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THE ROLE OF TRANSPORT PHENOMENA IN POLYMER SCIENCE

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ABSTRACT

Very often a contrast is constructed between so-called applied research and basic research. According to the present author, not only is basic knowledge in the usual sense (in physics, chemistry, etc.) of importance for engineers. The inverse situation can also occur. Branches of science, which typically emerged from technological problems, can become of particular interest for the solution of fundamental problems. One can almost say that many problems of a fundamental nature have not been solved because of a lack of feeling for technical problems at the hand of the pertinent expert. For many years the author has pointed to relations between, say, the measurement of flow birefringence of dilute polymer solutions (for the purpose of polymer characterization), polymer melt processing, and aspects of crystallization from polymer melts.

INTRODUCTION

A typical branch of science, as instigated by technology, is that of transport phenomena. The first balanced lecture course in transport phenomena was drawn up by Prof. J. Kramers at Delft University in the mid-1950s. The famous book *Transport Phenomena* by R. B. Bird, W. E. Stewart, and E. N. Lightfoot [1] came

†H. C. Brinkman in memoriam. Lecture presented by the author on the occasion of receiving the H. F. Mark Medal in Vienna on March 3, 1995.

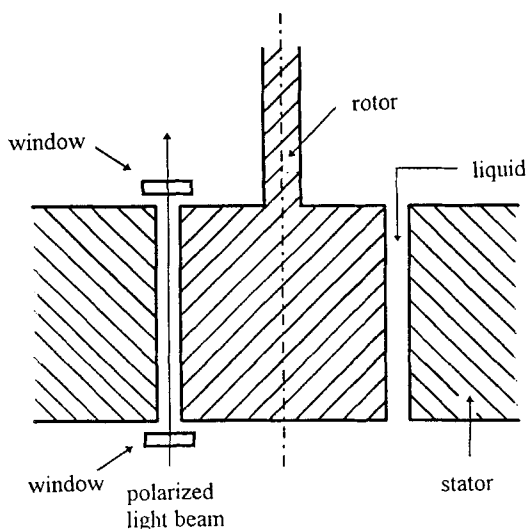


FIG. 1. Schematic presentation of an apparatus of the Couette-type for the measurement of flow birefringence.

out in 1960. It was clearly inspired by the initiative of Kramers. Later W. J. Beek, the successor of Kramers, continued the Delft tradition. A book with the same title was written by Beek and K. M. K. Mutzall [2] in 1975. Momentum, heat, and mass transfer are treated from a common point of view in these books. The first subject has grown out into a tremendously extended field, the field of rheology, which is of particular interest in polymer science. In that which follows the author will present three examples from his own research activities in which flow and heat transfer were of great importance, viz, for the construction of a suitable apparatus for the measurement of flow birefringence of polymer solutions, for an adequate interpretation of data from differential scanning calorimetry (DSC), and for the determination of kinetic data of crystallization from polymer melts.

FLOW BIREFRINGENCE APPARATUS

In the early 1950s the author was asked by his director at T.N.O. in Delft, Prof. A. J. Staverman, to develop an apparatus for the measurement of the flow birefringence of dilute polymer solutions. At that time there was great hope that this type of measurements would contribute considerably to the knowledge of single macromolecules, a hope which recently received a revival, as will be shown below. In Fig. 1 the principle on which the said apparatus is based is shown. The fluid to be investigated is contained in the concentric gap of a Couette-type viscometer. If the internal cylinder is rotated, the fluid becomes birefringent. In principle, this birefringence can be measured by any classical or advanced method [3, 4]. In this way one obtains two curves: The extinction angle and the value of the birefringence, both as functions of the rate of shear, which is sufficiently uniform if the gap width is small compared with the radii of the cylinders.

In Figs. 2 and 3 the said curves are shown for solutions of varying concentrations of an isotactic polypropylene with a weight-average molar mass $M_w = 480,000$ and a nonuniformity $M_w/M_n = 3.5$ [5]. *trans*-Decalin was used as a solvent at a temperature as high as 150°C . These pictures serve as illustrations of the type of measurements expected. The reader may notice that all extinction angle curves start at 45° with respect to the flow direction. In fact, the high temperature of the measurement, which is necessary for a crystallizable polymer, is sensational from the point of the experimental technique. It could only be reached with the apparatus to be described in this paper. Both types of curves allow important conclusions with respect to the nature (in particular, the molar mass distribution) of the polymer [6].

In conventional apparatuses the range of accessible shear rates is limited at high values by two effects: (a) The onset of turbulence (which can be shifted to higher values if a rotating outer cylinder is chosen [7]). However, with a gap as narrow as the one in our apparatus, this shift is not overwhelming). (b) The so-called "Björnsthål effect" [8]. This effect is a kind of Schlieren effect and is caused by internal friction in the streaming fluid if this heat is transferred to the thermostated (metal) walls of the cylinders. As a consequence, a parabolic temperature profile is formed over the cross-section of the gap, with a maximum in the center of

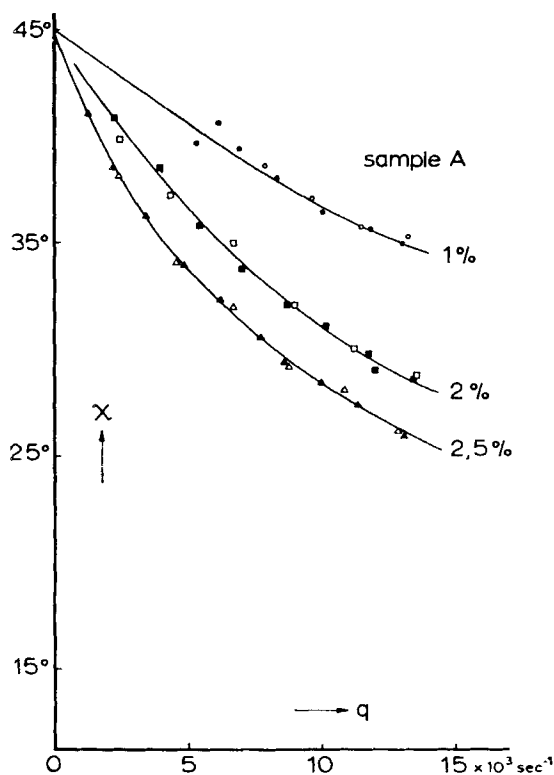


FIG. 2. Extinction angle as a function of the shear rate q for solutions of an industrial polypropylene in transdecalin at 150°C . The open and closed symbols indicate repeat measurements. (Courtesy of Dietrich Steinkopf Verlag Darmstadt.)

