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Flow-induced crystallization in polymer melts: on the correlation between nucleation and specific work

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Abstract A new counting technique for nuclei, as found after short-term shearing, has been developed with the aid of the plate-and-plate rheometer Linkam CSS450. For the purpose this apparatus was modified by the introduction of complementary polarizing optics (a polarizer and a λ-plate). With the aid of this technique the density of nuclei could be determined in a new way. When these number densities are plotted against the applied specific work, satisfactory agreement is found with results, which have been obtained previously with a sliding glass plate rheometer. Nevertheless, the limits of validity of the diagrams had to be discussed. A transition from a dynamic description with the aid of the specific work to a purely kinematic description with the aid of the frequency of successful encounters cannot be overlooked. In fact, with increasing specific work the influences of temperature and (non-Newtonian) viscosity appear to fade away.

Keywords Transparent rheometers · Melts of degraded PP · Polarization optics · Microscopy · Complementary colors · Pictures of high contrast · Counting technique · Activated nuclei

Introduction

Previously it has already been shown that at proper degrees of supercooling reasonable master curves as functions of the specific work can be obtained for the densities of activated nuclei [1–4]. Shear flow as well as extensional flow has been applied. The present communication shows that the usefulness of this evaluation can be underpinned with the aid of a new counting technique. Previously, the most common method has been to make cross-sections of the solidified sample, as

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obtained after the flow treatment, and count the number of the cross-sections of spherulites per unit surface. This number was then raised to the power 3/2 in order to obtain the number per unit volume. A few measurements were carried out also on extremely thin samples prepared by the evaporation of solutions. In these samples all spherulites could be seen [1, 5]. However, a crucial point was the accurate measurement of the extremely low sample thickness. Also, only permanently quiescent samples could be investigated in this way.

Experiments

Presently, use is made of a rotational rheometer, in which the development of the crystallization, which becomes observable some time after the cessation of the flow, can be monitored as in a movie. This machine (Linkam Scientific Instruments [6]) is of the "plate-and-plate" type. The plates are of glass permitting optical measurements. An extra polarizer and a λ-plate were introduced in our laboratory. The analyzer is provided by the microscope, which is part of the apparatus. One can choose a rather wide gap and insert relatively thick polymer samples. It will be shown that this possibility is of importance for our measurements. The commercial unit permits the heating of the sample to a desired temperature, where the sample is in the molten state. A relatively high temperature is chosen first, where residues of previous crystallization are erased. After some time the temperature is lowered to a proper temperature, where nucleation can be observed after a flow treatment. As long as the melt is kept quiet, the beautiful red of first order shows up as a complementary color of white light. This red of first order is particularly useful, as it switches quickly to blue or yellow, if a small phase difference is added or subtracted. We made use of this advantage.

After a shear treatment one observes the gradual appearance of nuclei. These nuclei manifest themselves in our experiments as blue specks. This fact means that the nuclei must be lengthy and oriented in the previous flow direction. Apparently, in these specks the addition of a small phase difference takes place. However, shortly after the cessation of the flow they are still so small that they cannot be observed in the microscope. During a time of waiting the specks are transformed into spherulites, which appear as white balls (white of higher order). Their (uniform) size increases continuously. A count of these balls can be carried out easily as long as the melt is translucent and the balls do not cover each other, which finally happens. In spite of the lengthiness the nuclei one gets spherulites. Apparently, the length of the original nuclei is very small compared with their mutual distances.

A drawback of the Linkam machine is that one cannot prevent slip of the sample on the glass surfaces. But meanwhile we have realized that this slip does not occur immediately after the onset of the flow. It happens only with continued deformation. It seems that corroding the surface of the inserted polymer sample with the aid of 30% hydrogen peroxide can help to prevent slip. In this way a polar surface is created on the sample. Such a surface should adhere more strongly to the polar glass surface.

