Model development and validation of crystallization behavior in injection molding prototype flows

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ABSTRACT: Injection molding of semi-crystalline \( \alpha \)-olefin polymers is a frequently applied production method. Solid-state properties, e.g. mechanical and optical, are related to the underlying material microstructure, which is largely determined by the processing conditions. During injection, the molten material is submitted to a complex thermal-mechanical history in which phase-changes occur in conditions far beyond equilibrium. This complex problem is coupled; the processing conditions determine the evolving morphology and type of crystalline structure, which, in turn, affect the melt rheology. To control the final properties of products, an accurate prediction of the material microstructure developed upon processing is required. To address this problem we model the experiments reported in\(^{[1,2]}\) in which the morphology development of an isotactic polypropylene (iPP) resin was studied using experimental setups specially designed to generate flows with fully controlled initial and boundary conditions. A model for flow-enhanced nucleation is proposed within the framework of molecular-based rheological modeling, which relates molecular deformation with the enhancement of crystallization. The model is implemented in a finite-element injection molding code in which flow-kinematics are computed. In a decoupled fashion, flow-kinematics are used to solve a coupled viscoelastic stress - crystallization problem. A morphological description concerning the number, size and shape of crystalline structures is predicted and a comparison between computational and experimental results is made.
1 Introduction

The microstructure of semi-crystalline polymers results from a variety of physical changes that occur during processing. Notably, in injection molding such changes take place under extreme conditions characterized by high shear rates, high-pressure levels, high cooling rates and steep temperature gradients. The morphology of the material develops accordingly to these conditions and the part geometry. An important physical process during processing is crystallization, which is coupled to the flow history: flow induces crystallization, crystallization changes the rheological behavior, and thus the flow. Furthermore, crystallization plays a dominant role in the final properties of injection molding parts. However, the effect of crystallization on macroscopic properties is difficult to predict and, therefore, also difficult to control. Typically the microstructure of an injection molded part, when visualized under polarized optical light microscopy, consists of different layers: a highly oriented layer close to the surface, a transitions layer, a second oriented shear layer, a fine-grained layer and a spherulitical core. This layer-type morphology introduces a high degree of anisotropy in physical properties. The effect of processing conditions on the morphology of the microstructure of injection molded parts has been extensively investigated. For example, Viana et al. found the oriented-layer/core ratio to vary most strongly with varying injection speed and injection temperature.

In order to unravel the intrinsic relation between product properties and the underlying crystalline morphology, research effort has been devoted to predict the microstructure of injection-molded parts of semi-crystalline materials. Most of the studies focused on
isotactic polypropylene (iPP), due to its high potential for property tuning and its vast use in applications where crystallinity determines the mechanical and optical properties. Pantani et al.\cite{7} gives an extensive review on available models and experimental techniques to predict and characterize the morphology of injection-molded parts. The authors propose a model to predict the morphology of injection-molded iPP, in which flow kinematics are computed using a lubrication approximation. Polymorphism was accounted for, using the Avrami-Evans-Nakamura equation to describe the crystallization kinetics of the mesomorphic phase, while the evolution of the $\alpha$ phase was modeled using Kolmogorov's model.\cite{8} The growth-rate of spherulites was described by the Hoffman-Lauritzen expression.\cite{9} Smirnova et al.\cite{10} used a differential set of Avrami equations to predict crystallinity and the average size of spherulites in injection molding, but in their study only temperature effects were taken into account. In a different study, Pantani et al.\cite{11} investigated the effect of varying the packing pressure on the morphology of injection molding samples.

The effect of pressure on crystallization kinetics was also assessed in a study by Watanabe et al.,\cite{12} in which the authors measured the half time, $t_{1/2}$, for crystallization (defined as the time at which the volume fraction of crystallized material reaches 50\%) and verified that pressure indeed simply acts as to increase undercooling. Van der Beeke in\cite{13} experimentally studied the combined effect of pressure, cooling rates and shear deformation on the specific volume of iPP, in a new PVT apparatus which allows PVT measurements at high cooling rates (100 °C s$^{-1}$) and pressures (up to 100 MPa). Additionally, the device makes it possible to generate flows prior to or during cooling with shear rates in the order of $10^2 - 10^3$ s$^{-1}$. Experiments like these, will certainly provide the input for further
improvement and validation of the theoretical models.

Flow effects on crystallization in injection molding simulations are often taken into account by adopting a modified version of the Nakamura equation.\textsuperscript{14} Within this approach, Hieber\textsuperscript{15} defined a characteristic time for crystallization that was made dependent on temperature, pressure and the absolute value of the shear stress. Kim et al.\textsuperscript{16} modified the crystallization rate constant in the Nakamura model, making it dependent on the shear rate. The authors tried to predict the thickness of the oriented shear-induced layer using a thermodynamic approach, in which viscoelastic stresses were computed to find changes in entropy associated with the flow. Making use of Flory’s expression\textsuperscript{17} that relates the equilibrium melting temperature, $T_m$, with changes in entropy, the authors could determine a new elevated nominal melting temperature resulting from the entropy decrease imposed by the flow. The transition from spherulitical core to oriented shear layer was assumed to take place when the local temperature would equal the calculated $T_m$. Even though their results qualitatively describe the experimental data, they still fall short from providing morphological detail.

Summarizing, most of the numerical studies on injection molding of semi-crystalline materials give few insight in the morphology developed, failing to provide information about the shape and dimensions of oriented crystalline structures. Also, the crystallization models employed lack molecular understanding, and they do not couple flow-induced crystallization with melt rheology. Furthermore, often similar growth mechanisms for non-oriented and oriented crystals are assumed, which is in clear contradiction with experimental evidence that shows the growth kinetics of a spherulite to be profoundly different from that of a
Advances in the physical understanding of flow-associated effects on crystallization have been recently reviewed by Somani et al.\textsuperscript{[19]} and Kumaraswamy.\textsuperscript{[20]} It has been experimentally observed that long chains, the high end tail of the molecular weight distribution, play a dominant and decisive role accelerating the kinetics of flow-induced crystallization.\textsuperscript{[21–24]} Seki et al.\textsuperscript{[23]} showed that with the addition of just 1% of chains with a number average molecular weight $M_w$ five times larger than that of the matrix resin, crystallization kinetics are profoundly changed. Special experimental setups have been developed to perform short-term shear experiments in semi-crystalline polymer melts at strain-rate levels close to real processing conditions.\textsuperscript{[22, 25–28]} In these experiments a polymer melt is held above its equilibrium melting temperature for some time, such that any residual ordering or structure becomes erased, and subsequently cooled to a desired crystallization temperature at which the material is subjected to a brief shear deformation. The crystallization temperature is chosen such that quiescent crystallization takes place over a time scale much larger than those being investigated. The changes in microstructure are monitored during and after the flow. These studies provide insight into the kinetics of flow-induced nucleation and its dependence on flow conditions, as well as morphological detail of oriented crystals. Mechanical deformation of the melt (shear or extension) was found to significantly enhance nucleation, and the increase of deformation rate to be more effective than that of deformation time. In their early work on dilute solutions under elongational flows, Keller and Kolnaar\textsuperscript{[29]} could already identify that upon a critical strain-rate an abrupt change in birefringence, that was associated by the authors to a coil-stretch transition of the chains.
conformation, occurs. Keller reasoned that such change in chains conformation could also occur in entangled polymer melts beyond a critical strain rate, and lead to the formation of oriented crystals (row nucleation). More recently, Seki et al.\cite{23} used short-term shear experiments on iPP melts at constant wall shear stress, and identified a critical shear stress that is needed to induce the transition from spherulitical to oriented crystal growth, which was found to decrease with the addition of long chains. The authors explain that a critical stress threshold has to be surpassed to generate threadlike precursors that template row-nucleated structures (shish).

In an attempt to unify all these findings, Van Meerveld et al.\cite{30} classified different flow regimes according to the Deborah number, defined as the product between strain-rate (in shear or elongation) and a characteristic relaxation time of the melt. Two time scales were considered: the disengagement time, $\tau_d$, associated with the reptation process and the Rouse time, $\tau_R$, associated with the fast chain retraction mechanism. For each time scale a corresponding Deborah number was calculated considering only the longest relaxation times associated with the longest chains, namely: a Deborah number based on the disengagement time $De_d$, and a Deborah number based on the Rouse time $De_R$. It was found that when $De_d > 1$ and $De_R < 1$, an increase of orientational order occurs leading to an enhancement of point-like nucleation. For $De_d > 1$ and $De_R > 1$, the onset of chain stretching occurs leading to the growth of oriented crystals (fibrillar regime). The latter regime was associated with changes in molecular conformation due to rotational isomerization.
Flow-regimes based models  From short-term experiments in a duct, Jerschow and Janeschitz-Kriegl[22] could relate the size of the oriented shear and fine-grained layers with the shear rate and shear time. It was found that at the boundary between the fine-grained layer and core $\dot{\gamma}_c^2 t_s$ was constant, with $\dot{\gamma}_c$ defined as a critical shear rate, and $t_s$ the shear time. In the same way the transition to the highly oriented shear layer was characterized by a constant $\dot{\gamma}_c^4 t_s$. Based on these findings Eder[3] proposed a model for flow-induced crystallization in which a critical shear-rate acts as a threshold to generate oriented crystalline morphologies. The model consists of a set of differential equations from which the number of flow induced nuclei, the total shish length per unit volume and the total volume of oriented crystals can be obtained. Later, Zuidema et al.[31] proposed a modified version of the Eder model, the S$_{J2}$ model, in which molecular orientation and stretch, computed from the second invariant of the deviatoric part of the elastic Finger tensor (also called recoverable strain tensor), $J_2(B_e^d)$, drives flow-induced crystallization. The non-linear increase in nucleation density as a function of the deformation applied is explained as the result of a self-enhancing process: flow induces nucleation and nucleation strengthens the flow. Zuidema assumed that flow-induced nuclei act locally as physical crosslinks increasing the relaxation time of the longest molecules. Thus, enhancing the molecular deformation and increasing the number of oriented chain segments, which are envisioned as precursors for new nuclei. Zuidema tested his model on the experiments of Jerschow et al.[22] and found that the $J_2(B_e^d)$ of the highest relaxation mode remains constant at the transition from spherulitical core to oriented shear layer, corroborating experimental evidences of the dominant role of long chains on flow-induced crystallization.
in polydisperse melts.