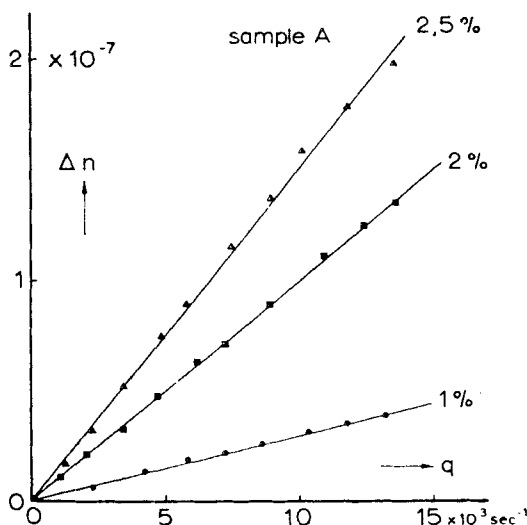


FIG. 3. Flow birefringence Δn as a function of shear rate for solutions of an industrial polypropylene in transdecaline at 150°C. (Courtesy of Dietrich Steinkopf Verlag Darmstadt.)

the gap. The height of this maximum is proportional to the square of the shear rate applied. Paradoxically, this effect is usually much more pronounced with dilute solutions than with polymer melts. In fact, the observed birefringence is roughly proportional to the shear stress τ with polymeric systems [6], whereas the frictional heat evolved per unit of volume and time is equal to the product of this shear stress with the shear rate q , which must be chosen much higher for solutions.

In a quiescent solution the elimination of the gap is adjusted so that reflections from the cylinder walls are avoided and, at the same time, a maximum amount of light passes through the gap. This subtle adjustment is gravely disturbed by the mentioned temperature maximum: With an increasing rate of shear, more and more light is diverted to the walls, where the temperature is lower than in the middle. This light forms bright bands of reflected light in the ocular. Their brightness between crossed polars points to the fact that parasitic phase differences are caused by (multiple) reflection from the metal walls which occur, in particular, if these walls still have grooves from their machining. A single reflection can cause a phase difference comparable with the one to be measured as a result of flow birefringence. The described severe state of depolarization was recognized and described first by Björnsthål [8], who did not see a way to avoid this disturbance. Other authors have ignored this effect. As a consequence, the values of their measurements remain rather dubious.

The present author, as a young guest researcher in the Netherlands, thought he could not afford a failure in developing a useful apparatus. According to the proverb "necessity is the mother of invention," he found the principle that makes it possible to avoid the Björnsthål effect: If the cylinder walls were adiabatic and the frictional heat could be removed by an axial convection stream, the said maximum would be replaced by a minimum of the temperature in the middle of the gap. The

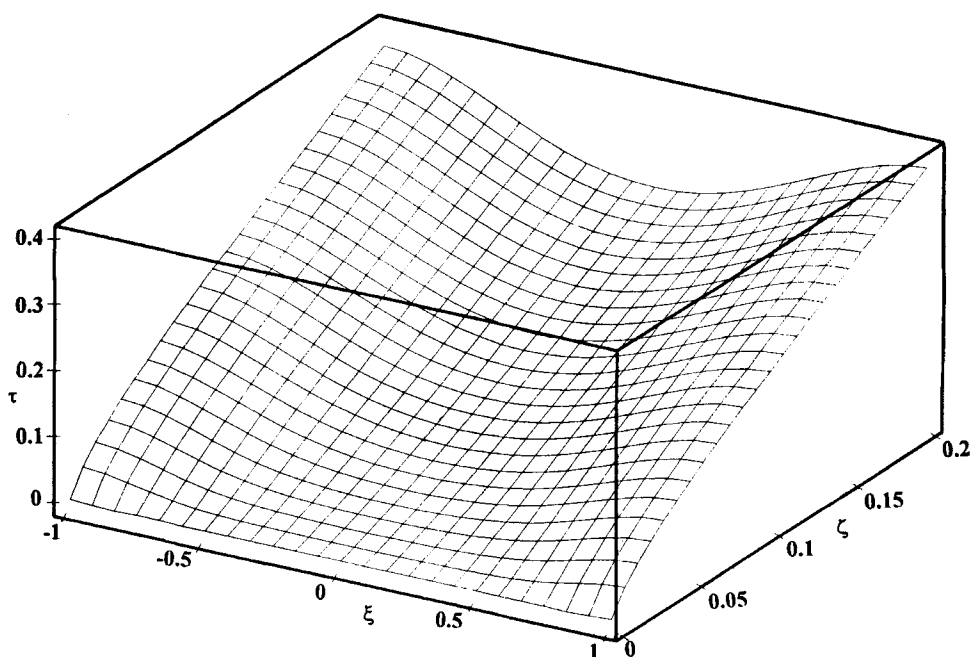


FIG. 4. Temperature distributions near the entrance of a convection stream in the z -direction superimposed in the gap on homogeneous heat production with adiabatic walls at $\xi = \pm 1$, Biot = 0. For the dimensionless variables, see the text. (Courtesy Dr. G. Eder.)

