

A rheological study of shear induced crystallization

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Abstract The isothermal crystallization of three isotactic polypropylene (iPP) types, with different molar mass (distributions), was studied after a well defined shear treatment of the melt at an elevated temperature and a subsequent quench to the crystallization temperature. For these experiments a standard rheometer of the cone and plate configuration was used. The development of the crystallization was monitored by dynamic oscillatory measurements. Shearing in the melt was shown to enhance subsequent crystallization at lower temperatures. Not only the total

shear at constant rate is of importance, but also the chosen combination of rate and shearing time. Moreover, a pronounced influence of molar mass was detected. The exploration of the melting temperatures and times which are necessary for an erasure of the memory effects showed that the effect of shearing could not completely be erased, possibly as a consequence of mechanical degradation.

Key words Isotactic polypropylene – isothermal crystallization – shear enhanced crystallization – rheological behaviour

Introduction

Crystallization of polymers is influenced by the mechanical treatment which the melt undergoes during the final stages before crystallization. This happens in almost all shaping processes, such as melt spinning, extrusion, film blowing, blow moulding and injection moulding. For instance, in injection moulded products skin layers are found with a highly orientated crystal morphology. They differ completely from the spherulitic bulk, and thus show considerably different properties. To study this, different approaches have been followed. Whereas McHugh et al. (1993) studied the influence of elongational flow on crystallization, most others focused on shear induced crystallization. Planar shear devices (e.g. Lagasse and Maxwell, 1976), rotary shear devices using parallel plates (e.g. Wolkowicz, 1978), Couette configurations (e.g. Kobayashi, 1970; Sherwood, 1978) and also geometries closer to practical conditions (e.g. Eder et al., 1990) have

been used. In most cases, shearing is performed at the crystallization temperature. Concentrating on shear deformation, it was shown that due to the high shear rates occurring in injection moulding, typically $10^2 - 10^4 \text{ s}^{-1}$ (Koppelman, 1987; Isayev, 1995), a strongly oriented layer is induced. Wolkowicz (1978) showed that lower rates ($\leq 12 \text{ s}^{-1}$) enhance crystallization as well, but do not influence the crystal growth speed, and a spherulitic morphology is induced. An approach developed in the group of Janeschitz-Kriegl (Liedauer et al., 1993) yields the possibility to distinguish between nucleation and growth processes. In some of their previous studies (see Eder et al., 1989, 1990) experiments were performed by shearing at temperatures high enough to prevent growth, followed by a subsequent isothermal crystallization process at lower temperatures.

The use of a rheometer has shown to be successful in studying the effect of nucleation (Khanna, 1993), in modelling a composite structure induced in a crystallizing melt (Carrot, 1993; Teh et al., 1994) and in analyzing

recrystallization (Hingmann et al., 1995). Unfortunately, many experiments that were meant to be isothermal, showed a start of crystallization during the cooling trajectory. In this study, a rheometer is used to examine the influence of low shear rates on crystallization. Following Eder et al. (1990), shearing was performed at high enough temperatures to prevent early crystal growth, followed by a monitoring of the crystallization process at much lower, constant, temperatures under quasi quiescent conditions, i.e. during dynamic oscillatory conditions with low amplitude.

Experimental

Materials

Experiments were carried out on the three types of iPP with different average molar masses and molar mass distributions. PP1: StamyranP 13E10 (DSM, Geleen, the Netherlands) $M_w = 500$ kg, $M_n = 100$ kg, $MFI_{230} = 4.0$ dg/min; PP2: StamyranP 15M10 (DSM) $M_w = 375$ kg, $M_n = 50$ kg, $MFI_{230} = 13$ dg/min; PP3: Himont 7073 (Himont, Italy) $M_w = 490$ kg, $M_n = 50$ kg, $MFI_{230} = 3.3$ dg/min. In a simplified characterization, PP1 can be seen as having a high molar mass and a narrow distribution, PP2 having a low molar mass and a medium distribution, and PP3 having a high molar mass and a wide distribution.

Pellets were pressed to 2-mm-thick sheets in a laboratory press at 230 °C, during 5 min at 2.5 MPa. Discs with 10 mm diameter were punched out of these plates.

Rheological tests

A Rheometrics RDSII rheometer was used in the cone and plate configuration, with a top angle 0.1 rad and a diameter of the plates of 25 mm, in the oscillatory shear mode with frequency $\omega = 10$ s⁻¹. Steady shearing was performed prior to the data acquisition in the oscillatory mode. To prevent oxidation, a N₂ atmosphere was used at all temperatures above 200 °C. At lower temperatures air was used to ensure a fast cooling and reproducible temperature. A maximal cooling rate of 20 K/min was reached. The thermocouple that was used for oven control was positioned in a hole drilled in the tool plate. This minimized differences between the sample temperature and read-out values. To ensure that the sample was retained between the plate and cone after shearing, we chose the sample diameter such that it did not completely fill the gap between cone and plate (diameter $d = 19$ mm, after adjusting the correct sample thickness) and the sample remained circular to a good approximation during the experiments.

During the complete solidification process from melt to solid, the auto-strain option was used and the initial strain of 10% was automatically decreased when the torque reached a preset value. To compensate for thermal contraction of the apparatus, the fixtures were manually adjusted twice during the cooling process, at 200 °C and at 165 °C.