**Motivation**  Most of the studies that deal with morphology development of semi-crystalline polymers upon processing, generally follow an approach that combines experiments with numerical simulations. However, most of the correlations drawn between processing conditions and morphology, e.g. skin layer thickness, are still based on models that lack physical detail, and on experiments performed in injection molding machines. The modeling of such experiments is over simplified by neglecting the flow history inside the machine during plastification. Recent findings suggest that even at high temperatures substantial order can be formed or remain in the melt. Azzurri et al.[32] measured the relaxation of shear-induced nucleation precursors in melts at temperatures slightly above the equilibrium melting temperature and found flow to affect the kinetics of crystallization, even when allowing the melt to relax for a considerable time before cooling it down to crystallization temperature. Furthermore, upon increasing the concentration of long chains in the melt the relaxation times of the nucleation precursors were found to increase. Similar results were found by Vleeshouwers et al.[21] They reported that after short term shearing of iPP at 200°C, followed by a waiting period of 30 minutes at 200°C, the influence of the flow-induced precursors on crystallization was still measurable. Regarding injection molding the implication of these studies is obvious: the complex deformation the material experiences inside the machine before injection is unlikely to be fully erased and therefore its effect on the developed morphology cannot be neglected. This strongly supports that morphological studies of semi-crystalline materials, in first instance should be carried out
under conditions in which the initial state of the material is known.

In the present study we make use of experimental results obtained using two experimental tools, a multipass rheometer and a capillary rheometer. Both allow to study crystallization phenomena at high shear-rates, but under controlled deformation and thermal histories, which, in contrast to the situation in real injection molding machines, are known a priori. Hence, the influence of flow on crystallization kinetics and developing morphology can be quantified and experimental conditions can be accurately translated into boundary conditions for numerical simulations. We develop a model for flow-induced crystallization, which revises the underlying model-ideas of the $S_{J2}$ model\cite{31} and the recently proposed model by Steenbakkers and Peters\cite{33} to predict the morphology of the oriented crystalline phase. Summarizing, we see the present study as a necessary step to validate kinetic models for flow-induced crystallization and to understand the morphological development of crystalline structures in flow conditions close to injection molding conditions.

2 Modeling crystallization

Under the combined effect of cooling and flow-induced molecular deformation, the resulting material morphology upon crystallization combines both spherulitical and fibrillar oriented structures. Both have to be taken into account if a realistic description of the final morphology is envisaged.
Quiescent crystallization

Spherulitical structures develop under quiescent conditions, their number and size depend on the cooling history and on the concentration of nucleating agents. To model this we use the Schneider rate equations,\(^3\) which are based on the Kolmogoroff-Avrami equation.\(^{34,35}\) They provide a complete picture of the morphology, in terms of number of spherulites, their radius, surface and volume, and consist of a set of nested differential equations that reads:

\[
\begin{align*}
\dot{\phi}_3 &= 8\pi \alpha \quad (\phi_3 = 8\pi N), \\
\dot{\phi}_2 &= G\phi_3 \quad (\phi_2 = 8\pi R_{\text{tot}}), \\
\dot{\phi}_1 &= G\phi_2 \quad (\phi_1 = S_{\text{tot}}), \\
\dot{\phi}_0 &= G\phi_1 \quad (\phi_0 = V_{\text{tot}}),
\end{align*}
\]

in which \(\phi_0\) is the undisturbed total volume \(V_{\text{tot}}\) of the spherulites per unit volume, \(\phi_1\) is the total surface \(S_{\text{tot}}\) of the spherulites per unit volume, \(\phi_2\) is 8\(\pi\) times the sum of the radii \(R_{\text{tot}}\) of the spherulites per unit volume, \(\phi_3\) is 8\(\pi\) times the number of the spherulites \(N\) per unit volume, \(\alpha = \alpha(T,p)\) is the nucleation rate and \(G = G(T,p)\) the crystal growth rate.

In order to correct for impingement, two different models can be employed, the Avrami model,\(^{34,35}\)

\[-\ln(1 - \xi_g) = \phi_0,\]  

or the Tobin model,\(^{36}\)

\[\frac{\xi_g}{1 - \xi_g} = \phi_0.\]
The degree of crystallinity $\xi$ can be obtained by multiplying the degree of space filling $\xi_g$ with the degree of crystallinity within each spherulite (maximum amount of crystallized material). Expressions for the nucleation density $N(T, p)$ and growth $G(T, p)$, yet to be specified, should accurately describe the kinetics of quiescent crystallization dependence on both temperature and pressure.

**Modeling flow effects on crystallization**

The ideas contained in the model proposed by Zuidema et al.,\cite{31} and in the recent model developed by Steenbakkers and Peters,\cite{33} for flow-induced crystallization, are here combined and adapted in a model to describe the process of flow-induced nucleation and growth of flow-induced crystals.

We start by considering the total number of nuclei $N_t$ to be the result of heterogeneous (thermally activated) nucleation $N_q$ and homogeneous (flow-induced) nucleation $N_f$:

$$N_t = N_q + N_f,$$

(7)

The number of quiescent nuclei at a given temperature and pressure is found solving Equation (1)-(4) and using the expressions given by Equation (31) and (32). The flow-induced nucleation rate is assumed to be a function of the stretch of the longest chains present in the melt. This assumption has been demonstrated by\cite{30} and validated in,\cite{33} who have shown that the stretch, $\Lambda$, of the high molecular weight chains indeed controls flow-induced nucleation. It is envisioned that the stretch of the high end tail of the molecular weight distribution increases the number of aligned chain segments whose conformation
is closer to the crystalline state. Furthermore, the growth of oriented crystals (shish-kebabs) was found to occur only when a critical molecular stretch was exceeded,\textsuperscript{[30]} implying that molecular orientation by itself does not suffice to induce shish growth. Following these ideas, the flow-enhanced nucleation rate was described, in\textsuperscript{[33]} using a fourth-order dependence on the molecular stretch of the slowest relaxation mode only:

$$\dot{N}_f = g_n \left( \Lambda^4 - 1 \right),$$

in which $g_n$ is a scaling parameter that depends on temperature only. Recently, Graham et al.\textsuperscript{[37]} simulated anisotropic nucleation based on the configuration of chains obtained from the advanced molecular flow model (the GLaMM model\textsuperscript{[38]}), via coarse-grained kinematic Monte Carlo simulations, and found an exponential dependency on the molecular stretch that, for a broad range of shear rates, overlaps with the fourth order dependence used here.

Some experimental observations have been reported that a saturation limit exists beyond which the rate of flow-induced nucleation becomes zero.\textsuperscript{[39]} Hristova et al.\textsuperscript{[40]} measured the number of flow-induced nuclei in iPP HD120MO as a function of shear rate in a Linkam shear cell. The authors identified different saturation levels of the total number of flow-induced nuclei created, depending on the shear rate applied. For the highest shear rate applied, a saturation value, $N_{f,max}$, equal to $3.1 \cdot 10^{14} \text{ m}^{-3}$ was measured. To include an asymptotic limit determined by $N_{f,max}$ in the expression for the rate of flow-induced nucleation we modify Equation (8), which becomes:

$$\dot{N}_f = g_n \left( \Lambda^4 - 1 \right) \left[ 1 - \frac{N_f}{N_{f,max}} \right].$$

Even though experiments do suggest the saturation level to be dependent on the shear
rate $N_{f,\text{max}}(\dot{\gamma})$, due to scarceness of experimental data, we take $N_{f,\text{max}}$ constant and equal to the value measured by Hristova at the highest shear rate.

Following the approach used in\cite{31} the number of flow-induced nuclei are assumed to act as physical cross links in the melt. Hence, the relaxation time of the high molecular weight (HMW) chains in the melt is made a linear function of the number of flow-induced nuclei:

$$\tau_j = a_T \tau_{j0} \left(1 + \alpha N_f\right), \quad (10)$$

in which $\alpha$ is a coupling parameter, which expresses the addition of physical crosslinks to the melt. However, this coupling requires some caution, since the cross-linking effect of the flow-induced nuclei on the relaxation time of the HMW chains, makes it almost impossible to relax the orientation and stretch of these molecules, with the consequence of flow-induced crystallization proceeding up to unrealistic time scales. To circumvent this, we introduce a pre-factor $\delta$ in Equation (9), which sets the rate of flow-induced nucleation to zero if the flow is stopped. Experimental evidences might support the use of such a pre-factor. It has been observed in short term shear flows under isothermal conditions, that all flow-induced crystals grown possess the same size, indicating that the onset of crystal growth is triggered when the flow is stopped. If flow-induced nucleation would continue after the flow, one would expect a distribution in size of flow-induced crystals. Thus, the final equation for flow-induced nucleation reads:

$$\dot{N}_f = \delta g_n (\Lambda^4 - 1) \left[1 - \frac{N_f}{N_{f,\text{max}}}\right], \quad (11)$$
with

\[ \delta = 1 \text{ if } \dot{\gamma} > 0, \]  
\[ \delta = 0 \text{ if } \dot{\gamma} = 0. \]  

Both quiescent and flow-induced nuclei are assumed to grow radially, and therefore the total number of nuclei \( N_t \) obtained from Equation (7) is given as input for the Schneider rate equations:

\[ \dot{\phi_3} = 8\pi\alpha (\phi_3 = 8\pi N_t). \]  

Based on the experimental evidence that a deformation threshold needs to be surpassed to change from the isotropic growth regime to the fibrillar-oriented regime, we expect that flow-induced nuclei can only grow out as cylinders (shish kebabs) once a critical threshold in terms of molecular stretch \( \Lambda_{\text{crit}} \) is overcome. Thus, at an early stage flow-induced nuclei are envisioned as spheres whose morphological evolution will depend on the flow conditions. In Figure 1, our model for the morphological development of flow-induced nuclei is illustrated.

It is commonly accepted that the nucleation process starts with a stretch-induced bundle of oriented chain segments which is assumed to be an embryonic form of a nucleus, see\,[33]\)

If a critical stretch is reached, a transition from isotropic to oriented (fibrillar) growth is assumed to occur, here denoted as regime I and II, respectively. Only nuclei created after the critical stretch is reached are assumed to grow into shish-kebabs. The growth mechanisms for isotropic (spherulites) and oriented (shish-kebabs) crystalline structures are illustrated in Figure 2.

The radial growth \( G(T, p) \), given by Equation (30), drives the growth of spherulitical
crystalline structures and the growth of kebabs, which is depicted by the model as an increase in diameter of the cylinder in Figure 2. The diameter of shish $D_0$ is in fact equal to zero, since shish are represented by the model as lines whose length grows with $\dot{L}$. The cylindrical representation of a shish-kebab is only valid if $\dot{L} \gg G$, which, at this moment, we state as an assumption. An equation for shish-growth (cylindrical length) $\dot{L}$ is specified next.

