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ORIGINAL CONTRIBUTION

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Flow as an effective promotor of nucleation in polymer melts: a quantitative evaluation

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Dedicated to Prof. D. Heikens, Eindhoven.

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Abstract An apparatus is presented which enables the application of defined portions of mechanical work to the polymer sample in its state of undercooled melt. For the purpose mainly intermittent shear creep is used. Results are presented for an industrial grade of polypropylene. A three-dimensional picture is presented, in which the resulting numbers of nuclei (per unit volume) are plotted against two responsible parameters: crystallization temperature and mechanical work. With *decreasing temperature* and with *increasing mechanical work* the number of nuclei increases by many decades.

At sufficiently high mechanical loads a transition to thread-like precursors (“shishs”) has been observed previously. Oriented structures (kind of “shish-kebabs”) are formed in this way. The periods of shearing applied have always been extremely short compared with the time until crystallization becomes observable. In this way an accumulation of various processes could be avoided. The description of shear induced crystallization, as previously given, is modified in the light of the present results.

Keywords Flow · Promotor · Nucleation · Polymer melt · Evaluation

Introduction

It has become well known that flow has an enormous influence on the nucleation processes in undercooled polymer melts. A first, discontinued series of pertinent papers is already quite old (Haas and Maxwell 1969; Wereta and Gogos 1971; Lagasse and Maxwell 1976). In these papers the undercooled polymer melts were sheared until solidification occurred quite abruptly. Such extreme situations, however, are not suitable for a more detailed study. In the present laboratory slightly undercooled melts of i-PP were subjected to rather strong but intermittent duct flows. Highly oriented zones were created in this way near the duct surfaces as in injection molding, with one distinctive feature: our experiments were isothermal. Because of the short term shearing this method enabled a separation into more elemental processes (Eder et al. 1989, 1990; Eder and Janeschitz-Kriegl 1997; Liedauer et al. 1993; Jerschow and Janeschitz-Kriegl 1996, 1997; Monasse 1995; Kumuraswamy et al. 1999, 2000). The purpose of the present investigation will be to close a large gap in our knowledge between what happens in the said more extreme situations, where kind of shish-kebabs are formed (see also Keller and Machin 1967; Keller and Kolnaar 1997), and in a permanently quiescent melt. Preliminary initiatives were taken in this respect by Wolkowicz (1978) and Tribout et al. (1996).

It seems important that the mentioned investigations could all be carried out successfully at low degrees of undercooling under isothermal conditions. The chosen “crystallization temperatures” could be reached by slowly cooling the available quiescent melt from a temperature well above the thermodynamic melting point (Marand et al. 1998), where nuclei from previous crystallization processes were destroyed. The slow cooling rates are permitted because of the fact that the growth rates of spherulites are extremely low in the range of mild undercooling, adjacent to the melting point (Gandica and Magill 1972; Ratajski and Janeschitz-Kriegl 1996). Because of the occurrence of the third power of these growth rates in the kinetic equations for quiescent melts (see, e.g., Avrami 1940), the corresponding crystallization kinetics are extremely sluggish in the temperature range passed during the said cooling. This is very fortunate because a rapid quench cannot be carried out in any equipment appropriate for the creation of flow.

The thermal situation changes drastically if, for comparison, the number of nuclei is to be investigated in a permanently quiescent melt. In fact, interesting numbers of nuclei (of the athermal type; see Janeschitz-Kriegl et al. 1999) are found in quiescent melts of – say i-PP – only at drastic degrees of undercooling. However, in this range of lower temperatures the growth speeds of spherulites have become many decades higher, as compared with the those found in the range of mild undercooling (Ratajski and Janeschitz-Kriegl 1996). However, this means that the crystallization kinetics are no longer sluggish. If a melt is cooled down slowly to the desired low "crystallization temperature", considerable crystallization starts long before this temperature is reached. As a result one gets a mixture of larger and smaller spherulites which started growing at different times. Only after a sufficiently rapid quench spherulites of uniform size are obtained. Their number per unit volume agrees with the number of (athermal) nuclei per unit volume characteristic for the chosen crystallization temperature. For the purpose, some appropriate quenching experiment (see Janeschitz-Kriegl et al. 1999) is required.

In that which follows, a machine, which was designed for a fast response to the applied shear stress, will be described in more detail. Other equipment, e.g., for rapid quenches or for the application of extensional flow, will be described only verbally. In fact, they have been described earlier or will be described in more detail in subsequent publications. The comparison with results obtained in quiescent melts will be extremely interesting: With the application of moderate amounts of mechanical work (to the unit volume), at relatively mild degrees of undercooling, one obtains already considerable numbers of nuclei, which are comparable with those obtained in quiescent melts at harsh degrees of undercooling of more than one hundred degrees centigrade (see Fig. 5). A double logarithmic plot, as given in Fig. 6, more clearly shows the tremendous increase of the number of nuclei with the mechanical work applied. This plot suggests an accumulation of rows of nuclei, as found previously by Keller and Machin (1967), into "shishs" (thread-like precursors), if the applied work is large enough.

Apparatus

In contrast to previous investigations, where extrusion through a duct of rectangular cross-section of large aspect ratio was used, for the present investigation an apparatus akin to the "sandwich-rheometers", as described by Laun (1982) and by Koran and Dealy (1999) was used. The design of our machine is described in Fig. 1.

