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A stretch-based model for flow-enhanced nucleation of polymer melts

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Synopsis

A phenomenological model for flow-enhanced nucleation in crystallizing polymers is developed and validated by short-term shear experiments [Housmans et al., Macromolecules 42, 5728–5740 (2009); Hristova et al., Proceedings of the 228th ACS National Meeting, Philadelphia (2004)]. The model extends earlier work on flow-induced oriented crystallization [Custódio et al., Macromol. Theory Simul. 18, 469–494 (2009); Peters et al., Macromol. Symp. 185, 277–292 (2002); Peters, Polymer Crystallization: Observations, Concepts and Interpretations, edited by G. Reiter and J.-U. Sommer (Springer, Berlin, 2003), pp. 312–324; Zuidema, Ph.D. thesis, Technische Universiteit Eindhoven (2000); Zuidema et al., Macromol. Theory Simul. 10, 447–460 (2001)] to flow-enhanced pointlike nucleation, which can lead to number densities of spherulites multiplied by orders of magnitude. Excellent agreement between simulations and experimental data is obtained, for a range of rates and durations of shearing, with only two adjustable parameters: a prefactor to the creation rate of flow-induced nucleation precursors and a parameter that governs their influence on the relaxation dynamics of the high-molecular weight (HMW) fraction of the melt. The two main conclusions of this paper are, first, that the creation of flow-induced precursors is driven by the average stretch, not by the average orientation, of the primitive paths of chains in the HMW tail of the molecular weight distribution, and second, that nucleation of these precursors is impeded by flow. © 2011 The Society of Rheology. [DOI: 10.1122/1.3545844]

I. INTRODUCTION

A considerable amount of experimental work has been done, especially over the course of the last decade, to unravel the origins of the phenomena observed in flow-induced crystallization (FIC) of polymers; see, for example, the review by Kumaraswamy (2005). From the point of view of predicting structure formation and the resulting properties of semicrystalline polymers, there is a need for improved models. The results of the experimental work mentioned are of direct importance in this respect, since the models proposed so far exhibit essential differences in their key assumptions. Crystallizing melts have been described as molecular mixtures [Bushman and McHugh (1996); Doufas et al. (1999, 2000a, 2000b); Doufas and McHugh (2001a, 2001b, 2001c); Van Meerveld

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(2005); Van Meerveld et al. (2008)], as suspensions [Boutahar et al. (1996, 1998); Carrot et al. (1993); Steenbakkers and Peters (2008); Tanner (2002, 2003)], and as physically cross-linking networks [Horst and Winter (2000a, 2000b); Pogodina and Winter (1998); Pogodina et al. (1999a, 1999b, 2001); Winter and Mors (1997)] or locally physically cross-linking melts [Custódio et al. (2009); Peters et al. (2002); Peters (2003); Swartjes et al. (2003); Zuidema (2000); Zuidema et al. (2001)].

In contrast to the molecular mixture concept, the picture of a suspension is in better agreement with the commonly observed microstructure, which consists of large-scale crystallites dispersed throughout an amorphous matrix. It has been shown by Steenbakkers and Peters (2008) that the linear viscoelastic behavior of crystallizing melts with a spherulitic morphology can be described by a simple suspension model [Christensen and Lo (1979, 1986); Christensen (1990)], except at low frequencies. Elevated storage and loss moduli, observed immediately after strong short-term flow [Housmans et al. (2009); Vega et al. (2009)], cannot be explained based on filling of the material by semicrystalline particles, for example, with a suspension model. The flow in such experiments is generally applied above the nominal melting temperature or in the early stage of crystallization, when the volume fraction of transformed material (often called space filling) is negligible. The change in the initial rheological properties occurs in conjunction with the transition to oriented crystallization [Housmans et al. (2009)]. This transition, and the increase in number density of pointlike nuclei, which already takes place under less severe flow conditions, must originate from structural changes in the amorphous phase, although in a later stage typical suspension effects, such as increased molecular stretch between particles, could play a role [Hwang et al. (2006)].

In an attempt to illustrate this, Coppola et al. (2006) carried out rheological measurements on isotactic poly-1-butene (iP1B) samples with different constant volume fractions of spherulites as well as on amorphous iP1B filled with glass beads. The experimental procedure for the semicrystalline melts consisted of cooling them to a constant temperature $T=T_c<T_m$, where $T_m$ is the nominal melting point, staying at that temperature for a certain waiting time, then applying the inverse quenching technique [Acienno and Grizzuti (2003)] to “freeze in” the semicrystalline morphology, and performing oscillatory rheometry at $T=T_{iq}$ with $T_c<T_{iq}<T_m$. This was done for different waiting times, i.e., different amounts of space filling. The storage modulus increased relative to that of the purely amorphous melt, especially at low frequencies, where a distinct “shoulder” developed. Similar behavior was observed for the particle-filled melt, containing 12 volume percent glass beads, but the effect was much stronger even in the most weakly crystalline sample, containing 0.58 vol % spherulites according to the authors. They therefore concluded that an unknown structure with a long relaxation time developed in the amorphous phase prior to crystallization. However, the fraction of spherulites was estimated by linear normalization of the storage modulus, measured at a fixed frequency, between the values at zero and maximum crystallinity [Gauthier et al. (1992); Khanna (1993)]. Volume fractions 14–43 times higher than those obtained by this method and, even more importantly, higher than that of the glass beads, were predicted by Steenbakkers and Peters (2008) using a linear viscoelastic suspension model; see their Table III. This model was validated by optical microscopy and differential scanning calorimetry measurements of Boutahar et al. (1996, 1998). The conclusion of Coppola et al. (2006) is thus unsupported by their data. It may be worthwhile to repeat their experimental protocol with shorter times of crystallization at $T_c$, so that the melts after inverse quenching to $T_{iq}$ are indeed in the early stage, where space filling effects are negligible.

Network formation in the amorphous phase was proposed by Winter and co-workers [Horst and Winter (2000a, 2000b); Pogodina and Winter (1998); Pogodina et al. (1999a, 2001); Winter and Mors (1997)] or locally physically cross-linking melts [Custódio et al. (2009); Peters et al. (2002); Peters (2003); Swartjes et al. (2003); Zuidema (2000); Zuidema et al. (2001)].
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1999b, 2001); Winter and Mours (1997)]. In their experiments, the rheology of different polymers, prior to impingement of spherulites, looked similar to that of a chemical gel: the loss tangent \( \delta = G'/G'' \) became frequency-independent. They hypothesized that, at the critical gel point, the spherulites were connected by amorphous “tie chains” into a sample-spanning network. However, Janeschitz-Kriegl (2003) correctly pointed out that, in the optical micrograph of Pogodina et al. (2001) taken at the critical gel point of a quiescent crystallizing isotactic polypropylene (iPP) melt, the spherulites were still widely separated. He therefore argued that the junction points of the network must have included structures that did not grow into visible objects, which were created gradually until they caused gelation. The spherulites, on the other hand, all started to grow immediately when the temperature of the isothermal crystallization experiment was reached, as shown by their uniform radii, measured as a function of time [Pogodina et al. (2001)].

Fetters et al. (1999) reported the following relation between the mean squared end-to-end distance \( \langle r^2 \rangle \) and the molecular weight \( M \) of iPP: \( \langle r^2 \rangle / M = 0.694 \, \text{Å}^2 \text{mol}^{-1} \). With the weight-averaged molecular weight \( M_w = 351 \, \text{kg/mol} \) from Pogodina et al. (2001), we get \( 2\langle r^2 \rangle^{1/2} = 99 \, \text{nm} \) as an estimate of the maximum allowable distance between junctions to form a sample-spanning network. This is orders of magnitude smaller than the average distance between spherulites in the micrograph of Pogodina et al. (2001) corresponding to the critical gel point.

Janeschitz-Kriegl (2003) plotted the logarithm of the number density of spherulites \( N_{sph} \) versus temperature for different amounts of mechanical work, applied to an iPP melt in short-term shear flow. He then fitted linear curves through data for the same work (also for zero work, i.e., quiescent crystallization) and extrapolated them toward lower temperatures. He found an approximate convergence of these “isoergons” at \( T \simeq 75 \, ^\circ\text{C} \), where \( N_{sph} \sim 10^{18} \, \text{m}^{-3} \). The explanation proposed by Janeschitz-Kriegl and co-workers [Janeschitz-Kriegl (1997); Janeschitz-Kriegl et al. (1999); Janeschitz-Kriegl (2003); Janeschitz-Kriegl and Ratajski (2005)] is that the melt contains “dormant” nucleation precursors, which become “active” (able to nucleate) at different temperatures, and that flow improves their structure so that they are activated at higher temperatures. From this point of view, the convergence of isoergons gives the total number density of precursors, dormant and active ones combined, which is the maximum number density of spherulites attainable by cooling and/or flow. The average distance between precursors is then \( N_{sph}^{1/3} (T \simeq 75 \, ^\circ\text{C}) \sim 1 \, \mu\text{m} \). This is still a factor of 10 above the maximum distance between network junctions, calculated in the previous paragraph [which is nearly the same for the iPP used by Janeschitz-Kriegl et al. (2003), with \( M_w = 322 \, \text{kg/mol} \)].

