Monatshefte für Chemie 138, 327–335 (2007)
DOI 10.1007/s00706-007-0615-4
Printed in The Netherlands

**Monatshefte für Chemie
Chemical Monthly**

Synopsis

An Unusual but Consistent View on Flow Induced Crystallization of Polymers[#]

Hermann Janeschitz-Kriegl[*]

Institute of Polymer Science, Johannes Kepler University, Linz, Austria

Received December 18, 2006; accepted February 7, 2007; published online March 29, 2007

Summary. There is a considerable difference of more than 40 degrees centigrade between the equilibrium melting point of the α-crystal modification of *i-PP* and the lower temperature, where the α-spherulites of this polymer melt. The equilibrium melting point represents the temperature, where ideal crystals melt. In these crystals the macromolecules are in a stretched conformation. In contrast, in the spherulites the molecules are contained in lamellae of finite thickness. As a consequence it seems that in the interval between these two characteristic temperatures the nucleation kinetics is very different from the kinetics observed at temperatures below the melting temperature of the spherulites. This observation is of importance because almost all measurements on flow induced crystallization have been carried out below the melting temperature of the spherulites. It can be shown that at these lower temperatures the kinetics of crystallization (including flow induced crystallization) has nothing to do with the classical ideas about sporadic nucleation.

Keywords. Phase diagrams; Phase transitions; Thermodynamics; Crystallization kinetics; Nucleation by flow.

Introduction

As is well known, flow induced crystallization occurs in semi-crystalline polymers during their processing. It influences the patterns of structure in all kinds of plastic parts. These structures can be decisive in many cases for the product quality (anisotropy of mechanical and optical properties, crack forming, shape stability, warping). Only little was known about the background, when investigations were started in Linz 23 years ago. Because of the fact that the present author had been involved in polymer rheology for more than 25 years and in screw extrusion for about 10 years, his starting point differed considerably from that of other authors. This is also the reason, why the first experiments at Linz University actually where carried out in the high temperature range, where structure elements, which were formed by the action of flow, readily relaxed after cessation of flow. It was only many years later that we started to understand the results obtained. This fact gives an explanation for the choice of these old results as the starting point of the present consideration. The interested reader may find summaries of these activities in two review articles from 1990 [1] and 1997 [2] and in a more recent compilation of 2005 [3].

Isothermal Duct Flow

This experimental configuration has been used in our group in connection with a single screw extruder. The polymer was pushed at a rather high speed through quite a long duct of rectangular cross-section of large aspect ratio. Flow was stopped just before the van of the melt, which was at the entrance, when flow was started, had reached the exit. The duct wall, which was kept at a low degree of undercooling of the melt, was quenched by ice water either immediately after the cessation of flow or after various time

---

[*] E-mail: gerhard.eder@jku.at

[#] Lecture presented at the 8th Austrian Polymer Meeting in Linz in September 2006

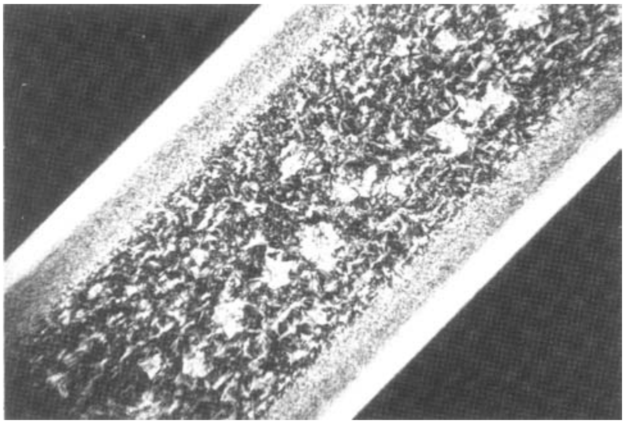

Fig. 1. Cross-section through a quenched sample of an industrial *PP* after short term extrusion at 150°C through a long duct of large aspect ratio. Shear rate at the large side wall was $68\,s^{-1}$ for 17.6 s. From Ref. [4], courtesy of Hanser Verlag