The exact mechanisms involved in the growth of a shish are still unknown and a matter for debate, however recently new experimental findings\cite{18} provide new insight. From elaborated experiments involving small-angle neutron scattering with deuterium labeling of specific chain lengths, Kimata et al.\cite{18} could identify the role of long chains in the processes of shish formation and growth. It was observed that shish, as opposed to the common understanding, do not predominantly consist of long chains, but instead they incorporate the full distribution of chain lengths. The authors propose a physical mechanism in which long chains play an important role in shish formation, but are not the dominant species in the shish growth. According to their explanation, the fast growth of a shish $\mathcal{O}(\mu s^{-1})$ does not give time to segregate chains from the bulk into the shish: ‘long chains greatly enhance the propagation velocity of a shish, with the kinetic consequence that all lengths of chains become incorporated as the shish advances’. Following their observations we assume the growth of a shish to be a non-selective process, in which all chains in the melt, regardless of their molecular weight, can participate. The average conformation of the chains, in terms of orientation and stretch is here assumed to influence the growth rate.
Accordingly, we write the shish-growth rate equation \( \dot{L} \) as:

\[
\dot{L} = g_1 J_2(B_e^{d\text{,avg}}); \quad \text{for} \quad \Lambda > \Lambda_{\text{crit}},
\]

in which \( J_2(B_e^{d\text{,avg}}) \) is the second invariant of the deviatoric elastic Finger tensor of a mode, representative of the average molecular weight distribution, which is added to the slow Rolie-Poly mode. The relaxation time of this mode is calculated by

\[
\tau_{d,\text{avg}} = \frac{\sum d,i G_i \tau_{d,i}^2}{\sum_i G_i \tau_{d,i}},
\]

which is the viscosity-averaged relaxation time. Thus, a two-mode Rolie-Poly model is used, in which one mode represents the long chains and the other an average contribution of all chains. In Equation (15), \( g_1 \) is a scaling parameter for the influence of \( J_2 \) on the thread-like growth of the nuclei. By considering an average relaxation time of the melt relaxation spectrum, we assume the growth of a shish to be a process in which all molecular chains participate, favored by the combined effect of molecular stretch and orientation, which is conveniently expressed by \( J_2(B_e^{d\text{,avg}}) \). From the growth rate of shish it is possible to calculate the total undisturbed length, surface and volume per unit volume, employing the rate equations of Eder,\(^[3]\) which read:

\[
\dot{\psi}_3 = 8\pi \dot{N}_t \quad \text{\((\dot{N}_t \text{ given by Equation (9))})\),}
\]

\[
\dot{\psi}_2 = 4\pi N_t \dot{L} \quad \text{\((\dot{L} \text{ given by Equation (9)) if} \quad \Lambda > \Lambda_{\text{crit}}))},
\]

\[
= 0 \quad \text{\((\text{if} \quad \Lambda \leq \Lambda_{\text{crit}}))},
\]

\[
\dot{\psi}_1 = G \dot{\psi}_2 \quad \text{\((\dot{\psi}_1 = S_{\text{tot}}))},
\]

\[
\dot{\psi}_0 = G \dot{\psi}_1 \quad \text{\((\dot{\psi}_0 = V_{\text{tot}}))},
\]

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in which $\psi_0$ is the total volume of shish-kebabs per unit volume, $\psi_1$ the total surface $S_{\text{tot}}$ of the shish-kebabs per unit volume, $\psi_2$ is $4\pi$ times the total length $L_{\text{tot}}$ of the shish per unit of volume times the number of flow-induced nuclei created with $\Lambda > \Lambda_{\text{crit}}$, which we denote as $N_{\text{ori}}$, and $\psi_3$ is $8\pi$ times the total number of flow-induced nuclei per unit volume. Since the model gives the undisturbed spherulitical and oriented crystalline volume, $\phi_0$ and $\psi_0$, respectively, we need to correct for impingement. We adopt the Avrami and Tobin model Equation (5) and (6) to take into account the contribution of both spherulitical and oriented crystalline structures. The modified models read:

$$-\ln(1 - \xi_g) = \phi_0 + \psi_0; \quad \frac{\xi_g}{1 - \xi_g} = \phi_0 + \psi_0. \tag{22}$$

The scaling parameters $g_n$ and $g_l$ are made temperature dependent according to time temperature superposition. Hence, at a certain temperature they are shifted with $a_T$ to a reference temperature:

$$g_n(T) = g_n(T_0)a_T, \tag{23}$$

$$g_l(T) = g_l(T_0)a_T. \tag{24}$$

The real total shish length per unit volume, taking into account impingement, and the real number of flow-induced nuclei per unit volume, taking into account impingement, can be directly found by solving the following equations:

$$\dot{N}_{f,\text{real}} = \delta g_n \left(\Lambda^4 - 1\right) \left[1 - \frac{N_f}{N_{f,\text{max}}}\right] (1 - \xi_g), \tag{25}$$

and

$$\dot{L}_{\text{tot,real}} = N_{f,\text{real}} g_l J_2(B_{c,\text{avg}}^d)(1 - \xi_g). \tag{26}$$
in which $N_{f,\text{real}}$ denotes the real number of flow-induced nuclei per unit volume and $L_{\text{tot,real}}$ the real total shish length per unit volume.

**Stress problem**

The Rolie-Poly model\cite{41} is used to calculate the part of the nonlinear viscoelastic response, necessary to solve the flow-induced crystallization problem. Namely, the stretch of the longest chains in the melt $\Lambda_{\text{HMW}}$ and the second invariant of the deviatoric part of the elastic Finger tensor of the viscosity-averaged mode $J_2(B_{e,\text{avg}}^d)$. The Rolie-Poly model was developed for the rheology of linear polymers and results of the model show a good agreement with rheological measurements in steady and transient regimes in both shear and extension flows. The model is of the differential type and its single-mode version reads:

$$\nabla \dot{B}_e + \frac{1}{\lambda_d} (B_e - I) + \frac{2(1 - \sqrt{3/\text{tr}(B_e)})}{\lambda_R} \left( B_e + \beta \left( \frac{\text{tr}(B_e)}{3} \right)^\delta (B_e - I) \right) = 0. \quad (27)$$

in which $B_e$ is the elastic Finger, or conformation, tensor. The deviatoric part of the elastic Finger tensor follows from:

$$B_e^d = B_e - \frac{1}{3} \text{tr}(B_e) I. \quad (28)$$

The molecular stretch $\Lambda$ follows from:

$$\Lambda = \sqrt{\frac{\text{tr}(B_e)}{3}}. \quad (29)$$

Each term of Equation (27) addresses a specific molecular mechanism, such as chain reptation, chain stretch and convective constraint release, which makes this model particularly
physically intuitive.\textsuperscript{[41]} In the model two time scales are of importance: $\tau_{d,i}$ the disengagement (reptation) times, and the Rouse (stretching) times $\tau_{R,i}$. Besides the Rouse times $\tau_{R,i}$, this model contains two nonlinear parameters, governing the stretch dependence of relaxation via convective constraint release, a pre-factor $\beta \in [0, 1]$ and an exponent $\delta < 0$; see Equation (27). For higher strain rates the Rolie-Poly model, in its single mode form, produces a faster stress growth when compared to the full theory.\textsuperscript{[41]} The explanation given by the authors, is that the full theory contains a spectrum of stretch-relaxation times, reflecting different parts of the chain, where as the single mode equation assumes uniform stretch. To compensate for the over prediction of the steady-state stress at large rates, the authors advise to set $\beta = 0$.

3 Injection molding prototype-flows, materials and experimental methods

Material selection

The research conducted on flow-induced crystallization in our group has been restricted to a small number of materials such that extensive material data, obtained from rheological measurements and crystallization studies, could be collected. Obviously, for modeling purposes in studies that aim at morphology prediction, the availability of extensive material data is crucial. In this study we restrict ourselves to a pure linear isotactic polypropylene (grade HD120MO, Borealis) which was studied previously,\textsuperscript{[1,2,13,33,40,42,43]} yielding molec-
ular weight-related properties and DSC-measured melting temperature, see Table 1. The thermal properties of iPP HD120MO as taken from Moldflow material database, are assumed to be constants, and are listed in Table 2.

**Quiescent crystallization kinetics in iPP HD120MO**

Van der Beek\[^{[13]}\] performed quiescent crystallization experiments in a dilatometer, measuring the specific volume of iPP HD120MO for different cooling rates at a pressure of 40 MPa. He could predict the evolution of the specific volume measured during cooling, using the Schneider rate equations and a state equation in which the dependence of density on the volume fraction of crystalline and amorphous material was taken into account. The spherulitical growth rate $G(T)$ and the number of nuclei per unit volume $N(T)$ were determined from polarized optical microscopy experiments. To describe specific volume at elevated pressures, both $G(T)$ and $N(T)$ were adapted in the following way:

$$G(T, p) = G_{\text{max}} \exp[-b(T - T_{\text{ref}} - f_g(p))^2], \quad (30)$$

$$N(T, p) = 10^{[n_0 + n_1(T - f_n(p))]}, \quad (31)$$

where

$$f_i = p_{i0} \Delta p + p_{i1} \Delta p^2 \quad i = g, n, \quad (32)$$

$$\Delta p = p - p_{\text{ref}}. \quad (33)$$

The parameters used in equations (30)-(32) are taken from\[^{[13]}\] and given in Table 3. Only for the highest cooling rate used (32.5°C s\(^{-1}\)) the model gave a poor result. The nucleation
curve and the growth rate curve at atmospheric pressure are given in Figure 3(a) and 3(b), respectively.

Regarding the heat of crystallization $H$, from literature it is known that for iPP the value lies between 170 up to 273 KJ kg$^{-1}$ for a a pure crystal. In this study we take it to be 170 KJ kg$^{-1}$. The degree of crystallinity $\xi$ is found by multiplying the degree of space filling $\xi_g$ with a factor indicating the maximum attainable degree of crystallinity $V_\infty$, which we take equal to 0.5.

**Flow-induced crystallization parameters**

The creation of point-like nuclei during flow is governed by the three parameters: $g_n$ and $N_{f,max}$ in Equation (11) and $\alpha$ in Equation (10). Using a model in which inactive nuclei (precursors) are created during flow, and activated after the flow is stopped, where the molecular conformation relaxes$^{[33]}$ obtained $g_{n0} = 6.04 \times 10^5 m^{-3}s^{-1}$, $N_{f,max} = 3.1 \times 10^{14} m^{-3}$, and $\alpha = 3.98 \times 10^{-8} m^3$ by fitting flow-enhanced nucleation densities in short-term shear experiments, which were determined by optical microscopy. In the simulations discussed here, the distinction between precursors and nuclei is not convenient. However, with the addition of the pre-factor $\delta$ to Equation (9) the current model mimics the model of Steenbakkers and Peters and therefore their parameters can used.

