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Shear-Induced Crystallization of Isotactic Poly(1-butene)

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Summary: In the present work the kinetics of the isothermal quiescent crystallization of the isotactic Poly(1-butene) (i-PB) is analyzed by means of rheological measurements and is used as an internal reference to study the effects of the shear flow. In particular, the flow-induced crystallization of two i-PB samples with different molecular weight is investigated by step-shear experiments at the crystallization temperature, T_C, of 95°C. Indeed, with step-shear experiments the effects of the applied shear rate and shear strain on the crystallization kinetics can be separately analyzed. In all the cases the overall-crystallization rate constant, k, defined as the inverse of the half-time of crystallization ($t_{0.5}$) has been evaluated. The results show that a critical shear rate (at a constant shear strain) and a critical shear strain (at a constant shear rate) are necessary to obtain the enhancement of k. These results significantly depend on the molecular weight revealing a stronger sensitivity to flow for the higher molecular weight sample. On the contrary, in the quiescent experiments no evidence of relevant molecular weight effects is detected. The in-situ optical analysis has shown that faster growth rates and a strong enhancement of nucleation density are observed in the step-shear experiments compared to the quiescent case.

Introduction

During the processing of semi-crystalline polymers the flow-induced crystallization (FIC) phenomenon can occur affecting the overall crystallization kinetics and the morphology of the final product. The study performed by Keller *et al.* [1] on the structure induced by elongational flows in the polymeric solutions showed a sharp coil-stretch transition at a specific strain rate. The authors also emphasized that a critical strain was necessary in order to reach a steady-state extension of the polymer chain and consequently shish-kebab structures developed. Similar results have also been obtained for polymer melts subjected to elongational flows [2]. In most polymer processing operations, however, the melts undergo both elongational and shear flow. The latter has been often considered a "weak" flow but recently experimental studies have amply shown that also a shear flow field is responsible for the flow-induced crystallization phenomenon in polymer melts [3-16]. Among these, Lagasse and Maxwell [6] developed a parallel plate rheometer equipped with a polarizing microscope to follow the rapid crystallization at small strains and large supercooling on thin films, avoiding viscous

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heating effects. The analysis of the induction times clearly showed the promoting effect of the shear flow on the crystallization of polyethylene samples. A resulting fibrillar-like morphology oriented in the flow direction was observed. Melt shearing experiments were performed with different devices by different authors and row-nucleated and shish-kebabs structures have been reported [4-5,7-11,13]. Tribout *et al.*[8] showed that the nucleation density is strongly enhanced by shear and accelerates the overall kinetics of isotactic polypropylene samples. Under shear the number of nuclei increases continuously, while no large spherulites are growing, as also reported by Wolkowicz [9] on a i-Poly(1-butene) sample. Very recently these results have been confirmed by Wassner and Maier [10] on i-PP and by Bove *et al.* for Poly(1-butene) samples [11]. Continuous shear crystallization experiments have been performed by Tan and Gogos [12] on a linear Polyethylene sample and the results, analyzed in terms of rheological induction times, suggest the formation of "extended-chain nuclei".

In this work the shear-induced crystallization of isotactic Poly(1-butene) samples with different molecular weights has been studied by rheological measurements. The kinetic analysis has been made in terms of the overall-crystallization rate constant for the shear flow experiments referred to the quiescent crystallization tests at T_C=95°C. The use of the step-shear experiments has allowed us to study separately the influence of the applied shear rate and shear strain. The on-line optical observation during the crystallization process, in quiescent conditions as well as in the shear flow experiments, has been also performed and the results have been compared with the rheological ones.

Experimental

Materials

The isotactic Poly(1-butene) (i-PB) samples used in this work, the i-PB400 and the i-PB200, were supplied by *Basell* (*Louvain la Neuve*) in the form of pellets, without nucleating agents. The i-PB is a semicrystalline polymer with a melting temperature, T_m, of 126°C. The molecular weight averages as obtained from GPC measurements by *Basell* are reported in Table1 together with the tacticity as measured by NMR C^{13} .

Table 1. Molecular characteristics of the Poly(1-butene) samples.