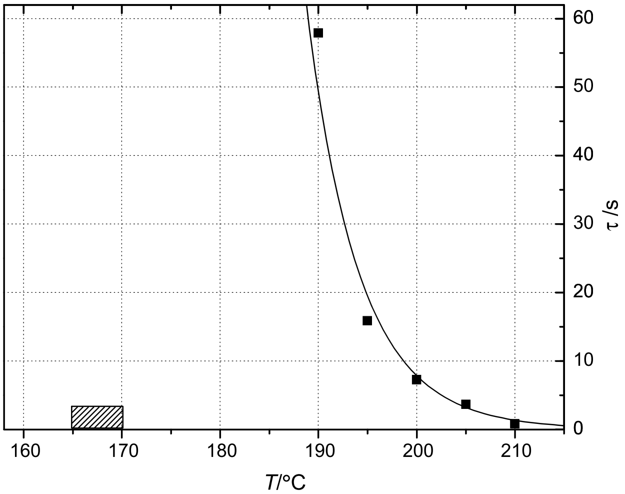

Fig. 2. Relaxation time *vs*. temperature of previous shearing for thread-like precursors of an industrial *PP*. Shear rate at duct wall was $1200\,s^{-1}$ for $\approx 0.5\,s$ [1]

spans reckoned from the moment, when the flow was stopped. In Fig. 1 the structure is shown, which was found in a cross-section of the solidified sample of an industrial polypropylene (*PP*) after an immediate quench. This cross-section was taken in a plane perpendicular to the large side wall of the duct. One observes highly oriented layers close to the duct wall, transitional fine grained layers and a spherulitic core. In the present context this figure is abused, as the build up of microstructures was investigated by *Liedauer*, whereas *Wippel* (see Ref. [1]) looked after the decay of those structures, which is of importance in the present context. *Liedauer*'s picture is only presented for being so useful for the explanation of the procedure in the following.

Relaxation of Thread-Like Nuclei

Obviously, the birefringence of the highly oriented layers can easily be measured. And it turned out that the values of this birefringence decreased exponentially with increasing waiting times introduced after the cessation of flow, before the quench occurred. In this way relaxation times could be determined for the temperatures, where the flow treatment had occurred. In Fig. 2 these relaxation times are plotted for the said *PP* against the temperature of the shear treatment. The shear rate at the duct wall for this treatments was permanently $1200\,s^{-1}$. (See Ref. [1], where *Wippel*'s diploma theses is cited, and where a table of the relaxation times is given.) The increase of these relaxation times with decreasing temperatures is remarkable. For comparison one finds the temperature range, where the spherulites melt, as a block located between 165 and 170°C. It seems as if the relaxation times of Fig. 2 almost reach infinite values at the temperatures where spherulites melt. In this respect one must emphasize that these relaxation times do not represent the relaxation of the structures shown in Fig. 1. This structures are formed only by the quenches. Before the quenches one has microstructures (presumably thread-like precursors), which are so tiny that a direct observation is impossible. They have no noticeable influence on the rheology of the melt and are not even reflected by the flow birefringence of the melt [5]. But Fig. 2 shows the relaxation of these tiny microstructures. And, apparently, halfway down to the temperature, where spherulites melt, they are already practically stable.

From an *Arrhenius* plot an activation energy of $334\,kJ/mol$ can be obtained. For viscous flow of the melt of *PP* an activation energy of only $44\,kJ/mol$ has been found [6]. So, one can see that the relaxation of Fig. 2 is not the relaxation of the orientation of free or entangled molecules. It shows that some microstructure containing more than one molecule, is decaying. Recently, a similar behavior has been found in our group for a high molar mass *PB*-1 [7]. Recently, *Azzurri* and *Alfonso* [8] published a review of their work on the relaxation of structure elements in undercooled melts of *PB*-1.

T,S-Diagram

The use of the *T,S*-diagram has been recommended by the present author already some years ago [9]. The advantage of this diagram is that it directly shows the temperatures, where several processes can occur. The specific entropy S is here the independent variable, which can easily be calculated from thermodynamic data existing for a great variety of polymers. The corresponding Fig. 3 holds for *i-PP*. On the right side one finds the liquidus line. On the left side two different solidus lines are given. The upper temperature of transition (melting) holds for the ideal crystals. *Marand et al.* [10] have determined the equilibrium melting point of α-*i-PP*. With a clever extrapolation method these authors found a value of 212°C. A direct way of obtaining ideal crystals in a sporadic nucleation process seems impossible. An explanation will be tried below. The transition at lower temperatures, as shown on Fig. 3, holds for the melting of spherulites. It is indicated by a double line. Between the two transitions (above the double line) one finds a shaded area of the shape of a parallelogram, which indicates the temperature range, where with decreasing temperature the thread-like precursors become more and more stable. Interestingly enough, however, one can obtain rather stable nuclei in this temperature range also with a departure from lower temperatures and in a quiescent melt. This effect will be treated in the next section.

