Phases of Flow-Induced Crystallization of i-PP: How Remote Pieces of the Puzzle Appear to Fit†

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ABSTRACT: A synopsis of already published results of very different characters, as obtained at four independent institutes, yields a congruent picture of the processes occurring during flow-induced crystallization of polymers like i-PP. The research groups mentioned only had a common starting point: They adopted the protocol of short term mechanical loading. With this protocol, a nice separation of the flow-induced nucleation process from the succeeding growth process is usually obtained. For this achievement, the largely differing time scales of loading and subsequent waiting are responsible. In Linz, the required mechanical treatments were characterized by harsh conditions, as occurring during practical processing (short loading times with high loads). Conclusions were drawn from the time-dependent optical retardation, as observed directly after cessation of flow, and from microphotographs obtained on cross sections of the finally solidified samples. The three other groups applied milder mechanical treatments, but used time-dependent small angle light scattering (SALS) and incipient depolarization. They could also follow the structure formation under the microscope. For this purpose they used transparent equipment. From a combination of the results of the four groups, one can draw the following conclusions: During flow a tremendously increasing number of nuclei of augmenting anisotropy are formed. Apparently, after cessation of flow, these nuclei act like pointlike nuclei, if their average lengths are still shorter than the average distances between their centers. In those cases, spherulites are formed, which fill the intermediate space. With light scattering, mainly the well-known invariant, reflecting density fluctuations, is of importance. It also appears that its time dependence can readily be predicted with the aid of the number density of nuclei and the growth speed of spherulites. With continued waiting, the internal structure of the just formed spherulites matures. As a consequence, orientation fluctuations of anisotropic entities, which grow larger, play a role. Along this route, the formation of "shishs", as well-known from oriented shish-kebab structures, may also be elucidated. The relaxation behavior of these threadlike precursors is discussed in connection with their stability at lower temperatures.

1. Introduction

The history of the research into the flow-induced crystallization of polymers starts with a series of publications in 1978 in the legendary Vol. 63 of *J. Polym. Sci.* In this volume, the papers that were presented at a conference on the said subject have been gathered. The content of these papers is recapitulated in a review by the research group in Linz.[3] Most important for the present purpose is a paper by Wolkovicz,[4] in which a poly(1-butene) of a molar mass of 180 000 Da is investigated at 100 °C. Wolkovicz could show in this paper that the number density of nuclei increases rapidly in a nonlinear way with the shearing time at various rates of shear. This result is in contrast to the outcome of a series of later theoretical papers, in which a linear increase of the said number densities with the shearing time is always predicted.

The research group of Linz University began to study the subject because of its interest in polymer processing.

In a first step, to make things not directly too complicated, quiescent samples were quenched in a typical experiment from above the equilibrium melting point to the desired crystallization temperature. For the purpose, thin samples (down to a thickness of about 1 μm) were embedded between cover glasses. The growth of spherulites can be interrupted by a second quench, as applied after various times of crystallization. After the second quench, the spherulites appear as thin disklike slabs separated by fine grained material. Their diameters, as measured under the microscope, appear to increase linearly with the applied crystallization times. With this and other methods, as described in a more recent review by Eder and Janeschitz-Kriegl,[5] the temperature dependence of growth speed could be determined over a wide range of crystallization temperatures. Microscopy could be used only at relatively high crystallization temperatures.

This left only the determination of the number density of nuclei as a function of temperature. For this purpose, cylindrical samples of 4 mm diameter were used. A fast enough cooling of these thicker samples is achieved in a countercurrent system, where the sample undergoes a rapid enough cooling in a stream of a very cold fluid. This cold fluid is replaced by a fluid of the desired crystallization temperature, as soon as this temperature is reached in the center of the sample, where a thin thermocouple is placed. After a sufficient waiting time the less seriously supercooled samples also solidify. This means that a second quench is not required in these experiments. One can obtain suitable cross sections by cutting the samples perpendicular to their axis. From the number of dissected spherulites, as counted in the unit surface of the cross-section near its center, the desired number density per unit volume is obtained by raising the count to the power $^3/_2$. In this way one obtains for i-PP number densities of nuclei which increase by a factor of 10^5, when the temperature is lowered from 125 to 85 °C.[6]

For a determination of the influence of flow on the number density of nuclei, a quite different experiment is required. For the attainment of shear rates of relevance in processing,

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† Dedicated to the research groups in Amherst,[1] Leuven, and Sophia Antipolis.[2]

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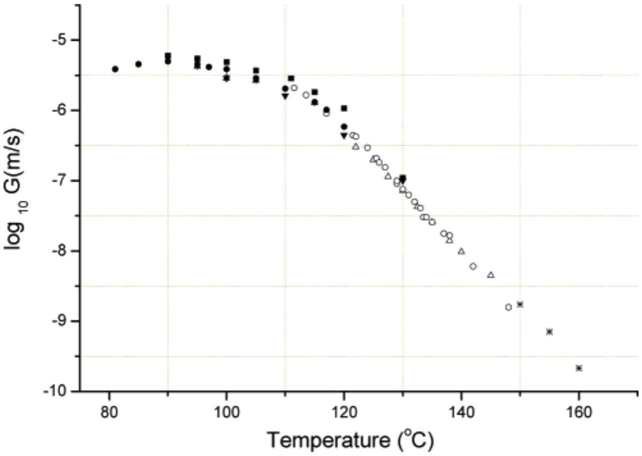