only disadvantage would be a nearly linear increase of the average temperature in the axial direction, but this effect could be kept within tolerable limits and would be of no optical consequence. The said minimum, however, would focus the light beam instead of breaking it up. In Fig. 4 the kind of temperature distribution expected in this case is shown.* The distribution resembles a gutter through which water flows. The dimensionless variables (ξ for the direction perpendicular to the gap, τ for the temperature, and ζ for the direction of the convection stream) will be explained below. But one thing is clear without such an explanation: The Björnståhl effect cannot occur in such an arrangement. It is also important to know that the shear flow of the Couette apparatus and the convection stream can be adjusted so that the shear flow remains dominant, as must be postulated, whereas at the same time the temperature increase in the direction of the convection stream remains acceptable. The only difficulty with this concept is that there are no materials from which adiabatic, viz., completely insulating, walls can be made. So, one has to choose a material with a heat conductivity as low as possible. For this purpose dark glass was chosen, which is also a material which can be machined extremely well by grinding and polishing on a lathe. An additional advantage of glass is that any inadvertently occurring reflection is of minor influence on the state of polarization.

*The author is very much indebted to his present cooperator G. Eder for producing the computer graphs. In 1955 the author used a method described in an epoch-making paper by H. C. Brinkman [9].

Unfortunately, with glass walls the full-fledged heat transfer problem, including the wall influence, had to be treated [10]. This had not been done before, as H. H. Winter confirmed to the author after having prepared a review on the influence of the wall on the temperature distribution in tube flow of polymer melts [11]. For the purpose of the flow birefringence apparatus, where the curvature of the cylinders can be disregarded, the treatment of the flat problem will suffice (as with the preparation of Fig. 4).

The above-mentioned dimensionless variables are

$$\xi = 2x/d, \tau = 1/\text{Br}, \text{ and } \zeta = 2/\text{Gz} \quad (1)$$

where

$$\text{Br} = \frac{\eta q^2 d^2}{\lambda_f T} \quad (2)$$

is the Brinkman number, viz., the ratio of the frictional heat produced in front of the unit surface of the wall per unit of time $-\eta q^2 d/2$ —to the heat transported per unit of time with the aid of the heat conductivity of the fluid to the said wall, where η is the viscosity, λ_f is the heat conductivity of the fluid, q is the shear rate, T is the temperature with zero level at the wall, and d is the gap width.

The dimensionless number occurring in the third Eq. (1) is the Graetz number:

$$\text{Gz} = \text{Re Pr} \frac{d}{4z} = \left(\frac{\rho d}{\eta} \frac{d^2}{8\eta} \frac{\Delta P}{\Delta L} \right) \left(\frac{\eta c}{\lambda_f} \right) \frac{d}{4z} \quad (3)$$

In this definition two other well-known dimensionless numbers, viz., the Reynolds and the Prandtl number, occur. They are explained for the present purpose by the expressions in parentheses, where, in addition to the variables occurring in Eq. (2), z is the distance from the entrance of the convection stream, ρ is the density, c is the heat capacity of the fluid, and $\Delta P/\Delta L$ is the pressure gradient in axial direction, which causes the convection stream. These terms are found in Brinkman's work although the present definitions are from a later date when the subject "transport phenomena" was established.

The influence of the wall is described by Winter in terms of the Biot number, which reads in the case of our problem:

$$\text{Bi} = \frac{\lambda_g}{\lambda_f} \frac{d}{2D} \quad (4)$$

where the conductivity λ_g and the thickness D of the glass wall appears as an additional parameter. In the original paper [10] this parameter is simply called c .

For the solution of the posed problem, a coupling of $\Delta P/\Delta L$ with q is unnecessary. However, an additional condition must be that the convection stream is of no noticeable influence on the measurement of the flow birefringence. As a consequence, the strength of the convection stream was chosen so that its maximum shear rate near the duct walls was always one-tenth of the shear rate q of the Couette flow. Because of the fact that the absolute value of the resulting shear rate of two streams of mutually perpendicular directions is the square root of the sum of the squares of the shear rates of the components (the sum according to Pythagoras), an error of about 1% is expected as the maximum error near the walls. The only

remaining open question is whether such a relatively weak convection stream can be effective enough. However, this could be shown by quantitative calculations.

In Fig. 5 the corresponding presentation is shown where, for reasons of the drawing technique, the difference between the temperature of the internal side of the glass wall and that of the external side (= thermostat temperature) is subtracted from the internal wall temperature. Because of this subtraction the temperature at the inner wall of the gap seems constant. The advantage is that the temperature profile in the fluid can now be drawn on a larger scale. For these calculations a Biot number of 0.043 was chosen, which seemed adequate for a normal organic solvent and glass walls with $d = 0.25$ mm and $D = 10$ mm. One notices the following tendency: With small values of ζ one obtains a strong concave curvature, whereas with increasing ζ one finally ends up with a convex parabolic temperature distribution with a maximum in the center of the gap. One can recognize a certain penetration depth for the concave profile. Interestingly enough, one obtains a smaller penetration depth if a wider gap is used. If metal walls are applied (with $c \rightarrow \infty$), the penetration goes no farther than $\zeta = 0.8$. This means that with metal walls there is no chance to realize the described concept.

