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ORIGINAL CONTRIBUTION

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How to determine high growth speeds in polymer crystallization

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Dedicated to Prof. Dr. D.W. van Krevelen, Arnhem

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Abstract With the fast crystallizing polymers HDPE and i-PP it is extremely difficult to extend the range of measurements of the growth speed of spherulites to temperatures as low as 80 °C. So far the lower limit for these measurements has been about 120 °C for both polymers. Several possibilities for this kind of measurements are explored in the present paper. It appears that none of these measurements is without uncertainties. So, only the comparison of results, as obtained with several independent measurements and with theory furnishes a sufficient credibility. Optical measurements, from light scattering to visual inspection, all under very special conditions of heat transfer, are described.

Key words i-PP – α- and β-modification – HDPE – crystal growth – induction – heat transfer

Introduction

If the growth speed of spherulites is to be considered, one should not overlook the difficulties arising from the fact that many polymers show polymorphism. For isotactic polypropylene (i-PP) four types of spherulites have been classified for the first time by Padden and Keith [1]. In a second publication [2] these authors have shown that types I and II crystallize monoclinicly, whereas types III and IV form hexagonal unit cells. Somewhat loosely, Turner-Jones and coworkers [3] called types I and II together the α-modification and types III and IV the β-modification. Quite a number of authors [1, 5, 6, 7] have investigated the growth speeds of α-spherulites. Because of epitactic growth the birefringence of these spherulites is weak. Nevertheless, the determination of the growth speed of the strongly birefringent β-spherulites, which show a bright appearance between crossed polars, is much more difficult because of the low rate of primary nucleation of this modification, so that special nucleation agents must be administered. For the observation of single spherulites, however, an extremely low dosage must be administered. Padden and Keith [1] were the first to observe that, in a temperature range between 128° and 132 °C, the β-phase grows faster than the α-phase by approximately 20%.

Lovinger, Chua and Gryte [4] succeeded in actually measuring the growth speeds of the spherulites of i-PP in a range of temperatures between 122° and 137 °C. For this investigation they used the so-called "zone solidification". With this method a rod-like sample crystallizes when drawn with constant speed through a stationary axial temperature gradient. In the steady state the growth speed of the crystal modification in question is equal to the speed with which the sample is moved. With this method the growth speeds of both modifications of i-PP could be determined. Because of the increase of the rate of primary nucleation of the α-modification at temperatures below 120 °C the separately crystallizing objects become too small for an observation under conditions of zone solidification. If the nucleation occurs at a surface, the crystallized area of the β-modification (of higher growth speed) expands as a cone from the spot where it is nucleated. From the bevel angle of this cone the ratio of the growth

K 713

speeds of the β- and the α-modification can be calculated quite accurately. Useful measurements were obtained by the mentioned authors in a temperature range between 120° and 140 °C.

More recently, Cheng and coworkers [8–10] reported growth speed measurements on i-PP of several degrees of tacticity. It appeared that with decreasing tacticity the growth speeds are lowered considerably and the transitions between the diverse crystal modifications become more clear. These authors used hot-stage microscopy for their purpose.

In the present investigation a presentation is given of a series of other techniques allowing measurements on the α- and β-spherulities of isotactic polypropylene down to a temperature as low as 80 °C. In this way also the maximum speeds of growth, which are expected for both modifications of i-PP somewhere halfway between their melting points and the glass transition temperature, could be grasped.

A similar success could be obtained for high density polyethylene (HDPE). The difficulty with this polymer is that it crystallizes much faster. On the other hand, normally there is only one crystal modification [11]. At temperatures between 120° and 130 °C Chew, Griffiths and Stachurski [12] succeeded in measuring the growth speed of spherulites of HDPE with a special thin layer technique, where a very thin sample of the polymer is embedded between cover glasses which are inactive with respect to primary nucleation. As a consequence, one obtains almost two-dimensional disklike "spherulites" of much larger radii because spherulites, which would be nucleated in neighboring layers in the bulk, cannot grow out into the layer under consideration and, as a consequence, do not interfere with the growth of the spherulites nucleated in this layer. This has also been emphasized by theory [13]. We succeeded in extending these data down to 80 °C. The validity of Van Krevelen's equation [14] for the growth speed of spherulites as a function of temperature could be checked with success for HDPE and with partial success for i-PP.

Materials

The following materials were used in the present investigation:

a) Industrial (isotactic) polypropylene Daplen KS-10 4095 DII (melt flow index 230/2.16 is 8 g/10 min).

b) Permanent Red E3B (cinquasia gold), as a nucleation agent for the β-modification of i-PP [15].

c) Industrial HDPE, (experimental grade of Petrochemie Danubia) MFI 230/2.16, 7.5 g/10 min., density $\rho = 0.965$ g/cm^3.

Transcrystallization against steep temperature gradients

Introduction

As is well-known, the wall of a vessel can be very active in creating nuclei. If the average distance between the nuclei at the quenched wall is much smaller than in the adjacent fluid, a crystallization front is formed, which starts with a growth speed characteristic for the growth of spherulites at the temperature of the quenched wall [16]. In metallurgy the structure created at the wall has been called the "columnar phase" [17]. In polymer science, one speaks of "transcrystallization" [18]. However, at some distance from the wall the front growth is usually superseded by diffuse spherulitic crystallization in the bulk of the fluid [19]. The reason is that, in a supercooled zone of the fluid, which always proceeds the front, the progress of diffuse crystallization is faster (see also below). These processes are schematically represented in Fig. 1 for the half infinite space, if the temperature in the bulk is uniform and above the melting point, and the wall at $x = 0$ is quenched at time zero to a temperature below the melting point. In order to avoid the occurrence of a diffuse crystallization zone in the bulk, an experiment has been developed in our laboratory in which transcrystallization occurs against steep temperature gradients. In this way an effective means has been found to suppress the mentioned spherulitic crystallization in the bulk, so that the growth of the front can be observed without disturbance.

Experimental set-up

For the purpose a tablet of, say, isotactic polypropylene is sandwiched in a horizontal position between two metal plates which form the end surfaces of two coaxial hollow cylinders. The diameter of the plates and the sample is 20 mm and the thickness of the tablet is of the order of 1 mm. The cylinders are heated with the aid of electric band heaters to a temperature well above the melting point of the polymer. At a certain moment the lower plate is quenched to a chosen temperature below the melting point with the aid of a water soluble heat transfer fluid (diethylene glycol) pumped through the interior of the lower hollow cylinder. Normally, the adjustment of the lower plate to the new temperature takes about 3 s. The opposite upper plate is kept at the original temperature above the melting point by the electric heater.