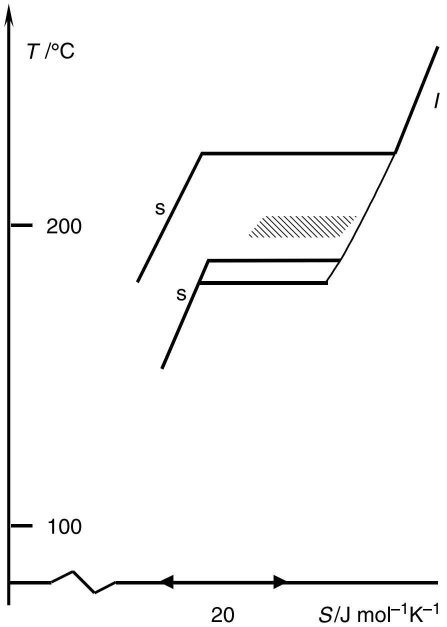

Fig. 3. *T,S*-diagram of *PP*. Upper transition for ideal crystals. Lower transition (double line) for spherulites. Shaded area: temperature range, where thread-like nuclei from high temperature shearing and nuclei from self-nucleation become stable

Self-Nucleation

This name was coined by *Keller et al.* many years ago [11]. It is well known that a spherulite, as observed under the microscope, can be regained at the same spot, when the temperature is lowered again after a careful melting procedure. Apparently the nucleus, around which the spherulite had grown, survived the melting process. And this nucleus also remained at the same spot. In fact, a sporadically formed nucleus will disappear during the melting procedure, and another one will appear at another spot in the following cooling process. Moreover, if melting occurs particularly carefully with a minimum of a temperature overshoot, one finds many more new nuclei within the domain of the melted spherulite. All these nuclei survived the melting of the spherulite. Isn't it a paradox that a big crystalline structure is less stable than some very tiny remainders of this structure? An explanation for this phenomenon seems overdue.

Local Alignments

Very surprisingly, nobody has ever thought of the role of local alignments. As a matter of fact, those alignments do exist without any doubt. If one considers an arbitrary macromolecule in a quiescent melt, one will find a polymer chain of statistical conformation. However, if one considers also a neighboring macromolecule, one will find that this second molecule cannot have a shape, which is independent of the shape of the molecule considered first. The two-dimensional case, which, of course, is unrealistic, is particularly restrictive. If one draws a statistically shaped line on a sheet of paper, the neighboring line must have practically the same shape, if the high density of lines is to be retained. In fact, a cross-over is not permitted in the strictly two-dimensional case. On the basis of this consideration *Pechhold et al.* [12] proposed his meander model at the time. Without any doubt, there is more freedom in the three-dimensional case. Nevertheless, if one would make a series of stiff three-dimensional wire models of arbitrary shapes, one should not entertain the hope that one could achieve the high density of a melt by throwing them on a heap. At best, one would get the density of a gas. But this means that, in reality, neighboring molecules must be flexible for a rather far going accommodation of their shapes. The result of this accommodation will be the existence of a spectrum of local alignments of varying quality.

It will be also clear that at temperatures below the melting temperature of the spherulites these local alignments will be stabilized and form a reservoir of athermal nuclei. Their shape will resemble the shape of fringe micelles. In fact, except for very low molar masses practically all alignments will be shorter than the lengths of the molecules. The corresponding overlengths will be disposed in the fringes or tangling ends.

Unfortunately, so far the topology of such a system has not been described mathematically.

On the Nature of Athermal Nuclei

Figure 4 shows a schematic presentation of a fringe micelle and a lamella formed by lateral association of macromolecules to this micelle. In the left picture the cone angle φ symbolizes the freedom of conformation of the tangling ends. If a lamella is formed by the said lateral association, which is possible by solely local rearrangements of the conformations, one obtains a lamella, in which the molecules are in a nearly perpendicular position with respect to the extension of the lamella [13]. The local rearrangements appear to be sufficient for the purpose. In fact, the growth speed of spherulites, which is based on the growth of the lamellae, does not depend on the molar mass, if this molar mass is large enough [14]. Only in the low range of molar masses the growth speed decreases with increasing molar mass [15]. If other than local rearrangements would be required, this tendency should continue to higher and higher molar masses.

