymers and the glass-transition temperature T_g (where the mobility of the molecular chains finally gets tied down), namely the range of truly metastable states (see Eq. 1), the extended range of spherulite growth (see Strobl) and, finally, a lowest range where only less-ordered structures are obtained. The occurrence of the smectic modification in i-PP below 80 °C, as found by Lotz [16] and recently confirmed in our group, may indicate this transition. (According to Van Krevelen [6] the glass transition of i-PP is at −8 °C .)

By the way, i-PP seems to be an extraordinarily useful model substance: its kinetics are not as fast as with HDPE, but still fast enough for Van Krevelen's condition of a sufficiently wide gap between the melting point T_m and the glass-transition temperature T_g. In fact, according to Van Krevelen's observations [17] the growth speeds of spherulites depend tremendously on this gap (or more accurately on the ratio T_g/T_m). The maximum growth speed, which occurs somewhere halfway between T_m and T_g, decreases by decades when this gap is reduced. In the past, however, growth speed measurements were carried out almost exclusively on polymers with low growth speeds for practical reasons. With those polymers, however, the glass-transition temperature is rather close to the melting point, so the observations predicted here could not be made: the characteristics of the lower temperature ranges mentioned are suppressed by the glass transition. This forms an example of the fact that generalizations in terms of corresponding states can be dangerous (Magill et al. [11]). This train of thought, however, will not be continued in the present contribution.

In that which follows, a series of previous observations which seem to underpin our points of view will be recalled. In fact, at the present state of development at least a vision is required, even if later perceptions may cause a "re-vision".

Number of athermal nuclei per unit volume as a function of temperature for i-PP

Recently, one of us (E.R.) succeeded in creating an ultrafast quenching procedure for the bulk of a sample. As is well-known, the use of a single heat-transfer fluid of given temperature leads to a cooling process, in which the interior of the sample reaches the temperature of the coolant asymptotically with time. If the sample is not very thin, this means that such quenching cannot be considered as very fast. In the new experiment two miscible fluids (water and ethylene glycol in our case) are used. These fluids are kept at different temperature levels. The "cold" fluid (water in our case) is applied first, but is replaced at a certain moment in a countercurrent by the "hot" fluid (ethylene glycol, if quenching is to be stopped above 100 °C, otherwise only water). This change occurs at the moment during fast cooling when the interior of the sample just reaches the desired

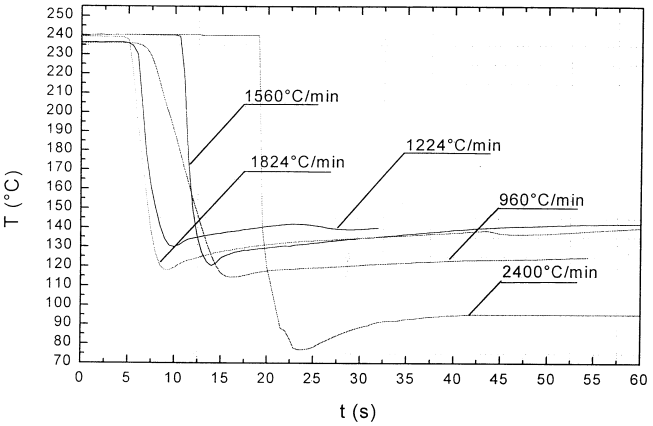

Fig. 1 Cooling curves, i.e. sample temperatures as functions of time for i-PP (average cooling rates are indicated near the curves)

