A Novel Flow Cell for the Investigation of Elongational Flow Induced Nucleation

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Abstract
Crystallization of semi-crystalline polymers can be strongly enhanced by chain orientation during flow. Elongational flow may cause extraordinarily large molecular orientations, specially for the high end tail molecular weight part, which then can act as nuclei during crystallization, since relaxation time of these molecules is very large.

In this study, a novel cross slot flow cell for polymer melts is described in which a stagnation flow can be created and for which the thermal history is controlled. Such flow is characterized by the presence of a free stagnation point, around which the extensional strain is high. With this flow cell, the influence of elongational flow on crystallization kinetics can be studied, using in situ Wide Angle X-ray Diffraction (WAXD) and point-wise birefringence measurements.

First results are presented for an isotactic polypropylene (iPP). The melt was annealed at a temperature of 220 °C for 90 minutes to erase crystal and flow memory. At the same temperature the flow is applied. Next, the cell is cooled to a temperature below the (quiescent) melting temperature (about 170 °C) to investigate isothermal crystallization.

A strong flow induced enhancement of turbidity in the birefringence experiments was found. This effect was larger at higher temperatures, but more difficult to detect at lower temperatures (< 130 °C), because the onset time of crystallization decreases exponentially with decreasing temperature. WAXD measurements showed in most cases an oriented α phase, despite the long cooling times. The orientation of the structure could be explained by the structure proposed by Fujiyama, with the c-axis oriented in inflow and outflow direction. In one experiment also the β phase was detected.

The reproducibility of the thermal history in the flow cell was excellent. Unfortunately, the stress controlled deformation history was not reproducible. Therefore, constant velocity experiments, which are much better reproducible, should be performed in future.

1 Introduction
Crystallization behavior has a large influence on final product properties of semi-crystalline polymers. Both thermal and deformation history determine crystallization kinetics, see for example Eder and Janeschitz-Kriegl (1997). Deformation history has an important influence on the orientation of the polymer chains and on the resulting anisotropy of the crystals formed on the backbone of the oriented chain(segment)s. Chain extension promotes crystallization for two reasons (Keller and Kolnaar, 1997). First, chain extension increases the crystallisation (and melting) temperature of the material. This thermodynamic reason is due to the lower entropy and the higher free energy of the extended chain compared to a random coil. Crystallization will be enhanced, since super-cooling for any temperature below melting temperature is increased. Second, the extended chain is closer to its final configuration state in a crystal and has therefore a lower kinetic barrier to overcome than a chain in the random state.

The influence of thermal history is found in the growth speed of spherulites, which is a function of temperature and is described by a bell-shaped curve with a maximum between the equilibrium melting point and the glass transition temperature, where at both temperatures this function equals zero. A second influence is the cooling rate. The number of spherulites is increased strongly with an increased
cooling rate, due to the combined nucleation and growth process during cooling. A third influence is the processing temperature and time. High temperatures and long times erase crystal memory and therefore decrease the number of nuclei. More details about the background of crystallization is given by Eder and Janeschitz-Kriegl (1997).

The material parameter that has the most pronounced influence on flow induced nucleation, enhancing crystallization, is the molecular weight distribution. It is believed that long chains have a marked influence due to the high relaxation time of the oriented state compared to that of oriented short chains. Vleeshouwers and Meijer (1996) investigated the influence of molecular weight (distribution) for three isotactic polypropylenes using a commercial rheometer (Rheometrics RDS2). The highest molecular weight material showed an enhanced onset of crystallization after flow at a high temperature, while the lower molecular weight material was hardly influenced by flow. Applying the same total shear, the influence of shear time and shear rate was compared \((\dot{\gamma} = t \dot{\gamma})\). High shear rates in short times had the strongest influence on the onset of crystallization.

The fundamentals of chain extension are described by Keller and Kolnaar (1997). Four different systems are discussed: dilute solutions, concentrated solutions, melts and cross-linked networks. A parallel was found for all systems between the coil-stretch transition in flow and the resulting fiber-platelet (shish kebab) morphology after crystallization. Fibers are only created beyond a critical elongational rate for high molecular weights. Lamellae are formed by the random coils of lower molecular weights. According to Keller, the fully stretched and the random chain are the two steady states with transient intermediate states.

Full chain extension can be achieved in stagnation flows. An overview of the different geometries to create such flow is for example given by Swartjes (1996) and Schoonen (1998). A stagnation flow can be created by impinging two liquid streams and is characterized by a free stagnation line where extensional strain becomes very high.