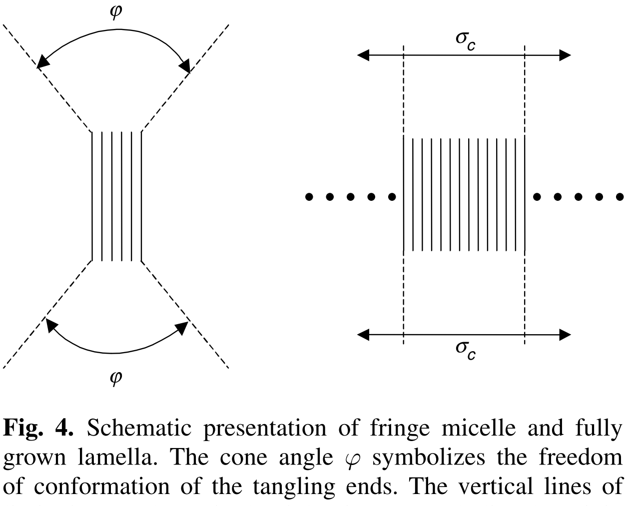

Fig. 4. Schematic presentation of fringe micelle and fully grown lamella. The cone angle φ symbolizes the freedom of conformation of the tangling ends. The vertical lines of limitation, as shown in the right picture, symbolize the origin of the surface tension σ_c as a consequence of the squeezing effect

Of course, the said association only occurs, if the specific free energy of the body of the micelle becomes lower than that of the melt. This occurs with decreasing temperature. However, as symbolized in the right drawing of Fig. 4, the tangling ends get into a squeeze, as they need more space in the lateral direction than the parts of the molecules incorporated in the body of the lamella. In fact, their freedom of conformation becomes much lower than in the original fringe micelle. This circumstance must cause a considerable tension in the rough surface of the lamella. Also back-folding [13] must contribute to this tension. This surface tension must cause a considerable melting point depression with respect to the ideal crystals. *Strobl* [16] has given a corresponding equation. It can be assumed that the difference in the melting temperatures of more than 40°C, as shown in Fig. 2 for *i-PP*, is caused by this surface tension.

The melting process of such a lamella is very instructive. Not only single molecules may be detached during this process. It can also happen that bundles of molecules are separated. And if such a bundle is thin enough for a sufficient increase of the conformational freedom of the tangling ends, as sketched on the left side of Fig. 4, this bundle is stabilized, as the tensions in the ends of its body are reduced. This reasoning would be a valid explanation for the self-nucleation phenomenon.

Interestingly enough, an analogy has been discovered for the case of droplet shaped nuclei [17]. In fact, as *Tolman* [18] has shown already a long time ago, the surface tension of droplets goes to zero with their size. (In the above case the tensions in the fringes goes to zero with the cross-section of the bundles.) This means that the classical theory for droplets, in which their surface tension is considered as a constant, must be modified. As a consequence of this modification one first obtains a shallow minimum of the free energy of the droplet with increasing size of the new phase [1, 17]. Only with further increasing size of the droplet this free energy rises to the well-known maximum forming the well-known barrier for continued growth. *Larson* and *Garside* [17] could explain in this way, why one finds stable clusters of sugar molecules or of other molecules in their saturated solutions. These clusters are still small compared with the wave-length of light (still clear solutions) but large enough for hardly moving under the influence of thermal motion. Only by stirring one can bring them to collide. Only by such collisions supercritical particles are formed, which lead to precipitation.

This consideration also opens the way for an understanding, why local alignments of decreasing orderliness (decreasing effective lengths of their bodies) become active as athermal nuclei only with decreasing temperatures. In fact, the mentioned barrier for growth is a consequence of a balance between the positive surface tension and the negative difference of the free energies of the body of the micelle and the fluid, as reckoned per unit surface of the cross-section of the micelle. But the latter quantity decreases, if the effective length decreases, which means an increase of the barrier. As the value of the said negative free energy difference not only decreases with the effective length of the micelle, but also increases in a well-known way with decreasing temperature, the conclusion must be: the lower the orderliness of the alignment is, the lower will be the temperature, where such an already existing stable alignment can form an active athermal nucleus. This fact forms a welcome selection rule for the activity of athermal nuclei. This fact will be demonstrated in the next section. The analogy with the droplets is obvious: also the droplets do already exist. But they start growing only, if the temperature is lowered according to their size. In this way the solution becomes considerably undercooled, so that stirring is no longer necessary.