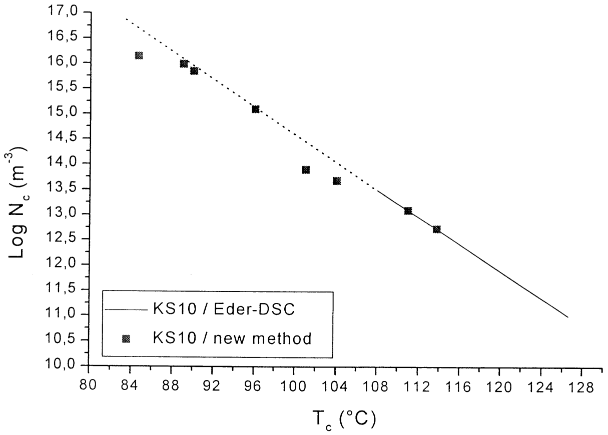

Fig. 2 Number of spherulites per unit volume as a function of crystallization temperature for i-PP

end temperature, which is chosen as the temperature of the "hot" fluid. In Fig. 1 several temperature traces are shown, as obtained at the central line of the cylindrical sample. The lowest points at the kinks are chosen as the temperatures responsible for the number of nuclei per unit volume (referred to room temperature!), as represented by the number of spherulites after complete crystallization. In fact, because of the fast quenching these nuclei should not be partially covered over by larger spherulites which started growing earlier at higher intermediate temperatures. The number of spherulites per unit volume is found by a subsequent counting procedure on a cross-section taken close to the central location of the thermocouple. The reason why larger samples (diameter ≅ 4 mm, length ≅ 20 mm) had to be used will be explained later. (The number per unit surface, as determined in first instance on the cross-section, is raised to the power 3/2 to obtain a very reliable approximate value for the number per unit volume: see Ref. [1].) As to the use of the lowest temperature at the kink, it can only be said that activated nuclei certainly experience some stabilization, so they do not disappear at a slight recovery of the temperature.

In Fig. 2 the number of (athermal) nuclei per unit volume, related to room temperature, as obtained with this method, is plotted against the crystallization temperature for an industrial polypropylene. One observes an increase by at least five decades with decreasing temperature from 130 °C to 80 °C. This result emphasizes the tremendous temperature dependence previously described. Above 130 °C the number of spherulites per unit volume is comparatively small. The solid line has been obtained for a higher temperature range in our laboratory by counting spherulites in cross-sections of DSC samples. For this purpose the peak temperatures had been corrected for a finite heat transfer coefficient in the upwards direction, as pointed out by Janeschitz-Kriegl et al. [18], by Wu et al. [19] and most accurately by Eder and Janeschitz-kriegl [1]. The range which can be covered by these latter measurements, however, is relatively small. Nevertheless, the extrapolation to lower temperatures (see the dotted line) still gives realistic values.

In emphasizing the correctness of the interpretation of Fig. 2 we should report that the second author was also able to measure the growth speeds of the pertinent spherulites of i-PP down to 81 °C [2], beating the previous record by as much as 40 °C. This was done with the aid of several independent methods. Particularly translucent was the method in which ultrathin slices (5 μm) were used according to Chow et al. [20]. With this method spherulites, which in the bulk would start in a neighboring layer, did not interfere. The only condition is that the confining cover glasses are not too active, So the spherulites nucleated in the "slice" can grow without too much restriction, as has also been shown theoretically [21]. As a consequence, their radii could be measured after quenching at widely varying periods of time (up to more than 20 s at the lowest temperature!). Also, quenching is very rapid in these thin slices. However, we were unable to deduce the number of nuclei per unit volume from these experiments for two reasons: the measurement of the thickness of the slices was too inaccurate, and also an uncertainty existed with respect to the number of extra nuclei created by the confining cover glasses. So, for the present experiments we needed relatively thick samples to avoid any wall influences. (These influences could clearly be seen in the cross-sections taken from the DSC samples where metal walls were involved.) In the growth experiments described [2] the radii of the spherulites, which by the nature of the experiment were actually disc-like (thickness 5 μm), showed a neat linear increase with time. In particular with the lower temperatures there were no noticeable induction times, and the spherulites were practically equal in size. They had started growing practically simultaneously at zero time. Some readers, who are not accustomed to the idea of athermal nuclei, may see this as an abnormality. However, other "abnormalities" could not be observed. Probably it should also be said that also in the thicker samples as used for the determination of the number of nuclei, no temperature gradients can be expected for the centers of the samples where the counting occurred. Temperature gradients are pronounced near the sample surfaces. A study of their influence is given in Refs. [1, 22].