In this way, a crystallization front is formed, which moves from below with a certain initial speed into the melt. After certain times both plates are quenched by tap water to about 12 °C. These times lie between 1 and 15 min,

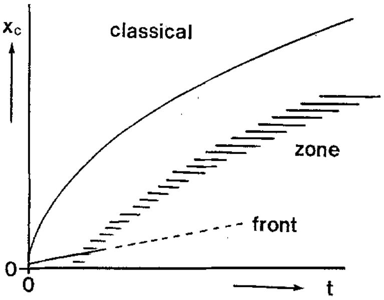

Fig. 1 Schematic presentation of several ways, in which crystallization proceeds from a quenched wall into a melt of initially uniform temperature [19]

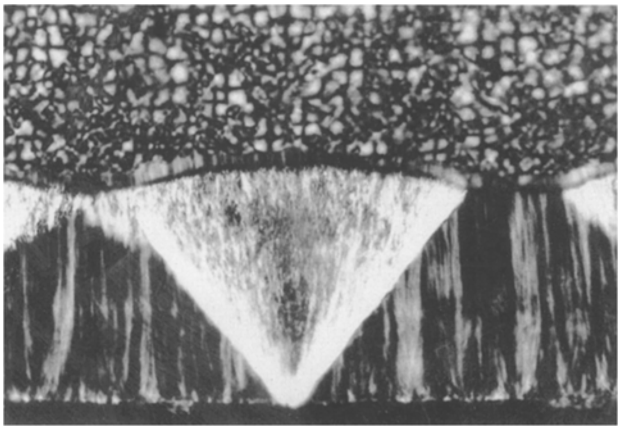

Fig. 2 Transcrystalline layer of the α-modification of i-PP at a wall temperature of 110 °C and a contact time of 103 s. A single β-nucleus at the wall produces a conical body as part of a β-spherulite which becomes dominant after a distance of 0.153 mm from the wall

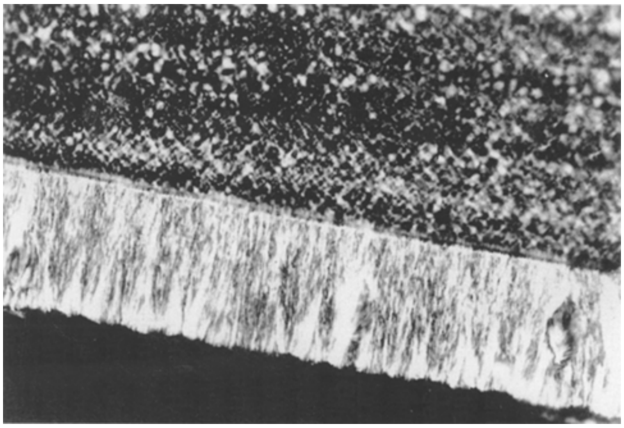

Fig. 3 Transcrystalline layer of the β-modification with a pear-shaped inclusion of a body of α-modification, as obtained at a wall of 110 °C after a contact time of 49 s. The layer thickness is 0.105 mm. The surface of the sample was rubbed with Cinquasia-Gold as a nucleation agent for the β-modification

dependent on the chosen experimental conditions (temperature of the first quench etc.). They have been called the "contact times" in our laboratory jargon.

From the solidified samples cross-sections of about 30 μm thickness were prepared by cutting the samples perpendicularly to the tablet surface. These cross-sections were investigated under a polarizing microscope. The area which solidifies during the second quench, shows a fine-grained structure and can easily be discerned from the structure formed during the contact time. As always a sharp boundary is found, one can conclude that diffuse spherulitic crystallization is successfully suppressed by the steep temperature gradients prevailing in the sample during the contact time.

In Figs. 2 and 3 two situations are presented. In both cases the lower sample surface was quenched from 200° to 100 °C. Figure 2 shows a cross-section of a sample, on which no nucleation agent for the β-modification was applied. In the beginning of the crystallization mainly α-phase was created at the quenched surface. Nevertheless, a few spots are discernable at the surface, where β-phase was nucleated. This happened at the apices of the bright cones which, understandably, do not lie exactly in the cutting surface.

Apparently, because of the higher growth speed of the β-modification, the growth surfaces of the few β-cones start to dominate the transcrystallization already at rather small distances from the wall. This effect is particularly pronounced at the wall temperatures of the lower plate between 90° and 115 °C. For this reason, the method of transcrystallization against a steep temperature gradient is not useful for the determination of the growth speed of the α-modification in this temperature range.

However, according to Lovinger et al. [4], one can calculate the growth speed of the α-modification in this temperature range, if the growth speed of the β-modification is known. The ratio of the growth speeds G_α and G_β of the α- and β-modifications, respectively, is equal to

$$\frac{G_\alpha}{G_\beta} = \cos\frac{K}{2}\,, \tag{1}$$

where K is the said cone angle.

In Fig. 3 a cross-section of a sample of i-PP is shown, of which the lower side was rubbed in with Cinquasia-Gold before the experiment was started. In this way, one obtains a transcrystalline β-layer, in which only a few α-"spherulites" are embedded. Because of the higher growth speed of the β-modification, these α-spherulites are pear-shaped (cf. [4]) and, as a consequence, do not seriously hamper the thickness measurement of the β-layer.

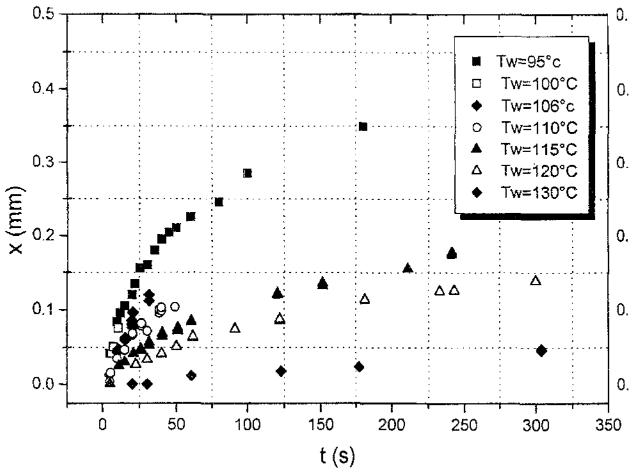

Fig. 4 Thickness of the transcrystalline β-layers as functions of the contact time for various wall temperatures. (Initial temperature of the bulk of the melt was 200 °C)

If these layer thicknesses are plotted against the pertinent contact times (see Fig. 4), one obtains curved lines, of which, in principle, the initial slopes furnish the growth speeds at the chosen wall temperatures. However, as the results of previous investigations [19] show, the determination of these slopes is not reliable enough. This was the reason why Eder [20] proposed a more reliable method which will be explained in the next section.

Approximate theoretical description of the front growth in a steep temperature gradient

The following assumptions are made:

a) In the surrounding of the chosen wall temperature T_w the growth speed can be approximated by an exponential function:

$$G = G_w e^{-\beta(T - T_w)} \,. \tag{2}$$

b) In a steep temperature gradient the evolution of latent heat of crystallization has no noticeable influence on the distribution of the temperature.

c) The heat diffusivity a is not influenced remarkably by the degree of crystallinity.

d) The Fourier number

$$Fo = \frac{at}{D^2} \tag{3}$$

(with D equal to the thickness of the tablet and t equal to the time) is large enough for an early adjustment of a linear temperature profile (a constant temperature gradient) over the cross-section of the sample. This is the case for $Fo \geq 0.5$.

For a sample thickness of 1 mm and a heat diffusivity of $a = 10^{-7}\ \mathrm{m}^2\ \mathrm{s}^{-1}$ this means:

$$t \geq \frac{D^2}{2a} = 5s \,. \tag{4}$$

After this time span one practically has:

$$T(x) = T_w + (T_i - T_w)\frac{x}{D} \,, \tag{5}$$

where T_i is the initial temperature which endures in the upper plate and x is the distance from the quenched wall.