An experiment typically consists of the following steps:

- A polymer disc (\varnothing 10 mm) is placed in the rheometer and melted at T_m under N₂ atmosphere. As soon as melting has occurred, the gap between cone and plate is adjusted, resulting in a sample with a diameter of 19 mm.
- The sample is kept at the melting temperature T_m during a time $t_m = 15$ min in an attempt to erase memories of previous treatments and to ensure an isotropic melt. In general, T_m must be chosen sufficiently high, so that a further increase of T_m has no significant effect anymore. However, T_m must not be too high to minimize the thermal exposure of the iPP.
- If shear is part of the experiment, the sample is sheared during a time t_s at a constant shear rate $\dot{\gamma}_s$, at T_m . Shearing time and rate t_s and $\dot{\gamma}_s$ were varied between $0 < t_s < 200$ s and $0 < \dot{\gamma}_s < 10$ s⁻¹.
- The oven containing the plates and sample is cooled to the crystallization temperature T_c , using a trajectory that prevents a through shoot to temperatures below T_c . The cooling step typically takes 5 min. Two different crystallization temperatures, $T_c = 138$ °C and 140 °C, have been used.
- At T_c , the crystallization process is monitored using the oscillatory shear mode. The time t_c from the start of the cooling process is used as a representative time scale. At the end of the experiment, the sample is removed from the rheometer and kept for further examination.

Results

In Fig. 1 a typical shearing experiment is illustrated. Sample PP1 was molten at 260 °C during 15 min. Subsequently, the sample was cooled and kept at 138 °C. In Fig. 1 the storage and loss moduli, G' and G'' , the tangent of the loss angle, $\tan \delta$, and the temperature T are plotted vs. the time elapsed from the moment the cooling step was started. The maximum cooling rate reached equals 25 °C/min. A small oscillation in temperature is noticed around 138 °C. The maximum amplitude is ± 1 K around $t = 800$ s, but rapidly decreases to ± 0.2 K. The temperature profile is found to be well reproducible for all experiments.

From the stagger in G' and G'' at short times it is clearly recognized when the tool distance was adjusted at

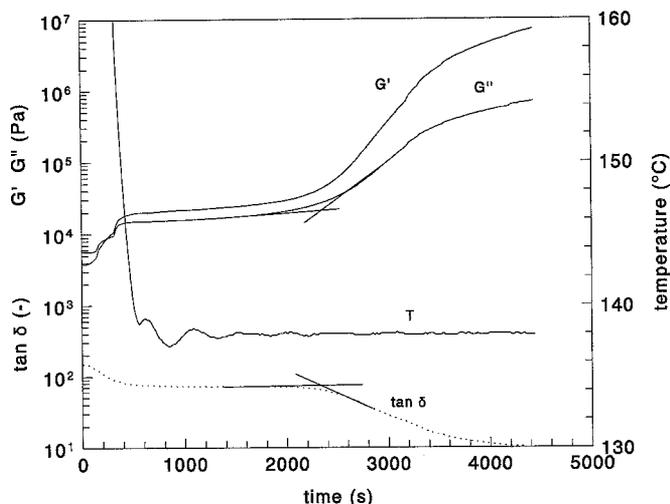


Fig. 1 Development of storage and loss modulus and the tangent of loss angle for PP1 during a quench from 260° to 138°C. The course of the temperature is given as well. Tangents are drawn to determine t_{onset} (solid lines)

200°C ($t = 100$ s) and at 160°C ($t = 200$ s) to compensate for thermal contraction of the apparatus. As soon as the temperature is (nearly) constant, only a slight but steady increase in G' and G'' is observed for $t < 2000$ s. At larger times, crystallization sets in and increases in G' and G'' of orders of magnitude are noticed. $\tan \delta$ decreases by a factor of ten. Within reasonable times, no complete leveling off of G' and G'' is found.

To define the onset of crystallization, tangents are drawn along either G' , G'' or $\tan \delta$ curves in the nearly horizontal regime ($600 \text{ s} \leq t \leq 2000 \text{ s}$ in Fig. 1) and in the regime of maximum changes ($2800 \text{ s} \leq t \leq 3400 \text{ s}$ in Fig. 1). The intercept t_{onset} is an arbitrary measure for the time evolved before crystallization sets in. In Fig. 1, t_{onset} is determined to be 2350 s.

To study the influence of the shear at T_m on crystallization, a constant shear rate of $\dot{\gamma}_s = 5 \text{ s}^{-1}$ was applied before the cooling step, during various times $t_s = 25, 38, 50, 100$ and 200 s, corresponding to 2, 3, 4, 8 and 16 rotations of the lower plate, respectively. The results for PP1 are shown in Fig. 2. As a reference, also the experiment with no shearing is shown. In this figure and in further figures, the $G''(t)$ and $T(t)$ curves are omitted for clarity and only $G'(t)$ and $\tan \delta(t)$ curves are presented. Probably due to slight differences in sample position between the tools, and to fluctuations in tool distance, which influence the sample diameter, the initially measured values for $G'(t)$ showed variations, of the order of less than one order of magnitude and the $G'(t)$ curves were shifted vertically to fit the initial values. This procedure does not influence the shown courses of the crystallization process and the determination of t_{onset} .