The objective of this research is to design and test an experimental setup for polymer melts to quantify the influence of extensional flow on the crystallization behavior. A cross slot device is developed and tested that can be used for in situ X-ray scattering and birefringence measurements at different thermal histories and flow conditions. In this way, the relation between molecular properties of the material, process conditions and final product properties can be determined.

A cross slot device, which creates a stagnation flow, was earlier used by Miles and Keller (1980) and Gardner et al. (1982) to investigate the interplay between flow and polymer conformation for a polystyrene solution. This geometry is chosen for its simplicity.

In this report, the cross slot device is discussed in detail. First results obtained with this completely new setup for an isotactic polypropylene are presented.

2 Design of the cross slot device

The cross slot flow device for melts is described. The basic design is shown in Figure 1. It consists of a cross slot and two reservoirs where two cams, which are connected with a ring, drive the melt. Several experiments with the same sample are possible without opening the flow cell. The whole design is described in detail in Swartjes (1999).

Flow

The maximum strain rate chosen (10 \([s^{-1}]\)) was used to estimate the flow rate. Three dimensional finite element analysis (SEPRAN; Segal (1992)) were used to calculate the exact strain, strain rate and pressure drop. To reduce computing time, three parts of the cell were modeled separately: the reservoir, the rectangular (inflow or outflow) channel and the center part of the cell. The total pressure drop was calculated by simply adding these partial pressure drops. The melt was modeled as a Newtonian fluid.
with a viscosity of 1000 [Pas]. A more realistic shear thinning behaviour would give smaller strain rates and pressure drops.

The pressure drop was the most important design parameter in the flow cell. The magnitude of this drop was used to calculate the window dimensions, the bolt dimensions and the force or torque needed to move the ring. The cam force was determined by multiplying the pressure by the cam area. This force can be transformed into the torque at the outer diameter of the ring.

The final dimensions and specifications of a cross slot with inflow and outflow channels height × depth 2 × 2 [mm²] and reservoir height × depth 5 × 2 [mm²] are given in Figure 2. In Figures 3 and 4 the calculated velocities and elongation rates on the center line, which is the symmetry line in the cell, are shown. Near the stagnation point velocities increase linearly, corresponding with a (small) area where the elongational rate is constant. An estimation for the total strain of a particle along a stream line was found by integrating the elongational rate over time.

$$\varepsilon = \int \ddot{\varepsilon}(t') \, dt'$$  \hspace{1cm} (1)

The maximum strain for a particle, which moves over a stream line on the center line, starting from point \(x_0 = 1.7 \cdot 10^{-6} \, \text{[m]}\) is equal to 10.6 [-]. However, as in reality a finite size beam is used, an average strain value depending on the diameter of the beam should be considered.
Figure 3: (a) Velocity versus position and (b) elongation rate versus position on centerline of cross slot. The broken line marks 0.5 times the height of the channel. Starting point $x_0$ is equal to $1.7 \cdot 10^{-6}$ [m].

Figure 4: (a) Velocity versus time and (b) elongation rate versus time on centerline of cross slot. The broken line corresponds to 0.5 times the height of the channel.

Temperature

Flow will be applied at a temperature $T_m$ well above the melting temperature of the polymer. After moving the ring, the cell is cooled to a crystallization temperature ($T_c$). Three oil baths (LAUDA K 6 KP (two) and UB 20) are used to control the desired thermal history (Figure 5) and to get ‘fast’ cooling rates. The first oil bath is set at the melt temperature. The second oil bath is kept at room temperature ($25 \, ^\circ C$) and is cooled by water. The largest oil bath (LAUDA UB 20) is used to keep the constant temperature $T_c$; due to its higher capacity, this bath is less disturbed by changes in the oil temperature.

The baths are connected with a valve system to the flow cell. This system consists of three mechanical valves (Klinger), which can be opened and closed with pneumatically controlled rotators (Bar GmbH). The pneumatic valves (Airtec) can be remote controlled electrically. The valve system was designed such that only one oil bath is connected with the flow cell at a time (i.e. in Figure 5(a) only the upper bath is connected).

The whole flow cell, which consists of four plates, is heated by a spiral oil channel. This oil channel is milled in the two inner plates, which are closed by the two outer plates (see Figure 7). For the ease of disconnecting the cell from the thermal system and opening the cell, four quick couplings (TEMA) are
used that connect the tubes from the valve system to the flow cell.

**Final design**

The final setup is shown in Figure 6(a). The cell is fully insulated and fixed to a frame with two bolts. Insulation reduces heat losses and prevents problems due to differences in thermal expansion of the plates in relation to the ring, since the ring is not heated by oil.