At this point a (qualitative) interpretation of the computer graphs of Fig. 5 seems adequate. For a fixed length of the cylinders at $z = L$ (with $L = 50$ mm in our case), one has a low value of ζ if a high rate of shear q is chosen (and $\Delta P/\Delta L$ is

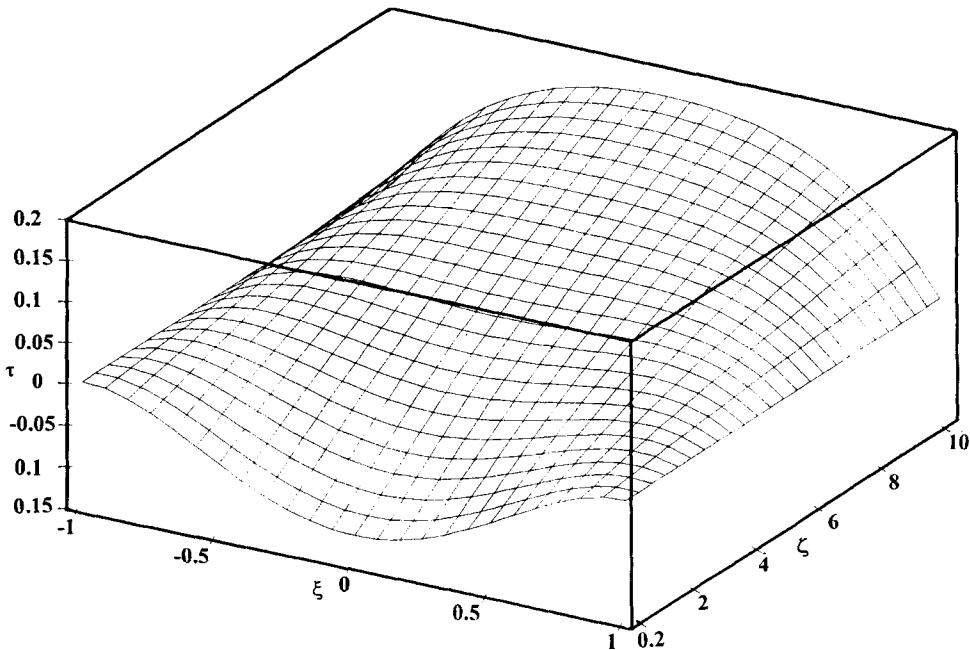


FIG. 5. Temperature distributions near the entrance of a convection stream in the z -direction superimposed in the gap on homogeneous heat production with heat conducting walls (Biot = 0.043). The temperature on the internal wall surface, which increases in the flow direction, is subtracted. As a consequence, this temperature appears constant. For the dimensionless variables, see the text. (Courtesy Dr. G. Eder.)

adequately coupled to q). At the same time, a high value of T corresponds to a certain value of τ . However, because of the concave curvature there will only be the desirable result of a strong focusing of the light beam. (Without a convection stream one would obtain a high maximum of T in the center of the gap and, as a consequence, a tremendous Björnståhl effect.) At low rates of shear (of the Couette flow) there are relatively high values of ζ . But, at the same time, only a low value of T will correspond to a certain value of τ . In other words, there will be a temperature maximum in the center of the gap, but this maximum will be harmless because of its low height. The final conclusion to be drawn is that the dreaded Björnståhl effect will no longer occur with such an arrangement.

Interestingly enough, there is also a second type of penetration depth which is of a mechanical nature. If one looks at Fig. 2, one notices that the mechanical relaxation time of the curves is of the order of 0.5×10^{-4} second (see the medium initial slope of the curves). On the other hand, one can calculate for the highest shear rate of $1.5 \times 10^4 \text{ s}^{-1}$ that a "particle" entering the gap with the convection stream will reach the other end of the cylinders (with $L = 50 \text{ mm}$) after 0.5 second. Comparing 0.5×10^{-4} second with this latter time span, one can conclude that the mechanical penetration depth is only 10^{-4} times the height of the cylinders, so that the steady-state flow birefringence is measured with high accuracy. This is typical for a system containing a fluid of a relatively high Prandtl number (low heat conductivity and normal viscosity) in combination with a low heat conductivity of the walls. The complete success of the concept is demonstrated in this way.

In Fig. 6 a drawing is shown of the apparatus as developed at TNO in Delft at the time [6].* The closer explanation of the parts is given in the legend to the figure. The rotor unit works in the following way: The light beam is indicated by the vertical line L-L. The design of the windows is that of a diving bell which prevents any contact between the fluid in the rotor unit and the (thick) fluid used for sealing purposes. As a consequence, even at a temperature as high as 150°C , no leaks are observed and, at the same time, no extra stresses are created in the windows by the hardening effect of a glue. The internal cylinder is driven by the very thin shaft (6). In this way any heat flow through the axle of the apparatus, as observed with previous models, is avoided, so that the whole unit, which is enclosed in a thermostat, is in thermal equilibrium. The core of the internal cylinder, which is made of stainless steel, is pressed around a bronze cylinder. The stationary axle (5) is mounted on the inner side of the cover and together with the bronze cylinder forms a journal bearing. The differing thermal expansion of the bronze cylinder is suppressed by the strong core of the internal cylinder so that there is no noticeable play between the bronze bush and the axle (but also no squeezing) over the whole temperature range envisaged. The convection stream is produced by the screw pump (9). With this apparatus one can perform impeccable measurements in the unprecedented temperature range between zero and 160°C . As a consequence, crystallizable polymers can also be investigated by high temperature measurements (i-PP, LDPE, HDPE, i-PS, and others) [6]. The thermal stability of this rotor unit is unique.

*In this connection the author wants to memorialize the merits of his old friend, the late R. Nauta, at the time instrument maker at the Central Laboratory TNO.

