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Lifetime of Shear-Induced Crystal Nucleation Precursors

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ABSTRACT: The relaxation process of shear-induced crystal nucleation precursors has been investigated in a temperature range slightly above the melting point using a series of commercial grade isotactic poly(1-butene)s with different molecular weights. Development of transcrystalline morphology from the surface of a fiber pulled through the molten polymer is ascribed to high concentration of ordered clusters promoted by the alignment of chain segments under the high-intensity shear flow at the fiber−melt interface. Sheared melts isothermally crystallized immediately after cessation of flow exhibit a well-pronounced cylindritic morphology, characterized by closely spaced fibrillar branches; on the other hand, prolonged relaxation in the molten state before crystallization leads to classical spherulitic morphology. The lifetime of shear-induced nucleation precursors, t^*, has been associated with the complete disappearance of the transcrystalline morphology. It has been found that systems composed of short chains relax much faster than those containing a large fraction of high molecular weight species. When relaxed slightly above the melting point of the tetragonal crystal modification the highest molecular weight samples keep memory of flow-induced structuring during several hours. Temperature has a dominant role on the kinetics of reequilibration of sheared samples: experimental data of t^* obtained in wide range of "relaxation" temperatures can be fitted by an Arrhenius-type equation with an apparent activation energy of around 700 kJ/mol. Results can be justified by considering a network of aligned and ordered polymolecular clusters, originated under the high-intensity shear flow field at the solid−melt interface, whose relaxation involves large scale restructuring.

Introduction

Crystallization kinetics and textural features of crystallizable materials are often sensitive to the flow history experienced prior to and during the progress of the phase transition. In view of their impact on processing and properties, these effects must be carefully considered when dealing with polymeric materials; in fact, because of the soft nature of the macromolecular constituents, segmental orientation and chain conformation are easily perturbed already at the low stress levels associated with melt flow. The relevance of processing conditions on polymer crystallization has been known for a long time; however, molecular understanding has been for many years rather elusive. Significant progresses have been made in the past decade thanks to ingenious experiments[1−11] coupled with the availability of sophisticated instrumentation[12−16] and powerful molecular modeling.[17−20]

Experimental results strongly suggest that, under elongational or shear flow, the initial stage of melt crystallization is the formation of bundles of aligned chain segments in a quasi-crystallographic register. The residual fraction of these unstable aggregates that resists relaxation and is preserved during cooling acts as crystallization nuclei from which development of folded chain lamellae takes place.[1,2,13−15,22,23] For example, in a thorough characterization of the shear-induced crystallization behavior of a high molecular weight isotactic polypropylene, Isayev et al.[2] were able to establish that the higher is the temperature the greater must be the shear rate to develop an oriented skin layer. They also evaluated the temperature dependence of the relaxation time of nucleation precursors from the decrease of the thickness of the birefringent skin layer as a function of rest time after flow and, in agreement with Janeschitz-Kriegl and co-workers,[1] an apparent activation energy of around 200 kJ/mol was estimated for the processes underlying disappearance of flow-induced oriented structures.

Observation of long-living metastable oriented structures in crystallizable polymer melts submitted to flow at high temperatures has been recently reported by several researchers.[2,11−14,16,24−27] The first direct experimental evidence for their existence was obtained by Chai et al. in their rheo-Raman investigation of sheared HDPE.[25] These experiments suggested that flow promotes the formation of all-trans sequences which, just above the melting temperature, can survive for several hours after the cessation of flow. More recently, in-situ and ex-situ investigations of flow-induced crystallization by means of rheooptical methods[16,24] and small- and wide-angle X-ray scattering[11,13,15,24,26−30] confirmed that these structured aggregates of oriented chain segments persist for long time after interruption of flow also at temperatures higher than the nominal melting point of the polymer.