Interaction of Three Transport Phenomena

It will be clear to the reader that three transport phenomena interact with flow induced crystallization. These phenomena are heat transfer, flow, and crystallization kinetics. In Fig. 5 the enormous influence of these phenomena on each other is demonstrated for an industrial *PP* [19]. This figure gives a three dimensional plot. On the left axis one finds the crystallization temperature for quiescent melts after the application of rapid quenches (heat transfer!). On the right axis one finds the specific mechanical work applied to the samples during flow. With the sandwich type machine, which is required for the application of this work (in rectilinear flow with shear rates up to $1000\,\mathrm{s}^{-1}$), a fast quench is not possible. This means that the measurements are restricted to a range of higher temperatures. On the vertical axis one finds the number densities of the nuclei created by these treatments. On the latter axis a logarithmic scale had to be chosen because of the tremendous changes in number densities experienced.

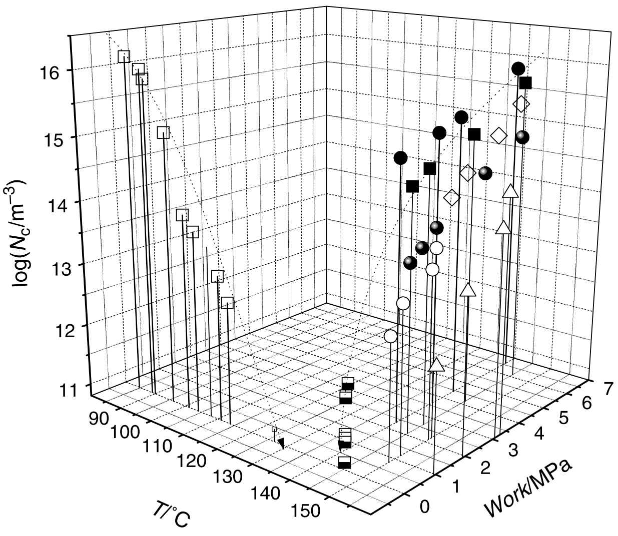

Fig. 5. Three dimensional plot of the logarithm of the number density of nuclei *vs.* crystallization temperature and specific mechanical work, as applied to a sample of an industrial *PP*. From Ref. [19], courtesy of Springer Verlag

One observes that with a change of temperature from 130 to 85°C the number density of nuclei increases in a quiescent melt of *i-PP* by more than five decades. It seems to us that this fact reflects the spectrum of local alignments, as dictated by the statistics: the number of alignments of a higher degree of ordering is very small compared with the number of alignments, which show a low degree of orderliness. In fact, the temperature, where spherulites melt, lies between 165 and 170°C and the equilibrium melting point is at 212°C. This means that the length of the temperature axis of Fig. 5 must be doubled, if the said critical temperatures are to be included on the scale. One can guess how low the number densities of nuclei will be at those temperatures.

The influence of flow on the number density turns out to be overwhelming. At those higher temperatures, where the said number density is extremely small in quiescent melts, one finds increases of at least six decades. At 145°C one finds points (open diamonds) for low specific works, which show a steep increase. These points were obtained in extensional flow [20]. By the way, in this presentation the said steepness comes from the fact that the logarithm goes to minus infinity, if the argument goes to zero. The remaining points of Fig. 5 have been obtained in shear flow [19]. With our machine of the sandwich type we could realize at most 7 MPa. In this range of specific works (seemingly) point-like nuclei were found. In order to include points for the transition to thread-like nuclei, the axis for the specific work should have been extended to about 25 MPa. (This value of the specific work corresponds with the transition from the highly oriented layer to the fine grained layer in Fig. 1 [4].) Also the axis for the work of Fig. 5 must be extended tremendously for an inclusion of the influence of high mechanical loads. This remark and the remark made at the end of the previous paragraph show the enormous range of interesting variables.

In a double logarithmic plot, where also for the work a logarithmic scale is chosen, one obtains practically straight lines with slopes between three and four in the range of temperatures between 140 and 160°C. This means that the dependence of the number density of nuclei on the specific work is highly non-linear. As long as unchanged external stresses are used, this also holds for the shearing time. In an early work *Wolkowicz* [21] has already demonstrated this non-linearity with respect to the shearing time for the undercooled melt of a *PB*-1. An important feature of those curves is that they show a zero initial slope, which means that there is a low shear region, where the melt behaves like a quiescent melt, a fact which has been observed several times in the past.