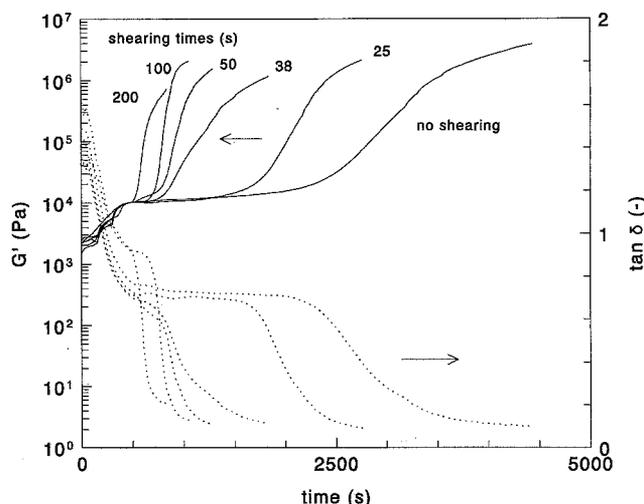


Fig. 2 Development of storage modulus and tangent of the loss angle for PP1 during a quench to 138° after melting at 260°C and subsequent shearing during the indicated times at $\dot{\gamma}_s = 5 \text{ s}^{-1}$

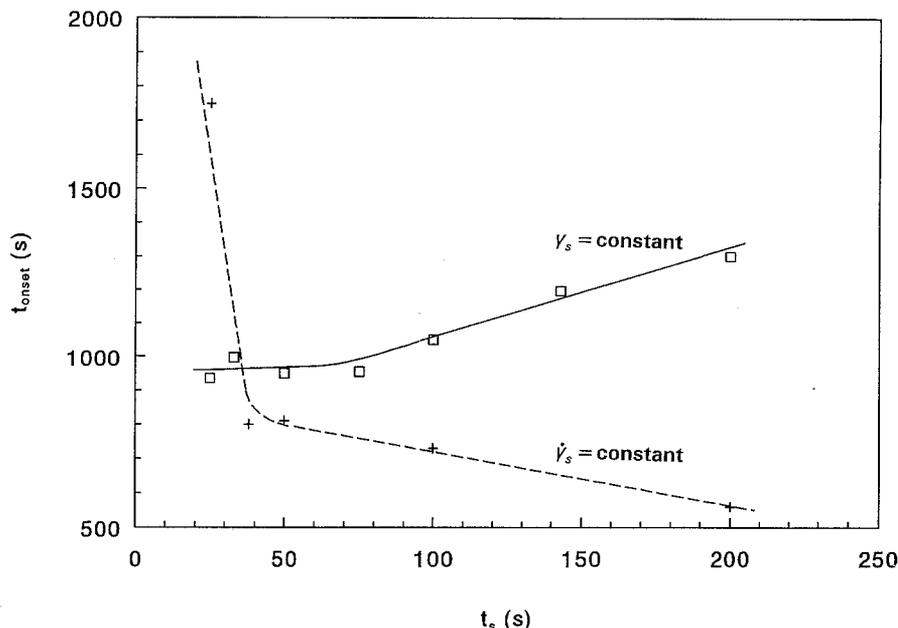
From Fig. 2 it is clear that shearing substantially accelerates the crystallization process. Several experiments have been repeated, resulting in a reproducibility of $t_{\text{onset}} \pm 50$ s. In Fig. 3 t_{onset} is plotted vs. t_s for the experiments shown in Fig. 2 ($\dot{\gamma}_s = \text{constant}$).

It must be mentioned that for the experiments with the highest shearing times t_s , crystallization already sets in before completely isothermal conditions are reached. This fact is reflected in Fig. 2 by relatively high $\tan \delta$ values at short times, found for $t_s = 100$ s and 200 s, but this does not alter the trend shown in Fig. 2. With the standard rheometer used, the time to reach isothermal conditions at 138°C was about 500 s, see Fig. 1, and this time could not be further shortened.

The total shear applied $\gamma_s = t_s \dot{\gamma}_s$ influences the rate of crystallization, as was shown in Fig. 2. However, it can be shown that the values of t_s and $\dot{\gamma}_s$ have pronounced independent influences. In Fig. 4 results are presented for combinations of t_s and $\dot{\gamma}_s$, of which the product $\gamma_s = 250$ is constant, which means eight rotations are made. Short shearing times at high rates are clearly found to be more effective, in spite of some experimental fluctuations. In Fig. 3, the respective values of t_{onset} are plotted vs. the shearing time t_s .

It was investigated whether the choice of melt temperature T_m had a considerable influence on the subsequent crystallization behaviour. First, an experiment was performed using $T_m = 200^\circ\text{C}$ and 260°C , without a shearing step prior to cooling and crystallization. The same value of $t_{\text{onset}} = 2350$ s was found. It is possible that at 200°C incomplete melting takes place, leaving small nuclei, while at 260°C some degradation occurs. Both

Fig. 3 Onset time for crystallization t_{onset} vs. shearing time t_s for the experiments shown in Figs. 2 (+, dashed line) and 4 (\square , solid line)



would cause an enhancement in the subsequent crystallization. To investigate this, shearing experiments with $t_s = 100$ and $\dot{\gamma}_s = 5 \text{ s}^{-1}$ were performed after melting during 15 min at temperatures T_m of 200°, 220°, 240° and 260°C. Results are presented in Fig. 5. The time t has been corrected in compensating for differences in the times needed for cooling from T_m to T_c . Values of $t_{\text{onset}} = 800 \pm 50 \text{ s}$ were found. The fact that at an intermediate temperature of 240°C a possibly significant maximum t_{onset} is found, could be an indication that $T_m = 200^\circ\text{C}$ might be too low and 260°C too high. Fur-

ther experiments should be carried out to clarify this issue.