The nature of these clusters, usually referred to as crystal nucleation precursors, is currently under investigation. Somani et al.[26] argued that, in isotactic polypropylene, they are metastable noncrystalline aggregates of sheared macromolecules, generated through assembling of bundles of oriented chain segments and characterized by a layerlike superstructure with an average spacing between layers around 40 nm, as indicated by the appearance of a meridional maximum in the SAXS patterns. On the other hand, the in-situ X-ray scattering experiments of Li and De Jeu[27−29] suggest that flow promotes an initial development of smectic domains, with periodicity of about 4 nm, that are able to act as nucleation sites onto which folded chain crystals grow epitaxially at later stages. By in-situ rheooptical experiments combined with synchrotron SAXS−WAXS X-ray

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diffraction, Kumaraswami et al.[16,24] have shown that the ordered precursors appear at times that decrease on decreasing temperature. Accordingly, they suggest a nucleation process through a nonclassical pathway in which formation of nuclei does not require an activated process.[24]

The structural and morphological evolution of nucleation precursors is not a peculiarity of the widely investigated polypropylene; it was also observed by simultaneous small- and wide-angle X-ray microdiffraction in isotactic polystyrene close to the interface of a glass fiber pulled through a thin layer of the molten polymer.[30] Experimental results provided evidence for the development, even above the quiescent melting temperature, of a small, but detectable, amount of oriented domains in which chain segments are packed in a crystalline register and whose concentration, dimensions, and orientation are strongly dependent on shear conditions (flow field intensity and temperature).

The aforementioned experimental evidences of long-living flow-induced nucleation precursors and of a crystal nucleation pathway that does not require to overcome an activation energy barrier have been qualitatively forecast and discussed in a simple theoretical model by Ziabicki and Alfonso.[31] Above the quiescent melting temperature of the crystals, this model postulates the existence of unstable ordered nanodomains (clusters) whose size and orientation distributions are altered when a flow field acts on the system and are strictly related to intensity of flow, flow temperature, and molecular weight of constituent chains.[13,32] Being unstable, these entities tend to disappear when the flow is stopped; however, the larger and better oriented clusters surviving relaxation behave as predetermined *athermal* nuclei on which crystal growth proceeds as soon as the system is cooled below the melting temperature.[6,33−35]

In this work we are not concerned with the type of order characterizing the flow-induced precursors; we rather focus our attention on their lifetime in the quiescent melt after cessation of flow as a function of temperature and average molecular length. The sensitive and straightforward marker of transcrystalline (cylindritic) morphology has been adopted to reveal residual memory of previous flow history in terms of concentration of nucleation precursors.[36−40] This approach was previously successfully tested by one of us on POE and PP,[41] and it was proved to provide reproducible data for the evaluation of the temperature dependence of the minimum time a sheared melt must be held in quiescent conditions to attain complete reequilibration of the system. Results obtained on a series of isotactic poly(1-butene) samples differing in their molar mass characteristics suggest that the relaxation mechanism leading to the unperturbed state involves large scale structural reorganization.

Experimental Section

Materials and Techniques. The semicrystalline polymers used in this investigation were a series of commercial-grade isotactic poly(1-butene)s (*i*-PBu-1) kindly provided by Basell Polyolefins. The molecular characteristics of all samples were also provided and are shown in Table 1. This series of i-PBu-1 samples has very similar isotacticity index and different molecular weights, covering a range of around 1 order of magnitude in M_w. Films, about 100 μm thick, were prepared from as-received pellets by compression-molding at 180 °C for 5 min in a Carver press, followed by quenching in cold water.

Table 1. Molar Mass Characteristics of PBu-1 Samples

sample code	M_n, 10^{-3} g/mol	M_w, 10^{-3} g/mol	M_w/M_n
BR200	125	850	6.8
PBu 0200	105	398	3.7
PBu 0300	64	295	4.6
PBu 0400	54	177	3.2
PBu 0800	37	116	3.1

A single coated glass fiber with diameter of 17 ± 1 μm was sandwiched between two thin polymer films, and the ensemble was confined between two microscope cover-glasses. The high-intensity shear flow field at the fiber−melt interface was imposed by means of a slight translation of the fiber along its axis as previously described.[41,42] Optical microscopy observations were performed by means of a polarizing optical microscope Polyvar Pol using an objective lens with magnification 10×. The instrument was connected to a photocamera, and three Mettler FP 82 hot stages were used to keep under control the temperature during the various stages of the whole thermomechanical treatment described in the next paragraph. A homemade fiber pulling device, enabling us to pull the fiber at constant linear velocity in the range between 0 and 14 mm/s over a distance up to 10 mm, was used to drag the fiber through the thin layer of molten polymer.