A strip of the polymer is cut from a slab produced in a press. Its thickness is chosen to be about 1 mm, length and width being about 10 cm and 1 cm, respectively. This strip is inserted at PM into the apparatus described in Fig. 1. It is sandwiched together with two Teflon strips on either side (for keeping the correct distance) between a bottom plate of glass PG and the glass slide GS. A weigher WE (kind of letter-weight) is put on the glass slide in avoiding a detachment of the polymer during the horizontal movement of the slide. With the aid of the furnace and the heated cover the polymer sample is melted and kept for some time at a sufficiently high temperature in order to destroy residual nuclei from previous crystallization. (For temperature control furnace and cover are fitted out with thermocouples.)

After this heat treatment the temperature is lowered to the level where the shearing is scheduled to occur. (As already explained in the introduction, no fast quench is required because of the fact that crystallization in the quiescent melt is extremely sluggish at temperatures higher and equal to the temperature level of interest.)

As a next step the compressed gas from the reservoir is suddenly admitted to the pneumatic cylinder with the aid of an electrically activated magnet valve MV. The reservoir is big enough for keeping the gas pressure practically constant. The distance, over which the glass slide can travel, is determined by the starting point of the piston: the closer the initial location of the clamp is chosen to the front of the furnace, where it is predestined to be arrested, the shorter the said distance will be. The displacement transducer DT monitors this movement. The higher the chosen gas pressure, the higher the shear stress to which the polymer melt will be exposed during its deformation. In principle, the corresponding shear rates can be read from the monitored course of the displacement with time.

The function of some other parts of the machine, which are indicated in Fig. 1, must still be explained. Near the end of the piston there is a yoke Y (in a horizontal position). At both ends of this yoke ropes are tied up. As one can see only on the side turned to the observer, these ropes run over a pair of wheels CW solidly interconnected by the axle, on which they are mounted. In addition, these wheels are connected also by a rung RU, which is in its lowest position, before the experiment is started. On this rung an adjustable weight (of sometimes many kilograms!) is suspended with a hook, not shown in the picture. This arrangement has been designed because during the shearing the sheared surface of the polymer sample decreases. In fact, the polymer melt behaves more like a fluid than a rubber-like solid. As a consequence, the force on the glass slide must also be adequately reduced during the deformation, in keeping the shear stress constant. The working of the sketched arrangement can best be explained by utilizing the following equation:

$$F_{\mathrm{red}} = \mathrm{P.A.} - \mathrm{M.g.sin}\alpha \tag{1}$$

where F_{red} is the reduced (adjusted) force on the glass slide, P is the (constant) pressure applied to the pneumatic cylinder, A is the area of the piston end surface in the cylinder, M is the mass of the weight, g is the acceleration by gravity, and α is the angle, by which the position of the rung is turned away from its lowest starting position during the period of flow. This starting position is depicted in Fig. 1. If the radius of the wheels is chosen not too small, angle α will never be very large. However, this means that sin α never deviates too much from α itself. In this way the reduction of the

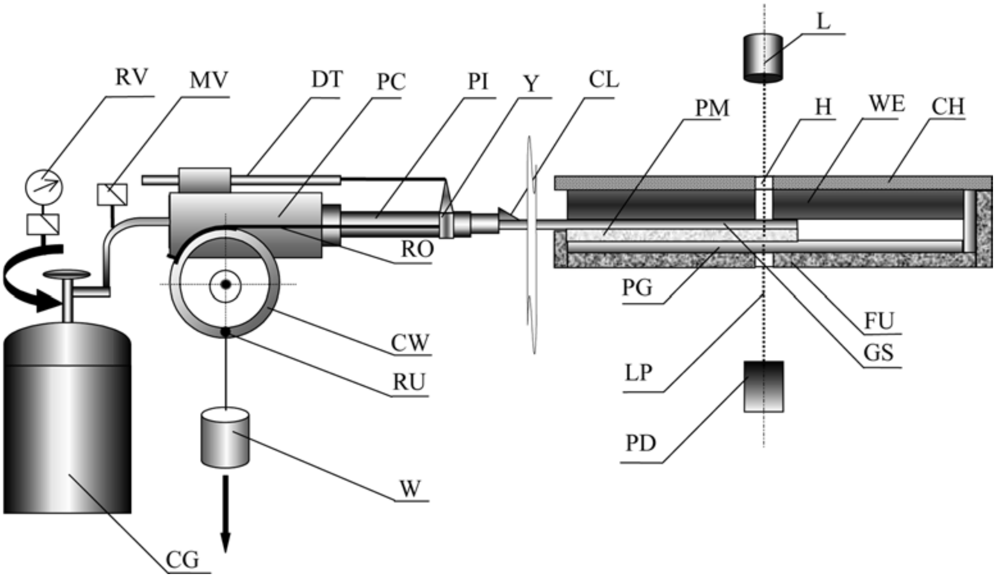


Fig. 1 PM – polymer melt (sandwiched), PG – glass pane, GS – glass slide, FU – furnace, CH – cover with heating elements, WE – weigher with Teflon bed, H – holes, LP – light path for polarizing optics, L – laser, PD – photo diode, CG – big steel cylinder, reservoir of pressurized gas, RV – reduction valve on the inlet pipe to the reservoir for pressure control, gas of higher pressure being provided by a central supply installation, PC – pneumatic cylinder, MV – magnetic valve, PI – piston, DT – displacement transducer, CL – clamp for glass slide, Y – yoke, RO – pair of ropes, CW – "cart wheels", RU – rung, W – adjustable weight. Reservoir and weight are not drawn on scale. The path length of the glass slide is 8 cm

shearing surface is compensated readily. Mass *M*, of course, must always be chosen proportional to pressure *P,* in an adequate relation. The application of the correction given by Eq. (1) appears to be helpful. Without this mechanism of correction the course of the displacement always shows a continuous upwards turn, as can be seen in Fig. 2.