Fortunately, slip can be detected. In fact, from the moment, when slip comes up, the appearance of the sample does not change any more. So one can put aside the photographs of those useless samples afterwards. But this means that the application of shear is restricted. However, as one can vary the shear rate, one can still obtain quite a selection of specific works w. Admittedly, the pertinent viscosities η must be determined separately in another apparatus. One has $w = \eta q t$, where q is the shear rate and t is the shearing time.

Results

For the present purpose a polypropylene was chosen, which had been degraded with the aid of a peroxide. Its molecular data are $M_w = 160.000$ g/mol and $M_w/M_n \sim 2$. One advantage of this low molar mass polymer is that steady state viscosity (as a mild function of the shear rate) is obtained within a short-time span, when after the onset of flow the deformation is still small. Another advantage for our purpose is that the number density of nuclei remains rather small under all conditions of flow. In fact, one finds that the number density of nuclei usually is about a hundred times larger with untreated polypropylenes. As a consequence, counts are much more difficult with those normal polypropylenes. Interestingly enough, polyethylenes pose still more difficulties with counting. In fact, in a quiescent melt and at 100 °C the number density of nuclei is a factor ten thousand larger than in the peroxide degraded polypropylene. These facts have been a point of discussion [1]. However, in this communication we are interested only in the advantage of an easy count of a low enough number.

Figure 1 is introduced in order to enable a judgment of the quality of such a count. In this figure the dimensions of the sample are indicated schematically in perspective. In fact, the thickness of the sample is comparable with the sides of the frame of the microscopic picture. This picture is shown on the forefront. If colors are reproduced, the gray background of the spherulites is red of first order. The complementary color of the spherulites is white of higher order. This special sample had been sheared at 145 °C and at a shear rate of 75 s^{-1} for 0.5 s. The picture was taken after 36 min. Clearly, the waiting time was long enough for considering the 0.5 s of shearing just as the moment, when the nuclei were born. In fact, the size of the spherulites is practically uniform.

In Fig. 2 the counts, as achieved with the Linkam unit, are presented on the right side of the figure as functions of the applied specific works (1 MPa = 1 J/cm^3). As in previous papers [1, 5] this figure is a presentation in prospect. On the left horizontal axis the temperature is given. The obtained number densities change quite a lot. As a consequence, the number densities are plotted on a logarithmic scale. On the upper left side of the picture the number densities, as obtained with zero specific work, are plotted as a function of temperature for comparison. These numbers were obtained on very thin samples after rapid quenching. Because of the logarithmic scale one finds very steep descents, when zero work or temperatures above 160 °C are approached. This is caused by the fact that the logarithmic scale inflates in the negative direction with decreasing argument. In previous graphs, as

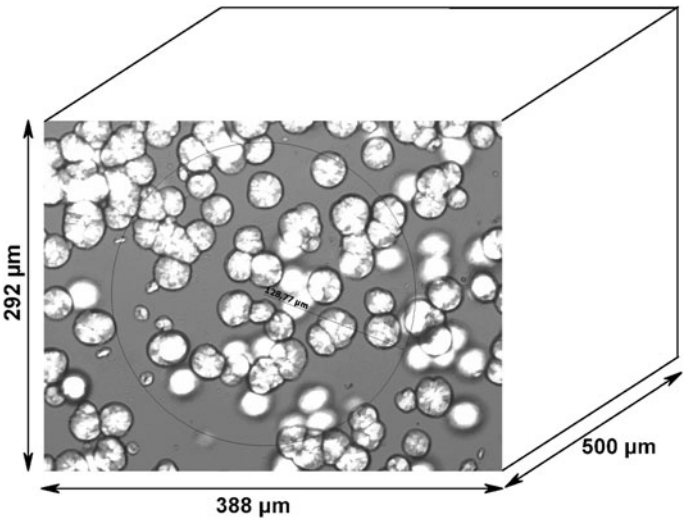

Fig. 1 The sample volume in the Linkam unit is schematically presented. On the forefront the actual microscopic picture is shown. One observes spherulites of a peroxide-degraded PP in a stage of development, which corresponds to a waiting time of 36 min. This waiting time is reckoned from the moment of the cessation of the flow. This flow was applied for 0.5 s at a shear rate of 75 s^{-1} and at a temperature of 145 °C. This treatment corresponds to a specific work of 1.26 MPa. In reality the *gray* background is red of first order in white polarized light