To determine the shish growth parameter $g_{l0}$, the flow-induced crystallization model is combined with a suspension model, Steenbakkers and Peters$^{[44]}$ and applied to the rheological measurements reported in$^{[43]}$ after short-term shear flow. Figure 4 shows that for $g_{l0} = 1.0 \times 10^{-7} ms^{-1}$, the onset time of the increase of $G''(t)$ is captured for two of the
four shear times, but is overpredicted for the shortest and underpredicted for the longest shear time. The shape of $G'(t)$ corresponds reasonably well with the experimental curves. The best agreement between model results and the experimental curves was found by setting the critical molecular stretch $\Lambda_{\text{crit}} = 40$ [-], beyond which the onset of the oriented growth regime occurs (regime II), see Figure 1.

**Viscoelastic material data**

The rheological properties at a temperature of 190 °C are given in Table 4. The linear viscoelastic behavior of the material is described by a seven-mode Maxwell model. The relaxation spectrum of the material was obtained using a discrete Maxwell relaxation time spectrum, satisfying:

\[ G'(\omega) = \sum_g g_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}, \quad (34) \]

\[ G''(\omega) = \sum_g g_i \frac{\omega \tau_i^2}{1 + \omega^2 \tau_i^2}, \quad (35) \]

where $G'$ and $G''$ are the storage and the loss modulus, respectively. The set of relaxation moduli, $g_i$, and times, $\tau_i$, were determined elsewhere. The temperature dependence of the horizontal ($a_T$) and vertical ($b_T$) shift factors is described using the WLF equation, Equation (45). A Cross model is used to describe the temperature and shear rate dependence of the viscosity. Using the viscoelastic data listed in Table 4 we find the viscosity-averaged relaxation time $\tau_{d,\text{avg}}$, given by Equation (16), equal to 12.2 s at $T = 190$ °C.

Uniaxial viscosity measurements, supplied by Borealis, are used to determine the Rouse
times. The strain rates $\dot{\varepsilon} = 0.3 \text{ s}^{-1}$, $\dot{\varepsilon} = 1 \text{ s}^{-1}$, $\dot{\varepsilon} = 3 \text{ s}^{-1}$, and $\dot{\varepsilon} = 10 \text{ s}^{-1}$ were applied at a constant temperature, $T = 180 ^\circ \text{C}$.

As stated before, flow-enhanced nucleation rates can be described well by a fourth-order dependence on the stretch of the slowest mode only, see Equation (8). Since the molecular conformations of different modes in the Rolie-Poly model are not coupled, only the dynamics of the slowest mode itself contributes to flow-enhanced nucleation. Therefore, although the uniaxial viscosity data can be fitted by different sets of Rouse times, we are only interested in obtaining a unique value for the longest Rouse time, $\tau_R$. This is accomplished by using the non-stretching Rolie-Poly equation for all modes except for the slowest. The only remaining free parameter is then found by fitting the model to the data for the two lowest strain rates: $\tau_R = 2.49 \text{ s}$. Its uniqueness is confirmed by starting from different initial values in the fitting routine. The shorter Rouse times can be found by adding stretching modes and including the uniaxial viscosity data for higher strain rates.

The Rouse time of the viscosity-averaged relaxation mode $\tau_{R,\text{avg}}$ can be estimated with the expression proposed in,[46] which in the case of the average mode reads:

$$\tau_{R,\text{avg}} = \frac{\tau_{d,\text{avg}}}{3Z},$$

(36)

in which $Z$, the number of entanglements per chain, can be calculated from the weight averaged molecular weight $M_w$ and the averaged molar mass between entanglements $\langle M_e \rangle$,

$$Z = \frac{M_w}{\langle M_e \rangle}.$$  

(37)

From[30] we took $\langle M_e \rangle = 5.5 \text{ kg mol}^{-1}$ and find $\tau_{R,\text{avg}} = 6.1 \cdot 10^{-2} \text{ s}$. 

24
Morphology development under quasi-isothermal conditions - the multipass rheometer

Recently a modified multipass rheometer (MPR) based on the original device developed in the group of prof. Malcolm Mackley, UK,\textsuperscript{[47]} was proposed by Housmans et al.\textsuperscript{[1]} In Figure 5(a) a schematic representation of the multipass rheometer is given. The pistons 'A' are driven by means of hydraulics that are not shown here. The MPR can incorporate different flow geometries and allows in-situ studies on the kinetics of flow-induced crystallization and its relation to the crystalline morphology, under a controlled thermal-mechanical history. Both steady and small and large amplitude oscillatory shear flows can be generated. Additionally, the double-piston configuration allows to study advanced injection molding processes, such as Push-Pull\textsuperscript{[48]} and Scorim,\textsuperscript{[49]} in which by reversing the flow inside the mold cavity during cooling, material solidification takes place under a continuous shear field.

In this study we focus on the experiments reported in,\textsuperscript{[1]} in which the MPR is equipped with a slit geometry of dimensions (120x6x1.5 mm). The material is held above its equilibrium melting temperature at 220 °C for 10 minutes, and subsequently cooled down to the desired temperature at which flow is applied. Such protocol has the purpose of erasing any deformation history prior to the flow. The flow time, $t_f$, is restricted to prevent material that passed through the contraction region between the cylinder and the slit from reaching the view point. Thus, entrance effects are excluded from the analysis. The flow time is
determined by:

\[ t_f = \frac{0.5L}{v_{\text{max}}}, \]  

(38)

in which \( L \) is the slit length, and \( v_{\text{max}} \) the maximum velocity inside the slit, which, for a Newtonian-fluid behavior, is estimated by \( v_{\text{max}} = 1.5v_{\text{avg}} \), in which the average velocity is prescribed for each experiment. The different flow conditions used are listed in Table 5.

Morphology development under non-isothermal conditions - the capillary rheometer

A capillary rheometer resembles early injection molding machines that employed, instead of a reciprocating screw, a plunger to pressurize and push the melt into a mold. Capillary rheometers are designed to measure the rheological properties of polymer melts at high shear rates, forcing the melt to flow into a capillary or a slit geometry. Since the material is homogeneously molten inside a cylinder under no-flow conditions, a uniform thermal-mechanical history is attained before injection. In[2] a capillary rheometer (Rheograph 6000, Göttfert Werkstoff-Prüfmaschinen GmbH, Germany) was adapted to make it perform as an injection molding machine, by adding a rectangular cavity of dimensions 2x12x135 mm, see Figure 5(b). A cooling clamp is used to thermostatically cool the mold walls. We consider the modeling of experiments using the capillary rheometer as a necessary step in between the MPR and an injection molding machine, since the experiments are conducted under non-isothermal conditions and the developed flow field is, like in injection molding, spatially inhomogeneous: behind the flow front, kinematics are shear dominated but near
the flow front, due to the fountain flow, significant extension takes place. The post-filling stages of injection molding, in which pressure levels are high and the fluid velocity inside the cavity is low, cannot be mimicked yet by the capillary mold and thus their effect on the morphological development is here disregarded. The effect of varying injection speed is assessed using the different flow speeds summarized in Table 6. For all conditions the injection temperature and the temperature at the slit walls are set to 220 °C and 80 °C, respectively.

**Morphology characterization**

**MPR experiments**

The morphology of the MPR samples is characterized ex-situ via polarized optical light microscopy (POLM). Micrographs are taken from thin cross-sections of 3-7µm, micromted at -130 °C on the flow-thickness direction, under cross polarizers rotated +/- 45° with respect to the flow direction. The cross sections are taken from the center of the slit, see Figure 6.

Only the samples processed at the highest flow speed conditions, MPR1 and MPR2, develop an oriented shear layer followed by a fine-grained layer, see Figure 7. Furthermore, the lower flow temperature of condition MPR2, significantly increases the thickness of the oriented layer. For the conditions MPR3 and MPR4 there is no development of oriented layers, only a fine-grained layer is found. For the condition MPR4 the morphological gradient across the thickness is very smooth, denoting a linear decrease in the size of
spherulites towards the walls and a pronounced effect of transcrystallinity. The thickness of the oriented and fine-grained layers are for all the conditions given in Table 7.

**Capillary rheometer experiments**

Samples are microtomed according to the same procedure explained for the MPR at three different positions along the length of the slit: close to the gate, at the middle and close to the end of the slit, see Figure 6. The micrographs for the different flow conditions are given in Figure 8. For all flow-conditions the morphology is inhomogeneous exhibiting a layer type of structure with a highly oriented crystalline region. Four different layers are identified from the edge to the core: a thin skin layer, a transition layer, and a shear layer that is followed by an isotropic core, see Figure 9.

In all samples the thickness of the oriented region, composed by the skin, transition and shear layers, increases towards the middle of the slit and decreases again towards the end of the slit, see Figure 10. Such variation is explained by the thermal and mechanical deformation experienced by the material. The skin layer, which originates from the deposition of stretched material in the flow front (fountain flow) that is subsequently quenched at the walls, remains constant along the slit length. However, thickness of the transition and shear layers result from the combined effect of cooling and shear deformation. Close to the gate the injection of molten material keeps the temperature relatively high, favoring the relaxation of orientation. At the middle of the slit, the material experiences a longer thermal and shear deformation history, which is reflected in the thicker oriented layers. The material that fills the end of the slit channel travels through the core region at low
shear rates experiencing a short cooling and mechanical history, thus the thickness of the oriented layers decreases towards the end of the slit. The increase of injection speed results in thinner oriented layers due to the larger amount of heat convected inside the slit per unit time as well as the higher contribution from viscous dissipation, which, combined, cause a lower cooling rate. Therefore the transition from oriented crystalline layers to spherulitical is shifted towards the walls. Moreover, the cooling time during filling is also obviously decreased. Hence, at higher injection speeds the shorter relaxation times that result from lower cooling rates and shorter cooling times during filling, explain the decrease in thickness of the oriented crystalline layers.

4 Computation of the flow kinematics

Viscous flow problem

The governing equations required to model the experiments of the MPR and capillary rheometer are presented. We consider the flow to be incompressible and inertial effects negligible, yielding an incompressible Stokes flow problem. Thus the continuity and momentum equations read:

\[ \nabla \cdot \mathbf{u} = 0, \quad (39) \]

\[ \nabla p = \nabla \cdot \mathbf{\tau}, \quad (40) \]

where \( \mathbf{u} \) is the velocity field, \( \mathbf{\tau} \) is the extra stress tensor and \( p \) denotes the pressure. The latent heat of crystallization is incorporated as a source term, \( \rho H \dot{\xi} \), in the energy equation,
with $H$ the heat of crystallization and $\dot{\varsigma}$ the rate of change of the degree of crystallinity. Heat conduction is described by Fourier’s law with an isotropic heat conduction coefficient. Neglecting thermal radiation and assuming compression effects to be negligible, the energy balance reads:

$$
\rho c_p \dot{T} = 2\eta \mathbf{D} : \mathbf{D} + \nabla \cdot (\lambda \nabla T) + \rho H \dot{\varsigma},
$$

where $\mathbf{D}$ is the rate of deformation tensor and $\eta$ the viscosity.