Procedure of Fiber Pulling. The as-prepared samples were first held at 180 °C for 5 min to erase the memory of the pristine morphology and of the mechanical history applied during the sandwich preparation. Afterward, samples were submitted to the thermomechanical history schematized in Figure 1. The experiment can be divided into three consecutive steps.

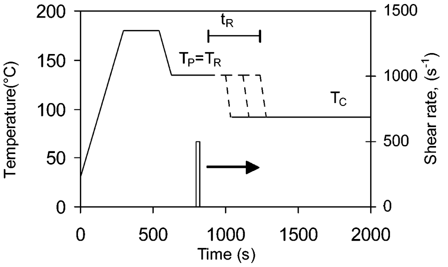

Figure 1. Scheme of the applied thermomechanical history.

Application of Flow. The relaxed sandwich of molten polymer was quickly placed into a hot stage already set at a suitable pulling temperature, T_P, that was always higher than the melting temperature of the tetragonal modification of *i*-PBu-1, the crystal form that is expected to develop under the adopted experimental conditions.[43] Typically, temperatures in the range between 130 and 150 °C were used. The sample was kept at T_P for 3 min before the fiber was pulled through the molten polymer. The pulling rate and the pulling distance were 5 mm/s and 5 mm, respectively. We remark here that the results were rather insensitive both to the extent of fiber displacement and to the rate of pulling; experiments in which the fiber was manually pulled by different operators always gave results differing for less than 10% from those collected by using the automatic device.

According to Monasse,[39] the shear rate at a distance r from the fiber axis is given by

$$\dot{\gamma}(r) = \frac{1-n}{n}\frac{1}{r^{1/n}}\left[\frac{1}{r_f^{\,1-1/n} - R^{1-1/n}}\right]V_f \qquad (1)$$

where n is the exponent of the rheological power law, r_f is the radius of the fiber (8.5 μm), R is the half-thickness of the polymer film (100 μm), r is the distance from the fiber axis, and V_f represents the pulling rate. By considering $n = 0.35$, as determined from rheological measurements,[44] under the adopted flow conditions the shear rate at the fiber surface attains values of the order of several hundred s^{-1}.

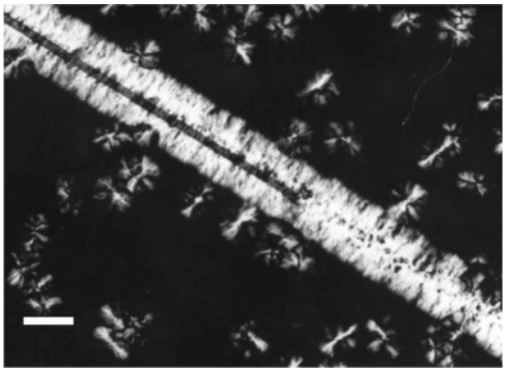

Figure 2. Example of cylindritic morphology around a pulled glass fiber in a matrix of *i*-PBu 0800, $M_w = 116\ 000$ g/mol. $T_P = T_R = 122.5$ °C, $t_R = 10$ s, $T_c = 90$ °C. The white bar corresponds to 100 μm. The transcrystalline morphology in the wake of the fiber demonstrates that flow is the only responsible for the high nucleation density.

*Relaxation***.** After pulling, the sample was held quiescent for a time, t_R, in the same hot stage or in second one, at a relaxation temperature, T_R, that, to avoid competition with crystallization, was always higher than the actual melting temperature of crystals.

Isothermal Quiescent Crystallization. After time t_R was elapsed, the sandwich was finally crystallized into a third hot stage set at a constant temperature, T_c, usually at 90 °C, at which the development of morphology was observed and documented.

