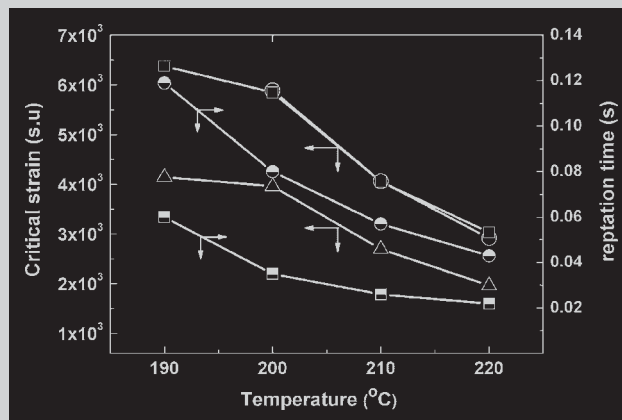


Summary: The effect of melt memory on shear-induced crystallization of a low-density polyethylene melt is evaluated with a new shear DTA instrument. A critical strain is identified as the controlling factor for saturating the crystallization. Variation of this strain with the temperature of the sheared melt is established, and the melt state responsible for saturating the crystallization is identified by shear-stress growth experiments at the steady-state. Reptation times have been evaluated in both viscoelastic nonlinear and linear regimes, and it is shown that small-angle oscillatory shear experiments cannot be used to probe effectively the effect of shear flow on the overall crystallization kinetics.



Evaluation of the Effect of Melt Memory on Shear-Induced Crystallization of Low-Density Polyethylene

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Introduction

Shear flow effects on the crystallization kinetics and morphology developed depend mainly on the shear strain level. Small amplitude oscillatory shear does not significantly affect the crystallization kinetics,^[1–3] and isotropic spherulitic morphology is generally formed under this weak shear flow. Moderate shear treatment not only strongly increases the nucleation density,^[2,4] but also leads to a certain level of chain stretch and orientation. As a result, crystallization kinetics is dramatically accelerated by several orders of magnitude and anisotropic oriented structures are generated.^[5] Under a strong shear flow, shish-kebab morphology is formed, and oriented chains (shish) serve as nuclei for the epitaxial crystal growth of chain-folded lamellae.^[5,6]

Regardless of the magnitude of the shear flow, long-lived shear-induced structures, which act as precursors of pri-

mary nuclei, are created. These structures were generated and observed in sheared i-PP melt by rapid quenching from the shearing temperature (above the nominal melting point) to room temperature,^[7] and also at 175 °C, after cessation of shear.^[8] These crystallization precursors with long-life (up to 2 h) are oriented layer-like structures, with a spacing between layers of around 430 Å.^[9] Upon application of a mild shear, long-lived smectic ordering of i-PP melt with a period around 40 Å was observed in a wide temperature range, up to 225 °C, their size decreasing with the sheared melt temperature.^[10] It is generally accepted that the survival of the oriented structures formed at a temperature well above the melting point directs the subsequent crystallization^[11] and explains the sheared melt memory effect.^[10]

From a physical point view, since the nucleation density cannot increase infinitely, and because the molecular chains in shear flows cannot be fully stretched,^[12] the size and

orientation of shear-induced oriented precursors, and therefore the crystallization kinetics, must saturate at some specific critical conditions. This saturation was reported in several works, although its controlling factor was not clearly established. The development of strongly anisotropic skin-core morphologies, and shear-induced crystallization kinetics, were found to saturate beyond a certain shearing duration.^[8] Both the shear-stress and stress-dependent strain were considered as the controlling factors. Small-angle light scattering experiments performed with a polyethylene, sheared in a Linkam shearing cell, have shown a saturation of the spherulite radius at strains of $\approx 10^3$ s.u.^[13] Analysis of shear-induced crystallization of i-PP with a shear DTA allowed the evaluation of strain $\approx 1\,800$ s.u. for saturating the crystallization.^[14] It was also reported that the anisotropy of PE and PP melts with DBS increases with shear strain, and saturates at about 10^3 s.u.^[11]

In this work, the effect of melt memory on shear-induced crystallization kinetics of a low-density polyethylene melt is studied. The key point is the evaluation of the critical conditions leading to the saturation of crystallization, which are further related to those leading to steady viscosity states in steady-shear experiments, and their temperature dependence is established. The shear-induced crystallization kinetics, after steady-shear and during oscillatory shear, is compared with quiescent crystallization and the validity of shear-induced crystallization studies in the linear viscoelastic regime is discussed.