Figure 1. Compilation of growth speeds for the α-modification of i-PP vs temperature from various sources. Literature data are indicated by open symbols [Lovinger et al., 1977 (rhombs), Padden and Keith, 1959 (circles), von Falkai, 1960 (triangles), Olley and Bassett, 1989 (stars)]. Values obtained in the Linz laboratory are given by closed symbols [β-trans-crystallization with the aid of Lovinger's cone angle (closed squares), Ratajski, 1993; from microtom slices (closed circles), Ratajski and Janeschitz-Kriegl, 1996; from DSC according to Eder's method (closed triangles pointing upward), Paulik, 1993; (closed diamonds) Ratajski and Janeschitz-Kriegl, 1996; from so-called incubation times (closed triangles pointing downward), Ratajski and Janeschitz-Kriegl. Reproduced with permission from ref 5. Copyright 1996 VCH−Wiley.

rectilinear flow is required. This type of flow is created in a sandwich construction, in which the melt is sheared between parallel glass plates.[7] The distance between these plates was chosen to be about 1 mm. In fact, a rapid quench to the temperature of the experiment is no longer necessary in these experiments. The reason for this alleviation is the fact that, because of the effectiveness of the flow, the experimental window can be shifted to higher temperatures, where the kinetics are still extremely sluggish, as long as the melt is not moved.

By a measurement of the time dependent optical retardation coming up after the cessation of flow, a first impression can be obtained about the processes taking place in the quieted down melts. For the same purpose, quite rapid extensional flow was also applied.[8,9] From the cross sections of the samples, the tremendously increased number densities of nuclei can be determined, as just described. Also, interrupted flow through ducts of rectangular cross-section (of large aspect ratio) has been used. See for instance refs 10 and 11. In these earlier papers, however, only the highly oriented surface layers were investigated. In the sandwich apparatus and in the extension rheometer, the deformation rates were insufficient for the formation of highly oriented structures.

The usefulness of (SALS) for an investigation of transient situations, as occurring after cessation of flow, has been demonstrated in two interesting papers, namely a paper by Devauxet al.[2] (at Sophia-Antipolis and Leuven) and a paper by Pogodina et al.[1] (at Amherst). A commercial rotational plate−plate rheometer was incorporated in this work (the Linkam unit containing two parallel glass plates). The mechanical treatment between rotating glass plates cannot be as effective as in rectilinear flow. Nevertheless, the results can readily be compared. This is due to a discovery made in Linz, namely that a forceful shearing for a short time is equivalent to a less forceful shearing for a longer period. The only condition is that the total specific work, as applied to the sample, is practically the same[7−9,12] (see also Figure 2).

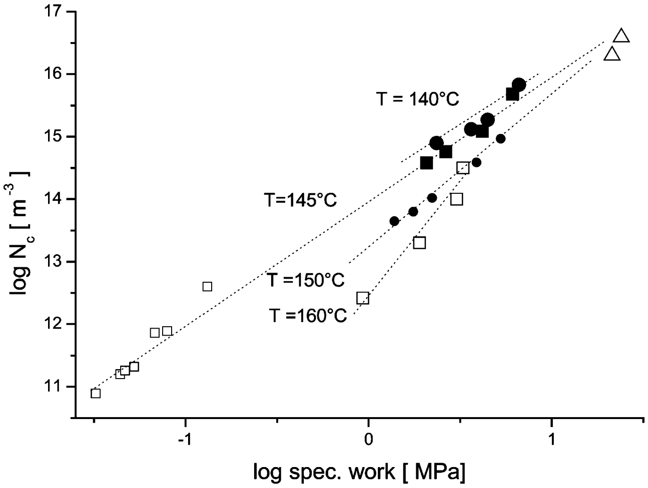

Figure 2. Double logarithmic plot of the number density of nuclei vs the specific mechanical work applied to an industrial PP for several indicated temperatures, according to ref 7. Left corner: from extensional flow at 145 °C, also according to ref 9. Upper right corner from duct flow experiments, transition to shishs. Reproduced from refs 7 and 9. Copyright 2003 and 2004 Springer Verlag and Society of Rheology.

2. Application of Realistic Mechanical Loads

Figure 1 shows the temperature dependence of the growth speed of α-spherulites of i-PP in the quiescent melt.[5] The results of many authors are compiled in this figure. The growth speed at 150 °C, which shows up in the right corner, has been determined by Olley and Basset.[13] To obtain more nuclei, on which growth could be observed, the sample was temporarily quenched to a lower temperature. Up to the maximum, the growth speed increases by four decades. Details can be found in ref 5.