The influence of average molar mass and molar mass distribution on the crystallization following shear has been studied by using a second iPP sample (PP2) with lower M_w and M_n and a little wider molar mass distribution. In Fig. 6 results are shown for a shear rate $\dot{\gamma}_s = 5 \text{ s}^{-1}$ and shear times $t_s = 0$ and $100 \text{ s} \leq t_s \leq 200 \text{ s}$. If the crystallization following quiescent melting is considered, i.e. with no shear, it is clear that low molar mass sample PP2 crystallizes much faster than sample PP1

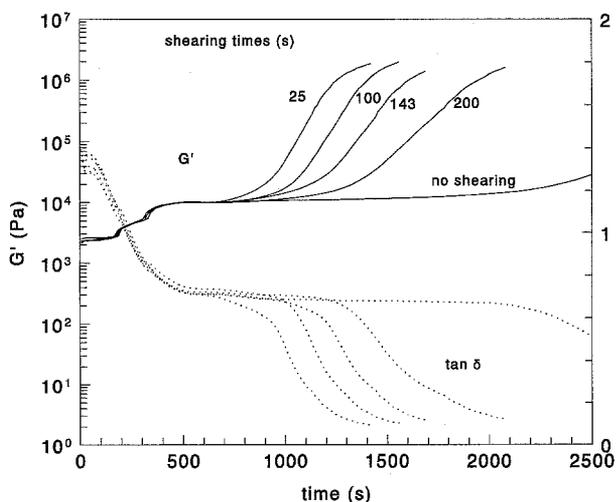


Fig. 4 Development of storage modulus and tangent of the loss angle for PP1 during a quench to 138° after melting at 260°C and subsequent shearing during the indicated times till $\gamma = \dot{\gamma}_s t_s = 250$

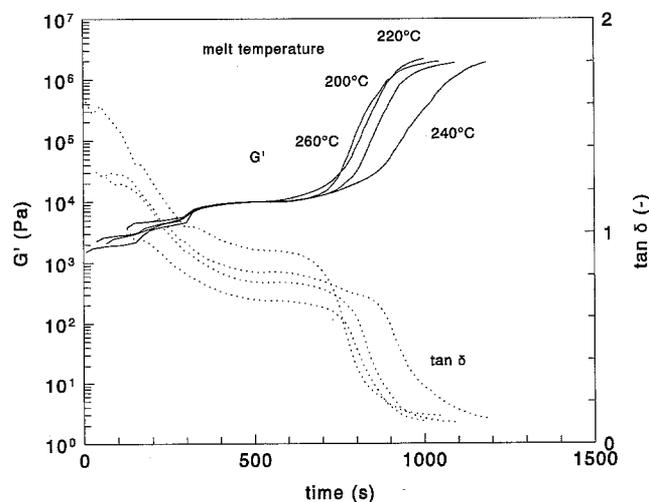


Fig. 5 Development of storage modulus and tangent of the loss angle for PP1 during a quench to 138°C after melting at the indicated temperature and subsequent shearing during $t_s = 100 \text{ s}$ at $\dot{\gamma}_s = 5 \text{ s}^{-1}$

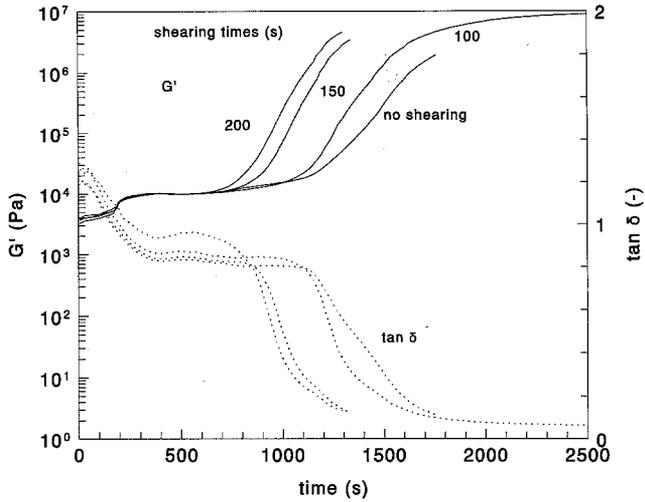
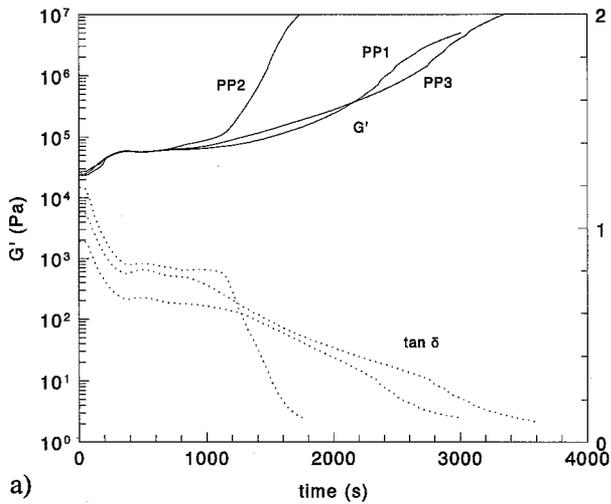