The flow kinematics are thus assumed to be determined by the kinematic boundary conditions and a generalized Newtonian description is adopted. Since we take into account the hardening effect of the crystalline structures on the viscosity, viscosity is here made dependent on temperature, the deviatoric part of the rate of deformation tensor $\mathbf{D}$ and space filling $\xi_g$:

$$
\eta = \eta(T, \mathbf{D}^d, \xi_g).
$$

According to the generalized Newtonian flow description, the extra stress tensor $\mathbf{\tau}$ reads:

$$
\mathbf{\tau} = 2\eta(T, \mathbf{D}^d, \xi_g) \mathbf{D}.
$$

The viscosity dependence on temperature and shear rate is described by a Cross model:

$$
\eta = \frac{\eta_0(a_T)}{1 + (K(a_T)\dot{\gamma})^{(1-n)}},
$$

with the shift factor $a_T$ given by the WLF equation:

$$
\log a_T(T) = \frac{-C_1(T - T_0)}{C_2 + T - T_0}.
$$

The values of the model parameters and the WLF constants are listed in Table 4.
**Crystallization effects on the flow** The growth of crystalline structures increases the melt viscosity (hardening), and during the filling stage this effect can become important. Lamberti et al.\cite{50} give a review on experimental studies concerning the viscosity hardening of polymer melts during crystallization. A list of available models to describe changes in rheology with the increase of crystallinity was given, distinguishing suspension-based from empirical models. The numerous different models illustrate the lack of understanding how crystallization kinetics and structural changes determine the viscosity hardening evolution. The authors proposed a new experimental method that combines differential scanning calorimetry, DSC, and rheometry, to determine the change in viscosity induced by the degree of space filling $\xi_g$. They found that the influence of crystallinity on viscosity can be described by a shift factor, $a_\xi(\xi_g)$, which is equivalent to adopt a time-hardening superposition. Hence, the viscosity is shifted according to the temperature and degree of space filling.

The effect of shear flow on the rheology of viscoelastic suspensions filled with rigid particles was analyzed by Hwang et al.\cite{51} using advanced finite-element methods, however their method was limited to 2-D flows. Even though the usefulness of such analysis in providing a more comprehensive insight of the rheological phenomena involved, they are computationally very expensive. This is certainly true when going to 3-D simulations, see.\cite{52} Thus, simple suspension models that can relate rheological properties of melts with the underlying crystalline morphology are more attractive to implement in injection molding codes. In a recent publication\cite{44} early work on suspension modeling was reviewed and applied a generalized self-consistent method\cite{53} to describe the evolution of linear
viscoelastic properties of crystallizing melts during crystallization and its completion. Their model allows to incorporate particles with different shapes, discriminating oriented from nonoriented crystals. Spherulites are represented by spheres and shish-kebabs by cylinders. Additionally, the mechanical properties of the particles and the matrix are transient and dependent on the ongoing microstructural changes. The approach of Lamberti et al.\cite{50} is a special case; crystalline particles are rigid and only space filling is accounted for, i.e. no influence of oriented structures.

Here, we follow the model proposed in\cite{50} in which viscosity is shifted according to the computed degree of space filling $\xi_g$. The generalized Newtonian viscosity then becomes:

$$\eta = \eta(T, \dot\gamma, \xi_g) = \eta_0(\dot\gamma \cdot a_T \cdot a_\xi) \cdot a_T \cdot a_\xi,$$  \hspace{1cm} (46)

with the shift factor $a_\xi$ given by:

$$a_\xi(\xi_g) = 10^{a \cdot \xi_g^b},$$  \hspace{1cm} (47)

where $a$ and $b$ are defined as hardening parameters. The authors used their model to describe experiments conducted with an iPP, ($M_w = 350$ kg mol$^{-1}$, $M_w/M_n = 5.3$), very similar to iPP HD120MO, see Table 1, and found $a = 3.875$ and $b = 1.236$. The evolution of the viscosity hardening shift factor $a_\xi$ with the degree of space filling is shown in Figure 11.

**Boundary conditions - MPR**

To make the problem computationally less expensive we approximate the MPR geometry by a 2-D problem in which the vorticity plane is depicted. A periodic channel is defined,
see Figure 12, and a mass flux is prescribed at the inflow boundary $\Gamma_p$. Dirichlet boundary conditions are used to impose a no-slip condition at the walls, $\Gamma_w$:

$$u = 0 \quad \forall x \in \Gamma_w.$$  \hspace{1cm} (48)

The wall temperature is set equal to the injection temperature, thus:

$$T = T_p(x, t) \quad \in \Gamma_p \cup \Gamma_w, \ t > 0.$$  \hspace{1cm} (49)

**Boundary conditions - Capillary rheometer**

We adopt a 2-D approximation of the original problem in which the flow history is only computed inside the slit. Such an approach avoids the solid-fluid interaction problem of the moving piston, considerably simplifying the numerical methods required to compute the flow kinematics. Local extensional effects at the contraction region are thus assumed negligible.

In order to track the polymer/air and polymer/gas interfaces we use a front-capturing technique, also known as *pseudo concentration method*, which was proposed by Thompson.$^{[54]}$ Each material point, or infinitesimal material volume element, is labeled with a scalar $c$, and the material labels for polymer, air and gas core are convected with the velocity $u$ throughout the domain. Boundary conditions are made dependent on $c$. The method requires the addition of a pure (passive scalar) convection equation that gives the evolution of the material label distribution:

$$\frac{\partial c}{\partial t} + u \cdot \nabla c = 0.$$  \hspace{1cm} (50)
As initial condition the material labels are set to zero over the entire domain $\Omega$, and at the inlet the following boundary conditions are assigned:

\[
c(x, t = 0) = 0, \quad x \in \Omega, \quad (51)
\]
\[
c(x, 0 < t < t_{\text{fill}}) = 1, \quad x \in \Gamma_e. \quad (52)
\]

The interface is captured for $c$ equal to 0.5. The material properties are made dependent on the local value of the concentration, $c$, and are discontinuous across the interfaces polymer-air and polymer-gas. For the air or gas phase, $c < 0.5$, the fictitious-fluid properties are assigned, while for the case $c \geq 0.5$ the polymer properties are chosen. We also perform particle tracking, using Equation (50), but instead of prescribing at the inlet boundary a concentration value $c$, we prescribe a time label, $t$, convecting basically the flow history. The boundary conditions in the computational domain $\Omega$, Figure 13, are specified at $\Gamma_e$, $\Gamma_w$ and $\Gamma_v$, designating the mold entrance, mold walls, and the air vents respectively. A fully developed velocity profile at the slit inlet $\Gamma_e$ is assumed. At the mold walls we employ dynamic boundary conditions to change from slip to no-slip condition depending on the material label $c$ at the wall. If air touches the wall, $c = 0$, a slip boundary condition is assigned, if instead polymer is, $c \geq 0.5$, a no-slip condition is imposed by setting a traction force at the wall. Accordingly, the boundary condition for the velocity and stress components $u_t$ and $\sigma_t$ in tangential direction read:

\[
a u_t + \sigma_t = 0 \quad \forall \ x \in (\Gamma_w \cup \Gamma_v), \quad (53)
\]
in which the dimensionless ‘Robin penalty parameter’ $a$ is defined as

$$ a = a(c) = \begin{cases} 
\geq 10^6 & \text{if } c \geq 0.5: \text{ no slip or leakage} \\
0 & \text{if } c < 0.5: \text{ slip or leakage} 
\end{cases} $$

Air is only allowed to exit the cavity at air vents, $\Gamma_v$. For this a Robin condition is assigned for the velocity and stress components $u_n$ and $\sigma_n$ in normal direction:

$$ u_n = 0 \quad \forall \mathbf{x} \in \Gamma_w $$

$$ a u_n + \sigma_n = 0 \quad \forall \mathbf{x} \in (\Gamma_w \cup \Gamma_v), $$

in which $a$ is again given by Equation (54). However, in this case the term ‘slip’ should be replace by ‘leakage’. The thermal boundary conditions are specified via Dirichlet boundary conditions at the walls.

$$ T = T_w(\mathbf{x}, t = 0, t) \quad \mathbf{x} \in \Gamma_w \cup \Gamma_v, \; t \geq 0, $$

**Viscoelastic stress problem**

As an initial condition for the MPR-flow computations, the melt is in an undeformed state:

$$ B_e = I \quad \forall \mathbf{x} \in \Omega, \; t = 0. $$

For both capillary and MPR computations the following boundary condition is prescribed at the inlet $\Gamma_e$:

$$ B_e = I \quad \forall \mathbf{x} \in \Gamma_e, \; t \geq 0. $$
Computational aspects

We use a finite element solution algorithm to solve the flow and heat transfer problems in 3-D, early developed in our group by Haagh et al.\cite{Haagh55} The Stokes and energy equation are coupled but solved within each time step in a segregated manner. The Stokes equations, Equation (39) and Equation (40), that compose the flow problem are solved by a velocity-pressure formulation that is discretized by a standard Galerkin finite element method (GFEM). Since during the filling phase the flow is incompressible, and in the subsequent phases (packing and holding) compressible, two different weak forms are found after performing the Galerkin finite element discretization. The system of equations is solved in an integrated manner, both velocity and pressure are treated as unknowns.

In case of 2-D computations the discretized set of algebraic equations is solved using a direct method based on sparse multifrontal variant of Gaussian elimination (HSL/MA41) - direct solver (HSL), for details the reader is referred to.\cite{HSL56-58} In 3-D computations the resulting system of linear equations consists of generally large sparse matrices, and often iterative solvers are employed which use successive approximations to obtain a convergent solution. Furthermore, they avoid excessive CPU time and memory usage. In our 3-D computations we use a generalized minimal residual solver (GMRES),\cite{GMRES59} in conjunction with an incomplete LU decomposition preconditioner. The computational domain is discretized with elements with discontinuous pressure of the type Crouzeix-Raviart - $Q_2^dP_1^d$, 2-D quadrilateral or brick 3-D finite elements, in which the velocity is approximated by a continuous piecewise polynomial of the second degree, and the pressure by a discontinuous
complete piecewise polynomial of the first degree. The degrees of freedom at the nodal points correspond to the velocity components while at the central node the pressure and pressure gradients are computed. The integration on the element is performed using a 9-point (2-D) or 27-point (3-D) Gauss rule.

Special care has to be given to solve the front-capturing convection equation. Convection dominated problems give rise to unstable solutions with spurious node-to-node oscillations, referred to as wiggles. To overcome this problem the Streamline-Upwind Petrov-Galerkin (SUPG) method, proposed by Brooks and Hughes,\textsuperscript{[60]} is the most employed and thus adopted in our model.