Figure 2 is from the research group in Linz. In a double logarithmic plot, the number density of nuclei is plotted against the specific work, as applied at several degrees of undercooling. An industrial PP of $M_w = 370\,000$ and $M_w/M_n \approx 5$ has been used. However, as shown in ref 9, these results are almost independent of the molar masses, if the specific work is used as the independent variable. On the extended time scale of waiting, all spherulites start growing simultaneously. This is because of the fact that the shearing or stretching times are so short compared with the growth times that are experienced after cessation of flow. As a consequence, the spherulites achieve a uniform size. However, because of the low growth speeds, which prevail as soon as the melt is quieted down again, one sometimes has to wait for a very long time for the final solidification. Cross sections are made from the solidified samples in order to determine the number density of nuclei, as explained in the Introduction.

Although Figure 2, which is taken from ref 7, has before been reproduced twice (refs 12 and 14), this figure will be needed also in the present paper. It also shows that the results are temperature dependent. The obtained number densities, however, seem to converge at high values of the specific work. At low specific works, the number densities, as obtained in extensional flow,[9] are given. At the highest specific works, the number densities, which are obtained in duct flow experiments, are given (see the two points given by open triangles). The transition to a highly oriented structure just occurs between these two points. This effect is depicted in Figure 3, which is taken from the work by Liedauer et al.[15] The pertinent experiment was something like an isothermal injection molding cycle at 150 °C. Because of the high temperature, the waiting time was

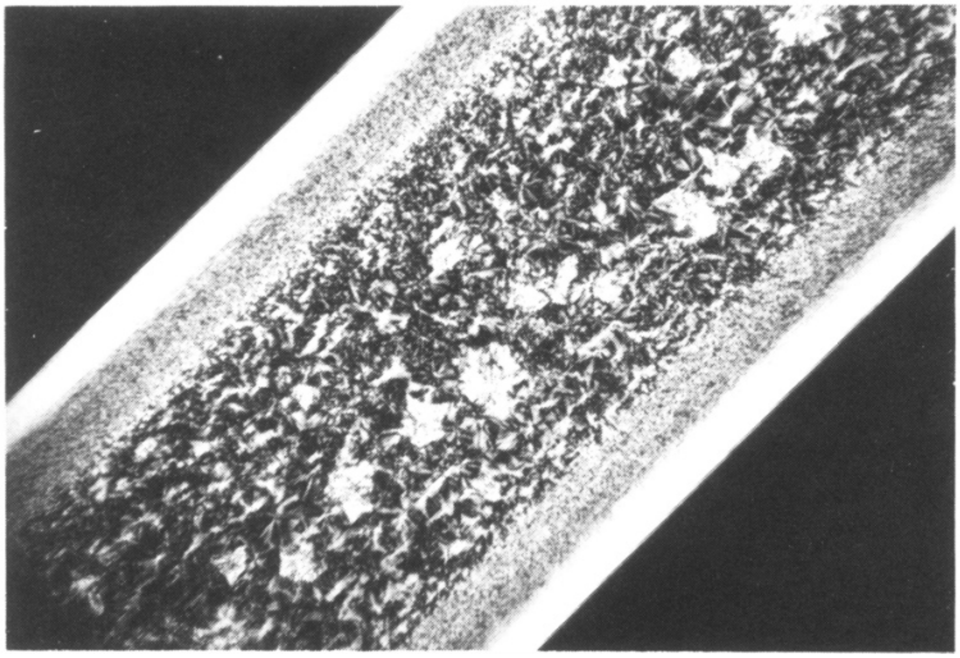

Figure 3. Cross section through a sample of an industrial PP after short term extrusion of 15.6 s at a temperature of 150 °C, with a shear rate of 68 s^{-1} at the large side wall of a duct of rectangular cross section of large aspect ratio. Reproduced with permission from ref 15. Copyright 1995 Hanser Verlag.

particularly long. In this picture, one notices three zones, a highly oriented zone near the duct wall, an intermediate fine grained zone, and a coarse grained spherulitic core. From the shearing time and from the local values of shear stress and shear rate, which occurred during the flow at the location of the transition from the highly oriented zone to the fine grained zone, the specific work was calculated by Dr. Ratajski and used in the graph of Figure 2 together with the number of grains.[7] For this purpose, the rheology of the still homogeneous melt could be used. This assumption is certainly permitted because of the extremely slow growth processes, which become of importance only after the cessation of the flow. (See also Figure 4.)