Memory effects in quiescent melts of i-PP

Interesting results have been published quite recently by Alfonso and Ziabicki [23]. The temperature program applied by these authors to quiescent samples of industrial polypropylenes of high purity is shown in Fig 3. The samples were first quenched with the aid of tap water and then, in a second step, reheated as fast as possible to a temperature T_l above the usually assumed melting temperature T_m, at which spherulites disappear in the thermo-microscope (say 165–170 °C). (One may notice that this T_m is not the thermodynamic melting point used in the Introduction, but more related to T_u!) At several temperatures T_l (180–260 °C) the samples were kept for varying time spans t_l (from a few minutes up to 400 min). After these tempering time spans the samples were cooled to a standard (optimum) crystallization temperature T_c of 127 °C (not too slow, not too fast crystallization). Every ensuing crystallization process was monitored with the aid of isothermal DSC. In this way, the crystallization tendency which was left over after the treatment at T_l was probed. Because the crystallization temperature of 127 °C was the same in all cases, the growth speeds of the spherulites were also assumed to be equal. This meant that the time t_p, at which the maximum heat flux was observed, should reflect the number of athermal nuclei which still existed.

In Fig. 4 this time t_p is plotted against the tempering time span t_l for a series of tempering temperatures T_l . A finite limiting value of t_p of about 8 min is observed for all tempering temperatures and sufficiently long tempering times t_l. This persisting crystallization tendency is ascribed to the presence of a small number of heterogeneous nuclei which are resistant to any heat treatment. (No purification treatment can be perfect !) From this picture it becomes obvious that the value of temperature T_l has a great influence on the results. A simple analysis, as given by the authors, has shown that t_p must be proportional to $N_0^{-1/3}$,where N_0 is the total number of nuclei which have survived the heat treatment at T_l . In pursuing their own argumentation the authors could calculate relaxation times which obeyed an Arrhenius-type temperature dependence with an activation energy of 90 kJ/mole, which is considerably higher than activation energies known from viscosity measurements on melts (about 46–67 kJ/mole for i-PP, see Refs. [24, 25]). At about 180 °C the relaxation times of the samples – which were not identical – appeared to be a factor of about 1000 higher than at 250 °C . The lowest value for the relaxation time at 200 °C, as quoted for sample SPLLI/103 of Himont, was 8.47 min.

One can draw several conclusions from these results. First of all it is clear that at temperatures below the melting temperature of spherulites of i-PP (165 –170 °C) the relaxation times mentioned are practically infinite. This corroborates the statement made in the Introduction that the ratio of the rates of attachment and

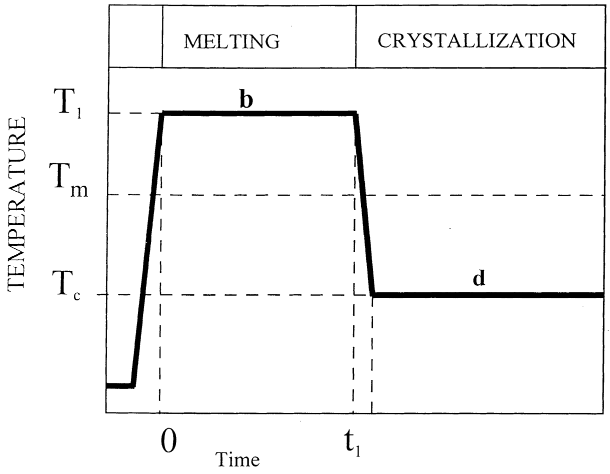

Fig. 3 Schematic representation of the standardized thermal history, $T(t)$, used in the experiments by Alfonso and Ziabicki [23]