In this case the growth speed of the front obeys the following differential equation:

$$\dot{x}(t) = G(T(x,t)) = G_w e^{-\beta \frac{T_i - T_w}{D} x(t)} \,. \tag{6}$$

For $x(o) = 0$ the solution of this equation reads:

$$x(t) = G_w \tau \ln\left(1 + \frac{t}{\tau}\right) \,, \tag{7}$$

where the characteristic time τ is defined as

$$\tau = \frac{D}{\beta(T_i - T_w)G_w} \,. \tag{8}$$

In logarithmic form Eq. (7) reads:

$$\log x(t) = \log G_w + \log\left[\tau \ln\left(1 + \frac{t}{\tau}\right)\right] \,. \tag{9}$$

For various values of τ the curves of $\log\,[\tau \ln(1 + t/\tau)]$ are calculated as functions of the logarithm of time t. Experimental values of $\log x(t)$ are plotted on a transparent sheet against $\log t$. The experimental curve is now shifted in a vertical direction until it coincides with the theoretical curve of the right shape. Equation (9) shows that the corresponding shift yields $\log G_w$. At the same time also the correct value of τ is found. With an admittedly low accuracy, also the value for β is obtained. In Fig. 5 an example for such a procedure is shown. For a rather large number of pertinent experiments the growth speeds G_w of the β-spherulites are plotted against the temperatures T_w on half logarithmic scales in Fig. 6. At temperatures above 122 °C our measurements nicely correspond with the measurements of Lovinger et al. At 130 °C there is even a reasonable coincidence with one of our points. Some microscopic measurements were possible at 140 °C. So, a rather complete picture is obtained for the growth speeds of the β-modification of i-PP in a range of temperatures extended down to 90 °C.

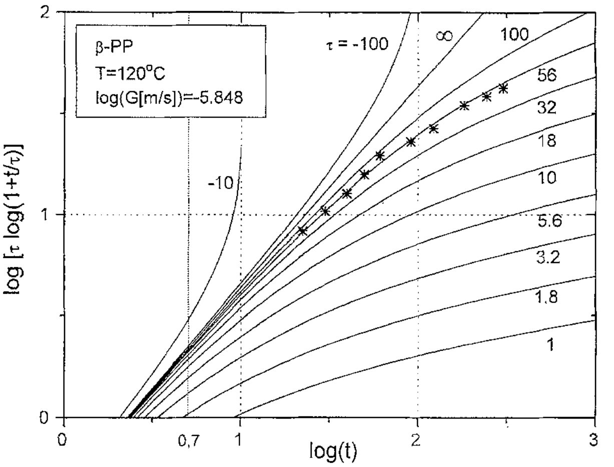

Fig. 5 Various theoretical curves log[τlog(1 + t/τ)] as plotted against log$t$ for changing values of τ (full lines). The stars give the positions of experimental points after a proper vertical shift. These points were obtained for the β-modification of i-PP at the wall temperature $T_w = 120\,^\circ$C. The corresponding values of G_w and τ are $0{\cdot}138\,10^{-5}$ m/s and 56 s, respectively

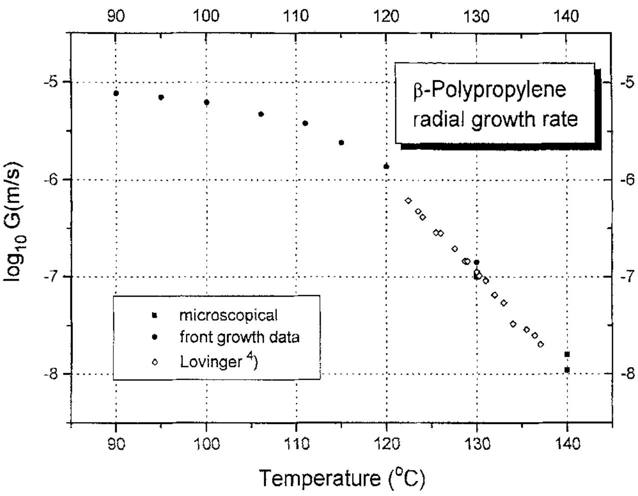

Fig. 6 Logarithm of growth speed of the β-modification of i-PP as a function of temperature. Open rhombuses give the values by Lovinger et al. [4]

The diffuse crystallization zone

Introduction

From Fig. 1, one learns that crystallization proceeds in two ways from a quenched wall into a sample which was originally at a uniform temperature above the melting point [19]. If the diffuse spherulitic crystallization is not suppressed by a steep temperature gradient, it takes over

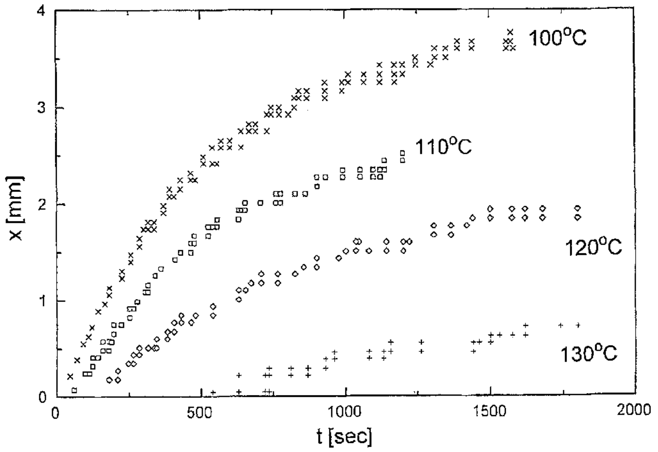

Fig. 7 Course of the experimentally determined "location" of the diffuse crystallization zone against time, as counted from the "moment" of the quench of the wall to various indicated wall temperatures for i-PP Daplen PT 55. The spherulites in the zone are almost exclusively α-spherulites. (Initial bulk temperature 200 °C)

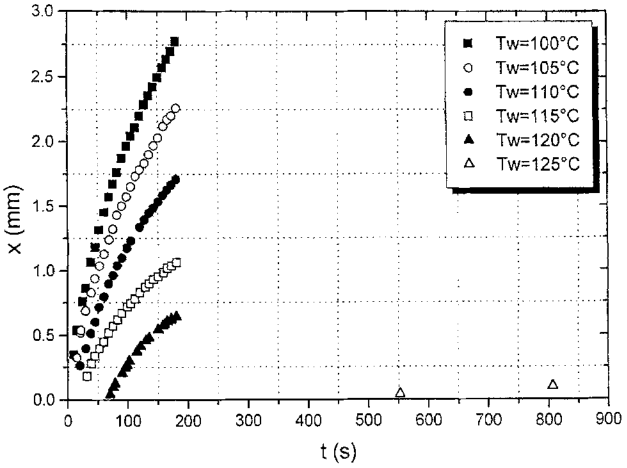

Fig. 8 Course of the "location" of the diffuse crystallization zone against time for a HDPE. Temperature of the quenched wall are indicated in the list of symbols. (Initial bulk temperature 170 °C)

the progress of crystallization at some distance from the quenched wall. The position of this zone is independent of the occurrence of transcrystallization. This zone solely depends on the nucleation in the bulk of the fluid. In Figs. 7–9 examples are given for the progress of the diffuse zone into the sample, as obtained by our previous optical measurements for several wall temperatures indicated in the graphs. Initial uniform bulk temperatures are given in the captions. From an inspection of these figures one learns that the zones for HDPE were much narrower than for i-PP, as may be judged from the respective spreads of the points. In an early paper by Schneider et al. [21], it has

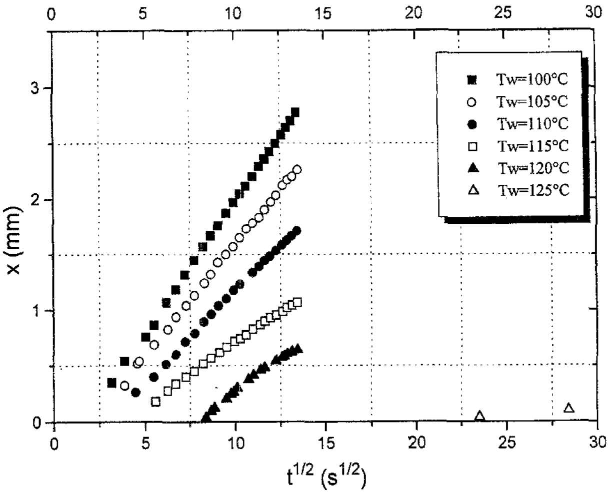

Fig. 9 Course of the "location" of the diffuse crystallization zone against the square root of time for the conditions of Fig. 8

been pointed out that, to a first approximation, the shape of the central lines of the zones (half conversion lines) is very similar to the shape of the classical square root law [22–24], but shows a vertical downward shift so that the line crosses the abscissa at some time larger than zero. As a consequence, one is inclined to believe that crystallization starts only after some induction time. However, no concept of induction is used in the mentioned theory. Only a smooth temperature dependent overall crystallization speed is assumed. From this preliminary theory one can expect that a plot of the said central lines against the square root of the time would straighten out these lines. This is really observed, as Fig. 9 doubtlessly shows. Such plots facilitate the determination of the rather short "apparent induction times" of HDPE.