The mentioned non-linearity invites for a proper interpretation. In the past the influence of a reduced specific entropy, as caused by the orientation of the macromolecules in flow, has been invoked (see *e.g. McHugh* and *Bushman* [22]). However, with this approach one obtains a linear relation between shearing or stretching time and number density of nuclei. This is understandable: during the period of flow the milieu for sporadic nucleation is improved. The longer this period lasts, the more nuclei are created. However, this means that we had to look for another explanation.

The representation of Fig. 5 suggests that flow has improved a lot of the low quality athermal nuclei, which as such are active only at low temperatures. This may explain, why after proper shearing the number density at 150°C is practically the same as it is without shearing at 90°C. According to this picture the non-linearity is caused by the fact that at lower temperatures there are so many more nuclei, capable of improvement. This picture has been developed in a recent paper [23]. The assumption is that the tangling ends of the fringe micelles are straightened out by the action of the flow, thus the fringes are "ironed".

With increasing shearing time (or specific work) the micelles will become longer and longer also by the incorporation of more and more neighboring molecules. In this way one finally obtains thread-like nuclei, interspersed between the mentioned "seemingly" point-like nuclei. In fact, only those scarce nuclei possessing already a proper shape in the quiescent melt, can grow out so far. This mechanism can also explain the large influence of the presence of a fraction of very long molecules on the formation of thread-like nuclei [24]. Now it can also be explained, why the term "seemingly" point-like has been used.

In this connection it must be emphasized that directly after the cessation of the short term shearing no changes in the optical properties can be observed. Normally it takes quite a long time, sometimes a factor hundred longer than the shearing time, until changes in the optics can be observed. Only then one notices an increase of the turbidity and finally a total depolarization. This depolarization is indicative of the space filling by spherulites. However, intermediately one always finds some indications for an optical anisotropy. This effect shows that the spherulites apparently grow on anisotropic nuclei, which are oriented in the direction of previous flow. But this means also that these lengthy nuclei remain shorter than the distances between neighboring nuclei. So they grow out into spherulites. But a spherulitic structure always gives the impression that its origin is in point-like nuclei.

Before giving something like a proof for the correctness of the just sketched mechanism, the author is tempted to introduce an intermezzo. At the 8th Austrian Polymer Meeting in Linz of September 2006 *G. Alfonso* of Genova gave an invited lecture just before the present author had his turn. *Alfonso* reported of recent measurements together with

F. Azzurri on a high molar mass *PB*-1. These authors sheared their samples at rather high temperatures, up to 190°C, before quenching them to a temperature below the melting temperature of the spherulites of Form I (124–136°C). This is the first time that after our early measurements [1, 5, 25] samples were sheared in the ominous temperature range between the equilibrium melting point and the temperature, where spherulites melt. Our experiments were carried out at very high shear rates but remained incomplete (no variation in shearing times). In contrast, the experiments of the Genova group were carried out at rather low shear rates, but were more systematic. To our surprise, these low shear rate experiments led to results, which could be evaluated. In fact, a linear increase of the number density of nuclei with the shearing time was found. This would mean that the entropy concept has found its application in this range of high temperatures between the equilibrium melting point and the melting temperature of the spherulites.

Returning to quiescent melts, the author is now tempted to discuss the possibilities for sporadic nucleation in the just mentioned range of high temperatures. As under those circumstances the probability for the occurrence of completely stretched conformations is extremely small, the sporadic formation of stretched nuclei is practically impossible. This seems also to be the reason for the enormous sluggishness of nucleation in quiescent melts in this temperature range. It also explains why ideal crystals can never be obtained directly in a process of sporadic nucleation. One can get those crystals only along an indirect way by recrystallization under quite severe conditions (high pressures and temperatures close to the equilibrium melting point [26]).

However, in the flow field molecules are stretched and oriented. This will improve the chances for sporadic nucleation tremendously. In this way the entropy concept can be saved, but only for the high temperature range between the equilibrium melting point and the temperature, where spherulites melt. This concept can never be used for the majority of measurements, which have been carried out below the melting temperature of spherulites. It will now also be clear, how difficult numerical simulation of structure formation will be. In fact, during the cooling process one moves down from one characteristic temperature range into the other. And pressurization, which is unavoidable with polymer processing, contributes to the difficulties, as will be shown in the next section.