Experimental Part

A low-density polyethylene, grade PE7324, supplied by Boralis, Portugal, was used in this work. The density and the thermodynamic melting temperature (T_m°) are $922\text{ kg}\cdot\text{m}^{-3}$ and 133.6°C , respectively. The melt flow index (MFI) was $3.3\text{ g per }10\text{ min}$ (230°C with a load of 2.16 kg , ISO 1133).

The quiescent isothermal crystallization was studied with a Perkin Elmer DSC-7, running in standard mode (temperature of the cold block at 5°C , purge-gas flow rate of $20\text{ cm}^3\cdot\text{min}^{-1}$, temperature calibration at $0.1^\circ\text{C}\cdot\text{min}^{-1}$). The sample was held at 170°C for 60 s , cooled down to the crystallization temperatures at $-60^\circ\text{C}\cdot\text{min}^{-1}$, and the data were recorded and treated following the usual procedures.^[15]

For comparison, similar experiments were also performed with a new shear DTA instrument,^[14] which was also used for analyzing the effect of the melt memory on shear-induced crystallization experiments. The shear DTA combines a capillary rheometer and a differential thermal analyzer. The capillary rheometer part allows the production of controlled shear pulses, where the controlled variables are the apparent shear rate at the channel wall and the time duration of the pulse, which may be applied to the sample at any prescribed temperature. The differential thermal analyzer part allows to monitor the sample's temperature in the capillary channel and its comparison with the temperature of a reference, as a function of time or temperature. The evaluation of the crystallization kinetics is similar to that

used for other thermal analysis instruments, by partial peak integration and normalization of the partial areas with the total peak area.

The rheological studies included oscillatory shear experiments in the viscoelastic linear regime, with a constant stress of 580 Pa , and shear-stress growth experiments, which were performed in a Physica MCR 300 (Paar Physica) and a Rheologica Stresss Tech (Rheologica Instruments AB, Sweden) rheometers, with parallel plate (25 mm diameter) and cone-and-plate (25 mm diameter plate and 2° cone angle) configurations. The parallel plate geometry was also employed for small amplitude oscillatory shear-induced isothermal crystallization experiments, which followed a similar temperature program of the quiescent crystallization experiments mentioned above. The temperature calibration of the devices and the evaluation of the average true sample temperature were described previously in detail.^[16] The temperature was recorded with an error of $\pm 1^\circ\text{C}$ for both rheometers, and the gap size was 0.7 mm for all experiments.

Results and Discussion

To evaluate the conditions leading to the saturation of crystallization kinetics with the shear DTA, a procedure similar to that used for the short-term shearing experiments^[7,8,17] was used but, instead of the procedure followed in this protocol, where intense and short shear pulses are applied at the crystallization temperature, the shear pulse was always applied at temperatures between 200 and 220°C , above the thermodynamic melting temperature of the polymer (133.6°C). The molten polymer was initially pumped from the accumulator to the capillary channel at a shear rate of 0.5 s^{-1} until the channel was filled with molten material, after which a relaxation time of 300 s was allowed to erase the previous thermal and shear history. Shear pulses with different duration and intensity were then applied, after which the material was cooled to the crystallization temperature at $-25^\circ\text{C}\cdot\text{min}^{-1}$ and the crystallization kinetics was recorded. The apparent shear rate at the wall was corrected with the Rabinowitsch correction for the non-Newtonian behavior of the material. The true shear rates were used for evaluating the strains of the melt.