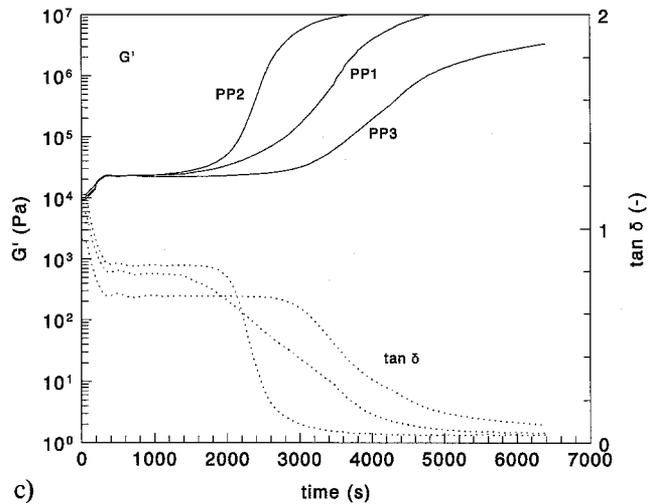
Fig. 6 Development of storage modulus and tangent of the loss angle for PP2 during a quench to 138° after melting at 200°C and subsequent shearing during the indicated times at $\dot{\gamma}_s = 5 \text{ s}^{-1}$

(compare with Fig. 2). For PP2 the application of shear hardly enhances the crystallization rate: after shearing for 100 s at a rate of $\dot{\gamma}_s = 5 \text{ s}^{-1}$, t_{onset} decreases for PP1 from 2350 to 830 s, while for PP2 only a change from 1200 to 1150 s is found, accompanied by an increase in slope of the $G'(t)$ curve. Now one should look at the results of a third sample PP3, characterized by a high average molar mass and a wide distribution. It is expected that especially the high molar mass tail is affecting the crystallization after shear. In Fig. 7 a (without shear) and b (after shearing) the crystallization of the three different PP's at

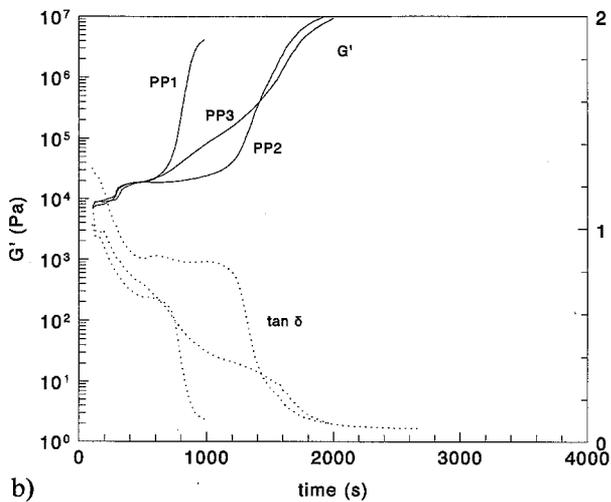
Fig. 7 Development of storage modulus and tangent of the loss angle for PP1, PP2 and PP3 during a quench after melting at 200°C. The conditions were: a) without shearing before quenching to 138°C; b) after shearing during 100 s at $\dot{\gamma}_s = 5 \text{ s}^{-1}$ before quenching to 138°C; c) without shearing before quenching to 140°C; d) after shearing during 100 s at $\dot{\gamma}_s = 5 \text{ s}^{-1}$ before quenching to 140°C



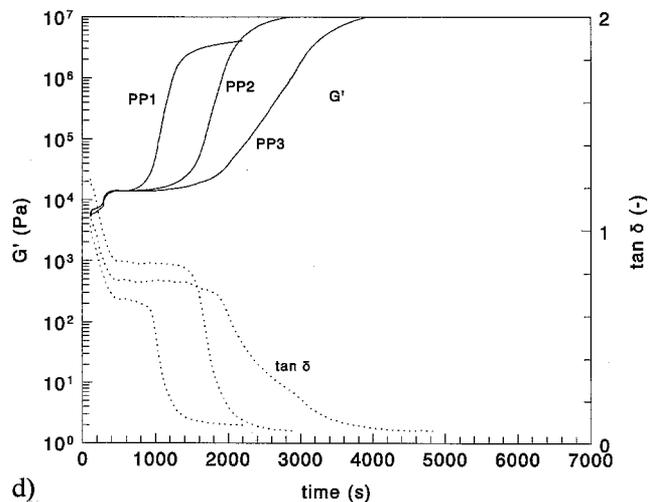
a)



c)



b)



d)

138 °C is illustrated. Shearing has a different effect on these samples. Whereas the low molar mass PP2 is hardly affected, PP1 shows the largest effect of shear. Without shearing the crystallization of PP3 is comparable with that of PP1, while after shearing the crystallization behaviour of PP3 lies between that of the two other samples: the start of the crystallization process of PP3 seems to be comparable to that of sample PP1, while the final crystallization overlaps with PP2. It is clear that in this case the definition of t_{onset} , as given above, is not satisfying, because PP1 and PP3 have the same value for this t_{onset} but show completely different crystallization behaviour at longer times.