The diameter of the flow cell is 130 [mm]. It consists of four cylindrical plates. A cross section of the cell is given in Figure 7. All parts of the cell are made from constructional steel (C45). Two different window materials were used: diamond windows for the X-ray and quartz windows for the birefringence experiments. The diamond windows (type IIA; Drukker International, Cuijk, the Netherlands) have a thickness of 0.25 [mm], a diameter of 4.0 [mm], and are glued in a stainless steel frame (clear aperture 3.0 [mm]) (see Figure 7(b)). The quartz windows have a thickness of 1.8 [mm], a diameter of 8 [mm] and replace, together with a rubber ring, the window holder in Figure 7(b). The thermocouple that measures the temperature in the flow cell is situated in the ‘X-ray entrance tube’.

Tas (1994) showed that in the film blowing process, mechanical properties of different LDPE correlate with stress rather than strain or strain rate. Therefore, a constant torque or force is applied by two weights, which are connected via iron wires with the ring at each side of the cell, to get stress controlled crystallization. Consequently, no resulting side force will act on the flow cell and therefore the alignment is not disturbed. The displacement of one iron wire is measured by a Linear Variable Differential Transformer (LVDT; Lucas Schaevitz). The starting moment of applying the weight is controlled by a pneumatic cylinder.

**3  Isotactic Polypropylene (iPP)**

Isotactic polypropylene can crystallize in three different unit cell modifications: the $\alpha$, $\beta$ and $\gamma$ phase. The monoclinic $\alpha$ phase is the most stable one. The trigonal $\beta$ is formed only as the sample has been subjected to large strain rates and/or specific crystallization conditions (high cooling rates, high crystallization temperatures or large temperature gradients). Meillle et al. (1994) proposed two possible models to describe this phase. Dorset et al. (1998) described it recently with a model of ‘frustrated’ chain packing. The $\gamma$ phase, which is for example formed under high pressure, has a face centered orthorhombic unit cell. All three phases show a three-fold helix ($3_1$) of the same length of 6.5 Å. An elucidation of iPP is given by Brückner et al. (1991) and a review and molecular analysis is given by Lotz et al.
Figure 6: (a) Cross slot flow cell. (b) Components of the flow cell (four plates and the driving ring with cams).

Figure 7: (a) Side view of the flow cell with a cross section of the upper part. 1. X-ray exit tube; 2. cross slot consisting of four plates; 3. driving ring with cams; 4. X-ray entrance tube. (b) Detailed drawing of the center of the flow cell. 1. X-ray exit tube; 4. X-ray entrance tube; 5. window holder; 6. diamond window; 7. channel with polymer melt.


An unique characteristic property of iPP is lamellar branching. It occurs within the $\alpha$ phase ($\alpha - \alpha$ branching) or between the $\alpha$ and $\gamma$ phase ($\alpha - \gamma$ branching). This feature was described on a molecular level by Lotz et al. (1996); Lotz and Wittmann (1986). Branching takes place when two successive ’ac’ layers have chains of the same hand. In spherulites, mother and daughter lamellae are 80 or 100 degrees apart. The last angle is the same as the $\beta$ angle in the monoclinic unit cell.

The WAXD experiments performed by Norton and Keller (1985) give the relation between X-ray pattern and morphology for four different spherulite types. The WAXD patterns of two oriented sections of an $\alpha$ and $\beta$ spherulite are given in Figure 8. The orientation of the lamellae correspond to the vertical direction.

Lovinger (1983) investigated the preferred growth direction of thin iPP films on mica. The diffraction pattern for moderate temperatures (120 - 140 [°C]) is shown in Figure 9. The pattern consists of two pairs of (110) reflections making an angle of about 80 degrees that are bisected by a single pair of (111)
Figure 8: Two dimensional WAXD patterns showing vertically aligned sections of $\alpha$ (a) and $\beta$ (b) spherulites according to Norton and Keller (1985).

Figure 9: Diffraction pattern showing $\alpha$-iPP crystallized as a thin film on mica according to Lovinger (1983). Sample thickness is equal to 50 [$\mu$m].

reflections.

Lovinger also investigated an unidirectionally crystallized sample of $\alpha$-iPP. The same diffraction pattern as Figure 8(a) was obtained. The angle of the two (110) reflections at the meridian was equal to 32 degrees. Earlier, Clark and Spruiell (1976) obtained the same diffraction pattern as Lovinger, Norton and Keller. However, in all these measurements thin samples were used (less than 100 [$\mu$m]).