More experiments are needed to check whether \( \log(N_{sph}) \) is indeed linear in \( T \) for the same amount of work, especially at lower temperatures, since Janeschitz-Kriegl’s extrapolation to \( T \simeq 75 \, ^\circ\text{C} \) was based on a limited amount of data in the relatively narrow range \( 140 \leq T \leq 160 \, ^\circ\text{C} \). A relation slightly stronger than linear can give a significantly higher number density of dormant precursors. Crystallization during flow, causing changes in rheological properties as well as in the flow itself, becomes a problem when going to lower temperatures. Therefore the flow should be applied before cooling. Another problem at low temperatures may be that the number density of spherulites is too high to be determined with optical microscopy. The method of Housmans et al. (2009), in which the number density is derived from oscillatory shear measurements by means of a suspension model, overcomes this problem. See also Ma et al. (2010).

The concept of flow-enhanced activation of intrinsic dormant precursors is a viable candidate to explain the huge effect of flow on the number density of spherulites. However, it does not explain the gelation process observed by Winter and co-workers [Horst and Winter (2000a, 2000b); Pogodina and Winter (1998); Pogodina et al. (1999a, 1999b,
The idea is that dormant precursors are intrinsically present in the melt. Their effect on the rheology should then be present from the beginning, whereas gelation occurs on a longer time scale. Coppola et al. (2006) also identified a critical gel point in their measurements, which occurred at 30% space filling according to Steenbakkers and Peters (2008). In the two-dimensional simulations of Hwang et al. (2006), regions of highly elevated molecular stretch between rigid disks in planar shear flow of a viscoelastic fluid became prominent at an area fraction of 30%. Admittedly, the stress field in a suspension of spheres has components in the third dimension, which were not resolved by these simulations. But it should be noted that the area fraction of intersections of spheres with a plane (for comparison with the simulations mentioned, the velocity gradient plane) equals their volume fraction in the bulk [Steenbakkers (2010)].

The accuracy between experimental and two-dimensional numerical results in terms of space filling is therefore encouraging. Moreover, qualitatively the same effect was observed in a three-dimensional simulation involving two spheres, initially separated by a distance on the order of their radius [Hwang et al. (2004)]. These results suggest that gelation in crystallizing melts is caused by hydrodynamic interactions between spherulites rather than structural changes in the amorphous phase.

Zuidema et al. (2001) developed a FIC model, in which both the creation and the longitudinal growth of threadlike nuclei were driven by the recoverable strain of the high-end tail of the molecular weight distribution. This was quantified by the second invariant of the deviatoric elastic Finger strain tensor, or equivalently the conformation tensor, of the slowest mode in a multi-mode rheological constitutive equation. The relaxation time of this mode was taken proportional to the number density of flow-induced nuclei, based on the idea that these act as physical cross-links if different molecules are involved in each nucleus. The model thus captures, in an averaged sense, the strong influence of high-molecular weight (HMW) chains on the overall rate of crystallization [Balzano et al. (2008); Heeley et al. (2006); Mykhaylyk et al. (2008); Seki et al. (2002); Vleeshouwers and Meijer (1996); Yang et al. (2004)] and the formation of an oriented morphology [Acierno et al. (2003); Van Meerveld et al. (2004)]. Reasonable agreement with pressure-driven flow experiments of Jerschow (1994) was obtained in terms of the transitions between morphological layers. A recent modification of the model by Custódio et al. (2009) was validated in more detail with respect to injection molding prototype flows. The most striking result was that the onset of an experimentally observable oriented skin layer could be correlated with a critical relative volume fraction of oriented crystalline material, for which the same value was computed in isothermal as well as in nonisothermal simulations.

The hypothesis that nuclei act as physical cross-links, which was a key element of the successes of the recoverable strain-based FIC model, remains unproven. Swartjes (2001) and Sentmanat et al. (2006) reported a slower relaxation of the stress after fast short-term flow of undercooled melts. But it is not sure whether the amount of HMW chains involved in nuclei (at least in those that actually become spherulites, which is a very small fraction of all molecules [Janeschitz-Kriegl (2003); Janeschitz-Kriegl et al. (2003)]) can explain this phenomenon, which may also be caused by the formation of a highly oriented (so-called shish) structure. Coppola et al. (2006) suggested that the evolution of a slow relaxation process in their quiescent inverse-quenched melts might be interpreted as evidence in favor of the hypothesis of Zuidema et al. (2001). However, referring to the discussion above, the samples were much more highly filled than estimated by the authors and the behavior observed was likely due to the spherulites acting as fillers rather than physical cross-links. Moreover, since the number density of spherulites, growing under quiescent conditions well below the nominal melting point, only depends on the
temperature [Eder and Janeschitz-Kriegl (1997)], it is believed that the corresponding nuclei are predetermined, existing in the melt in a dormant state until their temperature of activation is reached. These nuclei probably consist of heterogeneous substances in many polymers used in FIC studies, but the same phenomenon has been observed in very pure samples [Alfonso and Ziaibicki (1995); Piccarolo et al. (1992)]. From this point of view, no new nuclei were made in the experiments of Coppola et al. (2006) by prolonged crystallization at $T=T_c$, although it could be that sporadic nucleation became significant at the temperature $T_{iq}$, where the rheological measurements were performed, which was only slightly below the nominal melting point.

Several other FIC models with different levels of description exist. Examples are the continuum thermodynamics-based approaches of McHugh and co-workers [Bushman and McHugh (1996); Doufas et al. (1999, 2000a)], Isayev and co-workers [Guo et al. (1999); Kim et al. (2005)], Titomanlio and Lamberti (2004), and Van Meerveld et al. (2008), the introduction of a flow-induced free energy change, obtained from the Doi–Edwards model [Doi and Edwards (1986)], in the classical nucleation theory [Hoffman et al. (1969)] by Coppola et al. (2001) and Acierno et al. (2008), and kinetic Monte Carlo simulations by Graham and Olmsted (2009, 2010). All these models describe an effect of molecular orientation and/or stretch on the kinetics of nucleation, but none of them contain an effect of nuclei on the (local) relaxation dynamics, such as in the Zuidema model. Doufas et al. (1999, 2000a) and Van Meerveld et al. (2008) did incorporate changes in the rheology as a function of the degree of crystallinity or space filling, respectively, but these effects do not play a role in the early stage of crystallization. In general, agreement with FIC experiments was obtained in terms of changes in the time scale of crystallization. Only the simulations of Graham and Olmsted (2009, 2010) were validated with respect to direct morphological evidence, namely, microscopic observations of the number density of spherulites during continuous shear flow [Coccorullo et al. (2008)]. The shear rates in these experiments were very low, up to $\dot{\gamma}=0.3$ s$^{-1}$. Under much more severe flow conditions, the coupling between nucleation and the relaxation dynamics of the HMW fraction of the melt, as offered by the recoverable strain-based FIC model, was necessary to predict oriented structure development [Custódio et al. (2009); Zuidema (2000); Zuidema et al. (2001)]. It will be shown in this paper that this also holds for the spherulitic crystallization in moderate to strong flows. Therefore we focus on the recoverable strain-based model and adapt it to flow-enhanced pointlike nucleation.

II. OBJECTIVE AND OUTLINE

Physical cross-linking in the early stage of FIC was hypothesized by Zuidema et al. (2001) and in later work from the same group [Custódio et al. (2009); Peters et al. (2002); Peters (2003); Swartjes et al. (2003)] without providing a detailed theoretical argumentation. It was mainly an empirical way to capture the highly nonlinear effects of the rate and duration of flow on (in their case oriented) structure formation. Following their basic hypothesis, the probability of nucleation in the immediate vicinity of already existing nuclei is higher than in the bulk of the amorphous melt. Reasoning further along this line, one has to conclude that nuclei appear in clusters, as depicted on the left side of Fig. 1. If the relaxation times of chains within these clusters are increased, since they are connected by nuclei, then this increase should not depend on the global number density of flow-induced nuclei, as Zuidema et al. (2001) proposed, but on the local number
within each cluster. Only if the entire space is covered by clusters, as depicted on the right side of Fig. 1, the local number density within any arbitrary one of them (indicated by the circle) equals the global number density.

The objective of this paper is to develop a flow-enhanced nucleation model, able to predict the effects of the rate and duration of flow on the number density of spherulites. A global formulation (Fig. 1, right) is chosen. We refer to Chap. 3 of Steenbakkers (2009) for a preliminary model based on a local formulation and a discussion of opportunities for future efforts in that direction. A thorough investigation of similarities and differences between the two approaches is outside the scope of this paper, but we will point out a few of them along the way. The outline of this paper is as follows. Section III presents the experiments used for validation of the model, which is formulated in Sec. IV. The results are discussed in Sec. V and the conclusions are summarized in Sec. VI.