One of the most remarkable facts expressed by Figure 2 is the highly nonlinear relation between the number density of nuclei and the specific work. In this connection, one should not forget that the specific work is proportional to the shearing time or to the total shear, if the shear stress is kept unchanged. On the double logarithmic plot the slopes of the lines are between 3 and 4. The reader should be reminded here of the early work by Wolkovicz.[4] This nonlinear behavior, which does not match with any of the theoretical papers published so far—including those using entropy changes—was reason enough for the formulation of a new concept on the “transformation of dormant nuclei by the action of flow”. This concept was published very recently by Janeschitz-Kriegl and Ratajski.[12] In the more general case, when various stresses are applied, the shearing time can no longer be considered as the independent variable. A justification for the use of the specific work can only be derived from experiments. This fact will be discussed at the end of the present paper in connection with a special result from the Amherst group. In fact, the temperatures for the usual experiments always lay below the melting temperatures of the spherulites. Under this condition, the relaxation times of the structure elements, as created by the flow, are always extremely long. However, this means that the short loading times become irrelevant. Exceptions exist only for temperatures very close to the equilibrium melting point, where the relaxation times of structure elements, which show a much larger temperature dependence, become comparable with those relaxation times that govern the rheology of the undisturbed melt. So far those important (fast shearing) experiments have been carried out only in Linz.[3,16,17]

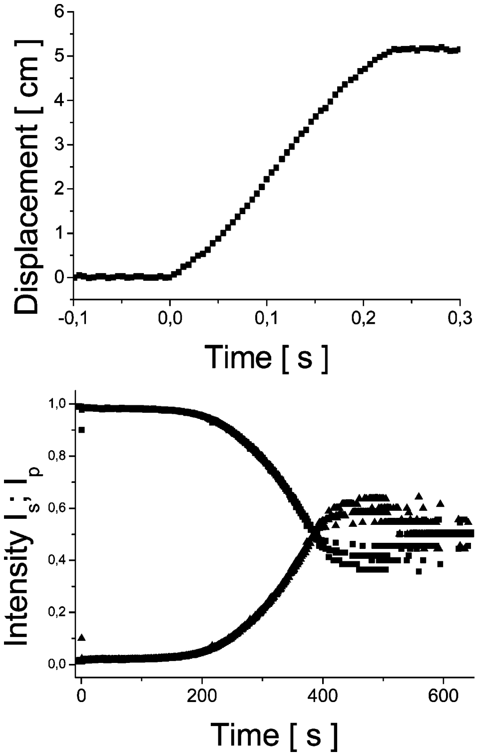

Figure 4. Documentation of a special shear treatment of an industrial PP at 150 °C and a shear stress of 106 kPa. Upper part: displacement of the upper glass plate of a sandwich type rheometer vs shearing time. A total shear of $\gamma = 50$ is reached after 0.2 s. Lower part: temporary optical retardation, as recorded as a function of time after cessation of the flow. The curve starting at a value of one gives the reduced intensity with parallel polars. The curve starting at zero gives the reduced intensity with crossed polars. A crossover occurs at almost 400 s. The large scatter on the right side is because of the low absolute intensities, which are the consequence of the increasing turbidity. Reproduced with permission from ref 12. Copyright 2005 Elsevier.

Finally, Figure 4 is taken from the just mentioned work.[12] It furnishes a remarkable insight into the crystallization process occurring after the cessation of short term shearing. For the purpose the i-PP of Figure 2 was used at 150 °C and at a shear stress of about 100 kPa. In the upper part of the figure, the displacement of the upper glass plate is shown. It occurred within 0.2 s over a distance of 5 cm, which means a total shear of $\gamma \approx 50$. The lower part of the figure shows the subsequent development of the optical retardation. The measured intensities are reduced with respect to the total transmitted intensity. The reduced intensities between crossed polars (lower curve) and between parallel polars (upper curve) are recorded as functions of time. Remarkably, it takes almost 200 s until any change in the optics can be noticed. After this time span, the curves converge to a crossover point at about 400 s. A maximum in the curve for crossed polars and a corresponding minimum in the curve for parallel polars is found at about 500 s. Of course, this phenomenon is blurred by the decreasing intensities measured as a consequence of the upcoming turbidity. Nevertheless, one can conclude that at about 400 s the system develops oriented anisotropic domains, which cause the said crossover. Finally, however, one obtains complete depolarization, which is characterized by a common value of one-half for both reduced intensities. In fact, a purely spherulitic structure is found later in the cross section of the solidified sample with no indication for a state of orientation. This means that the perceptible anisotropy, which is finally drowned in the depolarization, comes up during an intermediate process by the nestling of neighboring parts of molecules to elongated and oriented nuclei, which are born during the flow but which are too tiny to cause a measurable anisotropy by themselves. (See the long period of no measurable anisotropy, which must be a consequence of the low growth speed in the quieted down melt. This long period is remarkable in view of the short time of shearing of only 0.2 s.)

Finally an enlightening calculation will be carried out. It is based on the results of Figures 1, 2, and 4. In the caption to Figure 4, one reads that the depicted results were obtained at a shear stress of 106 kPa. If this value is multiplied by the total shear of $\gamma = 50$, one obtains for this experiment a specific work of $w = 5.3$ MPa. However, log 5.3 = 0.72. From Figure 2, one reads for this value of log w a number density of nuclei of $N \approx 10^{15}$ m^{-3}. In Figure 1 a value of $G \approx 1.8 \times 10^{-9}$ m s^{-1} is found for the growth speed of spherulites in a quiescent melt of i-PP at 150 °C. If the nuclei are there from the beginning, one finds, according to Kolmogoroff[18] (see also ref 5), a "space covering" ξ_g of

$$\xi_g = 1 - \exp\left[-\frac{4\pi}{3}NG^3t^3\right] \tag{1}$$

where t is the (waiting) time, as counted in our case from the moment of cessation of flow. Space covering (impingement of still loosely structured spherulites) is practically complete, if the expression in the square brackets of eq 1 is equal to -1. In this way a waiting time of 3500 s may be calculated, if the above data are used.