Fujiyama (1995), (1988) investigated an injection moulded specimen and compared the core with the skin of the samples. A fiber pattern was found in the skin with $a^*$, which is the growth direction of lamellar crystals (see Figure 11), highly oriented to the machine direction of the process. In the core, a weak c and $a^*$ orientation to the machine direction is found (see Figure 10). Sample thickness was about 0.4 [mm]. Additional SAXS measurements showed an oriented structure in the skin with only a peak on the meridian. This means that the $a^*$ oriented lamellae are small and imperfect. SAXS measurements on the core showed a random orientation of the lamellae. The structure in the skin of an injection moulded sample proposed by Fujiyama is given in Figure 11. It is a lamellar branched shish-kebab structure.

Kalay and Bevis (1997), Kalay et al. (1996, 1994) compared conventional injection moulded samples with samples from a SCORIM (Shear Controlled Orientation Injection Moulding) process using WAXD. The thickness of the samples was equal to 1.5 [mm]. These samples were cut from a round specimen with a diameter of 5 [mm], parallel to the injection direction. In the SCORIM samples the same orientation was shown as found by Fujiyama in the skin of his samples. The conventional moulding samples had the same orientation as the samples of Fujiyama in the core.
Figure 10: Two dimensional WAXD patterns showing orientation in the skin (a) and orientation in the core (b) in an injection moulded sample according to Fujiyama (1995)). The machine direction is vertical.

Figure 11: Proposed lamellar branched shish-kebab structure in the skin of injection moulded sample proposed by Fujiyama (1995). MD: machine direction.

4 Experimental conditions

4.1 Material

Experiments were carried out on a polypropylene (StamylanP 13E10; \( M_w = 501 \) [kg/mol] and \( M_w/M_n = 6.0 \); DSM, Geleen, The Netherlands).

Preforms for the flow cell were made in two steps. First, 2 [mm] thick plates were compression moulded at a temperature of 210 °C, doubling the pressing force each 15 min, starting from 5 [kN] to a maximum of 40 [kN]. Next, strips and arcs were cut out of these plates.

4.2 Thermal history

In the experiments done, the work of Vleeshouwers and Meijer (1996) is followed. Vleeshouwers used the same material, but in a shear flow created on a standard rheometer with a cone plate geometry. At high temperatures, simple shear flow was applied and at low temperatures crystallization is monitored using a dynamic oscillatory experiment with small amplitude. The same temperature history is used in our experiments. The influence of temperatures \( T_m \) and \( T_c \) and holding times \( t_m \) are discussed below.

The effect of the melt temperature \( T_m \) can be twofold. At too low temperatures incomplete melting can occur and at too high temperatures degradation (Vleeshouwers and Meijer, 1996). Of course both effects depend on the annealing time. In the experiments of Vleeshouwers, where a nitrogen environ-
ment was used, thermal degradation seems to be a minor effect compared to mechanical degradation. Especially the high molar mass tail degraded during each experiment on the same sample. Thermal degradation may be an important factor in our experiments, since no special environment like nitrogen is used and long processing (annealing) times are used.

Janimak et al. (1992) discussed the large range of equilibrium melting temperatures of isotactic polypropylenes. This temperature is claimed to be in a range of 185 °C to 208 °C. Samuels (1975) extrapolated a value of 220 °C for fully oriented chains.

Alfonso and Ziabicki (1995) considered the influence of annealing time and temperature for three kinds of polypropylenes in DSC experiments. Higher melt temperatures and longer melting times decrease the crystallization rate. This effect is subscribed to a decreasing concentration of athermal nuclei at a higher melt temperature or longer times. However, the influence of time shows an asymptotic behavior, above which longer times don’t affect the crystallization rate. This behavior is subscribed to heterogeneous nuclei, which are insensitive to annealing time and temperature.

Vleeshouwers also showed that an annealing time of one hour at a temperature of 260 °C after shear flow could not erase the effect of shearing completely. Very likely, this is also important in our experiments. Therefore, experiments without flow should only be performed on samples that have no flow history. However, sample preparation could influence these 'no flow' experiments, since material has flown in the mould. The exact conditions to erase the influence of flow are not known.

The following conditions for thermal history are chosen in our experiments. First, the melt was annealed at a temperature of 220 °C, which should be sufficiently high according to Janimak, for 90 minutes. It is unknown whether this time is large enough to erase previous flow history (Vleeshouwers). Next, the sample is cooled in about 200 [s] to the crystallization temperature T_c. Finally, isothermal crystallization is studied at temperatures between 126 °C and 138 °C. It is important that stable isothermal crystallization takes place (T_c < 138 °C). On the other hand, the material should not crystallize too fast otherwise crystallization dominated by supercooling would occur (T_c > 126 °C).