Experimental set-up

At this point the reader may ask how this type of measurement can be carried out. In the present context only the most recent and most practicable method will be described. For these measurements no thin tablets of the polymer are used, but rather thick cylindrical samples (of the same diameter of 20 mm) with a height of about 10 mm. Also these samples are sandwiched at their end surfaces by metal plates being formed again by the end surfaces of the hollow metal cylinders, as in the previous experiment. In lateral direction the sample is confined by a glass cylinder of an inner diameter of 20 mm, in which also the metal cylinders fit slidingly on both sides of the sample. Before insertion the sample is cut with the aid of a sharp blade along its axis. A microscale, as produced by a photographic technique (small scale reproduction), is clamped between the two parts of the sample. After the sample is melted this scale is completely embedded in the heart of the sample.

The sample is melted with the aid of the electric heating belts fixed around the metal cylinders. Through the interspace between the mentioned inner glass cylinder and an outer glass cylinder air or nitrogen of the same temperature is pumped. At a certain moment the lower plate is quenched to a desired temperature below the melting point with the aid of diethylene glycol (time of adjustment ≤ 3 s). At the same moment the temperature of the circulating gas is adjusted to a temperature which lies halfway between the enduring temperature of the upper plate and the temperature of the quenched lower plate. In this way, an approximately one-dimensional heat transfer problem is created.

After a certain "contact time" both metal cylinders are quenched by tap water. Even if the cooling of the interior of the sample takes much more time than in the tablet experiment, one still can recognize, at which distance from the lower plate the progress of the zone crystallization was stopped by the final quench. This result, of course, is much less important than in the tablet experiment. In fact, in the present experiment the progress of the zone crystallization is directly observed with the aid of a telescope which is oriented at an angle of 30° with respect to the end surface of the sample. The use of the embedded microscale is unavoidable, as the light rays are considerably bent in the rather steep temperature gradients occurring in the axial direction. So, a cathetometer scale will give wrong results. The criterion of progress is the time at which the nascent haze obscures a certain part of the scale.

Theoretical considerations concerning the progress of diffuse spherulitic crystallization

For the moment the exact prediction of the shape of the diffuse crystallization zone is out of scope. It is a consequence of the interaction between crystallization kinetics and heat transfer. Admittedly, the correct theoretical equations for such a description have recently been developed (for the first time in the history of solidification and structure formation! [25]). However, without the knowledge of the pertinent physical data (primary nucleation rates and growth speeds of crystalline regions as functions of temperature) such a calculation is impossible from a practical point of view. In fact, the results of the present paper are representative for part of our efforts in this direction.

A special spot, however, on the central line of the diffuse crystallizations zone is largely independent of the heat transfer problem and is, therefore, uncoupled. This is the point of intersection with the abscissa characterizing the apparent induction time. For this point the temperature of crystallization is fixed as the temperature of the quenched wall, if one disregards the short adjustment time of this wall. We are now going to emphasize that this apparent induction time is not really an induction time but a result of the physics of the observation.

It took us a rather long time to realize that during the initial state of crystallization the crystalline areas are so small that one can consider them as "Rayleigh Scatterers". But the scattering power of a Rayleigh Scatterer is proportional to the square of its volume. (The gross effect, which we envisage, is not changed if the initial scatterers are not ball shaped). As the volume of a ball shaped scatterer is proportional to $(Gt)^3$, one obtains for the scattering power of the unit of volume:

$$S = CN(Gt)^6 , \tag{10}$$

where C is an optical constant, N is the number of nuclei per unit volume, G is the growth speed of spherulites and t is the time elapsed from the moment of the quench of the wall.

If the scattering becomes so large that the microscale is obscured, Eq. (10) is certainly no longer valid. However, it is quite obvious that the onset of a more complex scattering phenomenon does not occur earlier than that of the scattering predicted by Eq. (10). As a parabola of sixth grade shows a quite rapid upswing after some time of unobservable development, one can explain without cerebral acrobatics the occurrence of an apparent induction time. If one now makes the additional assumption that in all our cases the development of the scattering structure occurs along the same route, one is able to construct an equation for the growth speed by rearranging Eq. (10), viz:

$$G = \left(\frac{S}{C}\right)^{1/6} \frac{1}{N^{1/6} \cdot t} , \tag{11}$$

where S is the (constant) critical scattering power at which the microscale is obscured and $(S/C)^{1/6}$ is a factor which can be calibrated at a temperature where crystallization is so slow that G and N can be determined along other routes (say under the polarizing microscope). As one may observe, in Eq. (11) there is still a dependence on the number of nuclei per unit of volume. In fact, this number may change with varying temperatures. However, the sixth root of this number is almost a constant, even if this number changes over about two decades within the interesting range of temperatures, as is the case with i-PP (see Fig. 10). For the way in which this numbers have been determined for i-PP, the reader is referred to the literature [26]. For HDPE the temperature dependence of N appears to be much less pronounced. Chew et al. reported a value of $1.1 \cdot 10^{14} \mathrm{m}^{-3}$ [12]. For a different HDPE our own measurements yielded a value of $5 \cdot 10^{14} \mathrm{m}^{-3}$. In the sixth root there is practically no difference between these values so that Eq. (11) seems to form an adequate equation for the determination of only G as a function of temperature T. The truth of this assumption, however, can only be verified by comparison with values of G, as obtained by independent methods. This was possible for i-PP. It will be shown that this experience was very welcome for HDPE because of the unobservable early development according to Eq. (10). This initially very slow development causes a welcome increase of the time of measurement with this rapidly crystallizing polymer. In Figs. 16 and 17 the corresponding points are marked by "zone".