III. EXPERIMENTS

A. Flow-enhanced nucleation

We compare our simulation results to experimental data of Hristova et al. (2004) for the polydisperse linear isotactic polypropylene (iPP) HD120MO, currently labeled HD601CF, from Borealis. Several aspects of the morphology, developing during and after different short-term shear flows, which were applied directly after cooling to a constant crystallization temperature, were investigated by means of different techniques. The pointlike nucleation densities, of interest here, were obtained from in situ optical microscopy using a Linkam shear cell. The number density of spherulites was estimated from the number of spherulites per unit area of observation, for which the relation

\[ N_{\text{sph}} \text{[mm}^{-3}] = (N_{\text{sph}} \text{[mm}^{-2}])^{3/2} \]  

was used [Gahleitner et al. (1996)]. This is based on the assumption that the square root of the number per unit area is a characteristic one-dimensional number density along a line, which is then cubed to obtain the volumetric number density. Spherulites out of focus were not counted, in order to get as close as possible to a number per unit area. Furthermore, numbers per unit area were determined in different parts of the sample and then averaged and, for small numbers, the magnification was decreased to increase the viewing area and thus obtain more reliable results. Errors were estimated on the order of 10% (Hristova, personal communication).

Simulation results are also compared to the experimental data of Housmans et al. (2009), which were obtained at a slightly different temperature for the same material and for two iPPs with a different molecular weight distribution: HD234CF from Borealis and 13E10 from DSM. The number densities of spherulites were determined from rheological
measurements after short-term shear, applying the Kolmogorov–Avrami equation, Eq. (12), in combination with the linear viscoelastic suspension model used by Steenbakkers and Peters (2008). Molecular characteristics of the materials are given in Table II. They are referred to as iPP1, iPP2, and iPP3 as indicated in the first column.

In both sets of experiments, the common short-term shearing protocol was applied. Samples were annealed above the equilibrium melting temperature to erase residual structures and then cooled to a temperature where crystallization occurs: \( T = 135 \degree C \) [Hristova et al. (2004)] or \( T = 138 \degree C \) [Housmans et al. (2009)]. Directly after the temperature became constant, a shear flow was applied for a duration \( t_s \) at a constant rate \( \dot{\gamma} \).

Hristova et al. (2004) determined the lamellar growth rate, \( \dot{R} \) in Eqs. (9)–(11), from successive microscopic pictures of spherulites. While \( \dot{R} \) turned out to be constant in each experiment, it varied considerably between experiments, from 37 to 70 nm/s, as seen in Table III. No correlation with the shear rate or shear strain was found. The experimental conditions \((T, \dot{\gamma}, t_s)\) and the number density of spherulites \( N_{sp} \) are also given in Table III. Furthermore, the presence of oriented crystallites is indicated. Their numbers were orders of magnitude smaller than those of the spherulites. The nucleation density is thus dominated by the pointlike nuclei and can be used to validate our flow-enhanced nucleation model. A snapshot of the morphology for one of the experiments with the largest amount of oriented crystallites is shown in Fig. 2.

No noticeable space filling occurred during flow in any of the experiments of Hristova et al. (2004), even for the longest shear time of 90 s. Furthermore, when the crystallites grew large enough to be detected, their number had already become constant. These observations confirm that the flow was always applied in the early stage of crystallization, characterized by unbounded nucleation and growth, as it should be in order to avoid disturbance of the flow, and hence of the crystallization kinetics, by growing crystallites.

B. Rheological characterization

The linear viscoelastic behavior of the three iPPs was measured and fitted with discrete relaxation spectra by Housmans et al. (2009). They estimated the Rouse time of the slowest mode using the Doi–Edwards result for monodisperse long linear chains [Doi and Edwards (1986)].
\[ \lambda_{0R} = \frac{\lambda_{0d}}{3Z}, \]  

(2)

in which they took \( Z = M_w/M_r \) as a characteristic number of entanglements for the high-end tail of the molecular weight distribution; \( M_r \) is the average molecular weight between entanglements. The longest relaxation times of the three iPPs are reported in Table II. The subscript 0 in Eq. (2) is explained in Sec. IV G.

Equation (2) is commonly applied in FIC studies, although it disregards the effect of shorter chains on the relaxation dynamics of the HMW fraction through constraint release. For bimodal blends, the Struglinski–Graessley criterion \( Z_{HMW}/Z_{LMW} \ll 0.1 \) [Struglinski and Graessley (1985)] can be used to verify Eq. (2) [Balzano et al. (2008)]. Here \( Z_{HMW} \) and \( Z_{LMW} \) are the molecular weights of the high and low molecular weight components, respectively, in units of \( M_r \). A similar criterion for polydisperse melts is lacking. For a discussion of issues, related to the determination of characteristic HMW relaxation times in polydisperse melts, we refer to Van Meerveld et al. (2004).

As an alternative to Eq. (2), the longest Rouse time is determined by fitting a multimode Rolie–Poly model [Likhtman and Graham (2003)] to uniaxial extensional viscosity data for iPP2. These were supplied by Borealis. Inspection of the transient viscoelastic extensional viscosity, calculated with the relaxation spectrum reported by Housmans et al. (2009), reveals a systematic underprediction of the data by approximately a factor of two. A previously determined spectrum for iPP2 (Vega, personal communication) does give a linear viscoelastic extensional viscosity curve in agreement with the data before strain hardening sets in. We attribute this to a difference between batches of the same iPP grade. Both relaxation spectra consist of six modes. The main differences are in the moduli, whereas the relaxation times are nearly identical. Vega’s rheological measurements, summarized in Table IV, were done around the same time as the FIC experiments on iPP2 at \( T=135 \, ^\circ\text{C} \) [Hristova et al. (2004)], which are used here to compare model results with the longest Rouse time determined by the two different methods.

Likhtman and Graham (2003) found that, to compensate for the overprediction of the steady state shear stress and first normal stress difference in fast shear flows, they had to take \( \beta=0 \) in the Rolie–Poly model; see Sec. IV G. This was not the case in the Graham–Likhtman and Milner–McLeish (GLaMM) model [Graham et al. (2003)], of which Rolie–Poly is a simplified version, and therefore, according to the authors, it should not be concluded that convective constraint release was insignificant. We also find that \( \beta=0 \) gives the best results. The remaining free parameters are then the Rouse times \( \lambda_{0R,i} \). Again, see Sec. IV G.

The extensional viscosities for iPP2, measured at four different strain rates, show minor strain hardening. The data for the lowest strain rate (\( \dot{\varepsilon}=0.3 \, \text{s}^{-1} \)) are excluded from the fitting procedure, since the calculated extensional viscosity always falls within the rather high scatter of these data. The other measurements are shown in Fig. 3. The Rolie–Poly model predicts a much too strong strain hardening at the two highest rates (\( \dot{\varepsilon}=3 \, \text{s}^{-1} \) and \( \dot{\varepsilon}=10 \, \text{s}^{-1} \)). The data for \( \dot{\varepsilon}=1 \, \text{s}^{-1} \) can be fitted reasonably well when only the slowest mode is described by Eq. (24), while for the other modes the non-stretching Rolie–Poly model [Likhtman and Graham (2003)] is used. Two additional stretching modes are sufficient to improve the fits of the other data, in terms of the onset of strain hardening. The strong strain hardening, predicted at longer times, cannot be prevented. It turns out that the result for \( \dot{\varepsilon}=1 \, \text{s}^{-1} \) is not affected much by these additional stretching modes, so we obtain a unique longest Rouse time, \( \lambda_{0R,6}=2 \, \text{s} \).

The uniaxial extension experiments were done at \( T=180 \, ^\circ\text{C} \). A time-temperature shift
to $T=138 \, ^\circ\text{C}$, with the Williams–Landel–Ferry (WLF) parameters given in Table IV, yields $\lambda_{0R,6}=7 \, \text{s}$. This is much longer than the 0.27 s obtained from Eq. (2) and reported in Table II. We have no physical explanation for this difference, but it is nevertheless interesting to test the effect of a variation in the Rouse time on the results of our flow-enhanced nucleation model. This is done in Sec. V.

IV. MODELING

A. Rheology

The Cauchy stress tensor for a polymer melt is written in the form

$$\sigma = -pI + \sum_{i=1}^{M} G_i (B_{e,i} - I),$$

where $p$ is the hydrostatic pressure and $I$ is the unit tensor. The subscript $i=M$ indicates the mode with the longest relaxation time. The elastic Finger tensor $B_{e,i}$ of mode $i$ follows from

$$\triangledown B_{e,i} = -A_i \cdot B_{e,i} - B_{e,i} \cdot A_i^T.$$  

The triangle denotes the upper convected derivative and $A_i$ is a slip tensor for mode $i$, which describes the non-affine deformation of the corresponding molecules. Several constitutive models can be written in this form with different expressions for $A_i$ [Peters and Baaijens (1997)]. A few are listed in Table I.