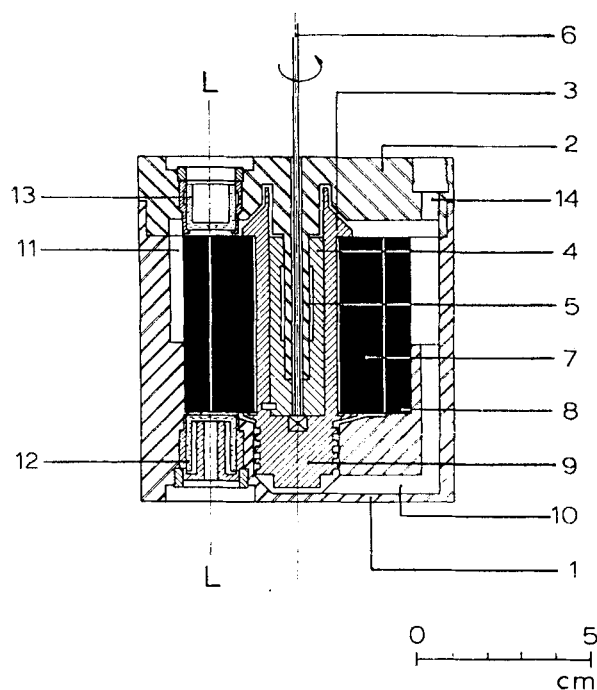


FIG. 6. Cross section of the rotor unit for measurements in a wide range of temperatures, as developed at the Central Laboratory TNO. (1) Pot, (2) cover, (3) rotor, (4) bronze bush, (5) axle, (6) driving shaft, (7) internal cylinder of black glass, (8) external (stationary) cylinder of black glass, (9) screw pump (the way to fasten the screw pump to the rotor is not shown), (10) bore for fluid circulation, (11) chamber, (12) lower window, (13) upper window, (14) filling hole. LL represents the direction of a light beam.

Comparable results have never been obtained before and after the moment when the activities had to be finished.

The described apparatus has recently evoked the interest of a research group around Prof. Ch. Öttinger [12-14] at the Technical University in Zürich. After this working group recently succeeded in improving the theory of the behavior of macromolecules in dilute solution to a considerable extent, it appeared that only the old measurements of the author and his cooperators to that time were useful. Unfortunately, at that time the author was obliged to concentrate at TNO on projects more relevant for industry. His superior, Prof. H. C. Brinkman, made him the leader of a newly founded group working on polymer melt extrusion because of his conviction that related problems of flow and heat transfer of great industrial relevance would occur in this field. As a consequence, the properties of the flow birefringence apparatus, as described above, could be exploited only insufficiently. The group at Zürich recently approached the author with an inquiry about the fate of this old apparatus. Fortunately, it appeared that all the relevant parts still existed thanks to the carefulness of the latest assistant of the author at TNO, Mrs. B. M. J. Baller. So, the apparatus could be restored, and it was sent to Zürich in 1994.

TRANSITIONAL CONSIDERATIONS

The work on screw extrusion resulted in the reputation of the author as a physical chemist familiar with industrial problems. As a consequence of this reputation, he was appointed to a professorship in the physics and chemistry of macromolecular compounds at Delft University of Technology in 1968. However, his research at this university quickly turned to more fundamental problems because other people considered themselves responsible for industrial subjects. However, near the end of his activities in Delft, and inspired particularly by the results of a famous thesis of one of his previous collaborators at TNO. (Wales [15]; see also Refs. 4 and 16), it grew clearer to him how the birefringence patterns in injection molded parts of amorphous polymers come into existence [17]. A maximum of birefringence is always found close to the wall of the mold. Its height and its distance from the wall are quantities which both have maxima about halfway between the gate and the end of the flow path where the mold is completely filled. It appears that these characteristics are the consequences of an interplay between the convection of heat in the flow direction and the local residence times at the cold mold wall. In fact, flow causes the flow birefringence which marks the location of the maximum because it is frozen in by the cooling process. This theory was later improved [4, 18] and verified almost quantitatively by a numerical simulation [19]. Meanwhile, knowledge about these processes was extended to fluids which show pronounced normal stresses [20], as well as to the explanation of residual cooling stresses and density distributions. The latter research was concentrated at Philips Research in Eindhoven in the search for further improvements of compact disks as molded from polycarbonate. In this connection one of the first graduate students of the author at Linz University was permitted to carry out his engineer's work in Eindhoven where he later obtained his doctor's degree [21]. These investigations were later perfected in Eindhoven [22, 23], so that the present author lost track of them.

However, one day the author asked himself why nobody had attacked the problems arising with crystallizing polymers during injection molding. This was the initiation of a new research field. The differences with the solidification of amorphous polymers are obvious. Solidification occurs with the latter polymers when the glass-transition temperature is passed. This transition occurs at slightly increasing temperatures with increasing cooling speed. The consequences of this effect are not very conspicuous with the steep temperature gradients occurring during mold filling. On the other hand, with crystallizing polymers the crystallization temperature decreases considerably with increasing cooling speed (effect of supercooling). Moreover, the crystallization kinetics very much depend on the thermal history and also on previous mechanical treatments (shearing, stretching of the melt) [24–27]. This complicated situation is the reason why the author does not intend to go into further detail in this lecture. He will restrict himself to two examples which form by-products of the development and which are also of more general interest.

ON THE CORRECT USE OF DIFFERENTIAL SCANNING CALORIMETRY

Usually only the temperature scale of a DSC apparatus is calibrated with the aid of the melting point of indium. During the investigation of the dependence of

the crystallization kinetics of polymers on the previous course of temperature, it appeared that the DSC apparatus can only be used in a quite restricted range of cooling speeds and, moreover, that a calibration of the effective heat transfer coefficient between the middle of the sample and the furnace is necessary [28, 29]. This coefficient does not only depend on the (varying) quality of the contact between pan and furnace. It also depends on the thermal properties of the polymer sample. This requires a renewed calibration with every measurement. In order to achieve comparability, the polymer samples must be fitted into the pan with great care. A special plot of the DSC curve was proposed by G. Eder [27], where the logarithm of the exothermal heat flux, after being multiplied by the cooling rate of the furnace, has to be plotted against the furnace temperature, which accepts the role of a time parameter because of its linear relation to the cooling time (constant cooling rate). Such a plot is shown for samples of equal masses (15.9 mg) of an industrial polypropylene in Fig. 7. Apparently a set of parallel straight lines is obtained on the low temperature side. From the common slope of these lines the pertinent effective heat transfer coefficient can easily be calculated. As a matter of fact, after completion of the phase transition, if the latent heat is completely released (or, with a heating cycle, absorbed), the DSC curve returns to the base line as an exponential function of time.