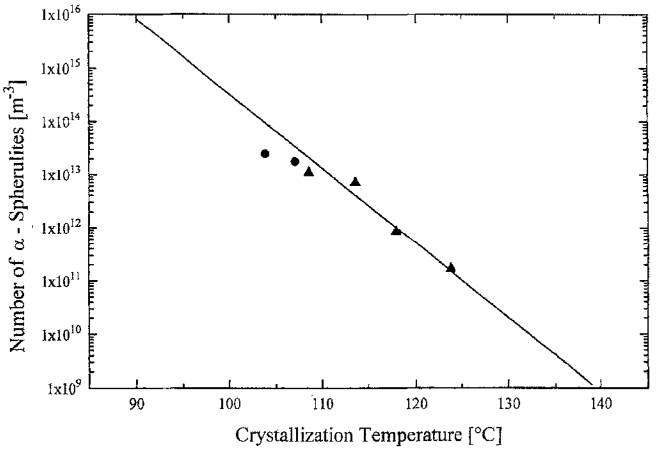

Fig. 10 Number of α-nuclei per unit volume for i-PP Daplen KS 10 as a function of crystallization temperature. The applied method has been described elsewhere [26]

Backward scattering of light

Introduction

Light scattering measurements have frequently been applied for the investigation of the development of crystalline structures in polymer melts. For the purpose, however, an extremely thin sample with a thickness of the order of 0.02 mm was required. Otherwise, multiple scattering would interfere with the usual possibilities of interpretation. According to Stein et al. [27,28], one obtains a characteristic depolarization effect between crossed-polars: For ideal spherulites a light scattering pattern is obtained on a photographic film similar to a four-leaf clover. The corresponding lobes emerge symmetrically under multiples of 45° between the directions of polarization of the polars. The distance between the intensity maxima in the hearts of these lobes and the point of intercept of the primary beam is a measure of the spherulite radius: with increasing radius the intensity maxima shift towards the center. The original work was started on polyethylene films. With more advanced techniques, Keyzers et al. [29, 30] determined the growth of spherulites of i-PS, Van Antwerpen and Van Krevelen [31] investigated the growth of spherulites of PET.

With the fast crystallizing polymers i-PP and HDPE the transient measurements were not very successful. Keyzers could show that the spherulites of i-PP seem to be not sufficiently well structured for the purpose. They show too many defects for being considered as ideal spherulites. Recently, it has been shown in our laboratory that rapidly quenched samples of HDPE and samples of i-PP containing nucleation agents do not show a noticeable depolarization effect at all [32]. Apparently, the spherulites are extremely small and irregular. Also, the development of a proper apparatus was not feasible within the budget and the available time of this research.

As a consequence, our light scattering method was only designed to improve the accuracy with which the moment can be determined when the diffuse crystallization starts at a suddenly quenched wall: A much shorter, almost zero time of adjustment of the surface of the polymer sample was achieved by bringing this surface into contact with a metal block of practically invariable temperature at time zero. The light beam evoking the scattering was directed through the transparent molten sample to the contact surface. Also the back scattering could be observed through the still remaining bulk of the transparent polymer melt.

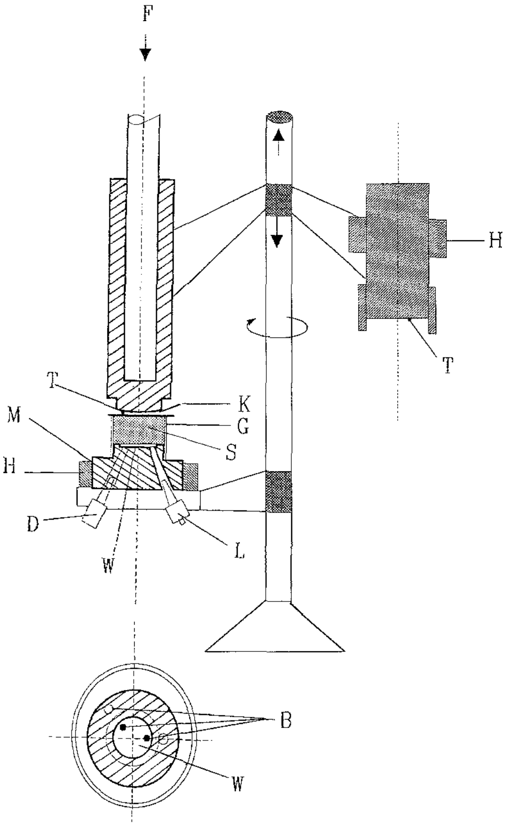

Fig. 11 Schematic presentation of the apparatus for the measurement of the "apparent induction time" with the aid of the back-scattering of light. S = sample, D = exit to diode, L = entrance of Laser light, W = window, M = lower metal block, T = temperature probe in the skin of the upper metal block, K = contact switch, G = confining glass cylinder, H = electric band heaters, F = heat transfer fluid, strongly shaded areas on the central column … clamping areas for the parts, B = collective symbol for the scanty bores (see text)

Experimental set-up

In Fig. 11 the design of the apparatus is shown. The lower metal block M, on which the sample S rests, contains two slanting bore-holes L and D for the entering laser beam and for the light reaching the detector, respectively. In order to prevent the polymer melt from entering these holes and for the sake of avoiding menisci, the holes are covered by a glass window W. The two holes are, in contrast to the impression created by the upper, vertical cross-section, not in the same plane of incidence. In this way it is avoided that reflected light from the originally shining surface of the aluminum foil covering the upper metal block can enter the detector. (The reason for the use of this foil is explained below.) See also the lower, horizontal section, where B is a collective symbol for both scanty borings, of which the entrances are indicated by open circles and the exits by full circles. Laterally, the sample is confined, as discussed in the previous section, by a transparent glass cylinder G for visual inspection. The upper construction of the apparatus is characterized by two rapidly exchangeable metal blocks. The compact block on the right side of the picture is embraced by a heating element by which it is heated up to the initial temperature, at which the lower block M is kept throughout the experiment. As a first step the upper compact block is lowered on the sample. In order to prevent the molten sample from sticking to this block, the sample is covered by an aluminum foil which rests permanently on it.

As soon as the sample is melted and becomes transparent, the mentioned upper heating block is exchanged rapidly by the block shown on the left side of the picture. (It goes without saying that the sample must have assumed a uniform temperature after a proper waiting time, before the exchange of the blocks occurs.) The block on the left side is kept at a desirable contact temperature below the melting point of the polymer. This occurs with the aid of a heat transfer fluid pumped through its interior. In order to improve the contact of the end surface of the left block with the aluminum foil and the polymer lying underneath, the end surface of this block is slightly convex. The temperatures in the metal blocks are checked by thermocouples situated close to their surfaces. The thermal influence of the aluminum foil is disregarded.

The physics of this experiment is characterized by the large difference between the heat penetration coefficients $\sqrt{\rho c \lambda}$ of the metal and of the polymer, where ρ is the density, c the heat capacity and λ the heat conductivity of the material [33]. In the present case the ratio

$$\frac{T_k - T_1}{T_2 - T_k} = \frac{\sqrt{\rho_2 c_2 \lambda_2}}{\sqrt{\rho_1 c_1 \lambda_1}}, \tag{11}$$

with T_k being the temperature at the contact surface, subscript 1 standing for the metal and subscript 2 for the polymer, has a value of about 0.03. As a consequence, one can assume that the upper surface of the polymer melt immediately adopts a temperature very close to the temperature of the metal block. With a difference in T_2 and T_k of the order of 100 °C, this would be about 3 °C. The influence of such a deviation on the measurements is of the order of the error in the measurements.

The moment when the cooled upper block makes contact with the melt is recorded by a contact switch K. A corresponding signal turns up on the computer screen. As soon as the contact between block and polymer melt is established, the crystallization is assumed to start at the contact surface. After some time the corresponding backward scattering becomes noticeable by visual inspection as a grayish coating. At the same time the detector records the increasing light scattering.

In Fig. 12 the corresponding picture, as it appears on the computer screen, is shown. On the abscissa the time is plotted, whereas the (inverted) diode signal of the detector is plotted at the ordinate. This figure is for a melt temperature $T_i = 170$ °C of i-PP and a wall temperature of 85 °C. The contact was made at 26.03 s, whereas the diode signal becomes noticeable at 26.75 s. So the "apparent induction time" is 0.72 s. After some time the diode signal levels off. This is to be expected. If this happens, the diffuse crystallization zone is fully developed and moves downward through the sample. From an optical point there is no change any more as soon as the diffuse crystallization zone departs from the metal surface. If the "apparent induction time" is long enough, which happens at the higher wall temperatures, also a stop watch can be used for its determination. With the aid of Eq. (11) the corresponding values of G can be calculated. The corresponding points are indicated in Figs. 16 and 17 by the codes "scattering/a" (diode measurement) and "scattering/b" (use of stop watch).