Looking at Figure 4, one observes that depolarization begins quite early, when compared with the just mentioned waiting time. In the course of the maturing process, a neighborhood of higher anisotropy seems to be formed around the primary nuclei, which appear during the previous period of flow. Apparently, these primary nuclei are oriented in the flow direction, but possess too low an optical anisotropy to be discovered. The finally obtained spherulitic structure is shown in a figure in ref 12. No signs of anisotropy can be seen in this picture. The fact that under this condition impingement is complete can be seen in many of our pictures.

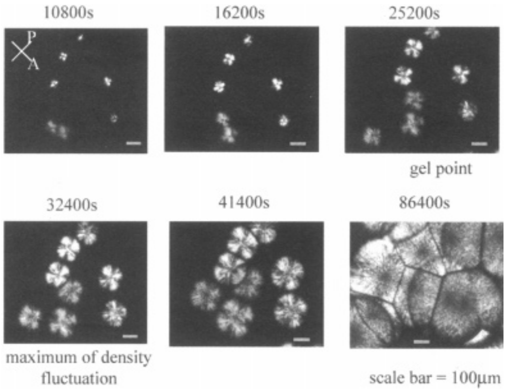

Figure 5. Development of spherulites, as observed in a polarizing microscope, during quiescent crystallization of an industrial PP at 148 °C. Scale = 100 μm, sample thickness 200 μm. Reproduced with permission from ref 1. Copyright 2001 Elsevier.

It may be instructive to realize that, in general, the well-known Avrami plot,[19] as based on equations similar to eq 1, cannot yield these subtle insights, just because there are no direct measures of crystallinity that are sensitive enough for the purpose. Indirectly, the occurrence of impingement can only be deduced from calculations with the aid of eq 1, on condition that the necessary kinetic data are available. The apparent failure of the Avrami plot at long times has nothing to do with a failure of impingement. It has to do with the maturing of the spherulites. A series of other objections against the use of the Avrami plot has been summarized by Eder.[20]

3. A Transparent Rotational Rheometer and Small Angle Light Scattering (SALS)

In Figure 5, as taken from the paper by Pogodina et al.,[1] six stages of the progress of (secondary) crystallization are shown for the quiescent undercooled melt (with $T = 148$ °C) of an industrial PP similar to our polymer. Because of the relatively high temperature, this progress was extremely slow. After 25200 s the authors observed a gel point, which indicated the formation of a continuous network.[21] The nature of the necessary junctions is still a point of discussion. It may be that dormant nuclei, as defined in ref 12, are at some of the junctions of the network. For our present purpose the photograph obtained after 32400 s is of a greater importance. The authors report that at this stage the invariant Q_η of SALS, which is responsible for density fluctuations, shows a maximum in its dependence on time. (For the theory of SALS see Stein and Wilson[22] and also refs 1 and 2.) It appears from the figure that at the time of this maximum about half of the volume was occupied by spherulites. This seems quite understandable. At longer times the still unstructured parts of the volume take over the role, which the spherulites have at shorter times, in a kind of reciprocity.

In Figure 6, which is taken from the paper by Devaux et al.,[2] the time dependences of both invariants of SALS ($Q_\eta(t)$ for the density fluctuations and $Q_\delta(t)$ for the fluctuations of orientation) are depicted for the quiescent melt of another, but also quite similar PP. The pertinent data were obtained at a temperature of 136 °C. From this picture we learn that the invariant $Q_\delta(t)$ became noticeable only after about 800 s, whereas $Q_\eta(t)$ was there already after about 200 s. $Q_\delta(t)$ starts to grow only, when $Q_\eta(t)$ is already at its maximum. In this picture there is also a third line showing the increase of the "Depolarized Light Intensity" (DLI). This function shows a still slower increase.

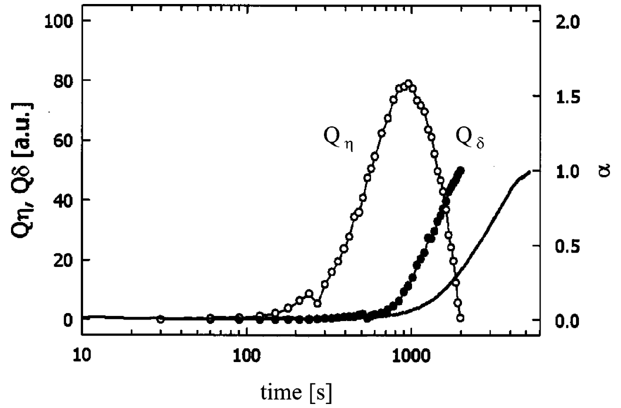

Figure 6. Evolution of the scattering invariants Q_η and Q_δ in a quiescent melt of an i-PP at a temperature ot 136 °C according to ref 2. The full line gives the course of the "Depolarized Light Intensity" α. Reproduced with permission from ref 2. Copyright 2004 Springer Verlag.