By the application of the said mechanism, however, the displacement clearly straightens out, as can be seen in Fig. 3. In this figure the courses of the displacements are shown for a polypropylene grade characterized below. However, a comparison between Figs. 2 and 3 also shows that an influence of friction cannot be avoided, even if one has to emphasize that, in addition to the application of the weight W (Fig. 1; Eq. 1), the sources for friction were also considerably reduced during extended experimentation, which is expressed by Fig. 3. In fact, one should not overlook that in Fig. 3 a final total shear of the order of 5 was reached at a shorter time than in Fig. 2, notwithstanding the fact that a lower initial shear stress was applied. In coping with these problems the work applied to the unit volume of the sample was calculated with the aid of the following equation:

$$w=\bar{\eta}\int_{0}^{t_s}\dot{\gamma}^2(t)dt, \tag{2}$$

where $\bar{\eta}$ is the viscosity, averaged over the shear rates experienced, $\dot{\gamma}$ is the time dependent shear rate, as obtained from the more or less increasing slopes of the lines in the figures, and t_s is the total time of shearing. One of the advantages of the more recent results, as depicted in Fig. 3, is that a value for $\bar{\eta}$ can be ascribed much more accurately. Also the physical picture becomes clearer, because of the fact that one can claim a certain (nearly constant) shear rate to be responsible.

Through Eq. (1) the shear stress is also known quite well.

The viscosity as a function of shear rate and temperature has been determined in a series of previous experiments in our laboratory as a routine. These results are condensed in the following two equations:

$$\eta(\dot{\gamma})=\frac{\eta_0}{\left[1+(\lambda\dot{\gamma})^m\right]^{\frac{(1-n)}{m}}} \tag{3}$$

which is the well-known modified Carreau equation, where $\dot{\gamma}$ is the shear rate, η_0 is the zero shear viscosity, λ is an adapted time constant, η_0 and λ are temperature dependent, whereas n – Power-Law-index – and m are constants independent of temperature. The pertinent values for the reference temperature of 200 °C ($T_r=473$ K) are: $\eta_0=7244$ Pa, $\lambda=0.52$ s, m = 0,51, n = 0.35.

The temperature dependence is given by the shift factor, which reads for $T_r=473$ K:

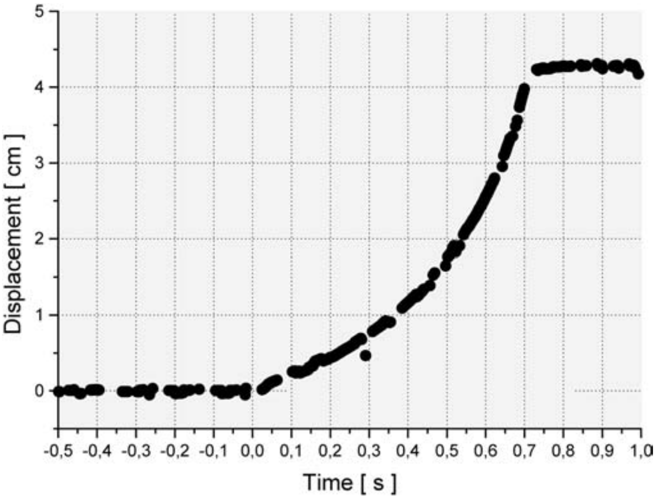


Fig. 2 Piston displacement vs shearing time for PP KS 10 at 145 °C for an initial shear stress of 50,800 Pa, if no correction mechanism is applied according to Eq. (1)

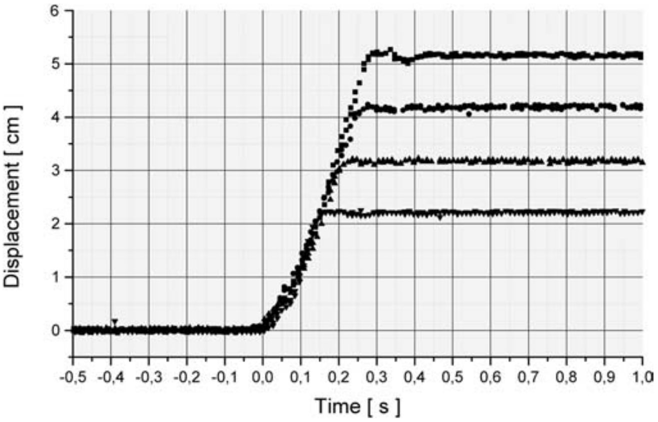


Fig. 3 Piston displacements vs shearing times for PP KS 10 at145 °C for a shear stress of 84,600 Pa, if the correction mechanism of Eq. (1) is used. Various shearing times were applied. The shear rate common to all curves was estimated to be 150 s^{-1}