Isothermal crystallization at 112°C , after a pre-shear at 220°C with different shear rates and constant shearing time, is shown in Figure 1(a). Figure 1(b) shows the crystallization at the same temperature for different shearing times and constant shear rate. As expected, the crystallization kinetics is accelerated with the shear rate and increase in shearing time. At the same average strain, of around $2\,950$ s.u., the crystallization kinetics saturates. Further increase in the shear rate, or the shearing time, does not lead to an acceleration of the process. Similarly to the results obtained for isotactic poly(propylene),^[14] the results in Figure 1 confirm the strain applied to the molten polymer as the controlling factor for saturating the crystallization from a sheared melt. As mentioned previously, strains with similar

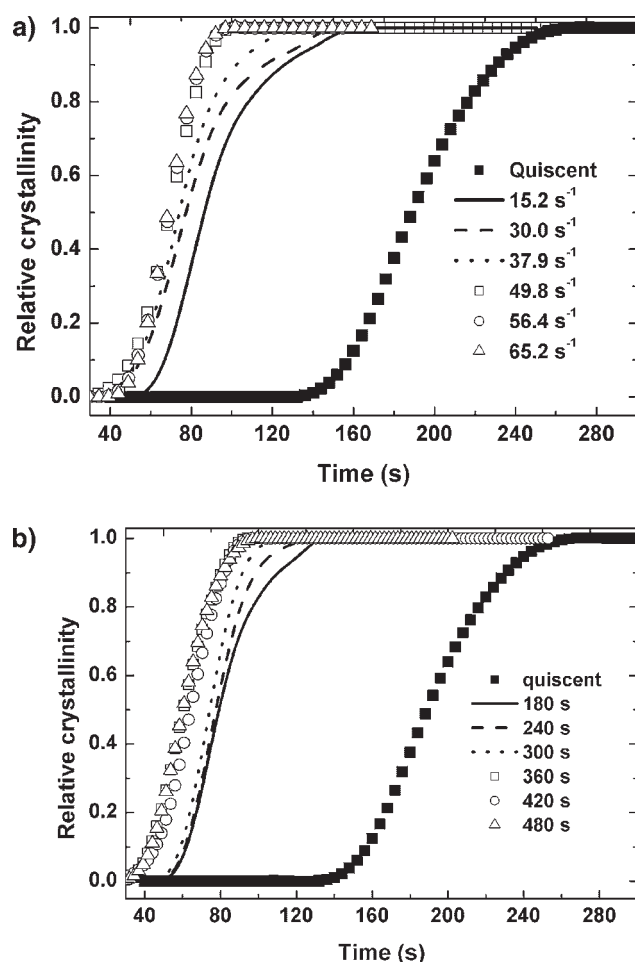


Figure 1. Isothermal crystallization at 112 °C after controlled shearing at 220 °C. (a) Constant shearing time (60 s) and increasing shear rates. The kinetics saturates at a shear rate at the wall $\dot{\gamma}_w = 49.8 \text{ s}^{-1}$, corresponding to a critical strain of 2 988 s.u. ($\pm 10\%$). (b) Constant shear rate at the wall (8.1 s^{-1}) and increasing shearing times. The critical strain is 2 916 s.u. ($\pm 10\%$).