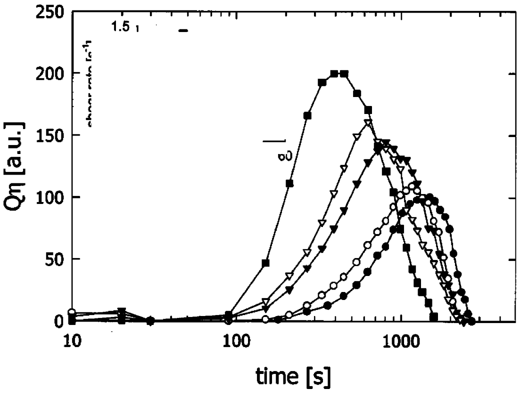

Figure 7. Effect of the shear rate on the evolution of the scattering invariant Q_η, according to ref 2. An industrial PP was investigated at 136 °C. Results are given for the quiescent melt and for four different finite shear rates: closed circles, 0 s^{-1}; open circles, 0.2 s^{-1}; closed triangles downward pointing, 0.8 s^{-1}; open triangles downward pointing, 1 s^{-1}; closed squares, 1.4 s^{-1} . The values of the scattering invariants are related to the transmitted light intensity at scattering angle 0°. Reproduced with permission from ref 2. Copyright 2004 Springer Verlag.

However, this function will only be scrutinized in the discussion of the present paper.

Now we switch to the shear induced behavior, which has been investigated by both groups of authors with the aid of the Linkam unit, which is a rotational rheometer of the parallel plate type with plates made of glas. Figure 7, which is taken from the paper by Devaux et al.,[2] shows the time dependent behavior of $Q_\eta(t)$ for the permanently quiescent melt and for four different previous shear treatments of the same polymer at 136 °C. Shearing time was in all cases $t_s = 30$s. Shear rates were increased in four steps from 0.2 to 1.4 s^{-1} . The effect of shearing on the position of the maximum was dramatic. Unfortunately, the authors had no possibility to compare these positions with the outcome of an independent calculation. However, such a calculation can be carried out with the aid of the data given in our Figures 1 and 2, if eq 1 is used.

For the purpose the viscosity of the fluid was guessed to be 10 kPa s at 136 °C. Shearing time was $t_s = 30$s. For a shear rate of 2 s^{-1} , which is a little higher than the highest shear rate quoted in Figure 7, the specific mechanical work can be calculated. One obtains $w = 1.2$ MPa. Using Figure 2 (with log 1.2 = 0.08) one guesses a number density of nuclei $N \approx 3.14 \times 10^{14}$ m^3 for this specific work at 136 °C. At this temperature, a growth speed of $G = 2.3 \times 10^{-8}$ ms^{-1} is found

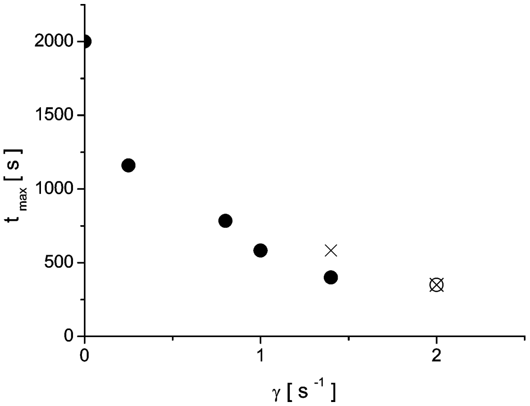

Figure 8. Time t_{max} , where the maximum of Q_η occurs as a function of the shear rate, if an industrial PP is investigated at 136 °C after a shear treatment of 30 s. Closed circles are according to ref 2. The crosses give the times for half space covering, as calculated with the aid of data given in Figures 1 and 2.

for the quieted down melt. Because 0.5 ≈ exp(−0.7), one can now calculate the waiting time for half space covering, if a value of −0.7 is used in the expression between square brackets of eq 1. One obtains in this way a waiting time of $t \approx 354$ s. Obviously this waiting time is much shorter than the waiting time calculated for 150 °C. This effect is certainly caused by the difference in the respective growth speeds, which enter eq 1.

In Figure 8, the waiting times for the maxima in Figure 7 are plotted against the shear rates. Our calculated point for a shear rate of 2 s^{-1} is inserted as an encircled cross into the figure. The position of a second cross for a shear rate of 1.4 s^{-1} is placed with the assumption that, to a first approximation, the specific work is simply proportional to the square of the shear rate and that the number density increases with the third power of the specific work. In fact, one will not find measurement points in Figure 2 at—e.g., 140 °C—for the corresponding low specific work. This fact is the reason why I desisted from calculating the positions for lower values of the shear rate. Nevertheless, my two points (crosses) appear to fit quite nicely into the picture, if one admits that a somewhat different polymer was used. Anyway, the consideration, which I gave at the end of section 2, seems correct.