**Stress problem** To perform the numerical integration of the Rolie-Poly equation, Equation (27), we use a second-order Adams-Bashford explicit scheme. For the first two time steps the numerical integration follows a first order forward Euler method. Accordingly, the time marching scheme reads:

for time step $\leq 2$,

$$
\bar{B}_e^{n+1} \approx \bar{B}_e^n + f(u, \bar{B}_e, \nabla u, (\nabla u)^T)|^n \Delta t, \quad (59)
$$

for time step $> 2$,

$$
\bar{B}_e^{n+1} \approx \bar{B}_e^n + \left(\frac{3}{2}f(u, \bar{B}_e, \nabla u, (\nabla u)^T)|^n - \frac{1}{2}f(u, \bar{B}_e, \nabla u, (\nabla u)^T)|^{n-1}\right) \Delta t. \quad (60)
$$
Computational procedure: decoupled approach

In our computations we adopt a decoupled approach in which the flow kinematics are assumed to be dominated by viscous forces. Every time step the rate of deformation tensor, $D$, and the temperature field, $T$, are used to solve the viscoelastic Rolie-Poly equation, Equation (27), to compute the stretch of the high molecular weight chains in the melt $\Lambda_{HMW}$ and the elastic Finger (conformation) tensor of the averaged relaxation times of the melt $J_2(B_{e, avg}^{d})$. The rate equations for crystallization are subsequently solved and the resulting degree of space filling used to update the viscosity via the hardening shift factor Equation (47). The decoupled procedure is illustrated in Figure 14 for the capillary-flow problem, which requires interface tracking between the polymer melt and air. For the multipass case the problem is simpler, since no interface has to be tracked.

5 Modeling results & discussion

MPR

The micrographs of microtomed injection molding samples, as the ones shown in Figure 7 for the MPR experiments, denote in many cases sharp transitions between morphological layers, i.e. oriented layer, fine-grained layer, and spherulitical core. The transitions between these layers should most probably be related to critical values of the model parameters that drive flow-induced nucleation and growth, $\Lambda_{HMW}$ and $J_2(B_{e, avg}^{d})$, respectively, and the morphological predicted parameters. Hence, we first look at the evolution of these
parameters at the transition from the oriented shear layer to the fine-grained layer for flow conditions MPR1 and MPR2, whose optical micrographs clearly exhibit an oriented shear layer, see Figure 7. The time scale of the flow analysis is limited to the influence of flow on crystallization, which is determined by the relaxation of $J_2(B_{e,avg}^d)$, since the flow-induced nucleation rate $\dot{N}_f$, given by Equation (11), becomes zero when the flow is stopped. After an elapsed time of $t = 1.5\ s$, $J_2(B_{e,avg}^d)$ becomes of $O(1)$ at the slit walls for conditions MPR1 and MPR2, thus the time scale of the flow analysis is limited to 1.5 s, after which the wall temperature is set to room temperature $T = 23^\circ\ C$. The crystallization kinetics are calculated until the degree of space filling $\xi_g$ is 1 everywhere. To better compare all the flow conditions, we list in Table 8 the Deborah numbers of each condition, based on the disengagement and Rouse times of the longest molecules, with $De_{d,R} = \dot{\gamma}_{wall} \cdot \tau_{d,R}$.

In Figure 15(a) we plot the time evolution of the molecular stretch ($\Lambda_{HMW}$) at the positions of the transition between the oriented shear and the fine-grained layers. Once the critical stretch, $\Lambda_{crit} = 40$, is reached the transition from regime I to regime II, see Figure 2, takes place, and shish start to grow on a rate, according to Equation (15), that is dependent on $J_2(B_{e,avg}^d)$, see Figure 15(c). The critical stretch is reached first for condition MPR1 $\sim t = 0.08s$, which is expected based on the higher Deborah numbers $De_{d,R}$ for this condition, see Table 8. The final values of the molecular stretch computed for both conditions are remarkably very close to each other (MPR1 $\sim 90$ and MPR2 $\sim 70$). The time evolution of the total number of real flow-induced nuclei $N_{f,real}$ at the transition between the oriented shear layer and fine-grained layer, calculated from Equation (25), is shown in Figure 15(b). $N_{f,real}$ is found to be very similar between both conditions, just
slightly lower for condition MPR2. Figure 15(d) shows the time evolution of the total real shish length per unit volume $L_{\text{tot,real}}$, calculated from Equation (26). $L_{\text{tot,real}}$ is found to be approximately three times higher for condition MPR1 than for flow condition MPR2, in agreement with the larger area underneath the plot in Figure 15(c). The values of $Λ_{\text{HMW}}, N_{\text{f,real}}$ and $L_{\text{tot,real}}$ for flow conditions MPR1 and MPR2, at the transition between the oriented shear layer and the fine-grained layer are listed in Table 9. The values are of the same order of magnitude for the two flow conditions. Based on the crystalline morphology shown by the optical micrographs, see Figure 7, one can expect the transition from the spherulitical core to the fine-grained layer to be defined by a characteristic total number of flow-induced nuclei $N_{\text{f,fg}}$. Likewise, the transition from the fine-grained layer to the shear-oriented layer should be identified by the properties of the shish, either or by a critical average shish length $\langle L \rangle_{\text{crit}}$, or, more likely, a critical total shish length per unit volume $L_{\text{tot,crit}}$, upon which an oriented crystalline morphology becomes noticeable at a micro scale. Therefore, we postulate that within the fine-grained layer either the kinetics of flow-induced crystallization take place within regime I, see Figure 2, and, in that case, only an increase in number of spherulitical structures occurs, or the growth rate of shish is so slow or takes place within a too small period of time, so the shish stay relatively short. Regarding the shear oriented layer, we expect flow to induce only fibrillar nucleation (regime II).

We proceed comparing the model predictions in terms of $L_{\text{tot,real}}, N_{\text{f,real}}$ and $\langle L \rangle$, at the transition between the different morphological layers for all flow conditions after no further morphological changes, due to flow-induced crystallization kinetics, take place. The
average length of shish-kebabs $\langle L \rangle$ can be calculated dividing the total shish length by the total number of flow-induced nuclei per unit volume:

$$\langle L \rangle = \frac{L_{\text{tot,real}}}{N_{f,\text{real}}}. \quad (61)$$

In Figure 16 we plot $L_{\text{tot,real}}$, $\langle L \rangle$ and $N_{f,\text{real}}$ over half of the normalized slit thickness, for flow conditions MPR1 and MPR2. The values predicted for condition MPR1 of $L_{\text{tot,real}}$, $N_{f,\text{real}}$ and $\langle L \rangle$ at the transition of the shear oriented layer, are tested if they can be used as critical values that have to be surpassed for an oriented layer to become visible, see Figure 16. $L_{\text{tot,crit}}$ denotes the critical value of $L_{\text{tot,real}}$, $\langle L \rangle_{\text{crit}}$ the critical average shish length, $N_{f,\text{ori}}$ and $N_{f,\text{fg}}$ the values of $N_{f,\text{real}}$ found at the transition of the oriented shear layer and at the transition of the fine-grained layer to the spherulitic core, respectively. To assess the predictive capability of the model, the values $L_{\text{tot,crit}}$, $\langle L \rangle_{\text{crit}}$, $N_{f,\text{ori}}$ and $N_{f,\text{fg}}$, taken from condition MPR1, are used as morphological criteria on the other flow conditions. The value predicted for a critical shish length $\langle L \rangle_{\text{crit}}$ is around 1 mm, which obviously is not realistic, making the comparison qualitative only and indicating that a further calibration of the model parameters is required. Typical shish lengths are thought to be in the order of microns. The computed $L_{\text{tot,real}}$ and $\langle L \rangle$ for condition MPR1 lie within the flow-induced crystallization region (did not cross the fine-grained layer to the spherulitical core), implying that the critical stretch $\Lambda_{\text{crit}}$ was reached only within this region. In the plots corresponding to condition MPR2 the open circles denote the critical values computed for condition MPR1. The circles fall almost on top of the curves, indicating that the different morphological criteria agree between these two conditions. However, the criterion based
on total shish length $L_{\text{tot,real}}$, seems to be in better agreement between the conditions than the one based on the average shish length $\langle L \rangle$. The total number of flow-induced nuclei $N_{\text{f,real}}$ at the transition between the different layers is also in good agreement between both conditions. Also for condition MPR2 the critical stretch, required for oriented crystals to grow (regime II), was reached only within the observed flow-induced crystallization region. Next, the flow conditions under which no oriented shear layer developed, namely MPR3 and MPR4, are considered. In Figure 17 we plot $L_{\text{tot,real}}, N_{\text{f,real}}$ and $\langle L \rangle$ for conditions MPR3 and MPR4. The model-predicted number of flow-induced nuclei at the transition between the fine-grained layer and spherulitical core for conditions MPR3 and MPR4 is relatively higher than the one predicted for condition MPR1 (open circles). The value predicted at the transition of the oriented shear layer $N_{\text{f,ori}}$ for condition MPR1 is also given as a reference at the wall, since there no oriented layer developed from conditions MPR3 and MPR4. The computed values for $L_{\text{tot,real}}$ and $\langle L \rangle$ are everywhere across the thickness smaller than $L_{\text{tot,crit}}$ and $\langle L \rangle_{\text{crit}}$, respectively, with the exception of $L_{\text{tot,real}}$ for condition MPR3 which equals $L_{\text{tot,crit}}$ at the wall. Such results are obviously important, since they imply that a critical, total or average, shish length, required for an observable oriented shear layer, was not reached. However, the computed local shish length, $L_{\text{tot,real}}$ and $\langle L \rangle$ for condition MPR3, went beyond the flow-induced crystallization region, implying that the critical stretch $\Lambda_{\text{crit}}$ was reached within the spherulitical core. This suggests that shish-kebabs might develop in the spherulitical region, however their size or volume fraction is too small.

Notice that these analysis, based on a coarse characterization done by means of optical
light microscopy, can only be aimed at qualitatively agreements. The definition of a critical shish-length should therefore be based on more resolved analysis based on techniques that allow to assess more detailed morphological information, such as small angle X-ray scattering (SAXS).