From Fig. 8 one learns what the influence of the internal heat transfer is on the course of the curve which describes the degree of crystallinity with decreasing

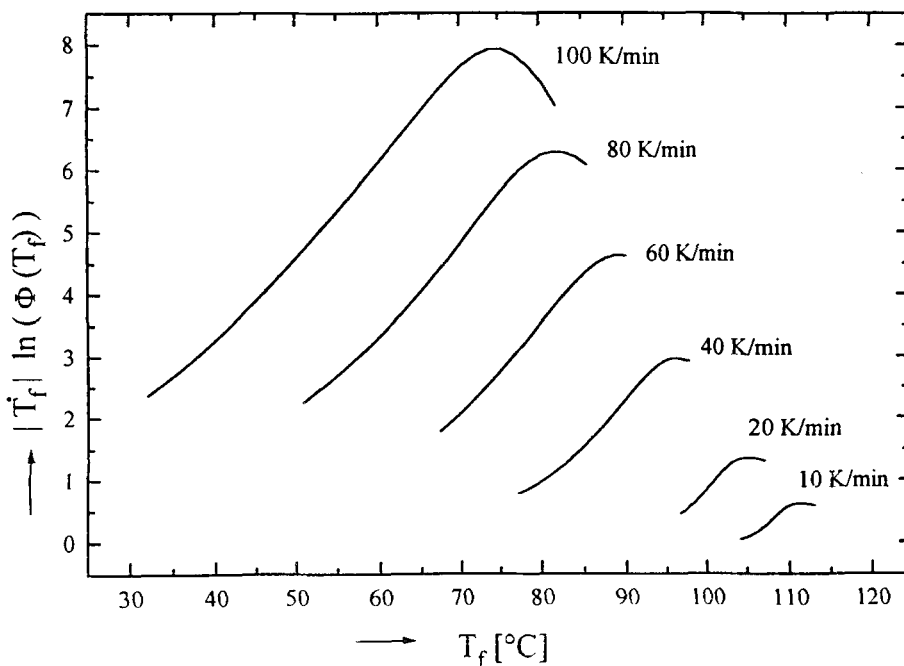


FIG. 7. Special presentation of DSC curves of an industrial polypropylene where the product of the pertinent cooling speed and the logarithm of the exothermal heat flow is plotted against the furnace temperature. (Courtesy of Verlag Chemie, Weinheim.)

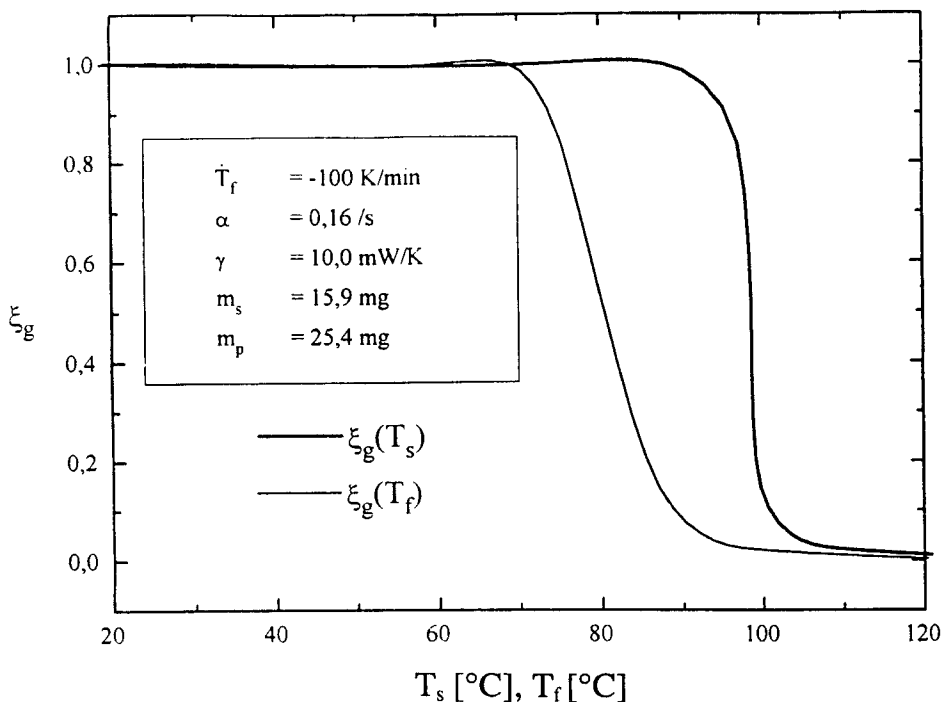


FIG. 8. Relative degree of crystallinity of an industrial polypropylene as obtained at a cooling speed of 100 K/min, plotted against the furnace temperature T_f and against temperature T_s prevailing in the center of the sample. (Courtesy of Verlag Chemie, Weinheim.)

temperature. (With i-PP the “final” degree of crystallinity is about 0.4. After room temperature is reached, this degree is enhanced only very slowly by secondary crystallization. The fraction 0.4 corresponds to the geometric degree of space filling by freshly formed spherulites, $\xi_g = 1$ in Fig. 8.) It should also be mentioned that the growth of ξ_g with decreasing furnace temperature T_f (left curve) is basically obtained by an integration of the surface of the original DSC peak down to the chosen value of T_f . However, in this case the correction for the finite internal heat transfer coefficient can be considerable [27]. This correction is zero only if the integration is carried out over the whole peak surface. However, the most conspicuous result, as shown in Fig. 8, is the fact that the internal sample temperature T_s , at which crystallization actually occurs at a nominal cooling speed of 100 K/min (right curve), is almost constant and lies much higher than the transition of the uncorrected curve of ξ_g vs T_f [27].