The Influence of Pressurization

The idea that nuclei of low quality can be improved by the action of flow has led us to the conclusion that also the application of pressure must lead to a similar effect. In fact, the density within the bodies of the fringe micelles will be higher than in the intermediate regions, where the fringes dominate. But this means that pressurization will mainly influence the latter regions. A kind of ‘‘ironing’’ will be the consequence. In fact, it has been known for quite a long time that the fold length is increased by the application of high pressures at sufficiently high temperatures [27]. But the first stages of such a process will improve the quality of nuclei in a similar way as flow does. And because of the higher number density of nuclei at lower temperatures (being of lower orderliness) the improvement of these nuclei must cause an increase of the number density at the temperature of the experimentation. In fact, without this concentration gradient in the quality of the nuclei pressure would not have a significant influence on the number density of nuclei. Admittedly, it is thinkable that new alignments are caused by the pressure. However, the quality of those new alignments will not directly be high enough for their participation in this game.

As a matter of fact, a remarkable influence of pressure on the number density of effective nuclei

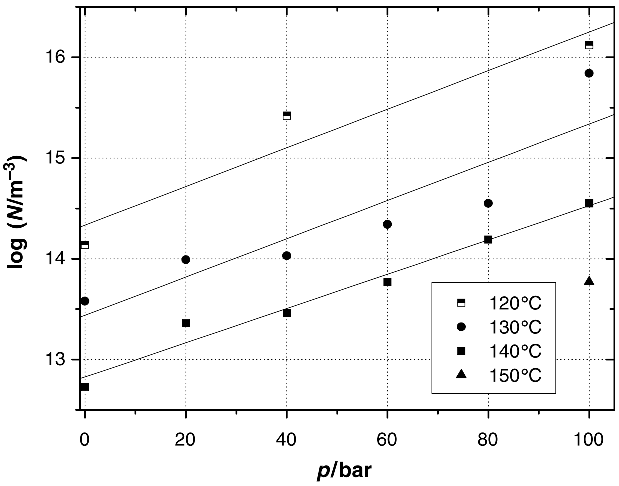

Fig. 6. Logarithm of the number density of nuclei against pressure at several temperatures for an industrial *PP* [28]

could be found. For various temperatures of experimentation this influence is demonstrated for an industrial *PP* in Fig. 6 [28]. If a pressure of 100 bar was applied, the number density of nuclei increased by a factor of one hundred. Even if the details of the process leading to the augmentation of the number density of nuclei are different, the results shown in Fig. 6 represent for us a direct proof for the correctness of our ideas, in particular with respect to the increase of the number density of nuclei by the action of flow.

Closing Remarks

Notwithstanding the obtained insights there remain various puzzles. For the investigations quoted above, quite severe experimental conditions were chosen in view of the corresponding conditions prevailing in practical polymer processing. In all cases rapid short term shearing or stretching was applied. For this purpose specific mechanical works (per unit volume) up to about 7 MPa were expended. In a few cases 25 MPa were reached.

Quite recently, however, some investigations were published [29–31], where instead of short term flow long term flow was applied. In these investigations flow persisted up to the moment, when the sample solidified. However, if one looks at the total specific mechanical works, which were applied in these experiments, one often finds specific works much lower than those applied in our short term shearing. One may also take into account that *Winter et al.* [32, 33] and *Winter et al.* [34] have discovered a rather slow gelation process in slightly undercooled quiescent melts.

However, growth speed, as enhanced by flow, has not got a sufficient attention in the past. Disentangled oriented molecules will be responsible. However, around a thin thread-like precursor crystalline volume increases with the square of time, if the growth speed is constant. So, also during flow it takes some time, until the effect becomes noticeable. However, if flow is stopped too early, as in our short term experiments, no enhanced growth will become obvious. In fact molecules coil up again in the quieted down melt. But a continued fast growth speed can overrule the effect of a greater number of nuclei or shishs as obtained in our rapid short term shearing.