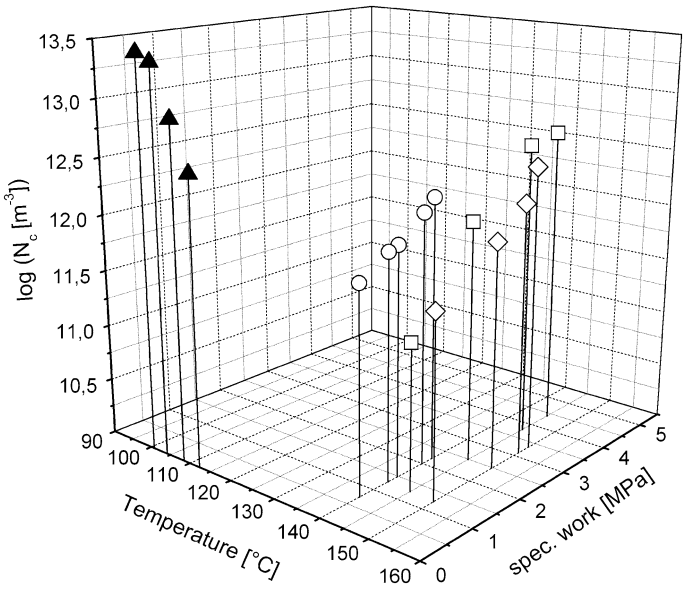

Fig. 2 Perspective presentation of the number densities of nuclei as functions of the specific work for various temperatures. For the application of the mechanical work the Linkam unit was used. The number densities of nuclei are equal to the number densities of spherulites formed. On the *left side* old results of our group are shown for zero shear rates. These results were obtained after rapid quenching of thin samples

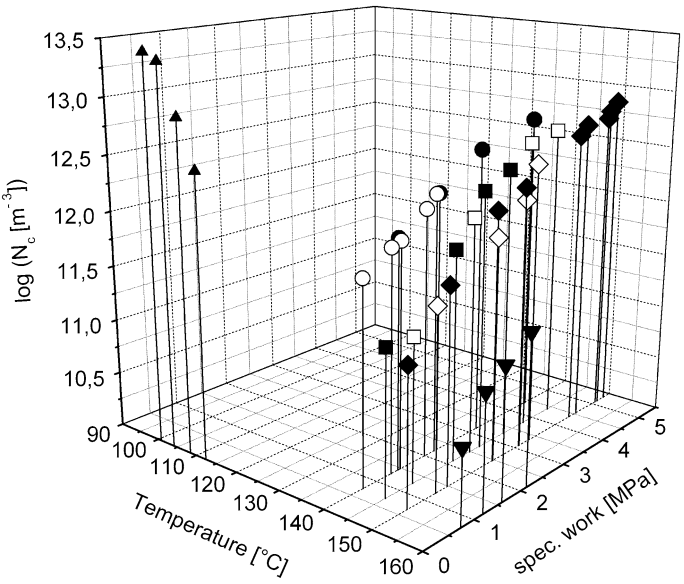

Fig. 3 Superposition of the results of Fig. 2 with old results (*closed symbols*), as obtained with the sliding glass plates apparatus [5]. The results with the Linkam unit are given by *open symbols*