**Oriented volume based criterion**  As it was suggested in,[61] the relative volume of oriented crystalline material, shish-kebabs volume over the total crystalline volume, could also be used as a criterion to define the transition between the oriented shear layer and the fine-grained layer. In Figure 18(a) to 18(d) we plot the relative undisturbed volume fraction of oriented crystals, $V_{ori}$, defined as $\psi_0/(\phi_0+\psi_0)$, after the completion of the crystallization process (after cooling to room temperature). The value of $V_{ori}$ computed at the transition from the oriented shear layer to the fine-grained layer in conditions MPR1 and MPR2 is almost the same $\sim 0.025$. Again, this value seems to be rather low and further calibration of the model parameter is required. For flow conditions MPR3 and MPR4 $V_{ori}$ is everywhere across the sample thickness smaller than the critical value $V_{ori,crit}$ defined from flow condition MPR1, see Figure 18(a). This is in agreement with the experimental results that no visible oriented shear layer developed under flow conditions MPR3 and MPR4. Comparing conditions MPR1 and MPR2, the values of $V_{ori}$ computed towards the slit wall for condition MPR2 are higher. To understand this we plot in Figure 19(a) and 19(b) the time evolution of the total shish-kebab and spherulitical volume close to the wall, where the highest volume fraction of oriented crystals is computed. As expected, the volume of shish-kebabs is higher for condition MPR2. Contributing to this, is the larger
computed value for $L_{\text{tot,real}}$, see Figure 16, and the radial growth of kebabs. The predicted spherulitical volume for condition MPR2 is also found to be smaller than condition MPR1, further favoring a higher volume fraction of oriented crystals. The time evolution of the radial growth rate $G(T, p)$, given by Equation (30), at the same position close to the wall after wall quenching is shown in Figure 20(a) for conditions MPR1 and MPR2. One can clearly see that the radial growth for condition MPR1, due to differences in cooling history, see Figure 20(b), is higher, explaining the larger spherulitical volume predicted for this condition.

**Capillary rheometer**

For the capillary rheometer the coupling of the viscosity with the degree of space filling gave rise to a non-smooth stress field. To circumvent this numerical problem, originated from a non-smooth viscosity distribution from the wall to the core, we did not couple the viscosity with the degree of space filling, Equation (46), with the consequence of reducing the effect of flow on crystallization. Figure 21 shows the computed total shish length per unit volume $L_{\text{tot,real}}$, the total number of flow induced nuclei $N_{\text{f,real}}$ and the local average shish length $\langle L \rangle$, across the thickness of the slit at position 2, see Figure 6, for the capillary experimental flow conditions. The corresponding micrographs are given on top of the figure.

The open circles denote the critical values computed from condition MPR1. The values for $L_{\text{tot,real}}$ computed at the transition of the oriented layer are close to $L_{\text{tot,crit}}$ obtained from MPR1. However, the predicted values for $\langle L \rangle$ for flow condition CA3 and CA1 is
3 orders of magnitude lower than the predicted value for the MPR experiments, which is explained by the higher predicted critical number of flow-induced nuclei $N_{ori} \sim 2$ orders higher. To verify the validity of morphological criteria based on shish length within the capillary experiments, the values of $L_{tot,\text{real}}$ and $\langle L \rangle$ computed from CA1 at the transition of the oriented shear layer to the spherulitical core are taken as critical criteria for condition CA3 (black dots). It can be seen that the dots fall on top of the curves, thus indicating that the model predicts at the transition of the oriented layer similar values for $L_{tot,\text{real}}$ and $\langle L \rangle$, for completely different filling conditions. The criterion based on the total shish length per unit volume $L_{tot,\text{crit}}$ is the one that gives the best agreement between the different experimental setups. It suggests that it is the total shish length per unit volume that determines the visibility of an oriented layer, and not the actual local shish length. The non-isothermal flow conditions under which the capillary experiments take place might explain the morphological differences. Nevertheless the model seems to give consistent results within each series of experiments, i.e., the average shish length criterion is valid within the MPR and the capillary rheometer experiments, and a reasonably good agreement in terms of $L_{tot}$. It is also interesting that the model captures the transition layer, between the skin and shear layers. For all the conditions, almost everywhere in this region the critical stretch of the high molecular weight $\Lambda_{HMW}$, which has to be surpassed for oriented crystals to grow (regime II), was not reached. It can be seen in Figure 21 that no shish-kebabs are predicted in that region by the model. This means that the coupling between the fast cooling close to the wall, and the transient viscoelastic behavior is captured quite well.
Oriented volume based criterion  The computed volume fraction of oriented crystals at the transition to the oriented shear layer for the MPR experimental condition MPR1 ($V_{ori} = 0.026 [-]$), was defined as a criterion $V_{ori,crit}$ to identify the transition to the oriented shear layer. We now test the validity of this criterion in the capillary rheometer experimental results.
In Figure 22(a-c) we plot the volume fraction of oriented crystals for capillary conditions CA1, CA2 and CA3, respectively. The critical value $V_{ori,crit}$, taken from the condition MPR1, is plotted as an open circle. For all flow conditions the predicted volume fraction of oriented crystals at the transition to the shear layer is remarkably similar, and the values are very close to the critical value $V_{ori,crit}$. For conditions CA2 and CA3 the agreement is excellent; $V_{ori,crit}$ falls on top of the computed curves. This strongly indicates that the criterion based on $V_{ori,crit}$ holds for experiments conducted under quasi-isothermal (MPR) and non-isothermal (capillary rheometer) conditions.

Due to start-up effects, which become more noticeable at high piston speeds (short flow times), the calculated average velocity in the slit for condition CA1, see Table 6, is overestimated. This could explain the lower predicted thickness of the shear oriented layer for this condition.

Based on the excellent agreement found for conditions CA2 and CA3, we plot for these conditions in Figure 23(a) and 23(b) the predicted and measured thickness of the oriented region along the slit length at different positions along the slit. The predicted thickness of the oriented layer is close to the measured values and agrees well with the experimental trends: the thickness of the oriented crystalline region is higher at the center (position 2) of the slit.
6 Conclusions

In conclusion, we present in this study a model to predict the resulting morphology of semi-crystalline polymers when processed via injection molding related flows. A model within the framework of molecular-based rheological modeling is proposed, in which quiescent and flow-enhanced crystallization processes are coupled to the flow-history, and the deformation of long chains is assumed to drive flow-induced crystallization. The model is tested on a set of experimental results obtained using special experimental devices in which the processing history, i.e. deformation and thermal history, is accurately controlled. The approach adopted in this study aimed at, first of all, predicting flow-induced crystalline morphologies created under quasi-isothermal conditions (MPR) and then under non-isothermal conditions (capillary rheometer) that mimic injection molding conditions. The model predictions in terms of number, size and shape of crystalline structures for both non-oriented and oriented crystals, allows to establish criteria in terms of total shish length per unit volume $L_{\text{tot,real}}$, average shish length $\langle L \rangle$ and volume fraction of oriented crystals $V_{\text{ori}}$, to identify the onset of an oriented shear layer. Such criteria are found to be in reasonably good agreement within the different experimental setups, between the tested flow conditions. Also, the predicted number of flow-induced nuclei at the transition of the morphological layers is found to be in agreement between all flow-conditions, within the MPR and capillary experiments. However, it is important to stress, based on the model results, that criteria defined by $\langle L \rangle_{\text{crit}}$ do not hold between isothermal and non-isothermal flow conditions. In contrast, criteria based on $L_{\text{tot,real}}$ and $V_{\text{ori}}$ seem to give a quanti-
tative agreement between all experiments, i.e. quasi-isothermal and non-isothermal flow conditions, in terms of a critical value for the transitions. We cannot make a quantitative comparison between measured and computed morphological measures due to lack of experimental data and, therefore, can also not tune our model parameters. However, the morphological information predicted by the model is essential to construct the material microstructure, which could be embedded in a multi-scale modeling framework, as proposed in,[62] to relate morphology to properties. Such approaches employ representative volume elements (RVE) of the microstructure to predict the material macroscopic mechanical response, thus using the microscale information to build an engineering scale material model.

Summarizing, we find the present results encouraging, in that a unified model for quiescent and flow-induced crystallization can be developed, sensitive to the molecular weigh of the material, with few fitting parameters and generalized to other materials.

**Practical aspects of crystallization modeling** The application of elaborated models to predict the morphology of semi-crystalline materials, as the one presented in this study, in commercial software is still restricted by reasons of economical and practical nature. The main difficulty originates from the extensive material characterization required. A complete rheological characterization of the material is needed to determine the spectrum of relaxation times. Additionally, the characterization of quiescent crystallization kinetics has to be done in experiments in which spherulites are counted under an optical microscopy for different thermal and pressure histories. Furthermore, the approach suggested here to
assess flow-induced crystallization kinetics combines the use of rheometry with numerical
modeling, in which changes measured in the elastic modulus $G'$ during crystallization, are
predicted and used to fit the model parameters $g_n$ and $g_l$. Last but not least, saturation
studies also have to be done to determine the saturation level of flow-induced crystallization,
which involve a shear flow device, e.g. Linkam shear cell, and optical microscopy. Hence, as the understanding of flow-enhanced crystallization phenomena improves, more
material data are required to feed constitutive and kinetic models.

From a numerical point of view, the model presented here also poses some difficulties
on current available software, as it requires two additional coupled problems to be solved:
a two-mode viscoelastic stress problem, and a crystallization problem. The spatial dis-
etization of the domain has to be sufficiently resolved to compute a smooth viscoelastic
stress field and, consequently, the crystalline morphology. If using explicit-type of integra-
tion schemes to compute viscoelastic stresses, as the one adopted here, time steps become
limited by the viscoelastic stress problem. Hence, computation times are significantly
increased.

Acknowledgements

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References


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Table 1: Physical properties of iPP HD120MO.

<table>
<thead>
<tr>
<th>Grade</th>
<th>$M_w$ [kg mol$^{-1}$]</th>
<th>$M_w/M_n$</th>
<th>$T_m$ [$^\circ$C]</th>
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<tbody>
<tr>
<td>HD120MO</td>
<td>365</td>
<td>5.4</td>
<td>163</td>
</tr>
</tbody>
</table>

Table 2: Thermal properties of iPP HD120MO.

<table>
<thead>
<tr>
<th>$c_p$</th>
<th>3175.3 [J kg$^{-1}$K$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>0.11 [W m$^{-1}$K$^{-1}$]</td>
</tr>
</tbody>
</table>

Table 3: Model parameters for the spherulitical growth rate $G(T, p)$ and effective number of nuclei $N(T, p)$ for iPP (HD120MO, Borealis).

<table>
<thead>
<tr>
<th>$G_{\text{max}}$</th>
<th>2.9669·10$^{-6}$ [m s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b$</td>
<td>1.3000·10$^{-3}$ [$^\circ$C$^{-1}$]</td>
</tr>
<tr>
<td>$T_{\text{ref}}$</td>
<td>9.00·10$^1$ [$^\circ$C]</td>
</tr>
<tr>
<td>$p_{g0}$</td>
<td>7.0333·10$^{-8}$ [K Pa$^{-1}$]</td>
</tr>
<tr>
<td>$p_{g1}$</td>
<td>-4.7000·10$^{-15}$ [K Pa$^{-2}$]</td>
</tr>
<tr>
<td>$p_{n0}$</td>
<td>2.7000·10$^{-7}$ [K Pa$^{-1}$]</td>
</tr>
<tr>
<td>$p_{n1}$</td>
<td>0.0 [K Pa$^{-2}$]</td>
</tr>
<tr>
<td>$n_0$</td>
<td>1.9067·10$^1$ [m$^{-3}$]</td>
</tr>
<tr>
<td>$n_1$</td>
<td>-4.9800·10$^{-2}$ [m$^{-3}$K$^{-1}$]</td>
</tr>
<tr>
<td>$P_{\text{ref}}$</td>
<td>1.0000·10$^5$ [Pa]</td>
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Table 4: Rheological parameters at 190 °C for iPP HD120MO: time-temperature shift-factors, \( a_T \) and \( b_T \), Maxwell relaxation spectrum, \( g_i \) and \( \tau_i \), and generalized Newtonian viscosity Cross model parameters.