Very recently *Kornfield et al.* at CALTECH succeeded in introducing a direct experimental proof for the correctness of our opinion about the nature of athermal nuclei. These authors kindly informed us of their results. They used an ingenious novel technique of levitation of a single particle of about 1 ng in an electric field [35, 36]. They were able to determine the ups and downs of the weight of a tiny particle of poly(ethylene oxide) (*PEO*) in a cyclically varying humidity (Scanning Activity Gravimetric Analysis (SAGA)). For *PEO* as a water soluble polymer the activity of the water takes over the role of temperature. At a humidity somewhat higher than the humidity, where the particle completely dissolved and formed a rather heavy droplet (as indicated by the proper light scattering pattern according to *Mie*), nuclei survived in such a droplet for at least two hours. This time span is much too long for a kinetic effect. An interpretation is given in terms of a surface tension decreasing with the distance from the center of a disk-like lamella.

Acknowledgements

The cooperation with Prof. *G. Eder* and Dr. *E. Ratajski* is gratefully acknowledged.

References

[1] Eder G, Janeschitz-Kriegl H, Liedauer S (1990) Progr Polym Sci **15**: 629
[2] Eder G, Janeschitz-Kriegl H (1997) Mat Sci Tech **18**: 269
[3] Janeschitz-Kriegl H, Eder G, Stadlbauer M, Ratajski E (2005) Monath Chem **136**: 1119
[4] Liedauer S, Eder G, Janeschitz-Kriegl H (1995) Intern Polym Proc **10**: 248
[5] Eder G, Janeschitz-Kriegl H, Krobath G (1989) Progr Colloid Polym Sci **80**: 1
[6] Van Krevelen DW (1976) Properties of Polymers, 2nd ed. Elsevier, p 345
[7] Braun J, Wippel H, Eder G, Janeschitz-Kriegl H (2003) Polym Engng Sci **43**: 188
[8] Azzurri F, Alfonso GC (2003) Macromolecules **38**: 1723
[9] Janeschitz-Kriegl H (1997) Colloid Polym Sci **275**: 1121
[10] Marand H, Xu J, Srinivas S (1998) Macromolecules **31**: 8219
[11] Blundell DJ, Keller A, Kovacs AJ (1966) Polym Letters **4**: 481
[12] Pechhold W, Hauber MET, Liska E (1973) Kolloid-Z **251**: 818
[13] Keller A (1957) Philos Mag **2**: 1171
[14] Gandica A, Magill JH (1972) Polymer **13**: 595

[15] Van Krevelen DW (1990) Properties of Polymers, 3rd ed. Elsevier, p 597

[16] Strobl G (1996) The Physics of Polymers, Springer p 166

[17] Larson MA, Garside J (1986) J Crystal Growth **76**: 88

[18] Tolman RC (1949) J Chem Phys **17**: 331

[19] Janeschitz-Kriegl H, Ratajski E, Stadlbauer M (2003) Rheol Acta **42**: 355

[20] Stadlbauer M, Janeschitz-Kriegl H, Eder G, Ratajski E (2004) J Rheol **48**: 631

[21] Wolkowicz MD (1978) J Polym Sci Polym Symp **63**: 365

[22] Bushman AC, McHugh AJ (1996) J Polym Sci Polym Phys **34**: 2393

[23] Janeschitz-Kriegl H, Ratajski E (2005) Polymer **46**: 3856

[24] Seki M, Thurman DW, Oberhauser JP, Kornfield JA (2002) Macromolecules **35**: 2583

[25] Janeschitz-Kriegl H, Wimberger-Friedl R, Krobath G, Liedauer S (1987) Kautschuk + Gummi-Kunststoffe **40**: 301

[26] Woodward AE (1989) Atlas of Polymer Morphology, Hanser, pp 106–109

[27] Prime RB, Wunderlich B (1973) Macromolecular Physics I, Academic Press, p 224

[28] Eder G, Janeschitz-Kriegl H, Rexhepaj E (2006) in preparation

[29] Samon JM, Schultz JM, Hsiao BS (2002) Polymer **43**: 1873

[30] Hadinata C, Gabriel C, Ruellmann M, Laun HM (2005) J Rheol **49**: 327

[31] Hadinata C, Gabriel C, Ruellmann M, Kao N, Laun HM (2006) Rheol Acta **45**: 539

[32] Winter HH, Chambon F (1986) J Rheol **30**: 367

[33] Pogodina NV, Lavrenko VF, Srinivas S, Winter HH (2001) Polymer **42**: 9031

[34] Acierno S, Grizzuti N (2003) J Rheol **47**: 563

[35] Olsen AP, Flagan RC, Kornfield JA (2006) Macromolecules **39**: 5946

[36] Olsen AP, Flagan RC, Kornfield JA (2006) Macromolecules, in press