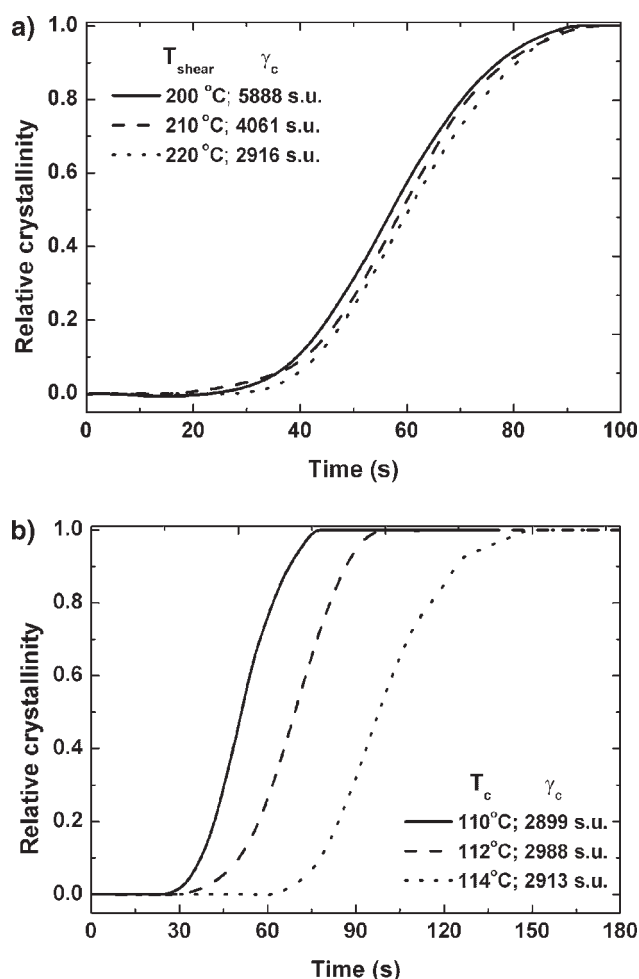


Figure 2. Effect of shearing and crystallization temperature on saturation of crystallization. (a) Constant crystallization temperature (112 °C) and shear rate (7.5 s^{-1}) for different shearing temperatures. (b) Constant shearing temperature (220 °C) and shearing time (60 s) for different crystallization temperatures.

magnitude ($\approx 10^3$ s.u.) were found to saturate the crystallization of a Ziegler–Natta-catalyzed LLDPE evaluated through rheo-optical shear and crystallization experiments,^[13] and to saturate the anisotropy of a sheared isotactic poly(propylene) melt with 1% of DBS.^[11]

While the effect of shear at different crystallization temperatures has been extensively analyzed in the literature, and also the effect of material parameters, such as the molecular weight and molecular weight distribution, the effect of melt temperature has been almost neglected. Higher shearing melt temperatures shortened the time needed for the detection of long-lived oriented structures during shear,^[8] but no linking was made to the strain applied to the melt, although this is implicit in the above results.

Figure 2 shows the effect of shearing and crystallization temperature on the saturation of crystallization kinetics. For the same crystallization temperature and higher melt

temperatures, the saturation of crystallization occurs at lower strains [Figure 2(a)], which is consistent with the lower time needed for the detection of long-lived oriented structures.^[8] These results also suggest that, at high melt temperatures, the long-lived structures have a smaller size, which, for isotactic poly(propylene), was confirmed experimentally by measurements of the smectic periodicity variation with the shearing temperature.^[10] An additional confirmation that the strain applied to the sheared melt is the controlling factor for saturating the shear-induced crystallization is provided by the results of Figure 2(b), where crystallization at different temperatures is recorded for the same temperature of the sheared melt. Under these conditions, it is shown that the saturation of crystallization occurs for the same strain of the melt.

The results of Figures 1 and 2 suggest the existence of a melt state where the melt morphology is not significantly

affected by an increase in the shear rate or the shearing time, and that, for constant shear rate, this melt state should appear at strains similar to those needed for saturating the crystallization. The existence of such a melt state can be identified in shear-stress growth experiments, where the transient shear viscosity is recorded as a function of time, while the melt is sheared with constant shear rate. Results of these experiments performed on polymer solutions^[18] and melts^[19] always show an overshoot at low strains, which is followed by a sharp decrease in viscosity and finally a steady-state at larger strains. Although the existence of this steady-state is a known and well-documented evidence, to our knowledge, no attention was given to the strains leading to this steady-state and to their variation with the temperature of the sheared melt.

By evaluating the strain at the onset of the steady-state, one can find that, at a specific temperature, the viscosity of polymer solution^[18] or melt^[19] always reaches the steady-state with the same strain, irrespective of the magnitude of the shear rate. Further, a strain of $\approx 10^3$ s.u., similar to that needed for stabilizing the anisotropy of sheared polymer melts^[11] and to saturate the crystallization from sheared melts,^[13,14] defines the onset of the steady-state in shear-stress growth experiments of a low-density polyethylene melt.^[19] However, a proof that the same strains are responsible for those effects was not given so far and it is important for identifying unequivocally the melt state responsible for the saturation of crystallization.