The experiments by which the effect of shear on the crystallization of different PP's is compared, have been repeated for a crystallization temperature $T_c = 140$ °C. Results are shown in Fig. 7c and d for crystallization without and with shear, respectively. As expected, the crystallization at 140 °C is much slower. In addition, after quiescent melting (Fig. 7c) an order differing from that at 138 °C is found. At 138 °C PP1 crystallizes faster than PP3, whereas at 140 °C the order is reversed. At this latter temperature the application of shear causes the crystallization of sample PP3 to be slower than that of PP2.

Discussion

Rheometry

The aim of this study was to investigate the influence of well defined shearing in the melt on the subsequent crystallization of PP. It is shown that crystallization and the influence of shear can be studied with the aid of rheometry. The complete process from melt to solid can be followed, which is accompanied by an increase in moduli of orders of magnitude. By using a small amplitude oscillatory shear flow, the sample can be tested in quasi-quiescent conditions.

From the experiments it is clear that melting during 15 min at 200 °C is sufficient for reproducible data. A further increase of T_m to 260 °C does not change results (Fig. 5). This has to be compared with results of Alfonso and Ziabicki (1995), who studied memory effects on PP, and found that melting during 10 min at different temperatures T_m , up to 260 °C, resulted in increasing delay of crystallization, as detected by differential scanning calorimetry. Choosing $T_m = 260$ °C, times needed for crystallization are levelling off at times ≥ 20 min (Alfonso and Ziabicki, 1995). In the present study we used a melting time of $t_m = 15$ min in order to minimize exposure to high temperatures. The effect of shearing is shown to be substantial and reproducible. Increasing the shearing time at a given shear rate, or combinations of short times and high rates at constant total shear are shown to be most effective (Fig. 4). Raising the crystal-

lization temperature T_c shifts the crystallization to longer times, as is expected (Fig. 7a and c). Shearing of the melt enhances crystallization at the two crystallization temperatures used, for all grades of PP. For the broad molar mass distribution type, PP3, the effect is large at 138 °C, but much smaller at 140 °C. It is shown that the influence of molar mass (distribution) on crystallization is pronounced. Characterization of the crystallization process in terms of an onset time t_{onset} is not unambiguous. The crystallization behaviour and its temperature dependence seem to be most sensitive to the presence of long molecules. Apparently, these molecules are strongly affected by the application of shear flow.

Memory effects

At this stage we will discuss the origin of the crystallization enhancement by shearing the melt. Because thermal degradation at $T_m = 260$ °C might lead to a decrease of molar mass and, consequently, to a faster crystallization, this possibility must be checked first. For this purpose an experiment was performed at $T_m = 260$ °C, without a shearing step. Results were obtained that were essentially identical to those shown in Fig. 1 (see Fig. 8a). Instead of the normal procedure, i.e. removing the sample from the rheometer and using a fresh sample for the next experiment, the same experiment was carried out a second time with the same sample. This resulted in practically the same t_{onset} . The absence of crystallization enhancement in the second experiment justifies the conclusion that thermal degradation is of no decisive importance. To check degradation due to shearing a shearing experiment was performed at $T_m = 260$ °C with $t_s = 100$ s and $\dot{\gamma}_s = 5$ s⁻¹. A value of $t_{\text{onset}} = 800$ s was obtained (see Fig. 8b). This is a similar experiment as shown in Fig. 2 (for $t_s = 100$ s). A second experiment with the same sample was performed, now without a shearing step at the melt temperature. After cooling, $t_{\text{onset}} = 1400$ s was found (see also Fig. 8b). This value lies between the values found after quiescent melting ($t_{\text{onset}} = 2300$ s) and after the shearing step ($t_{\text{onset}} = 850$ s). The same effect was found in a repeat experiment. Thus it seems that the effect of shearing can be erased only partially by melting. It was expected that the shearing effect, induced by the relatively low shearing rates, would be completely erased by melting. If shear would cause the formation of nuclei (Wolkowicz, 1978) that later, at the crystallization temperature, would grow to form crystallites, one would expect that these nuclei would disappear after sufficiently long melting. It should be noted that Eder et al. (1989) found that the ability to form a highly oriented skin layer vanished by relaxation above 210 °C within 1 s. In contrast, we are dealing with much lower deformations resulting in a spherulitic crystal morphology. However, discrepancies in apparent relaxation behaviour are ex-

treme and other mechanisms may be important. To further check the issue of erasability of the shearing effect, an experiment that included shearing was extended by a relaxation step after the shearing step. After a shear treatment at 260 °C during $t_s = 100$ at $\dot{\gamma}_s = 5 \text{ s}^{-1}$, the melt was not immediately cooled to the crystallization temperature $T_c = 138 \text{ °C}$, but offered the opportunity to relax at 260 °C during a time t_{relax} , $100 \text{ s} \leq t_{\text{relax}} \leq 3600 \text{ s}$. Surprisingly, no correlation between t_{relax} and t_{onset} was found. However, a large spread of the values for t_{onset} , i.e. $850 \text{ s} \leq t_{\text{onset}} \leq 1900 \text{ s}$, was found. These findings are in agreement with the experiments presented in Fig. 8 b, i.e. the impossibility to erase the shearing effect completely by a second melting step.