The elastic Finger tensor is taken equivalent to the conformation tensor, following Leonov (1976, 1987, 1992). It is written as

$$B_{e,i} = 3 \langle R_i R_i \rangle = 3 \Lambda_i^2 \langle n_i n_i \rangle$$

with the prefactor 3 derived for differential models [Rubio and Wagner (1999)]. The orientation tensor

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Symbols: measured uniaxial extensional viscosity of iPP2 at $T=180 \, ^\circ\text{C}$ for different strain rates. Lines: six-mode Rolie–Poly model with three stretching modes ($\lambda_{0R,4}=0.04 \, \text{s}$, $\lambda_{0R,5}=0.3 \, \text{s}$, $\lambda_{0R,6}=2 \, \text{s}$). Dashed line: linear viscoelastic response.}
\end{figure}
\end{center}
The average stretch of primitive paths is described by the scalar stretch parameter 

\[ \Lambda_i = \frac{\epsilon_{i,j} B_{i,j} + \epsilon_{j,i} B_{j,i}^{-1} + \epsilon_{k,k} J}{c_{i,j}} \]

Giesekus \[ \frac{\alpha_i}{2\lambda_{d,i}} \quad - \frac{(1 - \alpha_i)}{2\lambda_{d,i}} \quad \frac{1 - 2\alpha_i}{2\lambda_{d,i}} \]

XPP \[ \frac{\alpha_i}{2\lambda_{d,i}} \quad - \frac{(1 - \alpha_i)}{2\lambda_{d,i}} \quad \frac{1 - \alpha_i - 3\alpha_i^2 \Lambda_i S_{ij}; \Lambda_i}{2\lambda_{d,i} \Lambda_i^2} + \frac{1}{\lambda_{d,i}} \left( \frac{1 - 1}{\Lambda_i^2} \right) \]

Rolie-Poly \[ 0 \quad - \frac{1}{2\lambda_{d,i}} - \frac{\beta_i \Lambda_i^{2d}}{\lambda_{d,i}} \left( 1 - \frac{1}{\Lambda_i} \right) \quad \frac{1}{2\lambda_{d,i}} + \frac{1}{\lambda_{d,i}} \left( 1 - \frac{1}{\Lambda_i} \right) \]

\[ S_i = \langle n_i n_i \rangle = \frac{B_{i,j}}{tr(B_{i,j})} \] (6)

gives the average molecular orientation; \( n_i \) is a unit vector, tangent to the primitive path of a chain, and the angle brackets indicate an average over the orientation distribution. The average stretch of primitive paths is described by the scalar stretch parameter \( \Lambda_i = \sqrt{\frac{tr(B_{i,j})}{3}} \) (7)

and is assumed homogeneous along the chain, as usual for continuum-level constitutive models, which is why it can be taken outside the brackets in Eq. (5).

The Rolie–Poly model [Likhtman and Graham (2003)] is used throughout this paper. More advanced rheological models, like the GLaMM tube model [Graham et al. (2003)], of which Rolie–Poly is a simplified version, and the slip-link [Khaliullin and Schieber (2009); Schieber et al. (2007)] and slip-spring [Likhtman (2005); Ramírez et al. (2007)] models offer more detail. For example, they resolve the inhomogeneity of stretch along a polymer chain, which tends to increase from zero at the ends to a maximum near the center of the chain. However, these models are computationally too expensive for the problem at hand.

**B. Spherulitic structure formation**

We focus on spherulitic crystallization. The evolution of the morphology then follows from the rate equations derived by Schneider et al. (1988),

\[ \dot{\Psi}_3 = 8\pi N_n \quad (\Psi_3 = 8\pi N_n) \],

\[ \dot{\Psi}_2 = R \dot{\Psi}_3 \quad (\Psi_2 = 8\pi R_{tot}) \],

\[ \dot{\Psi}_1 = \dot{R} \dot{\Psi}_2 \quad (\Psi_1 = S_{tot}) \],

\[ \dot{\Psi}_0 = \dot{R} \dot{\Psi}_1 \quad (\Psi_0 = V_{tot}) \].

All quantities in these equations are expressed per unit volume in the hypothetical case of unrestricted nucleation and growth, meaning that nuclei can appear in the space already...
covered by the semicrystalline phase and that spherulites can grow through each other unhindered; \( N_n \) is the number of nuclei, \( R_{tot} \) is the sum of the radii of the spherulites, \( S_{tot} \) is their total surface area, \( V_{tot} \) is their total volume, and \( \dot{R} \) is the lamellar growth rate. The degree of space filling \( \phi \), i.e., the real total volume of the semicrystalline phase per unit volume of the material, is obtained from the Kolmogorov–Avrami model [Avrami (1939, 1940, 1941)].

\[
\phi = 1 - e^{-\Psi_0}.
\]

For a recollection of Kolmogorov’s derivation, see Eder and Janeschitz-Kriegl (1997). The real nucleation density follows from

\[
N_{n,\text{real}}(t) = \int_{-\infty}^{t} \dot{N}_n(s) [1 - \phi(s)] ds.
\]

Eder and co-workers [Eder et al. (1990); Liedauer et al. (1993)] developed a similar set of differential equations for the evolution of the oriented shish-kebab morphology, in which the rates of creation and longitudinal growth of threadlike nuclei were assumed proportional to the square of the shear rate. Zuidema et al. (2001) adopted this model but replaced the shear rate dependencies by linear functions of the second invariant \((J_2)\) of the deviatoric elastic Finger tensor, associated with the longest relaxation time, thus focusing on the molecules in the flow, rather than on the flow itself. This invariant, which they obtained from a multi-mode Leonov model, is a measure of the conformation, i.e., orientation and stretch, of the HMW chains in the melt. The modified Eder rate equations were used in parallel with the Schneider rate equations. Specifically, spherical and oriented nucleation and growth were supposed to be additive in terms of their unrestricted volume fractions: \( \Psi_0 = \Psi_{0,sph} + \Psi_{0,ori} \) with \( \Psi_{0,sph} \) from Eqs. (8)–(11) and \( \Psi_{0,ori} \) from the Eder rate equations. Peters et al. (2002) and Swartjes et al. (2003) later used the extended Pom–Pom (XPP) model instead of the Leonov model in the same FIC framework, which by then was called the SJ\textsubscript{2} (i.e., Schneider-J\textsubscript{2}) model. However, the effect of flow on the spherical crystallization process was not described and therefore the reference to Schneider et al. (1988) is misleading.

It has been known for a long time that the HMW fraction of a polydisperse melt most strongly affects the acceleration of crystallization by flow [Vleeshouwers and Meijer (1996)] and the transition from sphercial to oriented morphology [Acierno et al. (2003)]. Studies on bimodal blends [Balzano et al. (2008); Bashir et al. (1986); Heeley et al. (2006); Mykhaylyk et al. (2008); Seki et al. (2002); Yang et al. (2004)] have confirmed the role of HMW chains in the formation of threadlike nuclei. Interestingly, the fact that the shish structure consists of chains of all lengths [Kimata et al. (2007)] suggests that only the nucleation rate (and/or the initiation of longitudinal growth from a pointlike nucleus, but not the longitudinal growth rate itself) primarily depends on the conformation of the HMW fraction. Therefore, in the recent extension of the SJ\textsubscript{2} model by Custódio et al. (2009), the effect of flow on the longitudinal growth rate is formulated in terms of the average conformation of the melt.

For flow-enhanced pointlike nucleation, we could simply follow these previous works and formulate the nucleation rate as
\[ \dot{N}_n = \dot{N}_{nq} + g_n J_2 \left( B_{e,M}^d \right), \]  

where \( \dot{N}_{nq} \) is the nucleation rate in the quiescent melt and \( g_n \) is a scaling parameter for the effect of flow. However, this model cannot capture experimental spherulite number densities. The reasons will become clear in Secs. IV C–IV H. As an introduction, we will first discuss prior literature considering the nucleation process in polymer melts.

### C. Precursors of crystalline nuclei

The physics of early stage crystallization are still a matter of debate. For example, Olmsted et al. (1998) suggested that a *bicontinuous* structure of amorphous and mesomorphic domains is formed by spinodal decomposition and that crystallization occurs in the more dense, conformationally ordered mesophase. Strobl (2000, 2005, 2006) developed a fundamentally different theory, based on lateral growth and simultaneous thickening of *isolated* mesomorphic layers. Crystallization occurs where the layer thickness exceeds a critical size, resulting in a granular structure and eventually a fully crystalline lamella. Both views have been challenged by Lotz (2000, 2005). Based on the helical handedness in thin crystalline films of chiral polymers, he advocated the classical nucleation and growth theory [Hoffman et al. (1969); Lauritzen and Hoffman (1973)]. According to Cheng and Lotz (2005), however, the purely enthalpic nucleation barrier in the classical theory should be modified to include entropic effects.