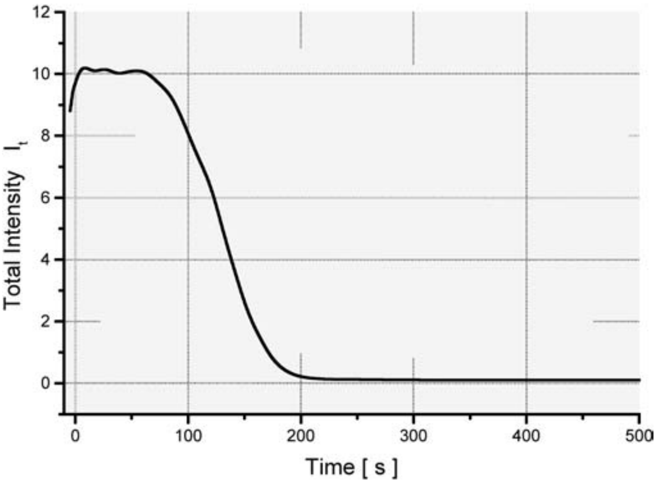


Fig. 4 Total light intensity vs monitoring time at 145 °C for the introduced PP grade. Previous shear stress was 84,600 Pa, and shearing time was 0.25 s

$$\log a_T = 5.5\left(\frac{473}{T} - 1\right) \tag{4}$$

These calculations hold for steady flow conditions. However, if transitional values of η were known, one would obtain only somewhat smaller values for the applied works. However, this would only exaggerate the results shown below.

In this connection one should not overlook the experimental difficulties encountered in a very short term (~0.1–0.3 s), shearing at considerable speeds, if a Spartan equipment is to be used.

Another point of interest is the use of the polarizing optics (see LP in the figure). Its parts are not indicated in the figure. A polarizer is inserted between the laser and the shearing unit. Its direction of polarization is – like that of the laser itself – at an angle of 45° with respect to the direction of flow. Between the lower side of the shearing unit and the location indicated by PD a beam splitter is inserted, so that – with the aid of actually two photo diodes – the intensities of the lights polarized perpendicular and parallel to the polarizer can be monitored separately and simultaneously. By adding up these intensities one obtains the total amount of light transmitted. When this total light starts to decrease noticeably, crystallization is already on the way. In fact, as has been shown elsewhere (Ratajski and Janeschitz-Kriegl 1996), the amount of light lost by lateral scattering increases with the sixth power of time, so that one cannot see an effect in the beginning. The two polarized beams, as emerging from the beam splitter, are only of separate interest, when the sample again becomes birefringent during the course of the crystallization (flow birefringence fades away very quickly after cessation of flow). As is well-known, one needs the separate intensities of these beams for an analysis of the birefringence. However, if no shishs are formed during the flow, no larger birefringence will return after the cessation of the flow. This was the case with our present measurements, which were carried out at shear stresses low compared with those involved in shish formation. Shishs were observed in the cross-sections of solidified samples only occasionally. It follows that those spurious shishs were obviously caused by impurities.

Light scattering is not noticeable immediately after cessation of flow. In fact, the scattering power of the particles, which start growing, is proportional to the square of their volume. However, those small particles could have had just as little an influence on the rheology of the melt during flow. This is one of the essential advantages of our technique. The correctness of this conclusion is made plausible by Fig. 4. In this figure the total light intensity is shown vs time for a sample, which had undergone shearing for only 0.25 s at a shear stress of 84,600 Pa. The light intensity, however, started to decrease only after about 80 s.

The optical situation (return of a considerable birefringence after cessation of flow) becomes more interesting with the application of a sufficiently high shear stress, as has been shown previously for duct flow. The main purpose of the present investigation, however, was to fill the gap at lower shear stresses, where no birefringence returns.

After complete solidification the sample is recovered. This solidification, however, takes some time because of the extremely low growth speed of the spherulites in the quieted down melt at the temperature of the previous shearing. A cross-section is prepared at room temperature in a plane containing the direction of previous flow and the normal to the shearing plane, which has also been called the direction of vorticity. A micrograph is prepared from the obtained surface. In this surface the existing spherulites are cut at varying distances from their centers, which causes a variety of surface areas even if the spherulites would have equal size. (Actually, these spherulites had simultaneously grown after the cessation of flow on the tiny nuclei, which were formed during the period of flow.) Thereupon the number of spherulites per unit surface is counted. An additional number of nuclei, as present already in a quiescent, untreated melt, can be disregarded anyway.

The number per unit surface is raised to the 1.5-th power. In this way a useful and practicable approximation of the number N_c of spherulites per unit volume is obtained. In fact, a dimensional analysis shows that N_c must be proportional to the said 1.5-th power. This holds in particular if one can assume that without impingement all spherulites would grow to the same size. The proportionality factor must be of the order of unity. A counting procedure, as carried out directly in a volume defined by the area and the thickness of quenched thin slices (~5 μm, with variation!) confirmed this assumption (Stadlbauer et al. 2001) for polyketones.

If the number of spherulites in the cross-section increases in a series of experiments, a direct counting becomes more and more difficult. In order to estimate higher and higher numbers of spherulites per unit surface, a photographic method was applied: Out of a cross-section, as cut from a sample, in which the spherulites were not too numerous, an area was photographed, on which the number of spherulites was still countable. Successively, from the same sample bigger areas were photographed with decreasing enlargements. Of course, on these photographs the spherulites became smaller and more and more crowded. However, because of the known reductions of the scale, the numbers of spherulites per field of vision were still known. These pictures were used for comparison with pictures from samples on which, also with the largest magnification, direct counting was no longer practicable. A whole catalogue of pictures was prepared for the purpose. There are two prerequisites for a successful application of this method: The cross-sections of the samples, from which the catalogue is prepared, must be sufficiently homogeneous over relatively large areas, and the quality of the spherulites in the "crowded" samples must still be good enough. Of course, there remains some arbitrariness. However, the obtained order of magnitude of the numbers, which will play a central role, will still be acceptable.