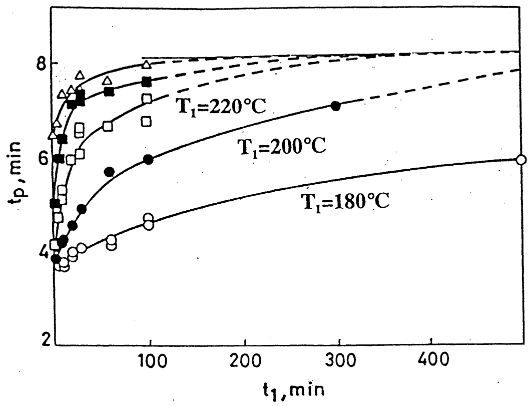

Fig. 4 Time-to-peak for isothermal crystallization of sample PP2 at T_c = 127 °C as a function of melting time t_l. ○: T_l = 180 °C; ●: T_l = 200 °C; □: T_l = 220 °C; ■: T_l = 240 °C; △: T_l = 260 °C according to Alfonso and Ziabicki [23]

detachment for sequences of proper conformation become practically infinite below the limiting temperature T_u, as given by Eq. (1). However, this also means that a tiny bundle of associated sequences which is, because of the smallness of its cross-section, not under tension by its tangling ends will stay practically forever at a temperature below the melting temperature of the spherulites of 165–170 °C.

Secondly, these results also give evidence that such small bundles of sequences apparently survive the melting of the spherulites for certain time spans decreasing with increasing tempering temperature.

Thirdly, the finite speeds of relaxation, which are easily measurable for temperatures T_1 above 180 °C, reflect the relative sluggishness of the kinetics in the temperature range of metastable states, where the bundles (athermal nuclei) which survive the melting of the spherulites become unstable. Remarkably, even at 260 °C, which is about 50 °C above the highest melting point of 208 °C, as reported by Monasse [7], a measurable relaxation time larger than those known from rheology for single macromolecules has been found.

In the next section rather unexpected support from measurements of shear-induced crystallization carried out ten years ago at Linz University will be provided for these conclusions.

Memory effects in sheared melts of i-PP

The idea for the pertinent experiments was born out of the first author's curiosity more than ten years ago: he asked himself what would happen if a melt was sheared for some time at a temperature well above the usual melting temperature (~165 °C) of the α-spherulites and then quenched to a temperature well below this temperature. Actually, the results of the first measurements, as carried out by Krobath (see Ref. [26]) stirred up some surprise and disbelief in the circles of rheologists and polymer processing specialists. In the cross-sections of samples which had been extruded through a slit die of rectangular cross-section and large aspect ratio, and quenched on a chill-role, we found the special type of oriented surface layer which was familiar from thin injection molded parts. If the extrudate was cooled sufficiently slowly instead of being quenched, no oriented surface layers were found. As is well-known, an investigation of the morphology of the oriented surface layers shows a so-called "shish-kebab" structure (see e.g. Ref. [27]). The "shishes" are very long strands, on which by lateral growth of lamellae the "kebabs" are grafted. The shishes may have thread-like (liquid ?) precursors in the sheared melt.

There were two big surprises. First, we found that an increase in the die length caused an increase in the thickness of the surface layers and in the intensity of their birefringence. At the same time, however, no influence of the die length could be recognized on the rheology of the melt. In fact, the flow birefringence, as measured with the aid of a light beam directed perpendicular to the large duct wall at the end of the duct, remained completely uninfluenced by the die length, which was varied between wide margins (12–121 mm). So, if precursors for the crystallization were formed during the flow through the duct, these precursors (of thread-like appearance) were too tiny (too thin) to have any measurable influence on the rheology of rectilinear flow. At the same time, however, they apparently had tremendous influence on the crystallization process occurring after quenching [28].

Secondly, it appeared that if the extrudate was not immediately quenched but was first put on a conveyor belt on which it could travel through an adequately heated tunnel of variable length, the crystallization on the chill-role became less conspicuous when the length of the tunnel was increased. Apparently, a relaxation process took place when the sample was kept at the extrusion temperature for a while [28].