Ryan and co-workers [Heeley et al. (2003a, 2003b); Ryan et al. (1999); Terrill et al. (1998)] analyzed several polymers in terms of the Cahn–Hilliard theory of spinodal decomposition. From small-angle x-ray scattering (SAXS) patterns during quiescent and flow-induced crystallization, they determined the growth rate of density fluctuations as a function of the magnitude of the scattering vector, \( |k| \). Typical Cahn–Hilliard behavior was observed, except for small \( |k| \), which was attributed to interference from stray radiation [Bates and Wiltzius (1989)]. However, Muthukumar and Welch (2000) found the same behavior with Langevin dynamics simulations, from which they concluded that the underlying process was not spinodal decomposition. Based on structural observations in these simulations, Muthukumar (2000) derived an alternative expression for the growth rate of density fluctuations. Although it may be seen as an improvement, the author’s claim that the new model is “fully consistent” with the experiments and simulations mentioned, is not supported. [Compare the theoretical growth rate of density fluctuations in Fig. 2 of Muthukumar (2000) to the numerical result in Fig. 4 of Muthukumar and Welch (2000).]

It must be noted that Muthukumar and Welch used a single-chain description. Simulations with multiple chains were discussed in an earlier paper by Liu and Muthukumar (1998) but were not analyzed in terms of density fluctuations. However, molecular dynamics simulations by Gee et al. (2006) qualitatively confirmed the single-chain Langevin dynamics results of Muthukumar and Welch. Curiously, Gee et al. (2006) interpreted this as a confirmation of the spinodal-assisted crystallization model.

Baert and Van Puyvelde (2008) reviewed small-angle light scattering (SALS) studies of polymer crystallization. These typically exhibit density fluctuations in the early stages, whereas orientation fluctuations are observed significantly later. Combining SALS with polarized optical microscopy during flow-induced crystallization of poly-1-butene, Baert and Van Puyvelde showed that the onset of density fluctuations coincided with the appearance of spherulites. From the absence of orientation fluctuations in these early stages, they concluded that the spherulites initially had a low crystalline content. Their results are
indicative of nucleation, followed by growth and perfection of the internal structure of the 
spherulites, rather than spinodal decomposition into a dense mesophase.

Panine et al. (2003, 2008) reported simultaneous SAXS and wide-angle x-ray diffraction (WAXD) measurements during quiescent crystallization of isotactic polypropylene, using a very sensitive wide-angle detector. Sharp WAXD peaks, corresponding to the crystalline α phase, developed around the same time as SAXS. Previous studies had shown a time lag between SAXS and WAXD and incited a discussion whether this was due to the lower sensitivity of the latter or a fingerprint of spinodal decomposition [Heeley et al. (2003b)]. The results of Panine et al. (2003, 2008) do not agree with the spinodal decomposition model, but suggest that crystalline nuclei are formed in the amorphous phase.

Blundell and co-workers [Blundell et al. (1996, 2000); Mahendrasingam et al. (1999, 2000, 2005a, 2005b)] showed that, during flow at high strain rates, nucleation is prohibited. The combined SAXS and WAXD measurements of Balzano et al. (2009) show a similar result at their lowest shear rate, where only metastable fibrillar precursors appeared during flow, which nucleated after cessation of flow. Interestingly, at very high shear rates in the oriented FIC regime, they observed that crystalline fibrillar nuclei were already formed during flow.

Based on these results, we distinguish between subcritical nuclei, which we call precursors, and supercritical nuclei, which are henceforth simply referred to as nuclei. Details of the structure of precursors, i.e., their degree of crystallinity, the number of monomers involved, and the number of molecules to which these monomers belong, are not considered. A precursor may nucleate due to a fluctuation in its size. As shown by the examples above, flow has a severe effect on this process, which is taken into account in Sec. IV E. For detailed simulations of nucleation in flow, we refer to Graham and Olmsted (2009, 2010). In our model, the number of precursors obeys the evolution equation

$$\dot{N}_p = I_p + T \frac{\partial N_p}{\partial T} - \frac{N_p}{\tau_{pn}} - \frac{N_p}{\tau_{pd}},$$

where the dot denotes the material time derivative and $I_p$ is the precursor creation rate. The second term on the right-hand side represents athermal activation [Fisher et al. (1948)]. This is not due to fluctuations, but involves dormant precursors, which only become active (i.e., able to nucleate) when the temperature is lowered sufficiently. The third term is the nucleation rate and the fourth represents an additional process through which precursors may disappear, namely, dissolution into the disordered bulk of the melt. The parameters $\tau_{pn}$ and $\tau_{pd}$ are characteristic time scales associated with these processes.

The nucleation rate is thus related to the number of precursors according to the expression

$$\dot{N}_n = \frac{N_p}{\tau_{pn}},$$

which was introduced by Avrami (1939). However, in his theory, $N_p$ only changes due to nucleation; no new precursors are created and the existing ones do not dissolve.

D. Quiescent and flow-induced precursors

The total number of precursors consists of “quiescent” precursors, i.e., those that would have been obtained after the same temperature history but without any deformation history, and flow-induced precursors:
\[ N_p = N_{pq} + N_{pf}. \] (19)

Nuclei are divided into quiescent and flow-induced nuclei accordingly and the corresponding nucleation rates are

\[ \dot{N}_n = \dot{N}_{nq} + \dot{N}_{nf} = \frac{N_{pq}}{\tau_{pn}} + \frac{N_{pf}}{\tau_{pd}}. \] (20)

We assume that \( \dot{N}_{pf} \) is independent of \( \dot{N}_{pq} \), so that both are described by uncoupled expressions analogous to Eq. (17) and the corresponding nucleation rates in Eq. (20) are also uncoupled. In this respect, our model differs from that of Grizzuti and co-workers [Acierno et al. (2008); Coppola et al. (2001)]. They proposed an additive decomposition of the free energy difference between the phases into a quiescent term and a flow-induced term, \( \Delta G = \Delta G_q + \Delta G_f \). This was inserted into the classical nucleation theory, where \( \dot{N}_n \) is an exponential function of \( \Delta G \). Thus the quiescent and flow-induced nucleation rates are not additive. In the kinetic Monte Carlo simulations of Graham and Olmsted (2009, 2010), the quiescent nucleation rate is multiplied by a function of the molecular stretch and hence the quiescent and flow-induced nucleation rates are coupled as well.

In quiescent melts at high degrees of undercooling, \( N_{nq} \) is a unique function of the temperature [Alfonso and Ziabicki (1995); Eder and Janeschitz-Kriegl (1997); Piccarolo et al. (1992)]. In the context of our model, this means that only athermal precursors are formed (\( I_p = 0 \)) and that these are immediately nucleated (\( \tau_{pn} = 0 \)). Equations (17) and (18) can then be rewritten into the single expression \( \dot{N}_n = \dot{N}_{pq} = \frac{N_{pq}}{\tau_{pn}} \). The minimum temperature for sporadic nucleation to become dominant was estimated by Janeschitz-Kriegl to lie approximately 50 K below the equilibrium melting point for isotactic polypropylene, which corresponds to the nominal melting point of this material typically between 160 and 165 °C [Janeschitz-Kriegl (1997); Janeschitz-Kriegl et al. (1999); Janeschitz-Kriegl (2003)].

In this paper, the sporadic creation of quiescent precursors is not taken into account. This is reasonable for most processing applications and common experimental protocols, where the corresponding regime of low degrees of undercooling is passed by very rapidly. Equation (17) is then split into

\[ \dot{N}_{pq} = \frac{\partial N_{pq}}{\partial T} - \frac{N_{pq}}{\tau_{pn}} \] (21)

and

\[ \dot{N}_{pf} = I_{pf} + \frac{\partial N_{pf}}{\partial T} - \frac{N_{pf}}{\tau_{pd}}. \] (22)

In Sec. IV E, it is shown that during flow \( \tau_{pn} > 0 \). Therefore, the distinction between precursors and nuclei is retained. The second term on the right-hand side of Eq. (22) accounts for the activation of dormant flow-induced precursors, which are too small to nucleate at the actual temperature of the experiment. These add to the part of the number density distribution \( \partial N_p / \partial T \) that lies below the actual temperature and are activated upon sufficient cooling. If the model is to be used to simulate nonisothermal flow-induced crystallization, information about the distribution of flow-induced precursors must be incorporated. A recommended first investigation is to apply different short-term flows above the nominal melting temperature, cool down to different temperatures for crystallization, and measure the nucleation density by means of optical microscopy or, alterna-
tively, small-amplitude oscillatory shear rheometry [Housmans et al. (2009); Ma et al. (2010)].