5 Experimental Results

In this section point-wise birefringence and Wide Angle X-ray Difraction (WAXD) results are described, which were performed in the stagnation point of the cross slot flow cell. In the birefringence experiments the setup developed by Fuller (1995) was used. Only the turbidity that is related to changes in the mean intensity I_0 at crystallization temperature T_c is discussed.

WAXD experiments were performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) at the micro-focus beam line (ID13-BL1), where a very small beam size of about 30 [µm] was used. Structural changes can be followed in situ due to the high flux. The wavelength λ of the beam was equal to 0.7817 Å.

Samples with an elongational flow history at the annealing temperature of 220 °C were compared with samples with no flow history using the same thermal history in both birefringence and X-ray experiments. The samples were used at most in four experiments. Quiescent experiments were not performed after flow experiments, since flow history is difficult to erase. Differential Scanning Calorimetry (DSC) is used to compare with the quiescent experiments in the cell. Experimental details can be found in Swartjes (1999).

5.1 DSC

DSC experiments were performed on a Perkin Elmer DSC Pyris 1 for the StamylanP 13E10. Seven different crystallization temperatures were used between 126 °C and 139 °C. The applied cooling rate was 27.5 °C/min, which is the same as obtained in the flow cell. Onset of crystallization and development of crystallinity are shown in Figure 12. The onset of crystallization increases exponentially
with increasing $T_c$. The final crystallinity of the samples is between 45 and 50 percent. The rate of crystallization increases with decreasing temperature.

![Graph (a)](image-a)

![Graph (b)](image-b)

**Figure 12:** (a) Onset time of PP 13E10 for different $T_c$. (b) Crystallinity (in percentage) of PP 13E10 versus time for $T_c = 126.6; 128.6; 130.7; 132.8; 134.9; 136.9; 138.9$ °C.

### 5.2 Turbidity

The conditions obtained with the cross slot setup for the experiments that will be discussed in this subsection are given in Table 1. The cooling rate ($T_{cool}$) is calculated by dividing the temperature difference of 220 °C (first oil bath) and the temperature at which was switched from the second to the third oil bath, with the corresponding time difference.

The mean intensity $I_0$ was determined each 50 [ms]. Diameter of the laser beam in the middle of the cell is equal to $1.05 \cdot 10^{-5}$ m and $2.29 \cdot 10^{-5}$ m at the windows (Siegman, 1986).

<table>
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<td>$T_{cool}$ °C/min</td>
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<td>129.8</td>
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<tr>
<td>$t_d$ [s]</td>
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<td>$T_{cool}$ °C/min</td>
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<tr>
<td>$T_c$ °C</td>
<td>133.5</td>
<td>134.0</td>
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</table>

**Table 1:** Conditions of the point-wise birefringence measurements on StamylanP 13E10. $t_d$: displacement time; $T_{cool}$: cooling rate; $T_c$: crystallization temperature.

### Temperature

The temperature curves are shown in Figure 13 for the quiescent and flow experiments together at a $T_c$ of about 130 °C and 134 °C, respectively. The reproducibility of the cooling rate is excellent. This is important because cooling rate influences the amount and perfectness of the crystals. Fast cooling rates give (less perfect) small crystals and therefore a lower degree of crystallinity compared to slow cooling rates. Switching between the cooling oil bath and the bath, which is on $T_c$, was done three degrees above $T_c$. This moment of switching was defined as the zero point for time in the following figures. Unfortunately, in some experiments the temperature dropped two degrees below $T_c$ just after $t=0$. This
was due to an error in the temperature calibration. The thermal history for the two experiments with $T_c = 130 \, ^\circ C$ is exactly the same as can be seen in Figure 13(a). The quiescent experiment that has $T_c = 134 \, ^\circ C$ shows a minimum compared with the flow experiment with the same $T_c$.

**Flow**

A total weight of 14 [kg] was used to induce flow at a melt temperature ($T_m$) of 220 [°C]. However, the displacement of the ring was not reproducible. Two different experiments showed different rotation speeds (Figure 14). A dependence on the number of runs on the same sample was found. A fresh sample gave a longer displacement time. This is probably caused by a some leakage out of the reservoir.