<table>
<thead>
<tr>
<th>Shift factors</th>
<th>( T ) [°C]</th>
<th>( a_T )</th>
<th>( b_T )</th>
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<tr>
<td>135</td>
<td>4.944</td>
<td>1.065</td>
<td></td>
</tr>
<tr>
<td>145</td>
<td>3.579</td>
<td>1.045</td>
<td></td>
</tr>
<tr>
<td>155</td>
<td>2.557</td>
<td>1.036</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>1.894</td>
<td>1.088</td>
<td></td>
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<tr>
<td>175</td>
<td>1.328</td>
<td>0.974</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>205</td>
<td>0.760</td>
<td>1.007</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>0.584</td>
<td>1.035</td>
<td></td>
</tr>
<tr>
<td>235</td>
<td>0.472</td>
<td>0.949</td>
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</tr>
<tr>
<td>250</td>
<td>0.358</td>
<td>0.974</td>
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<table>
<thead>
<tr>
<th>WLF</th>
<th>( C_1 )</th>
<th>( C_2 ) [°C]</th>
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<tr>
<td></td>
<td>2.149</td>
<td>225.8</td>
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<tr>
<th>Maxwell</th>
<th>Mode</th>
<th>( g_i ) [Pa]</th>
<th>( \tau_i ) [s]</th>
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<tr>
<td>1</td>
<td>9.0200</td>
<td>0.002</td>
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<td>2</td>
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<td>0.010</td>
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<tr>
<td>3</td>
<td>1.8200</td>
<td>0.051</td>
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<td>4</td>
<td>0.5620</td>
<td>0.258</td>
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<tr>
<td>5</td>
<td>0.0878</td>
<td>1.300</td>
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<td>6</td>
<td>0.0109</td>
<td>6.580</td>
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<td>7</td>
<td>0.0075</td>
<td>33.200</td>
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<th>Cross</th>
<th>( \eta_0 ) [Pa.s]</th>
<th>( K ) [s]</th>
<th>( n ) [-]</th>
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<tr>
<td></td>
<td>4.8489 \cdot 10^3</td>
<td>0.2674</td>
<td>0.3878</td>
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Table 5: Flow conditions for the MPR experiments.

<table>
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<tr>
<th>conditions</th>
<th>( t_{flow} ) [s]</th>
<th>( u_{avg} ) [m s(^{-1})]</th>
<th>( T_{flow} ) [°C]</th>
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<tr>
<td>MPR1</td>
<td>0.1875</td>
<td>0.2</td>
<td>165</td>
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<tr>
<td>MPR2</td>
<td>0.375</td>
<td>0.1</td>
<td>145</td>
</tr>
<tr>
<td>MPR3</td>
<td>0.375</td>
<td>0.1</td>
<td>165</td>
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<tr>
<td>MPR4</td>
<td>3.0</td>
<td>0.0125</td>
<td>145</td>
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Table 6: Flow conditions for the capillary rheometer experiments.

<table>
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<th>conditions</th>
<th>$t_{\text{flow}}$ [s]</th>
<th>$v_{\text{avg}}$ [m s$^{-1}$]</th>
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<tr>
<td>CA1</td>
<td>2</td>
<td>0.126</td>
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<tr>
<td>CA2</td>
<td>4</td>
<td>0.0662</td>
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<tr>
<td>CA3</td>
<td>8</td>
<td>0.03758</td>
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Table 7: Thickness of the oriented layers for the MPR experiments.

<table>
<thead>
<tr>
<th>conditions</th>
<th>oriented layer [mm]</th>
<th>fine-grained layer [mm]</th>
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<tbody>
<tr>
<td>MPR1</td>
<td>0.07</td>
<td>0.20</td>
</tr>
<tr>
<td>MPR2</td>
<td>0.16</td>
<td>0.25</td>
</tr>
<tr>
<td>MPR3</td>
<td>-</td>
<td>0.20</td>
</tr>
<tr>
<td>MPR4</td>
<td>-</td>
<td>0.10</td>
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Table 8: Computed Deborah numbers based on disengagement $D_{\text{d}}$ and Rouse $D_{\text{R}}$ times, for the highest relaxation mode.

<table>
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<tr>
<th>conditions</th>
<th>$D_{\text{d}}$ [-]</th>
<th>$D_{\text{R}}$ [-]</th>
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<tr>
<td>MPR1</td>
<td>$7.4 \cdot 10^4$</td>
<td>$4.4 \cdot 10^3$</td>
</tr>
<tr>
<td>MPR2</td>
<td>$6.7 \cdot 10^4$</td>
<td>$4.0 \cdot 10^3$</td>
</tr>
<tr>
<td>MPR3</td>
<td>$3.5 \cdot 10^4$</td>
<td>$2.1 \cdot 10^3$</td>
</tr>
<tr>
<td>MPR4</td>
<td>$0.8 \cdot 10^4$</td>
<td>$0.5 \cdot 10^3$</td>
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Table 9: Model parameters at the transition between the oriented and the fine-grained layers.

<table>
<thead>
<tr>
<th>conditions</th>
<th>$\Lambda_{\text{HMW}}$ [-]</th>
<th>$N_{f,\text{real}}$ [-]</th>
<th>$L_{\text{tot,real}}$ [m$^{-2}$]</th>
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<tr>
<td>MPR1</td>
<td>90</td>
<td>$10^{12}$</td>
<td>$0.9 \cdot 10^9$</td>
</tr>
<tr>
<td>MPR2</td>
<td>70</td>
<td>$0.35 \cdot 10^{12}$</td>
<td>$0.3 \cdot 10^9$</td>
</tr>
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</table>
Figure 1: Model for the nuclei growth.
Figure 2: Growth of isotropic and oriented crystalline structures.
Figure 3: (a) Quiescent nucleation rate $N_q(T,p)$ curve. (b) Spherulitical growth rate $G(T,p)$ curve.
Figure 4: Calculated (solid lines) and measured (dashed lines) storage modulus after different shear flows ($\dot{\gamma} = 30$ s$^{-1}$ and $t_s = 2, 5, 6$ and 7 s) at 138 °C, in.$^{[43]}$
Figure 5: (a) The multipass rheometer: A) piston; B) moving platen; C) heating/cooling barrel; D) slit-flow geometry. (b) The capillary rheometer: A) Piston; B) Material reservoir; C) Rectangular shaped mold; D) Pressure transducer.
Figure 6: Layout procedure to microtome samples for optical light microscopy.
Figure 7: Polarized optical micrographs for multipass flow conditions at the center of the slit, see also Table 5.
Figure 8: Polarized optical micrographs for capillary rheometer flow conditions at three locations along the flow slit-channel length, see also Table 6.
Figure 9: Identification of morphological layers over a cross section. Polarized optical micrograph corresponds to flow-condition 2CA at the middle of the slit.
Figure 10: Symbols: thickness of the oriented layer for the capillary-flow conditions at three positions along the slit length. Lines are shown to guide the eye.
Figure 11: Hardening shift factor $a_{\xi}(\xi_g)$ versus degree of space filling $\xi_g$, see Equation (47).
Figure 12: Periodic computational domain for the MPR flow simulations.
Figure 13: Computational domain for the capillary rheometer flow simulations.
Figure 14: Decoupled computational procedure: the kinematics of a viscous flow problem are used to solve a coupled stress-crystallization problem. The computed degree of space filling is used to update the viscosity.
Figure 15: Model results for flow conditions MPR1 and MPR2, at the position of the transition from the oriented shear layer to the fine-grained layer obtained from the optical micrographs Figure 7: (a) molecular stretch $\Lambda_{\text{HMW}}$; (b) time evolution of the total number of flow-induced nuclei per unit volume; (c) evolution of the second invariant of the elastic Finger tensor of the averaged relaxation times $J_{2}(B_{e,\text{avg}})$; (d) time evolution of the total shish length per unit volume $L_{\text{tot,real}}$. 
Figure 16: Distribution across half of the normalized slit thickness of the total shish length $L_{\text{tot,real}}$, the number of flow-induced nuclei per unit volume $N_{f,\text{real}}$, and the average shish length $\langle L \rangle$, after correcting for impingement, for flow conditions MPR1 and MPR2.
Figure 17: Distribution across half of the normalized slit thickness of the total shish length $L_{\text{tot,real}}$, the number of flow-induced nuclei per unit volume $N_{f,\text{real}}$, and the average shish length $\langle L \rangle$, after correcting for impingement, for flow conditions MPR3 and MPR4.
Figure 18: Distribution of the relative volume of oriented material, $V_{\text{ori}} = \psi_0 / (\phi_0 + \psi_0)$, across half of the normalized slit thickness: (a) flow condition MPR1; (b) flow condition MPR2; (c) flow condition MPR3; (d) flow condition MPR4.
Figure 19: (a) Time evolution of the undisturbed shish volume $\psi_0$, close to the slit wall, for flow conditions MPR1 and MPR2; (b) time evolution of the undisturbed spherulitical volume $\phi_0$, close to the slit wall, for flow conditions MPR1 and MPR2.
Figure 20: (a) Time evolution of the spherulitical growth rate $G(T,p)$, close to the slit wall, for flow conditions MPR1 and MPR2; (b) time evolution of the temperature $T$ after quench, for flow conditions MPR1 and MPR2.
Figure 21: Distribution across half of the normalized slit thickness of the total shish length $L_{\text{tot, real}}$, the number of flow-induced nuclei per unit volume $N_{\text{f, real}}$, and the average shish length $\langle L \rangle$, after correcting for impingement, for flow conditions CA1, CA2 and CA3, at slit position 2.
Figure 22: Distribution across half of the normalized slit thickness of the relative volume of oriented material, $V_{ori} = \psi_0/\left(\phi_0 + \psi_0\right)$, across half of the normalized slit thickness at slit position 2: (a) flow condition CA1, (b) flow condition CA2, and (c) flow condition CA3.
Figure 23: Symbols: measured and predicted oriented crystalline region thickness, based on the critical volume fraction of oriented crystals criterion $V_{\text{ori,crit}}$, for capillary flow condition (a) CA2 and (b) CA3. Lines are shown to guide the eye.