E. Interference of flow with nucleation

The microscopic pictures of Hristova et al. (2004), e.g., Fig. 2, show that all spherulites became visible at approximately the same time (i.e., within a few seconds) shortly after the cessation of flow, never during flow, and that their diameters were nearly equal. The same result was reported by Stadlbauer et al. (2004) for short-term uniaxial extension of two different iPP melts. The data from Hristova et al. (2004), summarized in Table III, prove that these observations are not simply a consequence of the shear time being too short to see any spherulites appear during flow or to end up with an observable distribution of diameters. The resolution of the optical microscope was $D_{res} = 2 \mu m$. In four experiments, the diameter of the earliest spherulites, grown from precursors nucleated between the end of the cooling step at $t=0$ and $t=t_{s} - D_{res}/(2\dot{\gamma})$, would have exceeded this limit before the end of the shear period at $t=t_{s}$. With $\tau_{ps}=0$, these would include all the quiescent and a fraction of the flow-induced spherulites. The diameter $D$ that the quiescent ones would have at $t=t_{s}$ is given in the last column of Table III and the four experiments mentioned are identified by $D > D_{res}$. In three of them, the number density of flow-induced spherulites exceeded that of the quiescent spherulites by three orders of magnitude. If the creation of flow-induced precursors is indeed a sporadic process, as in our model, then a clear distribution of diameters should have been observed in these experiments and possibly in some others as well, depending on the amount of precursors created during relaxation of the stress after flow. This was not the case, as shown in Fig. 2.

Based on these results, we assume that nucleation is impeded by flow. A possible explanation is that flow makes it more difficult for folded-chain lamellae to form, since the deformed long chains, attached to a precursor, have to relax before they can fold. Consequently, during flow, the creation of precursors is enhanced but the precursors are less easily nucleated. This assumption is supported by the works of Balzano et al. (2009) on short-term shear-induced crystallization of iPP (although they observed a renewed nucleation during flow well into the regime of oriented structure formation) and by Blundell and co-workers on film drawing of poly(ethylene terephthalate) [Blundell et al. (1996, 2000); Mahendrasingam et al. (1999, 2000)], poly(lactic acid) [Mahendrasingam et al. (2005a)], and poly(ethylene terephthalate-co-isophthalate) copolymers [Mahendrasingam et al. (2005b)]. The latter authors observed that, for high strain rates, no crystallinity developed until the moment when the draw ratio became constant, i.e., when the strain rate became zero. For lower strain rates, crystallization did start during flow. The onset of the fast drawing regime was correlated with the dynamics of chain stretch in the melt: when the strain rate was higher than the inverse of the stretch relaxation time, crystallization did not start until after cessation of flow. Pointlike nucleation during flow was observed by Coccorullo et al. (2008) for very low deformation rates and long observation times.

The shear rates in the experiments of Housmans et al. (2009) were chosen such that the Weissenberg number $Wi_{R}$, based on the Rouse time for each material in Table II as determined by Eq. (2), was always greater than 1. In the experiments of Hristova et al. (2004) on iPP, using the same Rouse time, $Wi_{R} > 1$ for all shear rates except $\dot{\gamma}=2$ s$^{-1}$. Based on the Rouse time fitted to the extensional viscosity data, all experiments fall in the stretching regime, $Wi_{R} > 1$. We therefore implement a step function,
to model the effect of flow on the nucleation process. According to Eq. (23), during the flow, precursors are created but not nucleated. When the flow is switched off, these precursors, and all precursors created afterwards, immediately become nuclei. Equations (20)–(22) can then simply be rewritten as one flow-enhanced nucleation equation of the form of Eq. (16). Of course, if the flow is applied for a sufficiently long time, sporadic nucleation will eventually be observed. Otherwise no crystallinity would develop in a continuous strong flow, which contradicts experimental evidence. A more realistic model for the dependence of $\tau_{pn}$ on the shear rate (and on the temperature) should be used in that case. However, it will be shown that Eq. (23) is a suitable approximation for the experiments considered here.

F. Dissolution of precursors

After cessation of flow, according to Eq. (23), the instantaneous nucleation of precursors prevents them from dissolving. During flow, we take $\tau_{pd}\rightarrow\infty$ since the time scale of dissolution of flow-induced precursors in iPP is much longer, already above the nominal melting temperature, than the shear times used here [Alfonso and Ziaibicki (1995); Eder et al. (1990)]. The same is true for other polymers, like isotactic poly-1-butene [Azzurri and Alfonso (2005)] and isotactic polystyrene [Azzurri and Alfonso (2008)]. The majority of quiescent precursors in our materials are probably heterogeneous and therefore do not dissolve (by definition of the term dissolution in the present context).

G. Coupling between flow and precursor creation

The Rolie–Poly model [Likhtman and Graham (2003)] is used to calculate $B_e$. Its upper convected derivative is then given by

$$\nabla^\ast B_e = -\frac{1}{\lambda_d} (B_e - I) - \frac{2}{\lambda_R} \left( 1 - \frac{1}{\Lambda} \right) \left[ B_e + \beta \Lambda^2 \delta (B_e - I) \right]$$

with the stretch parameter $\Lambda$ according to Eq. (7). The last term represents convective constraint release, which is controlled by the parameters $\beta \in [0, 1]$ and $\delta$. As explained in Sec. III B, we take $\beta=0$ and therefore $\delta$ does not play a role. The subscript $M$, see Eqs. (15) and (14), will be omitted in the remainder of this paper, but it is important to keep in mind that we only use the mode with the longest relaxation time in our flow-enhanced nucleation model.

Following the physical cross-linking hypothesis [Zuidema (2000); Zuidema et al. (2001)], the reptation time $\lambda_d$ and the Rouse time $\lambda_R$ are postulated as linear functions of the number densities of flow-induced precursors and nuclei,

$$\frac{\lambda_k}{\lambda_{0k}} = 1 + a(N_{pf} + N_{nfr,R<R^*}); \quad k \in \{d,R\},$$

where $R^*$ is a critical radius, on the order of the radius of gyration of the HMW chains, which determines whether a flow-induced nucleus acts as a physical cross-link ($R<R^*$) or as a viscoelastic particle ($R\geq R^*$). In the latter case, its effect on the rheology of the two-phase system is accounted for by a suspension model [Steenbakkers and Peters (2008)]. The critical radius can be seen as an empirical parameter to account for the swallowing of chain ends by the growing nuclei. A more detailed description can be found in Section 3.5 of Steenbakkers (2009) for the local formulation of our flow-
enhanced nucleation model. In the empirical approach taken here, it turns out that experiments are fitted most accurately with \( R^*/H_{11569} = 0 \). Then in conjunction with Eq. (23), the physical cross-linking effect, Eq. (25), is present only during flow, when no nucleation occurs. This yields the smallest possible size distribution of spherulites, in accordance with the experiments.

It has been suggested that, whereas molecules have to be stretched to form threadlike precursors, increased orientation already enhances the creation of pointlike precursors under moderate flow conditions. Here the terms stretch and orientation are defined on the level of primitive path segments of chains. Stretch of these segments corresponds to orientation on the level of Kuhn steps.

Coppola et al. (2001) extended the free energy in the classical nucleation theory with a term due to orientation, which they derived from the constitutive model of Doi and Edwards (1986). Changes in the time scale of crystallization were captured quite well by the model, also for bimodal blends [Acierno et al. (2008)]. Van Meerveld et al. (2004) presented a classification scheme for FIC experiments, in which different regimes were defined, based on the Weissenberg numbers associated with orientation and stretch of the HMW tail of the melt \( (W_{id} \text{ and } W_{ir}) \), respectively. They discussed different methods to obtain the relevant relaxation times. Applying the classification scheme to a large number of experiments, they found that the number of spherulites was already increased for \( W_{id} \approx 1–10 \) while still \( W_{ir} \leq 1–10 \). This seems to indicate that flow-induced orientation is indeed sufficient to create pointlike precursors. However, according to Eq. (25) in our model, the actual Weissenberg number related to the HMW chains, involved in the creation process, can increase tremendously during flow. Classification based on initial Weissenberg numbers should therefore be done with care, especially when long flow times are considered.

We will test an orientation- and a stretch-based flow-enhanced nucleation model. In the first case, Eq. (16) is replaced by Eqs. (20)–(22) with the precursor creation rate

\[
I_{pf} = g_p J_2^{(S^d)}; \quad \text{orientation-induced creation,} \tag{26}
\]

proportional to the second invariant of the deviatoric part of the orientation tensor, Eq. (6), which is given by

\[
J_2^{(S^d)} = \frac{1}{2} S^{d, S^d}. \tag{27}
\]

In the second case, the creation rate of flow-induced precursors is written as

\[
I_{pf} = g_p (\Lambda^{m} - 1); \quad \text{stretch-induced creation,} \tag{28}
\]

i.e., a power law in terms of the stretch parameter \( \Lambda \), given by Eq. (7). Similarly, a power law dependence on \( J_2^{(S^d)} \) could be introduced in Eq. (26). However, our results will show that any model based on this orientation invariant is unable to capture the effect of flow on the nucleation density.