**Measurements**

The intensity curves for the quiescent and flow experiments at a crystallization temperature of 130 [°C] and 134 [°C], are shown in Figure 15, together. The intensity curves in these plots were all scaled by its maximum intensity at $t = 0$ [s].

First, the increase of turbidity shows a clear influence of crystallization temperature $T_c$. Figure 15 gives the same trends as were found in the DSC experiments. A decreasing temperature decreases the onset of crystallization exponentially and increases rate of crystallization. However, the time scale of the quiescent experiments is shifted completely in comparison with the DSC experiments. For example, the onset of crystallization is lower than 200 [s] for the quiescent experiment with $T_c$ equal to 133.5 [°C]. The onset time in the DSC experiments for the same $T_c$ is equal to 511 [s] (Figure 12(a)). The corresponding temperature for an onset time of 200 [s] is according to the DSC experiments (Figure 12(a)) equal to 129.9 [°C]. The difference in onset time between DSC and these turbidity measurements can be explained by a difference in temperature of at least 3.5 [°C]. This might be caused by the better insulation of the small samples in DSC in comparison with the large samples in the flow cell, where the windows contact the 'cool' air.

Second, the influence of flow is shown clearly in Figure 15. Flow decreases the onset and increases the rate of crystallization. Since the sample crystallizes reasonable fast at about 130 [°C] in a quiescent experiment, largest changes are seen at a higher $T_c$. Probably, the effect is larger than shown in Figure 15(b), because the quiescent experiment was performed at a slightly lower $T_c$ where the initial $T_c$ started two degrees below the final $T_c$ (shown in Figure 13(b)).
Figure 13: (a) Thermal history for $T_c = 129.6$ [°C] (no flow) and $T_c = 129.8$ [°C] (flow). (b) Thermal history for $T_c = 133.5$ [°C] (no flow) and $T_c = 134.0$ [°C] (flow) (material: PP 13E10).

Figure 14: Displacement ($x$) of the ring for PP 13E10 versus displacement ($t_d$) time at $T_m = 220$ [°C]. (The symbols refer to $T_c$. A: 129.8 [°C] and B: 134.0 [°C]).

Figure 15: (a) Scaled intensity versus time at $T_c = 129.6$ [°C] (no flow) and $T_c = 129.8$ [°C] (flow). (b) Scaled intensity at $T_c = 133.5$ [°C] (no flow) and $T_c = 134.0$ [°C] (flow) (material: PP 13E10).
5.3 Wide Angle X-ray Diffraction

The conditions obtained with the cross slot setup for the WAXD experiments on StamylanP 13E10 that will be discussed in this subsection are given in Table 2. The cooling rate ($\dot{T}_{\text{cool}}$) is calculated by dividing the temperature difference of 220 [$^\circ$C] (temperature first oil bath) and the temperature at which was switched from the second to the third oil bath, with the corresponding time difference.

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<td>$T_c$ [$^\circ$C]</td>
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<td>131.8</td>
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<td>$t_d$ [s]</td>
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<td>$T_{\text{cool}}$ [$^\circ$C/min]</td>
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<td>$T_c$ [$^\circ$C]</td>
<td>135.6</td>
<td>136.0</td>
</tr>
</tbody>
</table>

Table 2: Conditions of the WAXD measurements on StamylanP 13E10. $t_d$: displacement time; $\dot{T}_{\text{cool}}$: cooling rate; $T_c$: crystallization temperature.

**Temperature**

The temperature curves are shown in Figure 16 for the quiescent and flow experiments together at a $T_c$ of about 132 [$^\circ$C] and 136 [$^\circ$C]. Switching between the cooling oil bath and the bath that is on $T_c$, was done ten degrees above $T_c$. This moment of switching was defined as the zero point for time in the figures. The $T_c$ for the quiescent experiments are lower than for the flow experiments (Figure 16). However, the temperature just after switching was for the quiescent experiments higher during a period of about 200 [s]. Moreover, cooling rates were faster for the quiescent experiments.

**Flow**

A total weight of 7.5 [kg] was used to apply flow at a melting temperature ($T_m$) of 220 [$^\circ$C]. The displacement of the ring is shown in Figure 17. Also here, displacement of the ring was not reproducible.