At this point the quenching techniques should be recalled, which have previously been required for the determination of the number of athermal nuclei in quiescent melts. As a matter of fact without flow crystallization mainly occurs in the low temperature range, which was called the range of unstable states. The pertinent implications have been explained in the introduction.

Fast quenches to well defined final temperatures were most conveniently achieved with the aid of a counter current principle. A cylindrical sample of about 5 mm diameter, containing a thin thermocouple in its center, was wrapped in aluminum foil and suspended in a horizontal position in a coil of a thin wire and heated by radiation to a temperature well above its melting point. After this annealing it was first rinsed with a fluid of rather low temperature (cold water), which directly caused a rapid decrease of temperature. When the target temperature was approached, the cold fluid was replaced in a counter current by a fluid of the desired final temperature. If this temperature was below 100 °C, water was used also as a medium for the final temperature. For a final temperature above the boiling point of water, diethylene glycol was used for the second fluid, because of its miscibility with water. The subsequent counting procedure was essentially the same as described above. It was carried out near the center of a cross-section perpendicular to the axis of the sample, in avoiding edge effects. For occasional thin slice quenches one could do without a counter current procedure. However, the possibilities for the subsequent counting of spherulites were restricted to a range of numbers around an optimum number.

Results

The polymer, on which the present investigation was carried out, was an industrial polypropylene with a relatively broad molar mass distribution (Daplene KS 10). This type of polymers was first characterized in the course of a working party by Lederer (Lederer and Mingozzi 1997) with the aid of size exclusion chromatography. The pertinent data, as kindly provided by Borealis, Linz, are $M_z \cong 1360\times10^3$, $M_w \cong 322\times10^3$, $M_n \cong 47\times10^3$ and $M_w/M_n \cong 6.8$. PP KS 10 has quite a long tail at high molar masses (see the value of M_z). The corresponding viscosity as a function of the shear rate is given in a graph by Jerschow and Janeschitz-Kriegl (1997) for T = 200 °C (cf. Eq. 3). One should look at the curve for the "modified" or "current" KS10. (Unfortunately, in Table 1 of Jershow's paper the molecular data for "current" KS 10 are incorrectly cited.)

In Fig. 5 really striking results are shown for this polymer. This figure gives a three-dimensional picture, in which the vertical logarithmic axis gives the number of nuclei per unit volume. On the two "horizontal" axes the temperature (down to rather low values) and the mechanical work, as applied during the periods of shearing to the unit volume, are plotted (MPa = Joule/cm^3). For zero work, i.e., for the quiescent melts (left side), values are taken from a previous publication (Janeschitz-Kriegl et al. 1999). For four relatively high temperatures (140, 145, 150, and 160 °C) the influence of shearing is recorded. For convenience, the same shear stress was used in most of these experiments, namely 84,600 Pa.

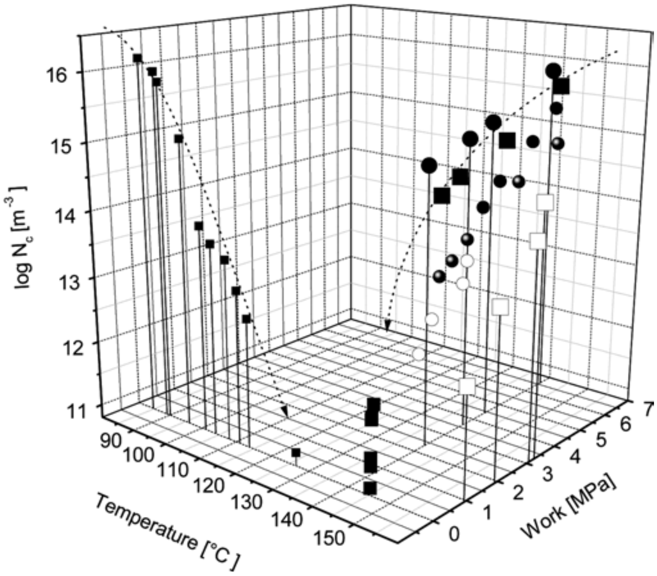


Fig. 5 Three-dimensional plot of the logarithm of the number of nuclei per cubic meter vs crystallization temperature and work applied to the unit of volume (MPa = J/cm^3), for PP KS 10. A shear stress of 84,600 Pa was applied in the majority of measurements: *large full circles* – 140 °C, *full squares* – 145 °C, *small full circles* – 150 °C, *large open squares* – 160 °C. Only at 150 °C also shear stresses of 50,800 Pa ("shining spheres") and of 25,000 Pa (*open circles*) were applied (see the text). At low works and at a temperature of 145 °C preliminary results were added, as obtained with extensional flow

In these experiments the change in the mechanical work was mostly achieved by a variation of the path length of the piston. Also two other shear stresses, namely of 50,800 Pa and 25,000 Pa, were applied at 150 °C ("shining spheres" and open circles). In the case of an initial shear stress of 50,800 Pa a less perfect line, of which one is shown in Fig. 2, was used for the integration of work. Nevertheless, the pertinent points fit into the general picture. Because after restored quiescence, the growth speeds are very low in the temperature range of 140–160 °C (10^{-8} to 10^{-10} m/s; see Eder and Janeschitz-Kriegl 1997 and Ratajski and Janeschitz-Kriegl 1996), these experiments are extremely time consuming. At 160 °C one has to wait, in particular after short paths of the piston, for many hours, until the spherulites have grown to full size, as limited by impingement. An early time saving quench to a lower temperature would introduce a lot of other spherulites in the still open interspaces between those spherulites, which grew on the original nuclei. These precautions demonstrate the fact that the vigilance in obtaining the shown width of the experimental window is enormous. At levels of undercooling near 90 °C the rate of growth is by many decades higher than at 160 °C (see the just mentioned papers).