Figure 3 shows the shear-stress growth results obtained with parallel and cone-and-plate configurations at 220 °C. The critical strains at the onset of the steady-state are evaluated, and the measurements with the cone-plate configuration are around two-thirds of those obtained with the parallel plate configuration. The critical strain needed for viscosity stabilization, measured with the parallel plate configuration, is similar to that needed for saturating the crystallization kinetics in the shear DTA at the same shearing temperature. Furthermore, both strains have the same temperature variation (Figure 5). Since the same strain saturates the viscosity and the shear-induced crystallization, the same state of the melt is reached for the experiments performed, both with rheometer and shear DTA. These results allow the establishment of the deformation conditions to be applied to the molten polymer for saturating the crystallization and stabilizing its anisotropy.

For further insight into the melt morphology at the steady-state, small-angle oscillatory shear experiments may be performed over samples sheared up to the steady-state and compared with unsheared sample's results. The storage (G') and loss moduli (G'') variation with the oscillation frequency for unsheared and critically sheared samples at temperatures from 190 to 220 °C, which were superimposed to yield master curves at 190 °C (Figure 4), allow the evaluation of the reptation time from the intersection of G' and G'' (Figure 5). It was ensured that the

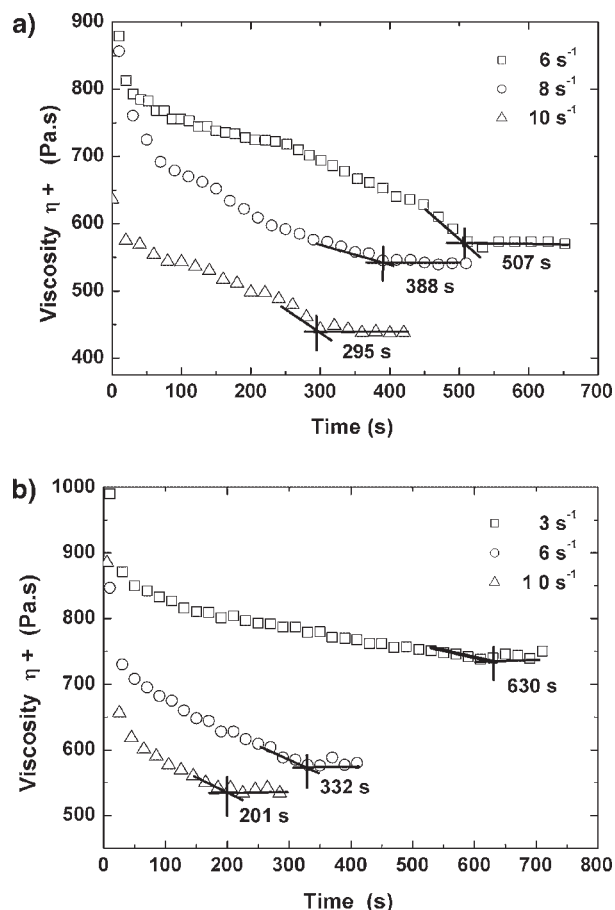


Figure 3. Transient viscosity measured at 220 °C with (a) parallel plate and (b) cone-and-plate configurations for PE7324. The solid lines show the procedure for evaluating the critical strain (indicated by the vertical lines) at the onset of the steady-state.

experiments in the two different melt states (unsheared and critically sheared) were performed in the linear viscoelastic regime, and the same constant stress was applied. The measured reptation time at the steady-state is around half that of unsheared samples. This behavior is explained by a decrease in the number of constraints at the steady-state, which is linked to an entanglement–disentanglement transition.^[20]

The above results question the utility of oscillatory shear experiments for studying shear-induced crystallization kinetics. In these experiments, the degree of conversion to the solid phase is evaluated from rheometry data by considering the storage modulus variation at time zero (or at a temperature greater than the thermodynamic melting temperature), at time t (or at the current crystallization temperature), and at time t_s (or a temperature T_s), where the liquid is fully converted to the solid phase.^[3] Figure 6 compares the crystallization kinetics under quiescent crystallization conditions (recorded with a DSC and the shear DTA), steady-shear (recorded with the shear DTA),