**Measurements**

The WAXD results for a crystallization temperature of about 136 [$^\circ$C] are shown in Figures 18-20. The two dimensional WAXD pattern after 3000 [s] is shown in Figure 18. The quiescent experiment (Figure 18(a)) shows the $\alpha$-phase. Intensities are weak and no orientation is seen. The flow experiment (Figure 18(b)) also shows the $\alpha$-phase and a small amount of the $\beta$-phase. This $\beta$-phase is oriented and is about 25 degrees tilted with respect to the equator. An orientation in the (040) reflection of the $\alpha$-phase is seen perpendicular to this orientation. These two orientation indicate a oriented structure, which is tilted in respect to the equator. The relative orientations are in agreement with Norton and Keller ($\beta$-phase; Figure 8(b)) and Fujiyama ($\alpha$-phase; Figure 10(b)).

The development of the peaks in time is shown in Figure 19. Some curves are missing for the quiescent experiment due to a refill of the synchrotron storage ring. The corresponding growth of crystallinity is given in Figure 20 (obtained by dividing the total area of the crystalline peaks by the total area below the curves). Flow enhances crystallization behavior of the material. Despite the higher $T_c$ for the flow experiment, crystallization starts earlier and the rate of crystallization is faster. The onset of the quiescent experiment (at 1335 [s]), is about 580 [s] slower than found in the DSC experiments for $T_c = 135.6$ [$^\circ$C].
Figure 16: (a) Thermal history for $T_c = 131.6 \, ^\circ\text{C}$ (no flow) and $T_c = 131.8 \, ^\circ\text{C}$ (flow). (b) Thermal history for $T_c = 135.6 \, ^\circ\text{C}$ (no flow) and $T_c = 136.0 \, ^\circ\text{C}$ (flow) (material: PP 13E10).

Figure 17: Displacement ($x$) of the ring for PP 13E10 versus displacement time ($t_d$) at $T_m = 220 \, ^\circ\text{C}$. (The symbols refer to $T_c$. A: 136.0 $^\circ\text{C}$ and B: 131.8 $^\circ\text{C}$.)

(linear interpolation gives 754 [s]; see Figure 12(a)). However, this difference can be explained by the slowly decreasing temperature just after $t=0$ [s].

The WAXD results for a crystallization temperature of about 132 $^\circ\text{C}$ are shown in Figures 21-23. Figure 21 gives the two dimensional WAXD patterns after 1500 [s]. Both the quiescent experiment and the flow experiment show the $\alpha$-phase. The quiescent experiment gives weak but oriented peaks (Figure 21(a)). Orientation at an angle of about 45 degrees with the equator is seen in the (110) reflection. Perpendicular to this reflection a weak orientation is seen in the (040) reflection. This pattern indicates a lamellar branched $\alpha$-phase. The flow experiment shows orientations in the (110) and (040) reflections both at the equator and meridian. This indicates a flow oriented, strongly branched structure.

The development of the peaks in time is shown in Figure 22. The corresponding growth of crystallinity is given in Figure 23. The same conclusions can be drawn as those based on the higher crystallization temperature. The onset of the quiescent experiment (523 [s]), is about 200 [s] slower than found in the DSC experiments for $T_c = 131.6 \, ^\circ\text{C}$ (linear interpolation gives 324 [s]; see Figure 12(a)). It seems that the X-ray measurements in the cell using diamond windows agrees better with the DSC measurements, than the birefringence measurements using quartz windows.
Figure 18: 2D-WAXD patterns about 3000 [s] after reaching $T_c$. (a) no flow and $T_c = 135.6 \degree$C; (b) after flow ($t_d = 195$[s]; $T_c = 136.0 \degree$C). Horizontal inflow and vertical outflow (material: PP 13E10).

Figure 19: WAXD intensity integrated along the Debye ring versus time and diffraction angle. (a) no flow and $T_c = 135.6 \degree$C; (b) after flow ($t_d = 195$[s]; $T_c = 136.0 \degree$C) (material: PP 13E10).

Figure 20: Degree of crystallinity for PP 13E10 versus time.
**Figure 21:** 2D-WAXD patterns about 1500 [s] after reaching $T_c$. (a) no flow and $T_c = 131.6$ [°C]; (b) after flow ($t_d = 315$ [s]; $T_c = 131.8$ [°C]). Vertical inflow and horizontal outflow (material: PP 13E10).

**Figure 22:** WAXD intensity integrated along the Debye ring versus time and diffraction angle. (a) no flow and $T_c = 131.6$ [°C]; (b) after flow ($t_d = 315$ [s]; $T_c = 131.8$ [°C]) (material: PP 13E10).

**Figure 23:** Degree of crystallinity for PP 13E10 versus time.
6 Discussion

A novel cross-slot setup to investigate structure development as a consequence of elongational flow of polymer melts is realized. First measurements were performed on isotactic Polypropylene using a point-wise birefringence technique and Wide Angle X-ray Diffraction (WAXD). The reproducibility of the thermal history was excellent. Unfortunately, displacement time of the ring at the same temperature for the same material is different for comparable experiments. Friction can have a large influence. Consequently, much better reproducible constant velocity experiments should be performed in future.