It appears striking that the application of mechanical work can lead to such enormous increases of the number of nuclei in the range of relatively higher temperatures. In quiescent melts comparable numbers are only achieved at extreme degrees of undercooling.

An extension of the range of applicable mechanical work is not so easy. As the path length of the piston is restricted, a widening of the range can be achieved only by the application of higher shear stresses. According to previous measurements in duct flow, shear stress has a more pronounced influence than shearing time. This gives hope, even if wall slip of the melt and the consequences of an increasing production of frictional heat will pose upper limits. As a consequence of the latter phenomenon, shear zones can show up because the temperature distribution becomes inhomogeneous in the melt. Also, the inertia of the melt can interfere: with a sudden start of the wall at high speed the internal layers of the fluid can seriously lag behind the tacitly assumed linear velocity profile. This will be the case, if the viscosity of the melt is relatively low and the gap width is relatively large.

On the other hand, for work lower than 1 MPa the present machine poses the problem of static friction between the glass slide and the weigher and, to a lesser degree, in the pneumatic cylinder. So, one would have to subtract some portion from the amount of mechanical work. One wonders, whether there will be a measurable downwards bent of *log* N_c with decreasing work, below 1 MPa towards the values found in a quiescent melt. Preliminary measurements, as carried out in a plate-and-plate rotational rheometer, indeed seem to show a pertinent descent with decreasing amounts of work applied. However, the work applied is not uniformly distributed in such a machine. An analogous descent is also shown by first measurements with a special extension rheometer, as built in this laboratory for these purposes by Lipp and Stadlbauer. The points obtained with the latter technique are shown in Fig. 5 for 145 °C. Experiments in extension are started with rather thick and short samples, so that after stretching the samples still have a body. A new clamping mechanism avoids necking effectively. The applied extensional rheometer works at constant tensile stress (tensile creep). The required tensile force, which decreases with the cross-section of the sample, is obtained with the aid of an aerodynamic system contained in an expansion tube. Stretching can be interrupted at every desired moment. Also compliance and recovery can be measured. The number of spherulites can be counted in the cross-sections of solidified samples. Optical anisotropy is still very low in the samples treated so far in this way and can be traced back to spurious shishs, obviously growing on impurities.

Another point of interest is the expected continuation of the lines in Fig. 5 to higher amounts of applied work. In a rather early investigation by Liedauer et al. (1995), in which duct flow was applied to KS 10 at various constant temperatures, two layers were found in the cross-sections between the outer surface of the solidified sample and its spherulitic core (see Fig. 2 of the mentioned paper). The outer layer was highly oriented. The inner layer was fine grained. The boundary between the highly oriented layer and the fine grained layer was found for 150 °C at a value of the applied work of the order of 25 MPa. In the region around this transition some thread-like precursors show up between spot-like nuclei.

In some respects a better overview is given, if the results of (the right side) of Fig. 5 are plotted in a double logarithmic plot. In such a plot the axis of the work is stretched to negative infinity, so that a comparison with data obtained in quiescent melts, as shown in Fig. 5, is no longer possible. Zero work goes to minus infinity. On the other hand, the linear scale on the work axis of Fig. 5 is not practicable, if large amounts of work, say above 25 MPa, have to be included. The announced double logarithmic plot is given in Fig. 6 for all temperatures applied at a shear stress of 84,600 Pa. In fact, the points for low amounts of work, stemming from the extensional rheometer, occupy an unreasonably big space on this graph, whereas the points from the old duct flow measurements optically come too close to those obtained with the apparatus shown in Fig. 1. On the linear scale for the work in Fig. 5 the work of 25 MPa would appear at the far right!

For duct flow the numbers of nuclei were obtained in a quite interesting way. In the Figs. 2 and 3 of the work by Liedauer et al. (1995) two situations are depicted, namely one where the boundary between the oriented and the fine grained layers is at a distance from the outer surface of the sample, and one where it is invisible, which means that it is very close to the duct wall. The latter picture, of course, corresponds to a lower mechanical load. The original photographs are still at our disposal. From these photographs suitable enlargements were made and compared with several pictures from our catalogue. The classification was not too difficult. The corresponding amounts of work were calculated with the aid of the data, which can be read from Figs. 6 and 9 of