H. Saturation

Housmans et al. (2009) recently studied the three isotactic polypropylenes with different molecular weight distributions, listed in Table II. Small-amplitude oscillatory shear measurements after short periods of steady shearing showed the fingerprints of different FIC regimes. Upon increasing the duration of flow, \( \log(G') \) versus \( \log(t) \) curves shifted to shorter times without changing shape, indicating that the number densities of pointlike nuclei were increased but remained constant after the flow was stopped. A saturation of this enhanced nucleation was clearly observed: identical results were obtained for longer
shear times. Yet a second acceleration occurred when the flow was maintained even longer. Not only did the log($G'$) versus log($t$) curves shift to shorter times again, but their shape also changed, indicating a transition from spherulitic to oriented crystallization. These interpretations were confirmed by ex situ micrographs of the final semicrystalline morphologies. In the saturation regime, the number densities of spherulites were indeed identical. This can be considered the first unambiguous evidence of a maximum pointlike nucleation density. For a polydisperse isotactic poly-1-butene, Baert et al. (2006) also reported a plateau in the time scale of crystallization as a function of shear rate, followed by a second acceleration at high shear rates. However, they compared experiments where the same strain was applied. This means that both the shear rate and the shear time varied, which confuses interpretation. The same strain with a different combination of rate and duration of flow does not yield the same molecular deformation in the transient startup behavior nor in the steady state. Nevertheless, the acceleration following the saturation plateau was concurrent with an upturn of the birefringence during flow, related to the growth of threadlike precursors, in agreement with the work of Kumaraswamy et al. (1999). These results are further supported by the fact that, for one of their materials subjected to two different shear rates, Housmans et al. (2009) detected an upturn in the first normal stress difference during flow exactly at the times marking the transition from the saturated pointlike nucleation regime to the oriented crystallization regime.

Martins et al. (2006) suggested that saturation of flow-enhanced nucleation is the result of the melt reaching its steady state. However, the first normal stress difference data of Housmans et al. (2009) showed that, in all their FIC experiments, the steady state was reached about ten times later than the onset of the saturation plateau. This was confirmed by viscosity measurements (Housmans, personal communication).

Saturation is implemented in the present model in a phenomenological way, writing $g_p$ in Eqs. (26) and (28) as

$$g_p = \left( 1 - \frac{N_{pf} + N_{nf}}{N_{f,max}} \right) g_{0p}.$$  

(29)

The saturated number density $N_{f,max}$ is expected to be related to a critical molecular weight for pointlike precursor creation, but is determined directly from nucleation data in Sec. V.

V. RESULTS AND DISCUSSION

The orientation- and stretch-based models for flow-enhanced nucleation, using Eqs. (26) and (28) for the creation rate of flow-induced precursors, respectively, are validated by the experimental data for iPP2 at $T=135 \, ^\circ C$ from Table III. The relaxation times from Table II were used in the simulations. The results in Fig. 4 show that the increase of the nucleation density as a function of shear time cannot be described by the orientation-
TABLE III. Number densities of spherulites $N_{sph}$ and presence of oriented crystallites in iPP2 after different shear histories at $T=135\, ^\circ\mathrm{C}$ [Hristova et al. (2004)]. Measured growth rate $\dot{R}$ and expected diameter $D$ of largest spherulites at the end of flow.

<table>
<thead>
<tr>
<th>$\dot{\gamma}$ ($\mathrm{s}^{-1}$)</th>
<th>$t_s$ (s)</th>
<th>$\dot{R}$ (nm $\mathrm{s}^{-1}$)</th>
<th>$N_{sph}$ (mm$^{-3}$)</th>
<th>Orient. cryst.</th>
<th>$D=2\dot{R}t_s$ ($\mu$m)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>42</td>
<td>$6.8 \times 10^2$</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>41</td>
<td>$6.8 \times 10^2$</td>
<td>-</td>
<td>2.5</td>
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<tr>
<td>4</td>
<td>15</td>
<td>51</td>
<td>$2.4 \times 10^3$</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>60</td>
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<td>$2.5 \times 10^4$</td>
<td>+</td>
<td>4.7</td>
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</tr>
<tr>
<td>90</td>
<td>40</td>
<td>$3.5 \times 10^5$</td>
<td>+</td>
<td>7.2</td>
<td></td>
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<tr>
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<td>-</td>
<td>0.52</td>
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<tr>
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<td>49</td>
<td>$7.1 \times 10^5$</td>
<td>+</td>
<td>3.5</td>
<td></td>
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<td>3</td>
<td>43</td>
<td>$8.6 \times 10^2$</td>
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<td>30</td>
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<td>0.19</td>
</tr>
<tr>
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<td>-</td>
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<td>0.62</td>
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</tr>
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<td>3</td>
<td>38</td>
<td>$6.8 \times 10^4$</td>
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<td>0.23</td>
</tr>
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<tr>
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<td>0.19</td>
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<tr>
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<td>50</td>
<td>$8.8 \times 10^4$</td>
<td>+</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>37</td>
<td>$1.8 \times 10^5$</td>
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<td>0.30</td>
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<td>$3.0 \times 10^5$</td>
<td>+</td>
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FIG. 4. Number densities of precursors (dashed lines) and nuclei (solid lines) versus time and experimental number density of spherulites versus shear time (symbols) in iPP2 for $\dot{\gamma}=60\, \mathrm{s}^{-1}$ at $T=135\, ^\circ\mathrm{C}$, according to the orientation-induced creation model.
based model. As it turns out, even replacing the linear dependence of $I_{pf}$ on $J_2(S^2)$ in Eq. (26) by a power law does not make a noticeable difference. The reason can be deduced from Fig. 5, showing the evolution of the orientation invariant. The area under the curve, i.e., the flow-induced number density, is only mildly affected by an increase of the shear time. In Figs. 4 and 5, $S_0p_l=10^3$ mm$^{-3}$ s$^{-1}$ and $a=10^2$ mm$^3$ were used. Similar results are obtained irrespective of the cross-linking parameter $a$. Hence, mere orientation of the primitive paths of the HMW chains is insufficient for the creation of flow-induced precursors.

On the other hand, the performance of the stretch-based model is excellent. We tested different (integer) values of the power law exponent $m$ in Eq. (28). Simulations with $m=4$ are shown in Figs. 6–9. For decreasing values of this exponent, the relative amount of precursors created after flow, during relaxation of the stretch, increases. This effect is more prominent for shorter shear times and, consequently, the final number densities for different shear times at the same shear rate become less separated than observed experimentally. On the other hand, we saw no improvement in the results for $m>4$. This
fourth-order stretch dependence agrees very well, up to $\Lambda = 3.5$, with the exponential relation found by Graham and Olmsted (2009, 2010). The parameters $g_0 = 1.4 \times 10^{-3}$ mm$^{-3}$ s$^{-1}$ and $\alpha = 1.0 \times 10^3$ mm$^3$ were obtained by fitting all experiments simultaneously. $N_{f,\text{max}} = 3.1 \times 10^5$ mm$^{-3}$ was estimated from the experimental data for $\dot{\gamma} = 60$ s$^{-1}$ and used as a fixed input parameter. For $m = 4$, the fit of the model to the experimental data is essentially the same as with the analog of Eq. (16) for the precursor creation rate. This is because

$$J_2(B^d) = 9\Lambda^4 J_2(S^d)$$

and, as shown in Fig. 5, $J_2(S^d)$ hardly changes as a function of the shear time.

In the Appendix, the stretch-based model, using Eq. (28) with $m = 4$, is compared to the experiments of Housmans et al. (2009) for all three materials at $T = 138$ °C. Again the agreement with experimental data is excellent, although we had to use a different set of
model parameters for each shear rate. As before, the relaxation times from Table II were used. For the experiments of Hristova et al. (2004), we now investigate the influence of a difference in the characteristic Rouse time, estimated for the HMW fraction, on the simulation results.

Figures 10–13 show the results of simulations with the longest reptation time from Table IV, which is approximately the same as the one obtained from the spectrum of Housmans et al. (2009), and the longest Rouse time \( \lambda_{0R} = 7.7 \text{ s} \) as determined from the uniaxial extensional viscosity data and shifted to \( T = 135 \degree \text{C} \). The parameters \( g_{0p} = 2.5 \times 10^{-4} \text{ mm}^{-3} \text{ s}^{-1} \) and \( a = 4.9 \text{ mm}^3 \) were obtained, again by fitting the number densities of spherulites for all shear rates. Especially the cross-linking parameter \( a \) is very sensitive to a change in \( \lambda_{0R} \). The results, in terms of the final number densities, are similar to those

**FIG. 9.** Number densities of precursors (dashed lines) and nuclei (solid lines) versus time and experimental number density of spherulites versus shear time (symbols) in iPP2 for \( \gamma = 60 \text{ s}^{-1} \) at \( T = 135 \degree \text{C} \), according to the stretch-induced creation model with the Rouse time estimated by Eq. (2).

**FIG. 10.** Number densities of precursors (dashed lines) and nuclei (solid lines) versus time and experimental number density of spherulites versus shear time (symbols) in iPP2 for \( \gamma = 2 \text{ s}^{-1} \) and \( \gamma = 4 \text{ s}^{-1} \) at \( T = 135 \degree \text{C} \), according to the stretch-induced creation model with the Rouse time fitted to extensional viscosity data.
shown in Figs. 6–9, obtained with the longest Rouse time determined by Eq. (2); see Table II. The model parameters from both approaches are included in Table V for comparison.