Sample	**M_n**	**M_w**	**M_z**	**M_z/M_w**	**tacticity** (%mmmm)
i-PB400	81700	244000	505000	2.1	79.5
i-PB200	107000	525000	1370000	2.6	82.7

It is noteworthy that the two Poly(1-butene) samples used in this work are good candidates to investigate the effect of the kinetics enhancement in the flow induced crystallization due to the increase of the molecular weight. The i-PB200 is, indeed, characterized by the weight average molecular weight, M_w, and the z-average molecular weight, M_z, much higher than the corresponding ones of the i-PB400 sample. On the other hand, the ratio M_z/M_w is quite similar for both samples showing a similar molecular weight distribution, MWD, in the high molecular weight tail; i.e. in the MWD region of interest for a flow induced crystallization point of view.

The crystallization process monitored by rheological tests

The crystallization process has been monitored by means of rheological experiments. The experiments for the isothermal crystallization in quiescent conditions (***a***), as well as during a steady shear flow (***b***) and after a step shear-flow history (***c***) were performed with the rotational stress rheometer, SR5000 (*Rheometric Inc.*) in a cone-and-plate configuration (∅= 25mm, cone angle= 0.1 rad) under N_2 atmosphere. The cone-and–plate configuration guarantees a uniform shear flow field; i.e. the whole sample is subjected to a homogeneous shear rate.

a- In the case of the quiescent isothermal crystallization, the following thermo-mechanical history has been investigated:

- the annealing treatment has been realized at T_a=160°C for 10 minutes to erase any crystalline fragments that could affect the subsequent crystallization process;
- the cooling step has been performed from the annealing temperature to the crystallization temperature, T_C, with a rate of about -10°C min^{-1}. The temperature profile was recorded by a thermocouple located under the lower tool. The isothermal crystallization was investigated at T_C= 95°C for both materials.

At the start of the cooling process the evolution of the storage modulus, G', has been monitored to follow both the cooling process and the isothermal crystallization by an oscillatory test at the constant stress, σ=1000 Pa and the frequency ω=1rad/s. Indeed, the choice of the values for these two parameters is crucial in order to reduce as much as possible the disturbance during the crystallization, as discussed in detail in a previous paper [16]. The storage modulus represents, therefore, our *probe* to follow the crystallization process.

b- To investigate the influence of a shear flow on the isothermal crystallization process, ***steady shear flow*** experiments at different shear rates were performed at T_c=95°C. Also in this case the samples have been previously annealed at T= 160°C for 10 min and then cooled to the crystallization temperature with a cooling rate of about -10°C min^{-1}, as described for the quiescent crystallization. The rheological induction times, for the crystallization process under continuous shearing, $\mathbf{t_{onset}}$, were determined at the time where the viscosity abruptly increases.

c- After the results of point *(b)* have been obtained, ***step-shear flow tests*** have been performed prior to the isothermal crystallization. Indeed, in our experiments the step-shear flow was applied as soon as the crystallization temperature of 95°C was reached. Moreover, since the aim of the step-shear experiments is to evaluate the influence of the applied shear flow on both the induction time and the overall crystallization kinetics, the shearing time at each chosen $\dot{\gamma}$ has been shorter than the corresponding rheological induction time, $\mathbf{t_{onset}}$, for the crystallization determined under the steady shear flow (point b). The latter, indeed, represents the maximum shearing times ($\mathbf{t_s^{max}}$) that can be adopted without causing a dramatic change in the rheology during the shearing step. The crystallization kinetics has been monitored by the measurements of G' at T_c=95°C just after the step-shear, as described at the point (a) for the quiescent case.

The step-shear experiments have allowed us to separately investigate the effects of the applied shear rate and shear strain. In particular, at each $\dot{\gamma}$ used, the shear strain influence was analysed by varying the shearing times (t_S). In the second set of experiments the total strain applied, γ, has been fixed and the effect of the shear rate has been investigated by modifying $\dot{\gamma}$ and the shearing times values on the basis of the following equation:

$$\gamma = \dot{\gamma}\, t_S \qquad (1)$$

In all the crystallization experiments a readjustment of the geometry was performed to compensate for the thermal contraction of the tools during the cooling step.

The morphological development

The morphological study has been performed by means of a polarized light microscope (*Leika DMLP*) in combination with the CSS 450 hot stage by *Linkam Scientific Instruments, UK*. For the temperature calibration the benzoic acid (T_m=122.12°C) has been used. In the CSS450 hot stage, crystallization experiments from the melt, both in quiescent conditions as well as under a steady shear flow or after a step-shear test, can be performed. The Linkam device is equipped with parallel plate geometry; i.e. the shear rate depends on the radius. The optical observation is therefore referred to a specific radius (r =7.5 mm) at which the sample experiences a uniform shear rate. In our experiments a gap of 150μm has been used.