The crystallization behaviour of StamylanP 13E10 is strongly enhanced by flow as shown by the birefringence and X-ray experiments. DSC showed an exponentially increase of the onset time of crystallization as a function of $T_c$. Therefore, the influence of flow is less, or more difficult to detect at temperatures lower than 130 °C for this material. The weak orientation in one quiescent experiment is unclear. Keller gives three mechanisms for orientation in absence of flow (Keller and Kolnaar, 1997). A moving temperature gradient, a nucleating surface and growing constraints can create orientation. The first leads to unidirectional spherulite-type growth along the moving temperature gradient. The second mechanism enhances nucleation at rough windows. The last exists when growth of a structure is constrained (for example within a very small channel).

In WAXD experiments lamellar branching of $\alpha$ isotactic polypropylene influences the orientation of the (110) reflection. Consequently, orientation was not only found at the equator, but also at the meridian (Fujiyama and Kalay). Branching depends not only on thermal history as shown by Norton and Keller, but also on deformation history. Previous in-situ WAXD experiments at ID-11 in Grenoble in a contraction flow cell, which was used in the past by Kolnaar and Keller (described in Bilsen et al. (1995)), showed a dependence on flow rate (Göschel et al., 1998a, 1999). Measurements performed at 158 °C during and after flow showed lamellar branching during flow at low flow rates. High flow rates showed orientation at the equator after flow, while during flow no crystallization was observed due to the short flow time.

WAXD experiments showed an oriented $\alpha$ phase. The orientation seen in many two dimensional patterns is given schematically in Figure 24. This structure could be explained by the crystalline structure proposed by Fujiyama (1995) with the c-axis oriented in inflow and outflow direction. In one of the experiments discussed also the $\beta$ phase was detected. This shows that flow conditions are severe enough to create this phase.

Deformation history in the material points situated in the measuring beam will be calculated in near future. A fully viscoelastic analysis of the cross slot can be preformed using the recently developed implementation by Bogaerds (1998). A full characterization of the material is necessary to simulate the resulting crystallization behaviour.

First X-ray experiments, using this setup, showed a competition between melting and recrystallization at a $T_c$ of 138 °C (Göschel et al., 1998b). However, Vleeshouwers and Meijer (1996) performed all
their measurements at 138 and 140 [°C]. At these temperatures crystallization was monitored by dynamic oscillatory experiments, while in the experiments described in this article no force was put on the sample at \( T_c \). This essential difference could explain the difference in isothermal crystallization conditions.

The quiescent birefringence and X-ray experiments showed a large difference in onset in comparison to DSC experiments. Crystalization in the birefringence experiments occurred much faster and in the X-ray experiments it occurred slower than in the DSC experiments. Since, the thermal history of the DSC and X-ray experiments was not exactly the same (\( T_c \) just after \( t=0 \) [s] was higher) a smaller difference is expected. The large difference in thermal conductivity \( (k) \) of the diamond window and the window frame, which is made of stainless steel, can induce thermal gradients in the sample. Diamond has the highest thermal conductivity at room temperature. Some values of \( k \) are given in Bejan (1993). Since the windows are in contact with air, sample temperatures close to the windows could be lower than in the center of the cell. A thermal calibration material, for example a liquid crystalline material with a known liquid to crystal transformation, has to be used in future to check for this thermal gradient.

The window material can influence the crystallization behaviour of the sample due to thermal gradients and/or rough surface of the window. A choice for a thermal history as proposed by Göschel et al. (1999), could remove these uncertainties. This thermal history uses the same annealing conditions as used in this article, but flow is applied at a \( T_c \) just below the melting temperature of the material (about 170 [°C]). In this case, the pure effect of elongational flow on crystallization during flow can be monitored. However, flow calculations at these temperatures may be difficult due to the high viscosities and long relaxation times. It is very likely that orientations at these high temperatures will be more pronounced.

In conclusion, this article shows how flow induced crystallization could be investigated. First, the material has to be characterized using DSC. Second, turbidity measurements can be performed to check the temperature range determined in DSC and to determine the influence of flow. Third, X-ray experiments give quantitative information about the relation between flow and crystallization behaviour. In the near future, a fourth step can be introduced that investigates the resulting morphology using microscopy (Transmission Electron Microscopy).

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**References**


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