However, there are still two other places, where the Linkam experiments concur with the results obtained in Linz. To show this, Figure 9 is introduced. It is taken from the paper by Pogodina et al.[1] In this figure, one can observe the development of shish-kebabs, as caused by lateral growth on the threadlike precursors. These precursors were formed in a shear treatment in the Linkam unit, as carried out at 148 °C. As already mentioned, the PP sample of the authors should also be quite similar to ours. The total shear was surprisingly high for this machine, namely $\gamma = 600$. The shear rate was 10 s^{-1}, and the shearing time was 60 s. The waiting times quoted below the pictures include the shearing time of 60 s. For us in Linz, the most important step is the calculation of the corresponding specific work.

From Figure 4 of ref 1 a viscostity of 4.25 kPa s is deduced for a shear rate of 10 s^{-1}, if the Cox−Merz rule is applied. The product of viscosity, shear rate, and total shear gives a specific work of 25 MPa. Remarkably, practically the same specific work was found in our early work for the transition from the fine grained layer to the highly oriented layer, as shown in Figure 3 of the present paper. (See the position between the uttermost two points in Figure 2, as presented by the open triangles.)

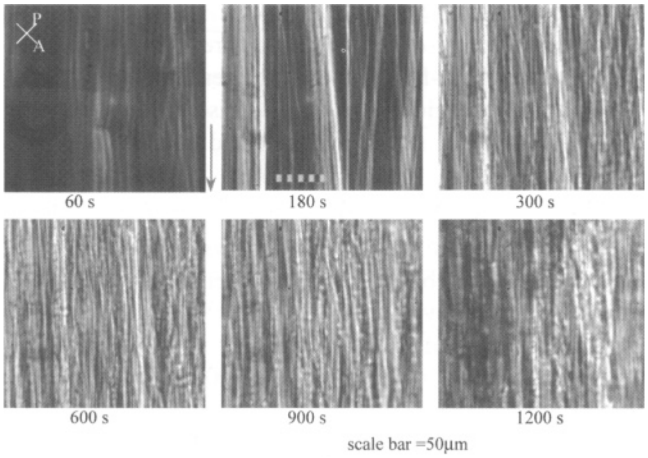

Figure 9. Microscopic images taken at different times after cessation of flow at 148 °C for a crystallizing melt of an i-PP of $M_w = 3.5 \times 10^5$, according to ref 1. The applied shear rate was 10 s^{-1} , shearing time was 60 s. A total shear of 600 was achieved in this way. The lateral growth of shishs, as being created during the shearing, can be observed. The shearing time of 60 s must be subtracted from the waiting times quoted below the pictures. Reproduced with permission from ref 1. Copyright 2001 Elsevier.

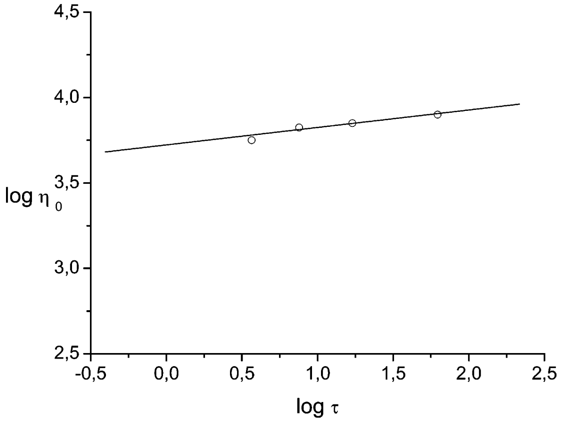

Figure 10. Double logarithmic plot of zero shear viscosity vs relaxation time of oriented semicrystalline surface layers, both as functions of temperature, for an industrial PP. Temperatures from left to right: 210, 205, 200, 195, 190 °C. (The relaxation times are deduced from the decay of the birefringence observed in samples quenched after increasing time spans). Cf. also ref 17 for PB-1 data. The shear rates applied for the creation of the surface layers were between 400 and 1300 s^{-1}. Shearing times (as residence times in the fluid layers of the duct flow) were between 4 and 1 s. Reproduced with permission from ref 17 and H. Wippel's Diploma Thesis. Copyright 1990 Pergamon Press.

Finally, it should be mentioned that Pogodina et al.[1] obtained shishs also at 190 °C. These shishs, however, are reported to relax after cessation of flow within 3−4 s. As a matter of fact, such phenomenona have been reported by the research group in Linz already as early as 1987[23] and described more extensively in a paper of 1989[16] and in the first review.[3] The present Figure 10 is reproduced from this review. In this figure, a double logarithmic plot is given of the zero shear viscosity vs the relaxation time of the shishs for the range of high temperatures. From the right to the left the points relate to temperatures from 190 to 210 °C. If the relaxation times of the shishs would follow the temperature dependence of the viscosity, a slope of 1 should be obtained. In reality, however, this slope is much lower. The relaxation time of the shishs shows a much stronger temperature dependence. In fact, quite recently, we were able to calculate an activation energy of 334 kJ/mol for the decay of the structure elements in the high temperature range, whereas the corresponding activation energy for the viscous flow of the melt is only 44 kJ/mol. (These energies hold per mole of the repeating unit.) These results point to a process of disintegration of aggregates, which differs considerably from the disentanglement process, which is of influence in the stress relaxation of the clean melt. A similar behavior has been found recently also for a polybutene-1 sample.[17] Because of the extremely high temperature dependence of the relaxation times of the shishs one finds extremely high relaxation times at lower temperatures, where most of the investigations were carried out so far. After their formation the shish-kebabs are practically stable at those lower temperatures on the time scale of the experiments. (See also a paper by Alfonso.[24])