The structure developments during the crystallization process has been followed for the isothermal crystallization at T_c= 86 and 95°C for samples tested both in quiescent and in shear flow under N_2 atmosphere with thermo-mechanical histories as described for the rheological experiments in the previous paragraph at the points ***(a)***, ***(b)***, and ***(c)***, except for the cooling rate that in this case has been of -25°C/min. For this reason, additional rheological tests have been performed with the cooling rate of -25°C/min in a strain controlled rheometer, the ARES (*Rheometrics Inc.*) in the cone-and-plate geometry (∅= 25mm, cone angle=0.1 rad) at T_c =86 and 95°C. The temperature calibration has been performed with indium (T_m=156.6°C) using a heating rate of 0.02°C/min and observing the relaxation of an applied normal force at the melting point.

The structure development observed in the Linkam cell can be, therefore, directly related to the change in G' (in the quiescent and step-shear tests) or in η (in the steady-state tests).

Results And Discussion

a) Isothermal crystallization in quiescent conditions

In Figure 1 the evolution of G' vs. time during both the cooling (after the annealing process at T=160°C) and the isothermal crystallization at T_c =95°C is reported together with the corresponding temperature profiles for three different *quiescent* crystallization tests on the i-PB400 polymer.

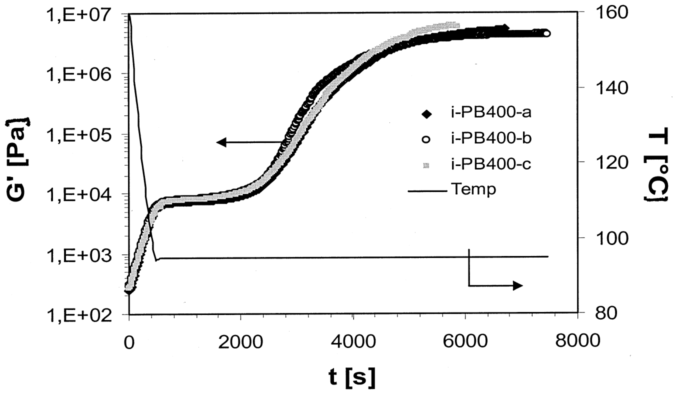

Figure 1. Reproducibility of three quiescent crystallization experiments of i-PB400 sample at T_C=95°C.

A very good reproducibility is obtained. The experiment shows that the storage modulus is very susceptible to structural changes in the polymer. After a first increase of G’, recorded during the cooling step, a plateau at T_C is observed, followed by a second growth of the modulus representative of the crystallization process. Finally, a second plateau is reached at the maximum percent of crystallinity of the material. A similar trend is also shown by the higher molecular weight sample, the i-PB200.

From the rheological experiment the “instrumental induction time” for the isothermal crystallization can be detected at the time where the storage modulus abruptly increases (the cooling time has been, of course, subtracted). Indeed, the log scale, necessary to represent the G’ results during the whole crystallization process, hides the induction time. Indeed, in the early stage of the crystallization, the G’ data would be better represented in a linear scale, as it will be shown in Figure 2.

The overall kinetics of the process has been estimated as the half- time of crystallization, $t_{0.5}$, determined at the time at which the storage modulus is half between its intial and final value. It is noteworthy that the evaluation of $t_{0.5}$ directly from the G’ data is equivalent to the evaluation of $t_{0.5}$ from the Khanna expression [17] at the transformed crystalline fraction α=0.5. The latter is, in fact, a normalized expression of G’. Indeed, so far no definitive ways to express the kinetics of the crystallization process from rheological experiments can be found in the literature. We consider satisfactorily reliable the method we have used based on the comparison between rheological and differential scanning calorimetry (DSC) data reported in a previous work literature[11] and on “in-situ” DSC experiments reported in the literature [18]. The inverse of $t_{0.5}$ represents, indeed, the overall crystallization constant, k, as defined by the Kolmogoroff-Avrami-Evans (KAE) expression, as previously reported [19]. Indeed, we have studied the quiescent crystallization kinetics in order to have the “reference” condition to estimate the effect of a shear flow on the crystallization kinetics. In this framework we consider the quiescent $t_{0.5}$ (i.e. the k_Q values) obtained from the G’ data as our “internal reference”. In the following we will, therefore, refer to the ratio between the overall-crystallization constant after the step-shear flow experiments (k_S) and the corresponding value in the quiescent case (k_Q).