If one knows the true crystallization temperature, one can count the number of spherulites per unit of surface in the center of a cross section of a sample taken from the pan and calculate the corresponding number of spherulites per unit volume. In this way one obtains the (minimum) number of primary nuclei per unit of volume as a function of the crystallization temperature. For an industrial i-PP investigated in our laboratory, this number increased by more than two decades when the crystallization temperature was lowered from 125°C to about 105°C. This

is an important result if structural development is to be predicted for certain industrial cooling conditions.

GROWTH SPEED OF HDPE SPHERULITES

In Fig. 9 the growth speed $G(T)$ of spherulites of a HDPE (high density polyethylene) is shown as a function of temperature. The growth speed is another parameter of great interest for the simulation of crystallization processes. In contrast to *i*-PP, the number of spherulites of HDPE is not very dependent on the crystallization temperature, but there are many more primary nuclei ($\sim 5 \times 10^{14} \text{ m}^{-3}$) and the growth speeds are larger. Up to now, growth speeds of HDPE could only be determined in a temperature range between 130 and 120°C (melting point 144°C) [30]. This was done with the aid of a complicated optical technique in which the microscopic picture was covered with a grid. In addition, extremely thin samples were used. These samples were embedded between cover glasses which do not produce nuclei on their surfaces. In this way, practically two-dimensional "spherulites" (=disks) can grow. These "spherulites" can grow to much larger radii than in three-dimensional space where their growth is disturbed by spherulites nucleated in neighboring layers of the material. This less-hampered growth facilitates the measurement of the growth speed. In our laboratory in Linz, Dr. Ewa Ratajski

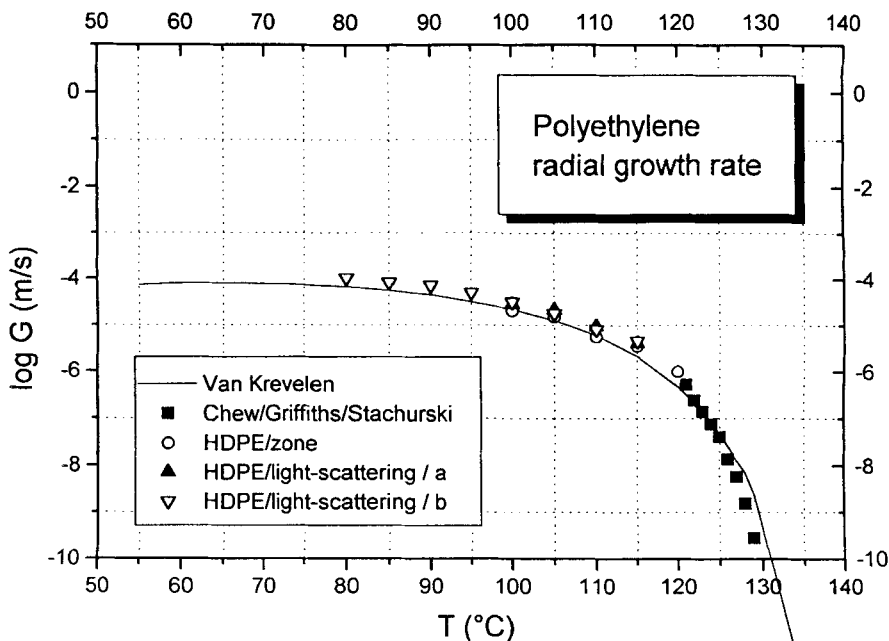


FIG. 9. Logarithm of linear radial growth speed of the spherulites of HDPE plotted against the crystallization temperature (courtesy Dr. Ewa Ratajski). The filled squares are from the literature [30]. The theoretical curve is from Ref. 31. The optical data are obtained according to a principle explained in Ref. 27.

succeeded in extending light-scattering measurements down to a crystallization temperature as low as 80°C. The basic idea for the interpretation of these measurements is that Rayleigh scatterers are formed first with incipient crystallization. Also, heat transfer considerations play an important role with these measurements. The temperature T_k at the contact surface of two bodies of different temperatures T_1 and T_2 , as obtained at the moment of the formation of the contact, can be calculated according to

$$\frac{T_k - T_1}{T_2 - T_k} = \frac{\sqrt{\rho_2 c_2 \lambda_2}}{\sqrt{\rho_1 c_1 \lambda_1}} \quad (5)$$

If body 1 has large values of density ρ and heat conductivity λ compared with body 2, the temperature of the contact surface will be practically equal to the temperature of body 1 ($T_k - T_1 \ll 1$). A metal block is used as body 1. Because the hot melt of the polymer, which is used as a rather thick layer, is transparent, the incipient light scattering at the contact surface can be observed through the transparent melt. A very satisfying result was that a semiempirical equation for $G(T)$, as obtained by Van Krevelen [31] from measurements on slowly crystallizing polymers, nicely fits the measurements reproduced in Fig. 9 for a polymer with extremely fast growth speeds. Remarkably, this semiempirical equation contains only two adjustable parameters; viz, the melting point and the glass-transition temperature.

As a consequence of these positive results, a comparison will be possible in the near future between structures experimentally obtained in quiescent but realistically cooled melts (objects cooled from outside!) and structures predicted by the theoretical approaches formulated by Schneider and Eder (Vienna-Linz) [27, 32].

CLOSING REMARKS

The author hopes he has demonstrated by way of example the usefulness of solutions of heat transfer problems for scientific tasks.

ACKNOWLEDGMENTS

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REFERENCES

- [1] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960.
- [2] W. J. Beek and K. M. K. Mutzall, *Transport Phenomena*, Wiley, New York, 1975.
- [3] G. G. Fuller, "Optical Rheometry," *Annu. Rev. Fluid Mech.*, 22, 387-417 (1990).