Evaluation of the Persistence of Flow Memory. As will be explained in detail in the next section, morphology is an exceptionally sensitive marker of any residual perturbation of the molten state. Even when all scattering, diffraction, or spectroscopic techniques fail in recognizing faint levels of segmental orientation and molecular deformation, the nucleation density and the growth morphology are affected to a substantial extent.[11] The presence of cylindritic morphology, or of high nucleation density, all around the pulled fiber has been adopted in our experiments as an indicator of the not fully attained reequilibration in the sheared melt. A trial and error procedure has been applied to evaluate the critical holding time needed to completely erase the memory of the applied flow in the quiescent melt, t^*. We identify t^* with the mean value of two times: the maximum holding time at T_R at which, upon cooling to T_c, transcrystallinity or high linear nucleation density is still observed around the fiber and the minimum time at which spherulitic morphology with uniform size is detected over the whole sample. For each sample, the experiments were feasible in a range of relaxation temperatures of 10−15 °C; this range shifts upward in the temperatures scale on increasing the molar mass of the sample.

Results and Discussion

Morphological Observation. As an example, Figure 2 shows the morphology observed with the lowest average molar mass sample sheared at 122.5 °C and relaxed at the same temperature for 10 s before being quenched to 90 °C, where it was held to crystallize for 10 min. According to results of similar experiments,[36−41] a very high nucleation density due to the shear flow at the fiber−matrix interface is responsible for the development of the cylindritic morphology, often referred to as transcrystallinity. The presence of transcrystallinity also in the wake of the fiber, in the right part of the micrograph, clearly indicates that the development of this morphology is due to row nucleation phenomena originated by the molecular alignment produced by flow and not by an intrinsic nucleating effect of the fiber surface in contact with polymer, as suggested by other authors for different substrates.[45,46] Far from the fiber, in the regions not perturbed by flow, only spherulites are detected. Their radius strictly matches the thickness of the transcrystalline layer; this indicates that in our experiments, in which crystals develop in quiescent conditions, the linear growth rate is not substantially affected by previous flow history. Therefore, the well-documented increase in the flow-induced overall crystallization rate should mainly be attributed to the large enhancement of nucleation density. We remark here that this experimental evidence does not contradict the results of Duplay et al.,[9,10] who have shown that, under continuous flow, also growth rate can be increased up to a factor of around 5.

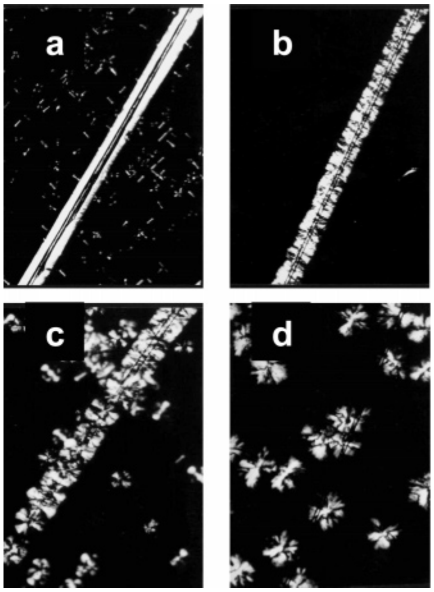

Figure 3. Examples of morphological evolution in *i*-PBu 0200 with the holding time in the melt after shearing. All samples were sheared and relaxed at $T_P = T_R = 132.5$ °C and isothermally crystallized at $T_c = 90$ °C. (a) t_R 6 s, (b) t_R 60 s c) t_R 420 s, (d) t_R 690 s.

During the pulling stage, a thin birefringent zone can be observed around the fiber. In agreement with what was already noted by Eder and Janeschitz-Kriegl.[4,47,48] and by Isayev et al.,[2] the birefringence quickly vanishes after cessation of flow while the effect of flow on nucleation density is preserved for a much longer time. The very fast disappearance of flow birefringence can be attributed to segmental dynamics leading to randomization of noncrystalline short sequences of aligned bonds; on the other hand, the long persistence of flow memory on nucleation density suggests presence of mutually connected pseudo-ordered nanodomains constituted by sequences of segments belonging to different macromolecules whose destruction needs large scale motions.