The results for the structure development during the isothermal quiescent crystallization have been obtained at T_c of 86°C and 95°C. They are reported in Figures 2a and b together with the evolution of G’ (in a linear scale) relative to the first part of the isothermal crystallization process for the i-PB200 sample.

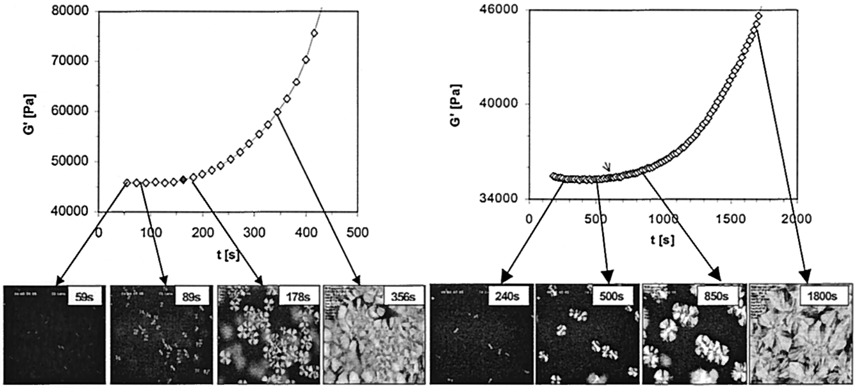

Figure 2. Comparison between rheological and optical quiescent isothermal crystallization experiments of i-PB200 sample **(a)** at T_c=86°C **(b)** at T_c=95°C (cooling rate -25°C/min).

The time scale starts at the end of the cooling step for both the rheological and the morphological tests; the times read from the figures are, then, directly related to the evolution of the crystallization in isothermal condition. The morphological investigation shows that spherulitites develop and grow until the impingement occurs; the nucleation density increases as the temperature decreases, as expected. Interesting is the comparison between the structure development and the G’ trend. Indeed, in all the cases it has been observed that spherulites appear and grow when the storage modulus is still constant at the first plateau value (representative of G' for the undercooled melt at T_c). This result is in agreement with the results reported by Bove *et al.* [11] and with the more recent ones by Pogodina *et al.*[20]. The increase in G' during time after the impingement is still related to the crystallization process itself. The whole time of the isothermal crystallization process, as monitored by G' data (for example t_{end}~9000 s for the i-PB200 at T_C=95°C) compare well, in fact, with the corresponding time as monitored by DSC (again t_{end}~9000 s for the i-PB200 at T_C=95°C).

b) Isothermal crystallization in steady-shear flow

The results of the *steady shear flow experiments* at different shear rates for the i-PB400 and the i-PB200 crystallization at T_C=95°C show that after the initial transient peak at short times, a constant value of the stress vs. time is recorded. At a certain point, that corresponds to the *"rheological induction time under steady shear flow"*, $\mathbf{t_{onset}}$, (here also defined as the maximum shearing time, $\mathbf{t_s^{max}}$), the stress begins to increase due to the crystallization process. The $\mathbf{t_s^{max}}$ values define the maximum shearing time that will be applied in the *step-shear experiments* performed on the i-PB400 sample at T_C=95°C. Indeed, in the analysis of the shear rate effects, the applied shearing times, $\mathbf{t_S}$, will be always shorter than the corresponding $\mathbf{t_s^{max}}$.

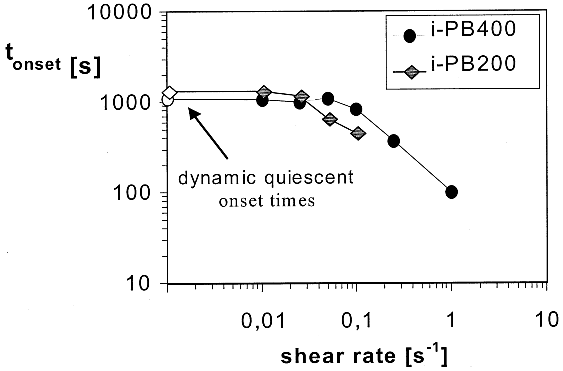

Figure 3. Effect of the shear rate on the crystallization onset time in the steady shear experiments: for i-PB400 (black full circles) and i-PB200 sample (black full rhombs). The empty symbols refer to the dynamic quiescent experiments.