Later less conspicuous but more accurate measurements, as carried out by H.W. in our laboratory [1, 29] revealed a more quantitative picture of this relaxation process. From these experiments we learned that the logarithm of the birefringence, as found close to the duct surface, decreased linearly with annealing time, as applied between the cessation of the flow and the quenching to tap water temperature. This type of a plot suggested the existence of a single relaxation time. For these experiments the extrusion speed was 200 mm s^{-1} (wall shear rate ≅ 1200 s^{-1}!). With decreasing temperature of this treatment from 210 to 190 °C the relaxation times obtained increased from about 1 to about 60 s. Besides the fact that the relaxation times in the experiments by Alfonso and Ziabicki were much larger, one finds qualitatively very similar phenomena. In connection with this, one should not forget that the surviving nuclei of Alfonso and Ziabicki were the remnants of a real crystallization process, whereas Wippel's associates had just been formed under the relatively mild conditions of shear flow. However, even if the much shorter relaxation times of our experiments increased by a further factor of 60 in the lower range between 190 and 170 °C, one should obtain a relaxation time of no less than 1 h at 170 °C. So, again, with approach of the magic temperature T_u one would obtain a virtually infinite relaxation time, which should mean that every attachment of another sequence is practically permanent.

The fact that in the shearing experiments the temperature dependence of the relaxation times for the precursors of oriented crystallization is much stronger than for the orientation of free molecules is clearly demonstrated in Fig. 5, as taken from Ref. [29]. In

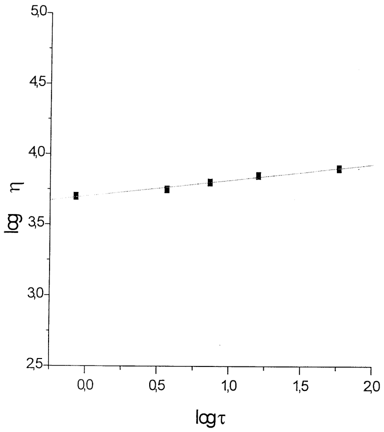

Fig. 5 Logarithm of the zero-shear viscosity versus logarithm of the relaxation time for the thread-like precursors of shear-induced crystallization of a polypropylene according to Wippel

Fig. 5 the zero-shear viscosities are plotted against the relaxation times for the precursors of oriented crystallization in a double logarithmic plot. If the relaxation times of the state of orientation of the free molecules showed the same strong temperature dependence as the relaxation times for the precursors of oriented crystallization, one should obtain a line under 45°. As this is not the case, Fig. 5 actually gives indirect evidence for the – rather slow – disintegration of supermolecular structures under the influence of the thermal motion in the temperature range between T_m and T_u of Eq. (1). In Fig. 5 the first experimental point on the left side represents the highest temperature of shearing, i.e. 210 °C, whereas the last point on the right side stands for 190 °C. The fact that above 210 °C the influence of shearing could not be observed seems to favor the thermodynamic melting point of 208 °C. If this coincidence is not incidental, one may suggest that the thread-like precursors – the shishes on which the kebabs are grafted later after quenching – are formed by cluster association as caused by the flow, the existence of these clusters being characteristic of the metastable state. In Larson's case [13] stirring caused coalescence of the clusters accompanied by an increase in their average size! In our case, because of the geometry of the clusters (bundles of segments), which are strongly oriented in the flow, a predestination is given for one-dimensional growth into thread-like precursors. As is clear, temporary clusters become very scarce above the thermodynamic melting point, where they are extremely short-lived. By the way, in shear average orientation of free molecules is virtually ineffective, as we showed in 1990 [29]. Below the magic temperature T_u the conditions of shear-induced crystallization for i-PP have also been investigated quite extensively at Linz University [1]. At these temperatures the thread-like precursors are quite stable. Ref. [1].

Self-nucleation in polymer melts

Self-nucleation (or self-seeding) is an old field of widespread interest. The discovery of this field goes back to the early 1960s and is connected with the names of Sharples and Keller (see Refs. [30, 31]). For newcomers to the field of polymer crystallization like the present authors it is almost impossible to read the pertinent literature without overlooking important arguments. For polymer melts (see also the three recent papers on i-PP by Fellon and coworkers [32–34] the phenomenon can be described as follows. If a single spherulite is formed at a suitable temperature as a thin disc in a melt sandwiched between two cover glasses of narrow spacing and heated carefully to a temperature level where this spherulite just disappears, one can observe after a subsequent cooling step that the contour of the original spherulite reappears. Inside this contour, however, a great number of new nucleation centers shows up.