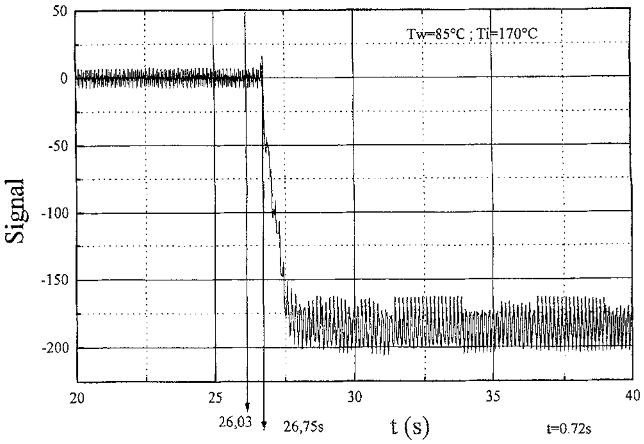

Fig. 12 A typical example for the picture obtained on the computer screen, if the "apparent induction time" is determined with the aid of the back-scattering of light for i-PP. The contact of the cool surface of the upper block with the upper surface of the polymer occurred at $t = 26.03$ s. At $t = 26.75$ s the (inverted) scattering signal starts to change rapidly. The "apparent induction time" is 0.72 s. For details see the text

Quenching of extremely thin films

Introduction

The basic idea of this type of measurements is that a crystallizing sample is suddenly quenched at a rather early stage of crystallization, so that the momentary structure elements can be observed microscopically. This is possible because of the fact that the final quench to a sufficiently low temperature (for i-PP the temperature of ice water is certainly adequate) causes an additional very fine grained structure which can easily be discerned from the structure formed during the primary crystallization. The difficulty with this method is only that primary structures become finer and the number of spherulites increases rapidly, when the primary crystallization temperature is lowered. Unfortunately, precisely in the lower crystallization temperature range physical data are very desirable.

A way out of this situation was shown in principle already by Barham, Jarvis and Keller [34]. These authors prepared suspensions of very small droplets of the polymer melt and quenched these suspensions. The concept of this procedure becomes clearer if instead of droplets ultrathin samples are embedded between cover glasses. The surfaces of those glasses are, like surfaces of real fluids, inactive in nucleation. In such a thin liquid film of the polymer the number of growing spherulites is drastically reduced when compared with a liquid layer of the same thickness when forming part of the bulk fluid. The reason is that all the spherulites which are nucleated in neighboring layers of the bulk, do not show up in the separated thin liquid film. Experimentally, Chew, Griffith and Stachurski [12] have made use of this insight. Theoretically, this effect has been predicted by Billon, Escleine and Haudin [13]. As a consequence the spherulites can grow out to much bigger size. In fact, they rather form disks instead of spheres. One can only hope that their growth speed is not too much influenced by the rim angle between the crystallization front and the glass wall. If the rim angle is finite, disklike, "spherulites" nucleated near the mid-plane will grow a little faster than those nucleated close to the glass surface. So, a comparison of the pertinent results with those obtained with the aid of independent methods will be of great importance. Such a comparison will be carried out in the next section. In fact, for all methods proposed in this paper some uncertainties are inherent, so that only the final comparison will provide the desirable trustworthiness.

Set-up of the measurements

In our case thin samples of i-PP of a thickness of 5 μm were cut with the aid of a microtome. These samples were placed between cover glasses of 0.15 mm thickness. To begin with, these sandwiches were kept for 10 min at 240 °C. In this period the i-PP film becomes fluid and transparent. Subsequently, these sandwiches were quenched in ethylene glycol of a chosen temperature of crystallization. They are kept at this temperature for various periods of time and are finally quenched in ice water. In Fig. 13, one finds the microscopic picture of a sample which was held at 110 °C for 32 s. Notwithstanding the fact that at these conditions of crystallization some spherulites have already impinged on each other, one will still find enough free spherulites of which the diameter can be measured. The same holds for Fig. 14. The pertinent sample was held at 95 °C for 39 s. As one can see in Fig. 13, there are areas where holes have been formed as a consequence of the shrinkage occurring during the crystallization process. In the neighborhood of these holes the spherulites can be deformed because of the shortage of crystallizable material. Nevertheless, at all chosen temperatures of crystallization some spherulites of good shape can be found. These spherulites are surrounded by a fine grained structure, apparently being formed during the final quench, as already pointed out.

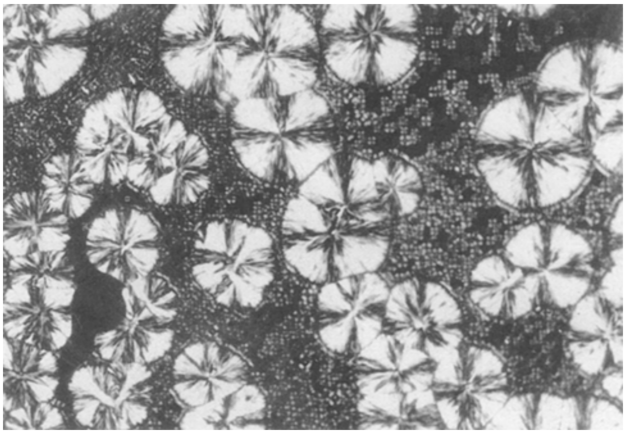

Fig. 13 Photograph of two-dimensional "α-spherulites" of i-PP Daplen KS 10, which grew in a bath of 110 °C for 32 s. The diameter of the largest spherulites is 0.14 mm. At several places, in particular on the lower left side holes can be observed. Apparently, these holes are a consequence of the shrinkage during crystallization

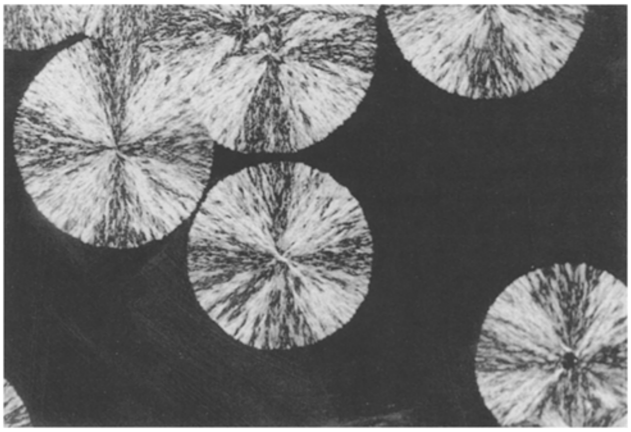

Fig. 14 Photograph of two-dimensional "α-spherulites" of i-PP Daplen KS 10, as obtained in a bath of 95 °C after a temper time of 39 s. The diameter of the biggest spherulite (upper left corner) is 0.177 mm

Interestingly enough, all intact spherulites are of the same order of magnitude. If there would be sporadic primary nucleation, one should find a great variety of spherulite sizes belonging to those nucleated immediately after the first quench to those smallest ones created just before the final quench. For the narrow size distribution there are three possibilities of interpretation: a) imperfect quench, b) pullulation only within a very short initial period and c) a finite contact angle between the "spherulite" surface and the glass surface. In the latter case "spherulites" nucleated in the middle of the sample will obtain the largest radii.