4. Discussion

Remarkably, for the effect of a strong flow at a high temperature, (see Figure 4 with a shear rate of 250 s^{-1} , a shearing time of 0.2 s, and a temperature of 150 °C), a waiting time of 3500 s is calculated for complete space covering. At practically the same temperature (148 °C) Pagodina et al.[1] find a waiting time as high as 86400 s for a quiescent melt. This means that flow has reduced this waiting time by a factor $^1/_{25}$. If the same growth speed is assumed for both processes because of equal temperature, irrespective of the fact that one melt was only quieted down whereas the other melt was permanently quiescent, the reason for this factor must exclusively lie in the differing nucleation densities. However, these densities enter eq 1 as their third root, which means that the increase of the nucleation density, as caused by the said flow, must be enormous. The difficulty is only, that for a permanently quiescent melt no direct measurement of the number density of nuclei exists for 150 °C. At 130 °C one finds 10^{10} m^{-3},[6] a value that is certainly too high for our purpose. After the said flow treatment at 150 °C, one finds a value of about 10^{15} m^{-3}. If, nevertheless, the ratio of these values is calculated, and the third root is taken, one gets a factor of $^1/_{47}$. This factor is of the right order. In reality, however, this factor should be much smaller in view of the fact that the number density of the quiescent melt at 150 °C would turn out to be smaller. Without doubt we have to do with an insufficient accuracy of the determination of the number density of nuclei in quiescent melts at high temperatures. Anyway, however, this result shows that the flow treatment is capable of increasing the number density to a surprising extent.

In ref 2, also the time dependence of the "Depolarized Light Intensity" (DLI) was measured. This method goes back to an idea by Magill.[25] The authors of ref 2 have put the polarizer in a direction parallel to the predetermined direction of flow. In this way, the crossed polars were in an extinction position with respect to the upcoming orientation. So only the depolarization proper could be detected. A look on Figure 4 of the present paper gives an indication of the time, at which maturing can occur at 150 °C. This maturing seems to start earlier than complete space covering occurs. A maturing can also be seen on Figure 6, as taken from ref 2. However, at this lower temperature of 136 °C maturing starts later, namely after space covering. This can be deduced from the course of DPI. Such an investigation must not be without significance. It probably points to the fact that the primary growth process and the maturing process do not show the same temperature dependence. At higher temperatures, the maturing process seems to be faster than at lower temperatures. Such an observation would concur with the experience that usually the degree of crystallinity of the final product decreases with increasing cooling speed. The process of maturing, which is relatively slow at lower temperatures, can probably be followed also by isothermal DSC, at least in a sample which has not been sheared.

In this connection the question arises, which fraction of latent heat will be evolved during the early stages of crystallization, when the loosely structured spherulites grow, and which fraction will be evolved during maturing. This question seems of importance also for an understanding of the heat transfer process, which can seriously be retarded by the evolution of latent heat. One question arises, for instance, about the temperature range in which oriented structures are formed during injection into a cold mold. Can latent heat be disregarded during the creation of the first shishs?

Interestingly enough, the relatively fast primary stages of crystallization—formation of a great number of "pointlike" nuclei or of shishes—determines the final structure of the sample. Maturing processes can only stabilize such a structure. The interaction with heat transfer only lies in the question about the temperatures, where these first stages of crystallization take place. For optimists in the field of numerical simulation of, e.g., the injection molding process of crystallizing polymers one can only emphasize that knowledge of the details of the process is still insufficient. Also, polypropylene is an extremely friendly polymer for the required investigations. One can show, for instance, that the overall crystallization speed of linear polyethylene in the relevant temperature range is a factor of 100 faster.[26,27] How can one manage to develop a similarly detailed vision on the behavior of this polymer? As a consequence, trial and error still governs this field a great deal.

Interestingly enough, Samon et al.[28] have recently published a note which shows that, independent of the kind of the polymer and of temperature, only the total deformation is responsible for the onset of crystallization in melt spinning. Many aspects of the present consideration are in accord with this result: Processes are not thermally activated (see the second and third paragraphs of section 2). Structure elements once formed do not relax to any extent, if the temperature is below the melting temperatures of spherulites (see the end of section 4). This latter fact will cause the independence of the kind of polymer. However, in our short term mechanical loading experiments, we only found that the multiplication of nuclei is governed by the specific work. In the note of the above authors also the lateral kebab growth, as stimulated without any doubt by the stretching flow, can be predominant in the final phase of solidification.

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