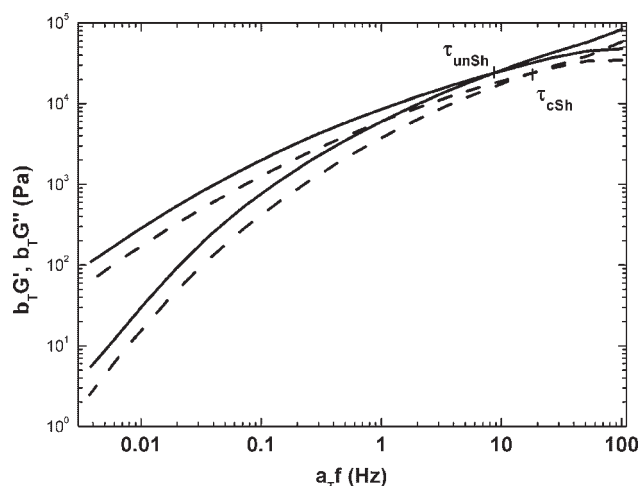


Figure 4. Reduced curves at a reference temperature of 190 °C for the variation of storage moduli (G') and loss moduli (G'') with the oscillation frequency (Hz) of unsheared (solid line) and critically sheared (dashed line) samples. The procedure used for evaluating the reptation time is indicated.

and oscillatory shear conditions for two crystallization temperatures. The difference between the quiescent crystallization recorded with the shear DTA and DSC is ascribed to different sample thermal environments and also to the effect that different metal surfaces have on the development of primary nuclei. The small amplitude oscillatory shear crystallization kinetics (strain of 3% at the beginning and around 0.1% at the end) is comparable with the quiescent crystallization, because the melt was subjected to small shear deformations that can only lead to a slight increase in nucleation density. After a steady-shear flow, the crystallization kinetics is accelerated due to the same effect, and an

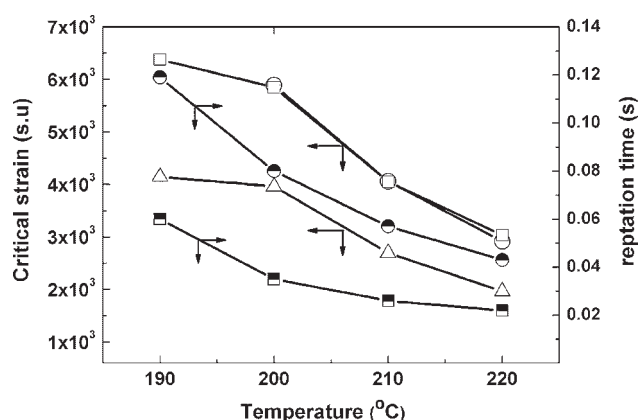


Figure 5. Temperature variation of the critical strain and reptation time. The critical strain measured with shear DTA (open circles), at the onset of the steady-state in shear-stress growth experiments with parallel plate (open squares) and cone-and-plate configurations (open triangles) is plotted as a function of the sheared melt temperature. The reptation time of unsheared (half-filled circles) and critically sheared samples (half-filled squares) show the same temperature variation as the critical strain.