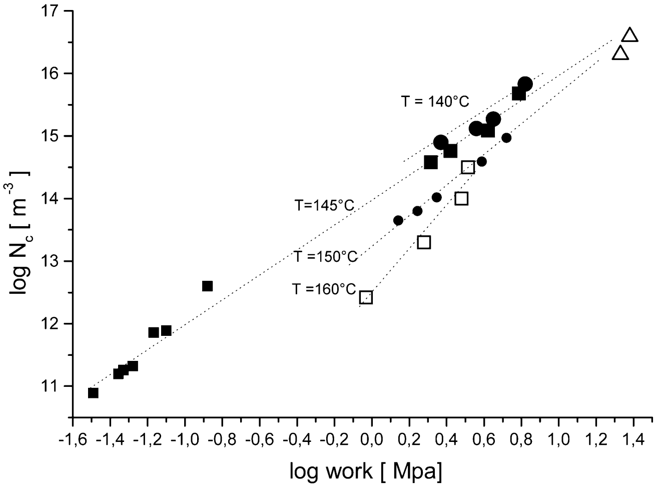


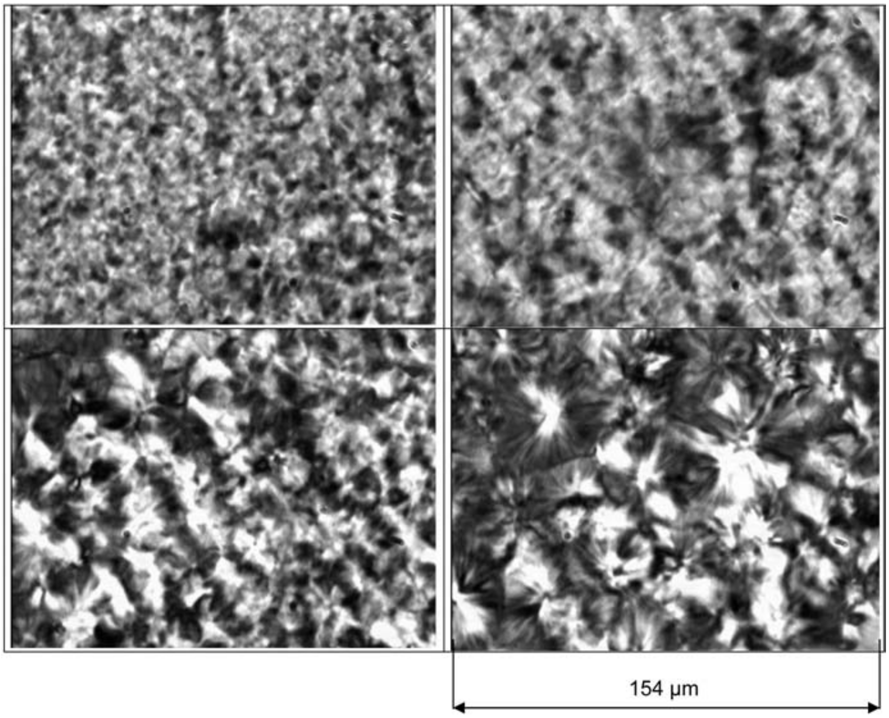
Fig. 6 Double logarithmic plot of the number of nuclei per cubic meter vs the mechanical work applied to PP KS 10 per unit volume for several temperatures. For the symbols see Fig. 5. Except for points obtained at very low amounts of work by extensional flow (M. Stadlbauer) and at very high loads in duct flow [38] all points are obtained at a shear stress of 84,600 Pa. The location between the *open triangles* indicates the transition to the formation of shishs

the cited paper. Existing viscosity values were used to calculate the shear stresses from the products of these viscosities with the corresponding shear rates. The technique followed with the extensional flow measurements will be published in due course (M. Stadlbauer et al.).

For a temperature of 145 °C the points at low loads lie quite reasonably on a line fitting the points in the middle range of loads. For 150 °C no points at low loads are available. As a compensation for this deficiency on one side one finds a nice correlation between the points in the middle range and the points stemming from duct flow and high work on the other side (open triangles). So, after all, one cannot escape the conclusion that points from three very different techniques arrange themselves quite reasonably. Our surprise should not be concealed, however, that the points from extensional flow do not go astray. Moreover, one should not overlook the convergence of the lines of Fig. 6 with increasing temperature. In fact, in a previous paper, in which results of duct flow (high mechanical work) was reviewed, a far-going reduction of results, as obtained at a variety of temperatures, was obtained with the aid of purely mechanical parameters (Fig. 5–53 of Eder and Janeschitz-Kriegl 1997), which is only possible, if the influence of temperature on shish formation is low. (The only temperature dependent parameter used was the growth speed in the quieted down melts, which played a role only after the formation of shishs was completed.)

For illustration purposes a Fig. 7 is finally introduced. It shows four photographs of cross-sections, as obtained at 150 °C and a shear stress of 84,600 Pa for four different total shear strains. The corresponding increase of the number of spherulites can clearly be seen with the unaided eye.

Fig. 7 A series of photographs of cross-sections of equal enlargement, as obtained on samples of PP KS 10 after shearing at 145 °C and a shear stress of 84,600 Pa. Total shears applied, from the upper left quadrant: $\gamma \cong 50$, 40, 30, and 20



Discussion

The most important point in this resumé is that Fig. 5 provides evidence that, with increasing duration of the shearing, the number of nuclei increases continuously. It should not be concealed that a similar result was found for a flowing polybutene – 1 melt in an early solitary paper by Wolkowicz (1978). This fact seems crucial to the validity of the two step model, which has previously been proposed for an explanation of the kinetics of the formation of highly oriented layers (Eder and Janeschitz-Kriegl 1997; Liedauer et al. 1993). As a first step the sporadic formation of primary nuclei was assumed. As a second step the growth of thread-like precursors (shishs), starting from these primary nuclei, was assumed. Each of both rates was supposed to be proportional to the square of the shear rate. The square of the shear rate was the simplest choice for an even function of the shear rate, as required for the independence of the direction of shearing. Admitting, however, for a certain limitation of the accuracy of the measurements we later preferred a more physical description. For this purpose it was assumed that the rate of formation of primary nuclei is proportional to the work applied per unit of time, being the product of two factors, the shear rate and the shear stress. In order to obtain the required shear stress, one just has to multiply one of the shear rates (out of the said square) by the corresponding (shear rate dependent) viscosity. This operation had no significant influence on the relative positions of the experimental curves, because the viscosities were varying not too much within the given experimental shear rate range. If, in addition, the first factor of the said product, namely the remaining shear rate of the square, is multiplied by the shearing time, one obtains the total shear. Total strain multiplied by the shear stress just yields the total work applied to the unit volume during the shear treatment.