obtained with normal polypropylenes, this effect could be shown more explicitly. In Fig. 3, the results of Fig. 2 are plotted together with previous results, which have been achieved for the same polymer with the sliding glass plate rheometer. The latter measurements are presented by closed symbols. The results, as obtained with the Linkam machine, are given by open symbols. The match is satisfactory. Of particular interest is the fact that the applied ranges of shear rates and shearing times are quite different. In the case of the Linkam unit maximum shear rates of less than 100 s^{-1} could be achieved at shearing times of seconds. With the sliding plate rheometer, in which short-term rectilinear flow was realized, shear rates up to more than 1,000 s^{-1} were reached at shearing times down to fractions of a second. (In the latter machine slip could be prevented by loading the upper-moving-glass plate with a proper weight.) The shown coincidence of results seems to be the best proof for the usefulness of the parameter "specific work". In this connection it is emphasized [1] that the rate of specific work is the product of the external stress, which reflects the degree of orientation in a rubber-like fluid, and the rate of deformation, which is a measure for the frequency of successful encounters.

Discussion

If not only the number densities but also the works are plotted on a logarithmic scale, one obtains nearly straight lines, as has been shown previously also for untreated polypropylenes [1, 5]. The corresponding graph for the present degraded polymer is given in Fig. 4. Again, the closed symbols are for the old measurements,

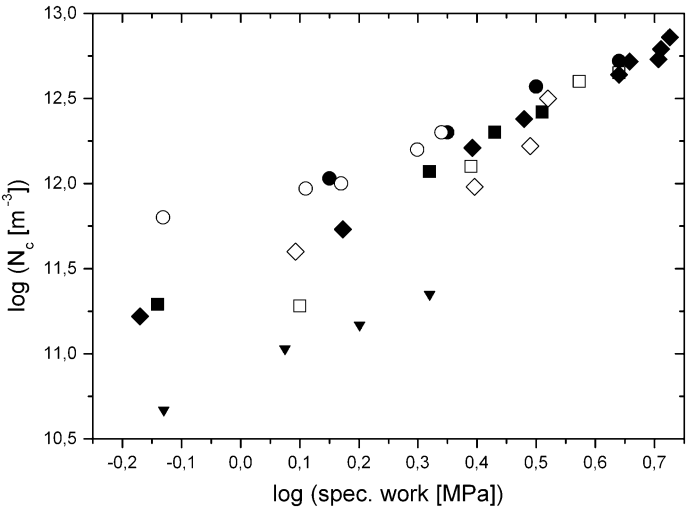

Fig. 4 Double logarithmic plots of the number densities of nuclei versus specific works for several temperatures: *circles* for 140 °C, *squares* for 145 °C, *diamonds* for 150 °C, and *triangles* for 160 °C, *open symbols* for results from the Linkam apparatus, *closed symbols* from the sliding glass plates rheometer

as carried out with the sliding glass plate rheometer, and the open symbols are for the present results, as obtained with the Linkam apparatus. Circles stand for 140 °C, squares for 145 °C and diamonds for 150 °C. The closed triangles were obtained only with the sliding glass plate rheometer at 160 °C. But it must be admitted that at this highest temperature there are some uncertainties. For the degraded polypropylene we are already quite close to the melting temperature of its spherulites. Also, for a spatial Poison distribution of nuclei a considerable spread of counts can be expected, if the number of observable nuclei is not large enough (G. Eder, personal communication). With untreated PP also the line for 160 °C converges with the other lines. However, be that as it may, one can easily observe a convergence of the points with increasing specific work.

In a more pronounced form the same tendency has been observed previously for untreated polypropylenes. With those polymers the range of specific works was from almost zero up to 25 MPa (log 25 = 1.4!). At this high-specific work the convergence of the lines for the number densities was almost perfect and, perplexingly, a transition to a highly oriented structure could be observed in duct flow experiments [1, 7]. With the degraded polymer a highly oriented layer has never been obtained in duct flow experiments. But we are particularly satisfied that a similar tendency of convergence could be found also with this degraded polymer. In other words: also with this degraded polymer the temperature dependence decreases with increasing specific work. With duct flow experiments on the untreated polypropylene we could observe that not only the temperature dependence but also the influence of the (non-Newtonian) viscosity dwindled. A simple dependence on the square of the shear rate was found. The said square was introduced as the most

simple even function. In fact, an even function is required because the process cannot depend on the direction of the flow.