Degradation

A check for degradation was performed by applying a frequency sweep experiment as proposed by Chambon (1995). In a plot of $\tan \delta$ vs. the product of zero shear viscosity and frequency, the inverse slope in the low frequency regime was found by Chambon to correlate with the molar mass distribution M_z/M_w . Applying this procedure in air, some degradation was observed at temperatures above 200 °C. However, under nitrogen, no change in M_z/M_w was found at 260 °C even after 30 min heating and including a shearing step at $\dot{\gamma}_s = 5 \text{ s}^{-1}$ during $t_s = 100 \text{ s}$ (see Fig. 9 a). Nevertheless, a decrease in η_0 was observed after shearing. The same experiments were used

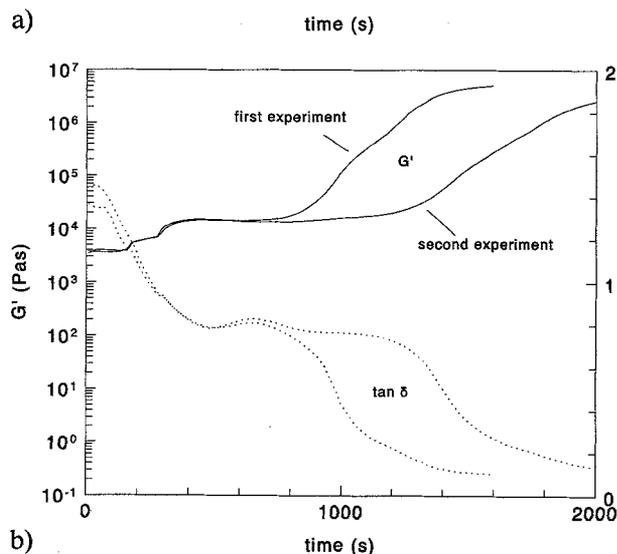
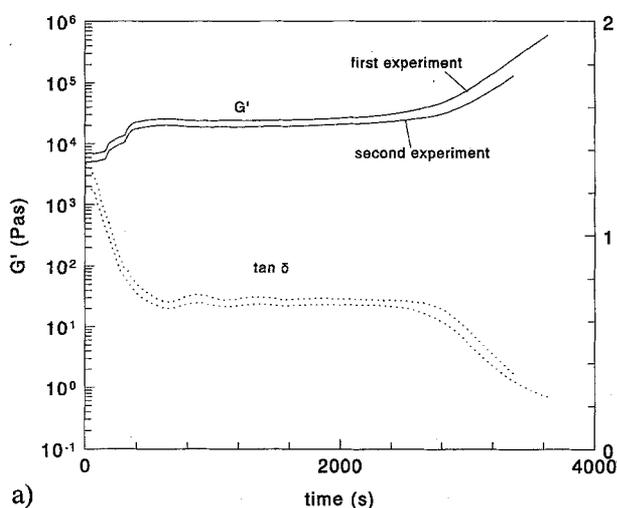


Fig. 8 Development of storage modulus and tangent of the loss angle for PP1 during a quench to 138 ° after melting at 260 °C. Two consecutive crystallization experiments were carried out with the same sample, as indicated in the figure: a) Both experiments without shearing; b) first experiment with shearing during $t_s = 100 \text{ s}$ at $\dot{\gamma}_s = 5 \text{ s}^{-1}$, second experiment without shearing

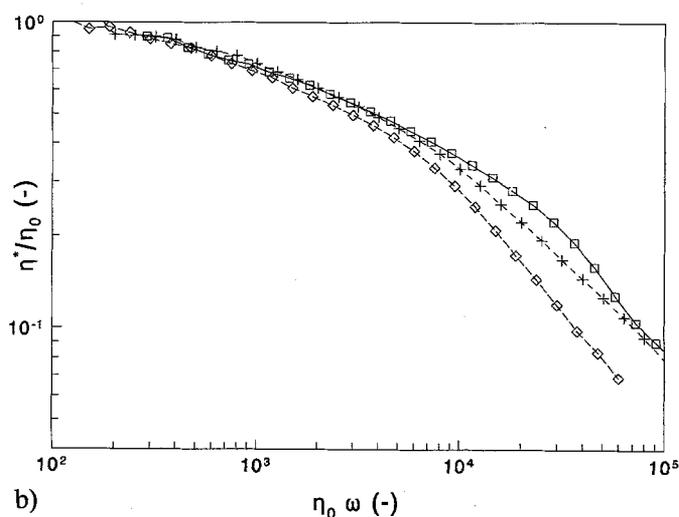
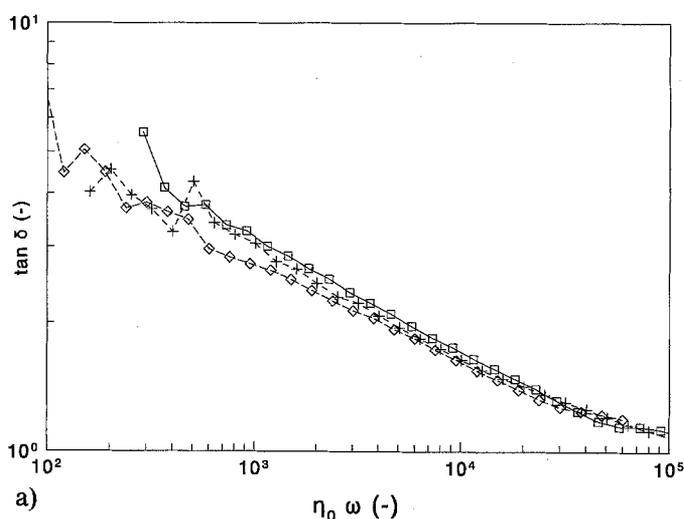