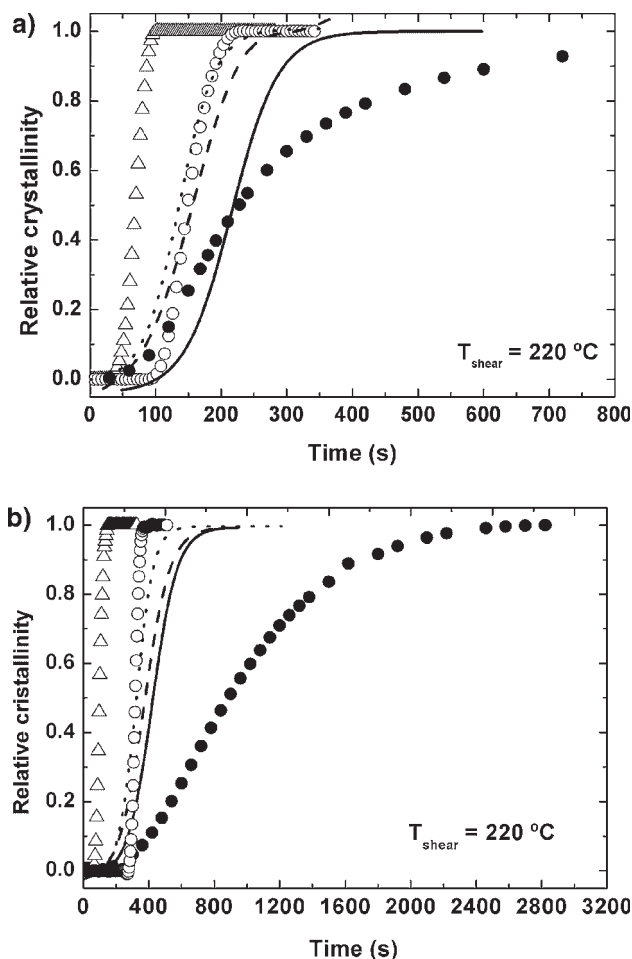


Figure 6. Isothermal crystallization recorded with a DSC, shear DTA, and parallel plate rheometer at (a) 112 °C and (b) 114 °C. The solid lines, dashed lines, and dotted lines represent the results obtained in a rheometer at frequencies of 0.1, 1, and 10 Hz, respectively. For comparison, the quiescent crystallization in a DSC (full circles) and shear DTA (open circles) is shown along with saturation of crystallization at a constant shearing time (60 s) and shear rates at the wall of 49.8 s⁻¹ (a) and 48.6 s⁻¹ (b).

additional acceleration may be observed if the supercooled melt is further sheared. Since the state of the melt probed by small amplitude oscillatory shear experiments, in a viscoelastic linear regime, is different from the one existing at steady-shear conditions, and also because of the different reptation times in the two regimes, it is concluded that the oscillatory shear experiments for studying the shear-induced crystallization kinetics are useless.

Conclusion

To our knowledge, this is the first work where the effect of different shearing melt temperatures on shear-induced crystallization has been analyzed. Particularly, it is shown

that crystallization at different temperatures from the same sheared melt temperature saturates at a constant strain, which is independent of the crystallization temperature. This result allowed us to identify the strain as the controlling factor for saturating the crystallization from a sheared melt. This critical strain may be defined as the minimum value of strain for aligning the maximum number of chain segments with the flow direction. Surprisingly, this same critical strain is required for defining a steady-state in steady-shear. The melt state responsible for saturating the memory effect of a shear flow, imposed at a temperature larger than the thermodynamic melting temperature, on the crystallization kinetics was therefore clearly identified for the first time. Also, for the first time, the temperature variation of the critical strain is established. It decreases exponentially with the sheared melt temperature. Although the time needed for the generation of shear-induced precursor structures^[8] and the smectic periodicity^[10] also decrease with the melt temperature, the physical explanation for the temperature variation of the critical strain is all but simple. It implies a precise understanding of the melt morphology at the steady-state, where shear-induced precursor structures coexist with a dynamic melt. The answer to these points involves the comprehension of the molecular mechanisms behind the formation of shear-induced precursors, which implies testing the basic assumptions of current flow models.

At the steady-state, the reptation time is smaller, and this is due to a massive loss of entanglements, which was assigned to an entanglement–disentanglement transition. However, the steady-state in steady-shear is not a disentangled state, and the ratio between the reptation time of critically sheared and unsheared samples may give us an indication of the number of entanglements at the steady-state, and therefore, of the entanglements lost during the transition. Their precise evaluation, however, requires more careful and detailed studies, and branched polymers, such as the one used in this work, are not the most suitable for this evaluation.

As a result of the different rheological behavior shown by unsheared and critically sheared samples, one is led to conclude that oscillatory shear experiments, which are always performed in the viscoelastic linear regime, cannot be used for

studying the shear-induced crystallization in steady-shear, where the flow behavior is viscoelastic nonlinear.

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