In Fig. 15 the largest spherulite radii of i-PP are plotted against the time of crystallization for a large number of crystallization temperatures. From the slopes of the neat

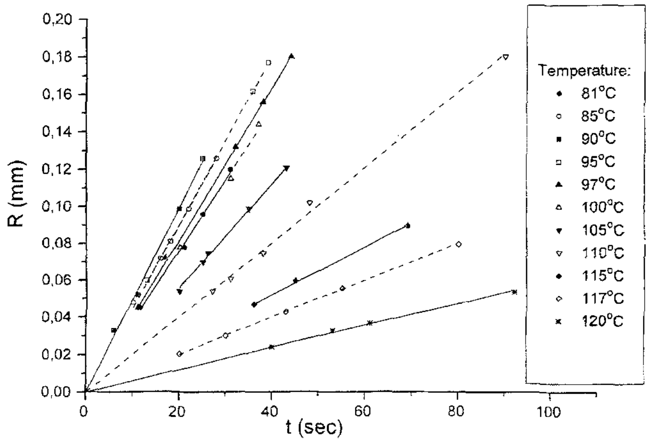

Fig. 15 Radii of the biggest α-spherulites of i-PP Daplen KS 10 against the temper times for a series of bath temperatures

straight lines connecting the points of measurement the growth speeds are obtained for the mentioned temperatures of crystallization. The accuracy of the method is remarkable. It is also striking that all lines go through the origin. But this means that there is no time of induction! This observation is very important in connection with the credibility of the methods described in this paper, and in particular for the usefulness of the back-scattering method. Also, from a theoretical point of view this result is satisfying. In fact, in previous papers we have argued that it will be practically impossible to determine the parameters of a complete activation time spectrum for all interesting temperatures. Our only way out of this difficulty was the hope that in athermal nucleation, which occurs at larger degrees of supercooling, the fluctuations preformed at the previous melt temperature and frozen in during cooling become immediately active, if the temperature, at which they are large enough for their growth, is reached. The number of these nuclei will be just a function of temperature. An argument in favor of this concept has been published elsewhere [19, 26, 35]. This concept means that the rate of nucleation simply becomes:

$$\frac{dN}{dt} = \frac{dN(T)}{dT}\frac{dT}{dt} . \qquad (12)$$

All the simplifying assumptions, as made so far by other authors, lead to unacceptable results: Actually, they are unable to predict realistic structures which, in general, have to depend on the cooling rate. Their "structures" are predetermined in some way and do not depend on the cooling rate. For this fact a formal proof has been given elsewhere [35].

Results

Growth data for i-PP

In Fig. 16 the data for the α-spherulites of several samples of i-PP are collected, as they were obtained with the aid of various methods and by several authors. Our own results were mostly obtained with PP-Daplen KS 10 4095 D II. The literature data were obtained on a variety of industrial polypropylenes. In this respect we are consoled by Magill's finding [36] that for polymers with a molar mass higher than a certain critical molar mass the growth speed of spherulites is independent of the molar mass. An influence of varying degrees of tacticity, however, cannot be excluded [8–10]. Nevertheless, data from various investigators fit quite nicely in the temperature ranges of overlap.

The symbols in Fig. 16 have to be explained. Below this figure there is a list of symbols with the pertinent references. In particular "from β" means that these points are calculated with the aid of Eq. (1) and with the use of cone-angles like those shown in Fig. 2 for the β-modification, as presented in Fig. 6 (open squares). These points almost perfectly coincide with the points obtained from microtome cuts (our Section 6, closed circles). Remarkably, with the latter method measurements could be extended down to 82 °C. The confidence in these measurements is improved by the coincidence with the values from the β-modification. Also Yu Long, Shanks and Stachurski [37] reported growth measurements obtained on thin layers. Their points are given by open triangles pointing downwards. One notices that these points lie a little higher than the points reported by Von Falkai [5] (open triangles pointing upwards), Padden and Keith [1, 2] (open circles) and Lovinger et al. [4] (open rhombuses). Interestingly enough, our lowest point (open square at 130 °C) "from β" lies quite close to the points by Yu Long et al. For the method using the "apparent induction time" we need a point of adjustment for the optical paramater of Eq. (11). This point is chosen as a full triangle pointing downwards at 130 °C just in the middle between the other points which are obtained at this temperature. The same point is also used for "scattering/a" (diode measurements) and "scattering/b" (use of the stop watch). Some points, which are calculated from electron micrographs as obtained by Olley and Basset [38] after crystallization in the high temperature range, are added as stars. One may observe that, within the apparently inavoidable scatter of the points also the points obtained from the "zone" (including those from back scattering) lie on the same trail. This is an important statement, because we shall see that for the rapidly growing HDPE an extension to low temperatures is only possible with the aid of the

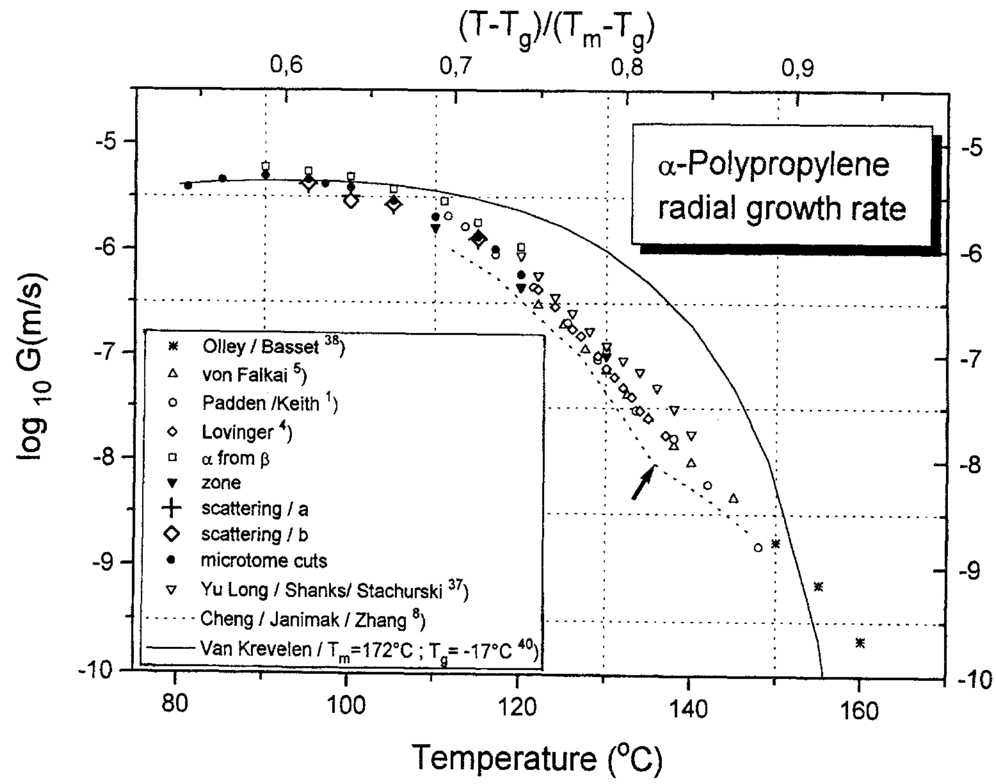

Fig. 16 Compilation of presently available data for the growth speeds of α-spherulites of i-PP. Below the figure the symbols are assigned to the respective references or, for our own work, to the methods used (α from β means: taken from figures like Fig. 2 with the aid of Eq. 1). Observe that the lowest crystallization temperature quoted in the literature is ≅110 °C. So, we could go down to 80 °C. The full curve is according to Van Krevelen's equation (Eq. (13))

back scattering method. The location of the line produced by Cheng et al. [8–10] for their highest degree of tacticity is indicated as a dotted line. This line clearly lies below the area of our results, notwithstanding the fact the degrees of tacticity of our industrial samples are certainly lower. This points to the suspicion that heat transfer in the hot-stage method is insufficient at lower temperatures. An interpretation of the full theoretical line, which is inserted into Fig. 16, will be postponed to a general discussion. At this point one may only state that the theoretical line correctly predicts the temperature range of the maximum growth speed as well as its height. There is no doubt that only our own measurements enabled us to make this comparison. None of the previous measurements could be extended down into the interesting temperature range of the maximum.