At that previous times we could not understand, why the occurrence of oriented structures did not depend on the usual parameters of rheology. Meanwhile we think that we can understand this phenomenon. In fact, as soon as—during fast flow—the molecular orientation reaches saturation (sometimes within fractions of a second [8]), the influence of the shear stress as a measure of orientation will loose its importance. This means that the favored *dynamic approach* looses its validity and, with it, the specific work. One is left with a purely *kinematic explanation*, i.e., with the frequency of successful encounters.

This vision is supported by completely forgotten results, as obtained by Stratton [9] a long time ago. Stratton investigated the non-Newtonian viscosities of melts of polystyrenes, which were obtained by anionic polymerization. As is well-known, those polymers have uniform molar masses, they are "monodisperse". Of course, these polystyrenes do not crystallize. Nevertheless, their rheology is very instructive for the present purpose. In Fig. 5 the results of Stratton are reproduced. At low shear rates he found the validity of the well-known Flory–Fox relation [10], which meant that the zero shear viscosities were proportional to $M^{3.4}$. This clearly is a very strong dependence on the molar mass. At increasing shear rates, however, this dependence becomes weaker and weaker and dies out finally with increasing shear rate. For those, who swear on the dominant influence of the longest molecules, the results of Stratton must be startling.

In fact, for general purpose polymers shear rates of the order of one hundred reciprocal seconds are of particular interest. Shear rates of this order occur in all kinds of manufacturing processes. For this reason one is also not so much interested in the behavior of polymers of too high a molar mass, as these polymers often show flow anomalies in the machines. But the preferred medium molar mass polymers have also another advantage. After the onset of flow they show very low adjustment times. These adjustment times are usually many orders of magnitude lower than the relaxation times, which are determined in the quiescent melts with the aid of dynamic mechanical measurements [8]. As a consequence, in many cases the birth

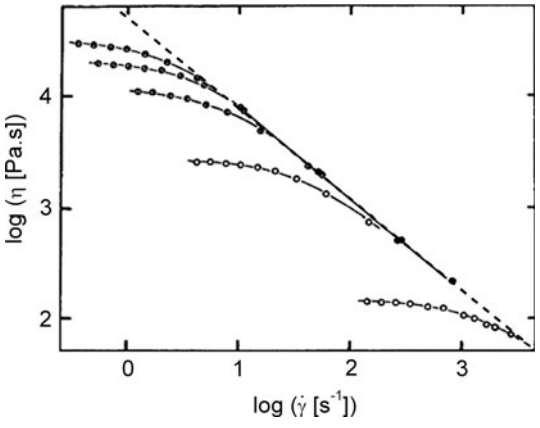

Fig. 5 Double logarithmic plot of non-Newtonian viscosities against shear rates for samples of monodisperse polystyrenes of different molar masses of 48,000, 117,000, 179,000, 217,000, and 242,000 according to Stratton [9]. All data are for 183 °C. The slope of the dashed line is −0.82 (not too far from the unattainable limit of −1). Courtesy Academic Press

of nuclei has been observed under steady flow conditions. Amongst others this fact has been demonstrated in the work by Hadinata et al. [11, 12]. These authors investigated a PB-1 of $M_w = 176{,}000$ g/mol and an $M_w/M_n = 5.7$. Figure 5 informs us that near a shear rate of 100 s^{-1} all samples of Stratton have been lined up except for that with the lowest molar mass. But this means that the longest molecules do not play a separate role in this range of shear rates. Only at much lower shear rates the viscosities diverge.

Of course, this does not mean that the longest molecules do not have a pronounced effect on the growth of threads. But this effect is no longer due to a diffusion controlled process. It has to do with forced association. A hint to rheologists should be that our pursuit of shear-induced crystallization has re-animated an old problem of rheology, i.e., the limits of validity of the rubber-like liquid hypothesis.

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