An explanation of this phenomenon in terms of the present consideration would be as follows. The lamellae of the original spherulite grew from a single (athermal) nucleus. When these lamellae are carefully melted, this melting process starts at a large number of spots within the spherulite simultaneously. After all, these lamellae cannot be perfect and must show a lot of weak spots. If this is true, a kind of circular melting front will proceed from each of these spots. After some time these fronts will impinge, leaving a lot of small areas unmelted. In fact, the surfaces of the "spandrels" in the corners, where the melting fronts meet, will become so small that the pertinent bundles of still-associated sequences become stable again for the reasons explained in the Introduction. (Regained freedom of the tangling ends.) It seems that by this reasoning a valid explanation is found for the tremendous increase in nuclei. Inversely, this augmentation of the number of (athermal) nuclei can also be considered as evidence for the correctness of the proposed nature of these athermal nuclei. Also the observation of Van Krevelen [17] would fit into this picture. Van Krevelen and his coworkers found that the number of nuclei in a melt of isotactic polystyrene was augmented by a factor of 10^5 when this melt was reheated after it had temporarily been cooled down below the glass-transition temperature.

Conclusions

As is well-known, spherulites disappear when heated under a thermo-microscope to a temperature T_u distinctly below the thermodynamic melting point T_m. The difference between these two temperatures, comprising the range of metastable conditions, can be estimated on the basis of thermodynamic considerations, as has been shown in a previous paper [5]. Only in this range of metastable conditions can the classical theory of nucleation in solutions [35] also be valid for melts. Compared with the large degrees of undercooling, as usually applied in polymer processing, the range of metastable conditions is rather small. Below T_u one can only find athermal nuclei [10].

The physics of these athermal nuclei is the subject of this paper. It appears that these nuclei are not sporadically formed but preexist in a characteristic temperature range between T_u and a much lower characteristic temperature, where less-ordered structures – compared with spherulites – must be expected. In this characteristic temperature range the athermal nuclei are dormant. They become activated only if their conditions for growth are fulfilled. These growth conditions are described, for example, in a recent theory by Strobl [15]. In this theory the growth of lamellae is directed into the right channels by the assumption of a positive extra free energy at the ends of the sequences which are ready for insertion. The shorter these sequences of correct (helical) conformation, the lower the temperature where the pertinent lamellae can grow. It has been made plausible, however, by one of the present authors [5], that this extra free energy has no constant value but is dependent on the thickness of the bundle of associated sequences. As long as this bundle consists of only a small number of sequences, this free energy can be disregarded. It increases (to a constant level) only because the tangling ends start to hinder each other with the growth of the lamella. This train of thought directly leads to the definition of the athermal nuclei. Also, the absence of this free energy with small bundles makes them survive, at least temporarily, when the sample is heated above the temperature where the spherulites melt. The number of these athermal nuclei increases tremendously with decreasing temperature because of the increasing probability of shorter helical sequences.

Experimental examples have been given which make this view very plausible. Also, the assumption of a number of nuclei per unit volume, which is a unique function of temperature, being so advantageous for the use in simulation projects, gets its physical justification along this route. This assumption was introduced by Eder et al. [29] because only in this simple way can one predict the well-known strong influence of an increasing cooling speed on a corresponding increase in the final number of spherulites without excessive mathematical effort. (The popular isokinetic approach of Nakamura et al. [36] is unable to predict such behavior, as Eder [22] and Eder and Janeschitz-Kriegl [1] have shown.) The tremendous sluggishness of the processes occurring under metastable conditions, which becomes evident from the experiments reviewed in this paper, is of great interest. The consequence of this sluggishness is that under industrial cooling conditions the processes occurring in the said temperature range of metastable conditions are of practically no influence on the structure formation, as long as flow is slow enough. In general, industrial cooling processes are too fast. Only the enormous acceleration of processes, as caused by fast flow, may breach this conclusion.

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