Figure 3 shows a series of micrographs taken at the crystallization temperature of 90 °C and illustrating the progress of decay in surface nucleation density around the fiber. Specimens of PB0200 were submitted to exactly the same thermomechanical history but the holding time in quiescent conditions. All of them were sheared and held to relax at 132.5 °C before quiescent isothermal crystallization at 90 °C. The sequence of micrographs demonstrates that the nucleation precursors gradually disappear upon holding the system above the melting temperature in quiescent conditions. In Figure 3a, corresponding to a specimen relaxed only few seconds ($t_r < 10$ s), cylindritic morphology characterized

Table 2. Critical Holding Times, t^* (in s), for Disappearance of Transcrystalline Morphology

	M_w, $\times 10^{-3}$				
T_R, °C	850 (BR200)	398 (PBu0200)	295 (PBu0300)	177 (PBu0400)	116 (PBu0800)
142.5	15−30	5−10			
141.5	60−90	10−15			
140.0	200−250	15−20			
137.5	900−1800	45−50	3−5		
135.0	1250−2100	110−120	25−30	3−5	
132.5	5400−8100	430−460	80−100	10−15	
130.0	55000−70000	1700−1800	330−400	20−25	
128.5			1500−2100		
127.5		16200−23600	2400−3000	50−60	
125.0			4200−5400	105−120	4−6
122.5				1800−2400	15−22
120.0				28000−30000	270−300
117.5					450−480
115.0					3000−4500

by closely spaced branches departing from the fiber surface is clearly evident. Samples crystallized after 60 and 420 s of relaxation at 132.5 °C are shown in parts b and c of Figure 3, respectively. The linear density of branches in the transcrystalline layer is evidently lower in the sample held quiescent in the melt for 1 min than in the one relaxed only during few seconds. After seven minutes of relaxation (Figure 3c), most of the flow-induced nucleation precursors have disappeared, and the resulting morphology is characterized by a series of embryonic spherulites preferentially nucleated onto the fiber. This weak memory of previous flow is completely lost in the specimen relaxed for more than 10 min. In fact, the spherulites in Figure 3d are evenly distributed over the whole field of view, with no trace of preferential nucleation close to the fiber. This is a further proof that, in itself, glass surface is ineffective in the heterogeneous nucleation of PBu-1 crystals.

The various morphologies obtained on holding the sheared system to relax for different times before crystallization imply that the shear-induced nucleation precursors gradually disappear. The holding time at which spherulites with uniform nucleation density are observed corresponds to the time needed to reduce the local concentration of shear-induced nuclei to a level indistinguishable from the natural one of the polymer in quiescent conditions. The progressive depletion of nucleation precursors during prolonged thermal treatment at temperatures above the melting point is a direct consequence of the existence of structured clusters generated by the flow field even at temperatures above the melting point of the crystals. This issue has been theoretically discussed and experimentally proved in the case of quiescent crystallization of i-PP.[49,50] The theory has recently been extended to molten oriented systems by simultaneously taking into account the distribution functions of cluster's size and orientation.[31] To a first approximation, it is expected that randomization of orientation and detachment of elements from the clusters leads to an exponential decay in the concentration of flow-induced athermal nuclei.

Dependence of t^* on Relaxation Temperature and Weight-Average Molar Mass. We now address ourselves to the main issue of our experiments: the lifetime dependence of shear-induced nucleation precursors on temperature and chain length. The trial and error procedure previously described enabled us to determine the survival time of the precursors in a temperature range of about 10−15 °C for each PBu-1 sample. The intrinsic limit of our experimental approach is related to the limited efficiency of the temperature jump from T_R to T_c that makes impossible to investigate conditions in which the relaxation processes completes in less than few seconds. On the other hand, we remark again that, despite its simplicity, our approach has no rivals in terms of sensitivity, being semicrystalline morphology the most powerful indicator of melt perturbations.

The obtained results are reported in Table 2. At each temperature, two values of time are included for all samples with different weight-average molecular mass. The first one corresponds to the maximum holding time in quiescent conditions after which around the sheared fiber the nucleation density is appreciably larger that in the unperturbed regions far from the fiber (vanishing transcrystalline morphology). Instead, the second value corresponds to the minimum holding time after which only spherulites with uniform size distribution are observed in the whole sample. The two reported time values thus provide the accuracy with which the estimation of precursors' lifetime has been obtained. In principle, this representation is analogous to the one adopted by Isayev et al. to describe the conditions for existence of shear-induced crystallization layer in stopped-flow extrusion experiments.[2]