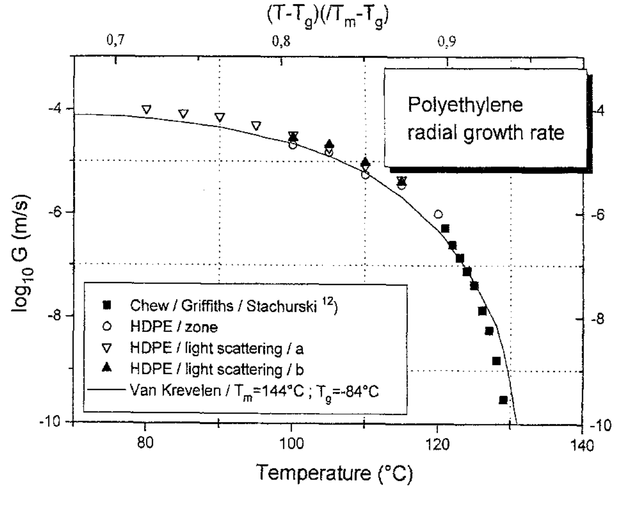

Fig. 17 Growth speeds for HDPE. Our scattering and zone results are calibrated at 120 °C by the results of Chew et al. [12]. Light-scattering/a was detected by the diode, light-scattering/b by visual observation with the use of a stop watch

Growth data for HDPE

In Fig. 17 the data for HDPE are collected. For the range for higher temperatures – roughly between 130° and 120 °C excellent measurements are available as obtained by Chew, Griffiths and Stachurski [12]. Also these data are obtained by the two-dimensional thin layer method, as driven to high perfection by the mentioned authors. For HDPE a special method was developed by these authors for an optical registration of the rather rapid growth of the spherulites of HDPE. Our zone and back-scattering method was adjusted at 120 °C. One may observe that the spread in these points is much lower than with i-PP. The reason is that the zone is much "sharper" with HDPE. Our achievements with respect to the temperature range are quite impressive. Whereas Chew et al. had to stop at 120 °C, we went down to 80 °C. A theoretical line according to Van Krevelen [14] is inserted, which fits the data quite well. The pertinent interpretation will be given in the general discussion.

General discussion

On the basis of many experimental results on slowly crystallizing polymers possessing a single crystallization modification, Van Krevelen [14] proposed two equations for the temperature dependence of the growth speed of spherulites, one for the temperature range between the glass transition temperature T_g and some temperature T_k about halfway between glass transition and melting point T_m. In this equation the transport processes are described with the aid of the WLF-equation [39]. In the temperature range between the melting point and the mentioned temperature T_k an Arrhenius type of equation is used, because of the fact that the WLF-equation, which describes a much steeper temperature dependence, only holds to about 100 °C above the glass transition temperature [39]. This remark will be of some importance in this discussion.

As the measurements presented in this paper are carried out in the upper range of temperatures, between T_m and T_k, only the second equation by Van Krevelen is presented here. It reads:

$$\log G = \log G_0 - 2,3\frac{\xi}{1-\delta} - \frac{115}{T_m}\frac{\xi^2}{\xi - 1}\,, \tag{13}$$

where G_0 is a universal constant equal to about 10^{12} mm/s, $\xi = T_m/T$ and $\delta = T_g/T_m$, with T being the temperature where the crystallization is observed.

Interestingly enough, this equation seems to hold quite well for HDPE, if the values for $T_m = 144\,°C$ and $T_g = -84\,°C$ are used, where the T_m-value is adjusted to the points reported by Chew et al. [12]. This is demonstrated by the full line in Fig. 17. This fact furnishes an important support for our measurements as carried out with the aid of backward scattering of light (zone crystallization), which were the only measurements possible in the temperature range between 80° and 120 °C. (For HDPE Eq. (13) is quite insensitive to the precise choice of T_g.)

Apparently, the situation with i-PP is much more complicated. If an effective melting point of $T_m = 172\,°C$, and an effective glass transition temperature of $T_g = -17\,°C$ are used, as proposed by Van Krevelen [40], one obtains the line drawn in Fig. 13. This line goes through the points by Olley and Basett in the high temperature range and describes the height and the location of the maximum on the temperature axis quite well. An objection may be that a very low value of T_g is chosen. In fact, if a value of $-9\,°C$ is used, the height of the maximum will be insufficient (about a factor two too low). An excuse for the low value of T_g, as proposed by Van Krevelen, may be that the glass temperature should be influenced by the degree of crystallinity [41]. In fact, the molecules are much more hampered in their movement if they are connected to several crystalline regions. So, in a thoroughly amorphous sample the glass temperature may actually be 12° lower than in a semicrystalline sample. It seems that, at the onset of crystallization, as occurs in the high temperature range, the molecules in the amorphous regions still are much more mobile than at the final degree of crystallinity.

In a temperature range in the middle of the experimentally available range the positions of all experimental points are much lower than expected from the prediction of the theory. Certainly, the reason for this deviation is the complicated crystallization mechanisms of i-PP. Nominally, Fig. 16 holds for the α-modification. However, as already mentioned in the introduction, there are two types (type I and type II) of α-modifications. Some elucidation is obtained, when the dotted line as obtained by Cheng et al. for the highest tacticity, is observed. From the shapes of the curves for the samples with decreasing tacticity, which gradually shift to lower G-values, it becomes evident that the transition from type I to type II should occur at the little arrow shown in Fig. 17. It seems that also the results gathered by us reflect this transition.

With i-PP, however, there is still another discrepancy with the mentioned theory. According to this theory the shape of the curve for the growth speed only depends on the ratio of the glass to the melting temperature $\delta = T_g/T_m$. The larger this ratio, the higher the growth speed in the whole temperature range. In this theory, however, the fact remains unexplained, why the growth speeds of the β-modification should be higher in a considerable temperature range, notwithstanding the fact that the melting point of this modification must be considerably lower, viz ≈ 145 °C, than that of the α-modification.

The better fit of HDPE can also be due to the fact that with this polymer the temperature T_k of the maximum speed is safely 100° above the glass temperature. As a consequence, the validity of the WLF-equation is certainly restricted to a range below T_k. With i-PP this is not so evident. With this polymer the distance between T_g and T_k is smaller so that the maximum speed may be influenced by the lower branch of Van Krevelen. Also this may explain, why one must insert a surprisingly low value of T_g into Eq. (13), in order to enable this equation to describe the correct height of the maximum.

Another important conclusion of this research is that the "effective" melting point can easily be adjusted to the growth speeds at high temperatures, which can be determined experimentally quite accurately. At lower temperatures, however, more experimental measurements are indispensible even if these measurements are rather difficult. For i-PP we have gathered many experimental points from a series of independent approaches, so that there is no doubt about the extraordinary behaviour of this polymer.

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