Returning to Fig. 5 one observes that the shape of the curves for the logarithm of the number of nuclei vs the applied work resembles that of a plot of $log\ Cw^n$ vs w. For $n = 1$ this would mean that the number of newly formed nuclei increases linearly with shearing time or work. However, a look at Fig. 6 teaches us that n is of the order of 2! This is a disturbing fact. It means that the creation of new nuclei cannot be independent of the number of already present nuclei. Indeed, such an independence has sensibly been assumed so far in our previous considerations, in view of the enormous dilution of the molecules taking part in nuclei. In fact, one cubic meter of a polymer melt contains a number of 10^{23} to 10^{25} macromolecules, depending on the molar mass. For our PP grade one has an initial number of nuclei of at most 10^{10} m^{-3} (see the line for zero work in Fig. 5) in a temperature range between 140 and 160 °C, where the mechanical measurements were carried out.

As a consequence, the initial fraction of molecules engaged in these nuclei must be of the order of at most 10^{-11}, admitting – say – 100 molecules per nucleus. Even after shearing, when the number of nuclei has grown to 10^{16} m^{-3} or so, the fraction of engaged molecules is still incredibly low. If our observations are correct, a fabulous long distance (mechanical?) interaction must exist during flow, using the already existing nuclei as "centers of mass". However, there seems no doubt about the reality of our observations. In fact, a set of measurements, which will be published soon, indicates that the exponent n increases tremendously with the molar mass, in particular, if the molar mass distribution shows a "tail" at very long molecules. See also the work of Gahleitner et al. (1996, 1999). Such an observation is, without doubt, in favor of the interaction hypothesis.

An important point of discussion will now be the mechanism of the shish formation. At the time we assumed that thread-like precursors grow out from the primary nuclei in the direction of flow. At present, however, we believe much more in an accumulation process: as soon as the number of nuclei becomes large enough, an aggregation occurs quite suddenly. In this connection one should keep in sight the relative closeness of the two open triangles in Fig. 6. In fact, shish formation happens in the range of work between these two points. Also, in a recent publication of some preliminary measurements in opposite nozzle flow (Janeschitz-Kriegl et al. 2001) a similar impression was conveyed. Interesting enough, a technical term, as coined in an early stage (Keller and Machin 1967), namely "row nucleation", gets a new livelihood, even if shishs do not resemble a row of nuclei. Previously we argued that the superposition of two steps, both linear in their dependence on the applied work, was necessary for the explanation of the observed second order dependence on the work. Now we arrive at the supposition that, possibly, a one step non-linear process can fulfill the same task.

To some extent such an accumulation process may have a similar macroscopic effect as a process based on the uniform decrease of the average entropy per unit volume, as proposed by Doufas et al. (1999). However, such an argument overlooks the long pre-history of the accumulation of almost point-like nuclei, which we could document in the present paper. Moreover, we have shown already in an early review (Eder et al. 1990) that the first normal stress difference, which can readily be determined for the shear flow of a polymer melt even at rather high shear rates, is a useful measure for this decrease of the overall entropy per unit volume. In fact, as rubber-like liquid character is assumed anyway, one has just to divide the first normal stress difference by the absolute temperature. The values of the normal stress difference can also be estimated with the aid of flow birefringence in a slit-rheometer up to shear rates as high as 10^3 s^{-1} (Wales and Den Otter 1970; Janeschitz-Kriegl 1983). However, it turns out that this decrease of overall entropy may be insufficient in many cases, even in fast flowing polymer melts, for a significant increase of the melting point.

The mechanism of the coalescence of large numbers of primary nuclei seems much more plausible. It is also preferable in view of the sporadic appearance of shishs interspersed in the transition zone between point-like nuclei (Liedauer et al. 1993, Fig. 2). This fact points to the statistical character of this transition. Careful future experiments will have to show the final truth. The view, as put forward by Monasse (1995) at the time, is in extensive agreement with this argument.

At this point it should also be mentioned that the model proposed by us has been slightly modified for a first use in a simulation of structures occurring in injection molding by Zuidema et al. (2001). However, the flow induced increase of the number of spherulites, which are interspersed between the shishs in the zone of transition, has not been tackled.

Finally, it should certainly be stressed that the type of results, as extended over many decades and presented in Figs. 5 and 6, has never been obtained before. An extension to other polymers is on our schedule. Also, a new extensional rheometer has been designed in our laboratory for an investigation of the influences of extensional flow on nucleation, enabling also large total extensions (see a previous section of this paper). As in the shearing experiments the deformation can be stopped at any desired value. Preliminary experiments are very promising. (See also the insertions in Figs. 5 and 6.) At this moment it can already be said that also in extensional flow the process paving the way is a gradual multiplication of the number of primary nuclei.

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