- [4] See also H. Janeschitz-Kriegl, *Polymer Melt Rheology and Flow Birefringence*, Springer, New York, 1983, p. 506.
- [5] H. Janeschitz-Kriegl and U. Daum, "On the Flow Birefringence of Polypropylene in Solution," *Kolloid-Z.*, *210*, 112 (1966).
- [6] H. Janeschitz-Kriegl, "Flow Birefringence of Elastico-Viscous Polymer Systems," *Adv. Polym. Sci.*, *6*, 170-318 (1969).
- [7] See, e.g., R. W. Whorlow, *Rheological Techniques*, Ellis Horwood, Chichester; Wiley, New York, 1980, p. 144.
- [8] Y. Björnsthål, "Thermal Effects in Flow Birefringence (on the Upper Limit of Measureable Flow Birefringence)." *Z. Phys.*, *119*, 245 (1942).
- [9] H. C. Brinkman, "Heat Effects in Capillary Flow," *Appl. Sci. Res.*, *A2*, 120 (1950).
- [10] H. Janeschitz-Kriegl, "On the Avoidance of Thermal Effects with the Measurement of Flow Birefringence," *Physica*, *22*, 1197 (1956).
- [11] H. H. Winter, "Viscous Dissipation in Shear Flow of Molten Polymers," *Adv. Heat Transfer*, *13*, 205-267 (1977).
- [12] H. C. Öttinger, "Gaussian Approximation for Rouse Chains with Hydrodynamic Interaction," *J. Chem. Phys.*, *90*, 463 (1989).
- [13] H. C. Öttinger and Y. Rabin, "Renormalization—Group Calculation of Viscometric Functions Based on Conventional Polymer Kinetic Theory," *J. Non-Newtonian Fluid Mech.*, *33*, 53 (1989).
- [14] J. Bossart and H. C. Öttinger, "Orientation of Polymer Coils in Dilute Solutions Undergoing Shear Flow: Birefringence and Light-Scattering," Submitted to *Macromolecules*.
- [15] J. L. S. Wales, *The Application of Flow Birefringence to Rheological Studies of Polymer Melts*, Delft University Press, 1976; see also Ref. 4, p. 426.
- [16] J. L. S. Wales, J. van Leeuwen, and R. van der Vijgh, "Some Aspects of Orientation in Injection Molded Objects," *Polym. Eng. Sci.*, *12*, 358 (1972).
- [17] H. Janeschitz-Kriegl, "Injection Moulding of Plastics: Some Ideas about the Relationship between Mould Filling and Birefringence," *Rheol. Acta*, *16*, 327 (1977).
- [18] H. Janeschitz-Kriegl, "Injection Moulding of Plastics 2: Analytical Solution of Heat Transfer Problem," *Ibid.*, *18*, 693 (1979).
- [19] H. van Wijngaarden, J. F. Dijkman, and P. Wesseling, "Non-Isothermal Flow of a Molten Polymer in a Narrow Rectangular Cavity," *J. Non-Newtonian Fluid Mech.*, *11*, 175 (1982).
- [20] A. I. Isayev, C. A. Hieber, and D. L. Crouthamel, "Orientation and Residual Stresses in the Injection Molding of Amorphous Polymers," *SPE Tech. Pap.*, *27*, 110 (1981).
- [21] R. Wimberger-Friedl, "Orientation, Stress and Density Distributions in Injection-Moulded Amorphous Polymers Determined by Optical Techniques," Doctoral Thesis, Eindhoven University of Technology, 1991.
- [22] F. P. T. Baaijens, "Calculation of Residual Stresses in Injection Moulded Products," *Rheol. Acta*, *30*, 284 (1991).
- [23] F. P. T. Baaijens and L. F. A. Douven, "Calculation of Flow Induced Residual Stresses in Injection Moulded Products," in *Integration of Theory and Applications in Applied Mathematics* (J. F. Dijkman and F. T. M. Nieuwstadt, Eds.), Kluwer, Dordrecht, 1990, pp. 73-90.

- [24] H. Janeschitz-Kriegl, G. Krobath, and S. Liedauer, "Physical Background of Mould Filling With and Without Crystallization," in *Integration of Fundamental Polymer Science and Technology* (L. A. Kleintjens and P. J. Lemstra, Eds.), Elsevier, London, 1986.
- [25] G. Eder, H. Janeschitz-Kriegl, and S. Liedauer, "Crystallization Processes in Quiescent and Moving Polymer Melts under Heat Transfer Conditions," *Prog. Polym. Sci.*, *15*, 629-714 (1990).
- [26] S. Liedauer, G. Eder, H. Janeschitz-Kriegl, P. Jerschow, W. Geymayer, and E. Ingolic, "On the Kinetics of Shear Induced Crystallization of Polypropylene," *Int. Polym. Process.*, *8*, 236 (1993).
- [27] G. Eder and H. Janeschitz-Kriegl, "Structure Development during Processing 4: Crystallization," in *Material Science and Technology*, Vol. 18 (H. E. H. Meijer, Ed.), Verlag Chemie, Weinheim, In Press.
- [28] H. Janeschitz-Kriegl, H. Wippel, Ch. Paulik, and G. Eder, "Polymer Crystallization Dynamics, as Reflected by Differential Scanning Calorimetry I. On the Calibration of the Apparatus," *Colloid Polym. Sci.*, *271*, 1107 (1993).
- [29] C. H. Wu, G. Eder, and H. Janeschitz-Kriegl, "*Idem.*, II. Numerical Simulations," *Ibid.*, *271*, 1116 (1993).
- [30] S. Chew, J. R. Griffith, and H. H. Stachurski, "The Crystallization Kinetics of Polyethylene under Isothermal and Non-Isothermal Conditions," *Polymer*, *30*, 874 (1989).
- [31] D. W. Van Krevelen, "Crystallinity of Polymers and the Means to Influence the Crystallization Process," *Chimia*, *32*, 279 (1978).
- [32] W. Schneider, A. Köppl, and J. Berger, "Non-Isothermal Crystallization of Polymers," *Int. Polym. Process.*, *2*, 151 (1988).