Fig. 9 Tangent of the loss angle (a) and reduced zero shear viscosity (b) vs. the product of zero shear viscosity and frequency for PP1 at 260 °C. Immediately after melting (\square); after 15 min at T_m ($+$); after 30 min at T_m and a shear treatment during $t_s = 100 \text{ s}$ at $\dot{\gamma}_s = 5 \text{ s}^{-1}$ (\diamond). Lines are drawn for clarity

to monitor the molar mass distribution M_w/M_n via a procedure proposed by Zeichner and Patel (1981). An earlier drop in the plot of the reduced zero shear viscosity η^*/η_0 vs. the product of zero shear viscosity and frequency indicates a larger value for M_w/M_n . Applying this procedure, a minor change in M_w/M_n was found at 260 °C after 15 min heating (see Fig. 9b). However, after 30 min at 260 °C and including a shearing step at $\dot{\gamma}_s = 5 \text{ s}^{-1}$ during $t_s = 100 \text{ s}$, a substantially broader M_w/M_n was detected. Thus it seems that, due to shearing, mainly the high molar mass tail is subject to degradation, causing M_z and M_w to be lowered to a larger extent than M_n .

Experimental conditions

It was checked whether the slight deviation of sample shape from circularity, due to positioning and shearing, might influence the crystallization. A sample (which does not completely fill the 25 mm diameter gap between cone and plate) was purposely placed eccentrically. An experiment under quiescent melt conditions resulted in a long t_{onset} , typical for these experiments. The sample position and shape is therefore not very critical and cannot explain results presented so far.

To clarify the influence of shear on the morphology of the crystallized samples, wide angle x-ray scattering (WAXS) and polarized light microscopy were used. Using a WAXS flat film camera, no orientation was detected in samples recovered after experiments including a shearing step. No orientation in the original discs, to be placed in the rheometer, was found and only the α crystal modification of iPP crystals was detected. Samples recovered from the rheometer after experiments with and without a shearing step showed reflections of the α crystal structure, accompanied by minor traces of the β structure. These findings were confirmed by light microscopy. In the recovered samples, a few randomly positioned spherulites of high birefringence (β modification) were found among a majority of spherulites of low birefringence (α modification). To study the occurrence of orientation in the melt due to shearing, a small part of a recovered sample was heated slowly in a hot stage under a light microscope, using polarized light. Immediately after melting of the spherulites, no traces of birefringence could be detected,

which would have been an indication of orientation in the crystallizing melt.

A new experimental set-up was built in our laboratory to overcome some of the experimental drawbacks of the cone and plate configuration of the standard rheometer. For this purpose an oil-heated Couette configuration was chosen. Both the bob and the cup are internally flushed with oil from one of two thermostat baths, connected by a set of valves that enable an instantaneous change-over from one oil bath to the other. In this way, the sample temperature can be changed from e.g. 260 ° to 138 °C within a reasonably short time. However, a disadvantage of this set-up is the lack of compensation for thermal expansion or for shrinkage due to crystallization (which was taken care of in the cone and plate device by the adjustment of the position of the two confining walls) and the impossibility to study the whole crystallization process due to torque values exceeding the transducer limit. These factors impeded the use of this set-up, but modifications will be realized in due time.

Rheometry is shown to be a useful tool to study shear enhanced crystallization. Using a standard rheometer, we were able to study in detail the crystallization of several types of polypropylene. Influences of the melt temperature and time, of the crystallization temperature and of different shear treatments could be identified. Surprisingly, the enhancement of crystallization by low shear rates ($< 12 \text{ s}^{-1}$) is, at most, partly caused by orientation of molecules in the melt. Orientation as an important factor is ruled out by the inability to erase the crystallization enhancement by prolonged relaxation in the melt. In contrast, the crystallization enhancement seems to be, at least partly, caused by mechanical degradation. Thermal degradation is not observed. The higher moments of the molar mass distribution indicate that especially long chains are susceptible to scission.

Irrespective of the precise reason for the crystallization enhancement, as caused by shearing, this enhancement manifests itself already under conditions of very low shear rates, much lower than can be envisaged in, for example, injection moulding. In particular, this enhancement is found in combinations of relatively high shear rates and short shear times. This might indicate that this effect may be important in many practical applications.

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