In Figure 3 the induction times under steady shear flow vs. the shear rate are reported for both the i-PB200 and i-PB400 samples. As the shear rate applied decreases, the $\mathbf{t_{onset}}$ values increase until they become, for very low shear rates, independent of $\dot{\gamma}$ and representative of the induction time for the crystallization in quiescent condition. Indeed, at these very low shear rates relaxation allows recovery of the molecular deformation obtained during the shear flow. For both samples, such a value coincides with the "*rheological induction time measured by G' for the quiescent case*" (see the previous section) that is also reported in Figure 3. This event confirms the validity for G' as a probe for the crystallization process.

Once the shear flow becomes effective to enhance the crystallization, the higher molecular weight sample, the i-PB200, shows induction times shorter than the corresponding ones of the i-PB400. Therefore, the higher the molecular weight of the polymer, the stronger is the influence of the flow on the kinetics of the crystallization process, as expected. Of course, since both samples are polydisperse samples, it means that their higher molecular weight fractions are the main responsible for the discussed enhancement of the kinetics; i.e. the M_w and M_z are the most effective averages in the study of the FIC phenomenon. On the other hand, we are comparing two samples with a similar MWD in the region of the high molecular weight tail (see Table 1 for the value of M_z/M_w) and thus our results specifically refer to the molecular weight effect. More evidence of the effect of the molecular weight on the crystallization process will be shown in the next section.

c) Isothermal crystallization after step-shear flow

The step-shear tests, as mentioned in the introduction, are used in order to study the influence of a "controlled" shear flow separating the effects of the applied shear rate and shear strain. The step-shear experiments have been performed at the instant the sample reaches the crystallization temperature, T_c=95°C, after annealing and cooling from T_a=160°C. In Figure 4 the evolution of G' is reported during the cooling and the isothermal crystallization after the step-shear at different shear rates with a constant strain deformation, γ, of 60. For comparison also the quiescent case is reported.

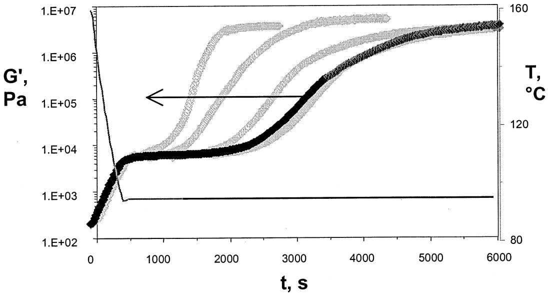

Figure 4. G' vs. time for step-shear crystallization experiments performed at T_C=95°C with different shear rates at the same strain (γ=60) for i-PB400 sample. Black curve: quiescent test; gray curves: step-shear tests with $\dot{\gamma}$ = 0.05, 0.1, 0.25, 1 s^{-1}, increasing as indicated by the arrow.

The analysis of the rheological results for both samples is reported in Figure 5 in terms of the k_S/k_Q ratio vs. the applied shear strain for different values of the shear rates.

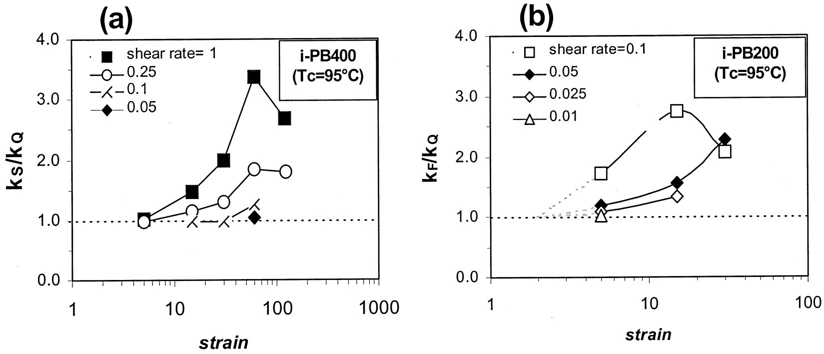

Figure 5. k_S/k_Q ratio versus shear strain at different shear rates for: i-PB400 sample **(a)** and i-PB200 sample **(b)** crystallized at T_C=95°C:

The results show that at a given shear strain, a critical value of the shear rate, $\dot{\gamma}_c$, is necessary to influence the crystallization kinetics. For example, in the case of a strain γ=30, for the i-PB400 sample (Figure 5a) the k_S/k_Q is close to one for a shear rate of 0.1s^{-1}, while it monotonically increases with increasing the shear rate. Below the $\dot{\gamma}_c$ value, the oriented chains might have enough time to relax, while beyond $\dot{\gamma}_c$ the fraction of polymer chains with higher molecular weight (and therefore long relaxation times) can preserve their orientation obtained during flow. They can form primary nuclei for the crystallization process, as also reported in literature by Somani *et al.*[13] from SAXS measurements on an i-PP polymer. This is confirmed by the data reported in Figure 5b for the higher molecular weight i-PB200. In this case at the same strain γ=30 the shear rate of 0.1s^{-1} is very effective to enhance the crystallization kinetics giving a k_S/k_Q is about 2.5.

The results in Figure 5 show that the deformation is also a critical factor for the orientation alignment of the polymer chains to form stable nuclei. Finally, a decrease of the sensitivity to flow is recorded if a high strain is applied probably due to the breaking of the crystalline structure.

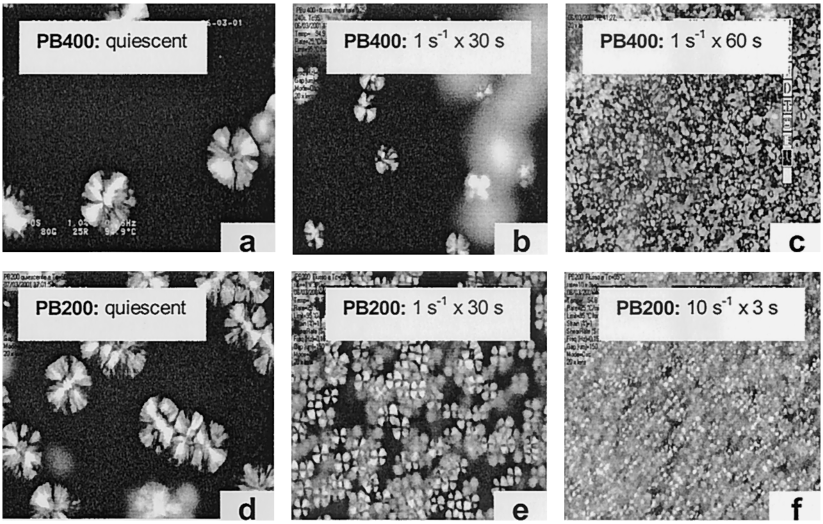

Figure 6. Morphology development during the isothermal crystallization at T_C=95°C for i-PB400 in quiescent conditions **(a)** and after step-shear (**b** and **c**) in the reported flow conditions; and for i-PB200 in quiescent conditions **(d)** and after step-shear experiments (**e** and **f**) in the reported flow conditions.

Some results of the morphological investigation are reported in Figure 6. The spherulites developed after 900 s in the isothermal crystallization at T_C=95°C in quiescent conditions for the i-PB400 (Figure 6a) and for the i-PB200 (Figure 6d) are shown. The morphologies observed after the step-shear experiments in all cases refer to 400 s (Figs. 6b,c,e,f). It is noteworthy that in all the step-shear experiments the crystals appear earlier than in the quiescent case.

For the i-PB400 sample a larger number of small spherulites is observed in the step-shear experiments compared to the quiescent case. Moreover, with increasing the applied deformation from $\gamma = 30$ to 60 (Figs. 6b and 6c) the nucleation density dramatically increases With increasing the shear rate value from 1 to 10 s^{-1} (Figs. 6e and 6f) an increase of nucleation density is also observed for the i-PB200. Moreover if we compare the experiments performed on the two i-PB samples in the same flow conditions (Figs. 6b and 6e) we can note the great influence of molecular weight on the morphology development: a higher nucleation density is obtained for the i-PB200 polymer characterized by the higher M_w and M_z values.

Conclusions

The shear-induced crystallization of two isotactic Poly(1-butene) polymers with different molecular weight has been investigated in this paper. The step-shear experiments has allowed us to separately analyze the effect of the applied shear rate and strain. The results show that a critical shear rate (at a constant shear strain) and a critical shear strain (at a constant shear rate) are necessary to obtain the enhancement of the crystallization kinetics. Both the strain rate and the level of deformation are, therefore, critical factors to form stable nuclei for the crystallization process from the flow oriented polymer chains. The evident effect of the higher molecular weight in increasing the crystallization kinetics is revealed in the rheological analysis as well as in the enhanced nucleation density.

Acknowledgments

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