The main difference occurs in the evolution of the number density of nuclei after flow. Due to Eq. (23) and the choice of the critical radius \( R^* = 0 \) in Eq. (25), the cross-linking effect vanishes at \( t = t_s \). However, for a longer Rouse time, the stretch needs more time to relax (Fig. 14) and consequently more flow-induced nuclei are formed after the flow has stopped. If \( R^* > 0 \), some flow-induced nuclei formed at times \( t > t_s \) also act as physical cross-links. The simulation results exhibit progressively worse agreement with the experimental data upon increasing \( R^* \), in terms of the number densities as well as the distribution of sizes of spherulites, which becomes very broad, contrary to microscopic observations.

FIG. 11. Number densities of precursors (dashed lines) and nuclei (solid lines) versus time and experimental number density of spherulites versus shear time (symbols) in iPP2 for \( \dot{\gamma} = 10 \) s\(^{-1}\) and \( \dot{\gamma} = 20 \) s\(^{-1}\) at \( T = 135 \) °C, according to the stretch-induced creation model with the Rouse time fitted to extensional viscosity data.

FIG. 12. Number densities of precursors (dashed lines) and nuclei (solid lines) versus time and experimental number density of spherulites versus shear time (symbols) in iPP2 for \( \dot{\gamma} = 30 \) s\(^{-1}\) and \( \dot{\gamma} = 40 \) s\(^{-1}\) at \( T = 135 \) °C, according to the stretch-induced creation model with the Rouse time fitted to extensional viscosity data.
The local flow-enhanced nucleation model, presented in Chap. 3 of Steenbakkers (2009), predicts a negligible effect of the relaxing deformation after flow on the number density of spherulites, similar to the global model used here with $R^* = 0$. In the local description, flow-induced precursors as well as nuclei are allowed to act as physical cross-links. However, after the cessation of flow, newly created flow-induced species remain in the clusters (see Fig. 1) to which the cross-linking effect is restricted, and whose volume is on the order of HMW chain dimensions. Consequently, the enhanced creation process does not lead to growth of separate spherulites. Therefore, the local flow-enhanced nucleation model does not require the use of the empirical parameter $R^*$. According to Steenbakkers (2009), it is also a viable candidate to capture the spherulitic and oriented crystallization regimes in a single theoretical FIC framework.

Another issue with the present model is that the increase of the longest reptation time and Rouse time as a function of the number density of flow-induced precursors, Eq. (25), leads to unrealistically high stretch values; the worst case is shown in Fig. 14. A rheological model with finite extensibility (Kabanemi and Hétu 2009; Stephanou et al.)

### Table IV. Old relaxation spectrum of iPP2 at $T_{ref} = 135$ °C.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$a_T$</th>
<th>$b_T$</th>
<th>$i$</th>
<th>$G_i$ ($10^4$ Pa)</th>
<th>$\lambda_{td,i}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>7.96</td>
<td>0.01</td>
</tr>
<tr>
<td>145</td>
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<td>3.998</td>
<td>0.06</td>
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<td>1.533</td>
<td>0.36</td>
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<tr>
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<td>4</td>
<td>0.344</td>
<td>2.16</td>
</tr>
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<td>5</td>
<td>0.0356</td>
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</tr>
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<tr>
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<tr>
<td>235</td>
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<td></td>
<td></td>
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<td>0.07241</td>
<td>0.91455</td>
<td>135</td>
<td>3.159</td>
<td>198.1</td>
</tr>
</tbody>
</table>

**FIG. 13.** Number densities of precursors (dashed lines) and nuclei (solid lines) versus time and experimental number density of spherulites versus shear time (symbols) in iPP2 for $\gamma = 60$ s$^{-1}$ at $T = 135$ °C, according to the stretch-induced creation model with the Rouse time fitted to extensional viscosity data.
might yield similar results in terms of number densities, while maintaining realistic stretch values. Note that an exponential dependence of the creation rate on the squared molecular stretch, inspired by Graham and Olmsted (2009, 2010), would not have improved our results. Figure 14 shows that, without the physical cross-linking effect, stretch values remain in the range of values where our power law, Eq. (28) with $m=4$, nicely fits the exponential function [Graham and Olmsted (2009)]. Moreover, from a practical point of view, it would have introduced another adjustable parameter: the quiescent nucleation rate, appearing as a prefactor, which cannot be obtained experimentally when quiescent nucleation is mainly predetermined.

VI. CONCLUSIONS

A phenomenological model for creation and nucleation of flow-enhanced precursors has been developed, based on a coupling of the characteristic reptation and Rouse times of the HMW chains with the number density of flow-induced precursors, similar to the

FIG. 14. Evolution of stretch without flow-induced precursors (solid lines) and in the simulations of Fig. 9 (dashed lines) and Fig. 13 (dash-dotted lines) for iPP2, $\dot{\gamma}=60$ s$^{-1}$ at $T=135$ °C.

FIG. 15. Number densities of precursors (dashed lines) and nuclei (solid lines) versus time and experimental number density of spherulites versus shear time (symbols) for iPP2.
The creation rate of flow-induced precursors is found to depend on the average stretch of the primitive paths of the HMW chains. Thus the coupling of relaxation with early stage structure development makes the creation of flow-induced precursors a self-enhancing process. This coupling is necessary to explain the strong effect of flow on the number density of spherulites. With only two adjustable parameters, a prefactor to the creation rate and a parameter quantifying the effect of flow-induced precursors on the HMW relaxation dynamics, excellent agreement with shear-enhanced nucleation data has been obtained for different shear rates and shear times.

In order to explain the absence of spherulites during flow as well as their narrow size distribution when they appear after cessation of flow, it must be concluded that the nucleation of precursors is impeded during flow. The fact that this is the case in the experiments considered here, with stretch-based Weissenberg numbers greater than 1, is...
in accordance with experimental observations during film drawing of different polymers [Blundell et al. (1996, 2000); Mahendrasingam et al. (1999, 2000, 2005a, 2005b)].

ACKNOWLEDGMENTS

We thank Susana Filipe and Markus Gahleitner from Borealis for the extensional viscosity measurements on iPP2.

APPENDIX: SIMULATION OF FIC EXPERIMENTS OF HOUSMANS et al. (2009)

For the three materials listed in Table II, only those experiments are considered in which the transition to oriented structure formation did not yet occur. Attempts to fit the number densities of spherulites for all shear rates with the same parameters \( g_0p \) and \( a \), as in Sec. V for the optical microscopy data of Hristova et al. (2004), were not successful. Therefore individual results for each shear rate are presented in Figs. 15 and 16. For iPP1 (Fig. 17) only one shear rate is considered because, for the other one, the saturation regime was obscured by the transition to the oriented FIC regime and only one shear time was applied before this transition [Housmans et al. (2009)]. The model parameters are summarized in Table V. The most conspicuous is \( g_0p \) for iPP1. This is very high compared to the other materials due to the lower quiescent number density, determined by means of a suspension model [Steenbakkers and Peters (2008)]. Consequently, the flow-induced number densities in the experiments on iPP1 need a stronger increase relatively to the quiescent number density (governed by \( g_0p \)) than with respect to each other (governed by \( a \)).

The results for iPP2 at \( T=135 \, ^\circ C \) from Sec. V are included for comparison. There is a big quantitative as well as qualitative difference between the parameter sets at the two temperatures. This can be understood if one notes that the number density of precursors increased much more strongly, by one decade, for \( \dot{\gamma}=30 \, s^{-1} \) and \( t_s=1 \, s \) at \( T=138 \, ^\circ C \) (Fig. 15) than for similar flow conditions at \( T=135 \, ^\circ C \) (Fig. 8) as determined by optical microscopy.

<table>
<thead>
<tr>
<th>iPP</th>
<th>( \dot{\gamma} ) (s(^{-1}))</th>
<th>( g_0p ) (mm(^{-3})s(^{-1}))</th>
<th>( a ) (mm(^3))</th>
<th>( g_0p ) (mm(^{-3})s(^{-1}))</th>
<th>( a ) (mm(^3))</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>2.0 \times 10^3</td>
<td>4.0 \times 10^{-4}</td>
<td>39</td>
<td>7.3 \times 10^{-3}</td>
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<td>15</td>
<td>23</td>
<td>2.8 \times 10^{-3}</td>
<td>28</td>
<td>7.9 \times 10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>0.7</td>
<td>6.8</td>
<td>6.0 \times 10^{-3}</td>
<td>28</td>
<td>6.0 \times 10^{-5}</td>
</tr>
<tr>
<td>5</td>
<td>28</td>
<td>10^{-5}</td>
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</table>

TABLE V. Model parameters for the three iPPs. Those at \( T=135 \, ^\circ C \) were fitted for all shear rates (Table III) at once with \( \lambda_{R}=0.29 \, s \) (top line) or \( \lambda_{R}=7.7 \, s \) (bottom line) depending on the method to estimate the Rouse time, as explained in Sec. III B.
References

FLOW-ENHANCED NUCLEATION


Struglinski, M. J., and W. W. Graessley, “Effects of polydispersity on the linear viscoelastic properties of...