The data in Table 2 clearly indicate that the lifetime of nucleation precursors is a very sensitive function of both relaxation temperature and molecular size of constituent chains. For example, in the sample with the highest molecular weight, the time required to erase the memory of flow on morphology development increases from around 20 s at 142.5 °C to more than 15 h at 130.0 °C. On the average, the critical times increase of around 3 orders of magnitude when the relaxation temperature is decreased of 10 °C. The strong effect of chain length can be appreciated by comparing the critical times at T_R = 130 °C: several hours are needed to attain complete relaxation with the highest molecular weight sample, while less than one second is the extrapolated critical time for the sample with the lowest value of M_w. It should be observed that slightly above the melting temperature the relaxation processes underlying recovery from the sheared state proceeds very slowly, on a time scale that is much longer than reptation times. In their model of flow-induced crystallization memory, Ziabicki and Alfonso justify such long times by considering a complex two-step relaxation process.[31] The final equilibrium state is attained through fast relaxation of dangling sequences of amorphous chain segments, evidenced by the fast disappearance of birefringence, followed by the slow relaxation of crystal nucleation precursors. To this second process contribute random-

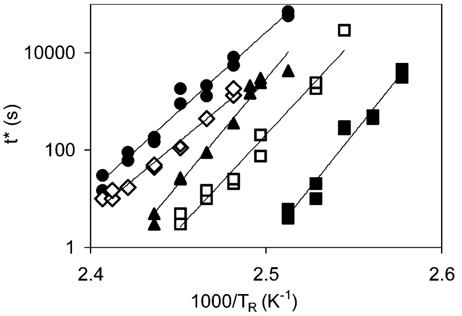

Figure 4. Critical holding times as a function of reciprocal relaxation temperature for samples with different weight-average molar mass: M_w 850 000 (●), M_w 398 000 (◊), M_w 295 000 (▲), M_w 177 000 (□), M_w 116 000 (■).

ization of orientation of the initially aligned clusters, through slow rotation of the aggregates in the viscous medium of amorphous segments, and detachment of elements from the cluster's surface.

The data of Table 2 are plotted in Figure 4 as a function of the reciprocal absolute temperature of relaxation. A family of parallel straight lines, shifted upward on increasing molecular weight, is obtained in this Arrhenius plot; independent of the length of the constituent chains, the value of 720 ± 50 kJ/mol is estimated for the apparent activation energy of the rate-determining step in the complex processes underlying disappearance of flow-induced structures. This value is substantially higher than the one found by Janeschitz-Kriegl et al.,[1] by Isayev and collaborators,[2] and by one of us for the decay of nucleation precursors structures in sheared[41] and quiescent[50] polypropylenes.

The large difference in the apparent activation energy between isotactic polypropylene and poly(1-butene) indicates that the decay of nucleation precursors is related to structural and morphological features of the flow-induced ordered domains rather than to chain mobility in the amorphous matrix. Furthermore, the very high sensitivity of the lifetime of nucleation precursors to relaxation temperature and the evidence that the flow-induced structures can persist in a time scale that is incommensurate with the segmental or molecular dynamics suggest that they consist in polymolecular bundles of locally aligned chains segments in which a quasi-crystalline order is attained. If one further considers that a single chain can simultaneously be involved in the formation of a few clusters, the complete macromolecular recoiling requires disengagement of all segments from the precursors, this being possible only through "melting" of individual cluster. This rough picture also explains why longer times are needed to erase flow memory from systems containing high molecular weight species: the longer is the chain, the larger is the number of clusters to which it contributes.

An isothermal section of the plot in Figure 4 allows one to evaluate the molecular weight dependence of the lifetime of the nucleation precursors. To this aim, we obtained the *t** values for the different polymer grades from the intercept of the straight lines with a vertical line drawn at 130 °C, in the middle of the temperature range in which the experiments were performed. The results are plotted in the log−log plot of Figure 5. If one neglects the sample with the lowest molecular weight, for which the *t** value at 130 °C was obtained by extrapolation and can be severely underestimated, the slope of the best line fitting the data is 3.4. The coincidence of this value with the scaling law of Newtonian viscosity with molecular weight is surprising; however, since we have used commercial grade polymers, characterized by a rather wide molecular weight distribution, this coincidence might be fortuitous. In fact, the important role of the high molecular weight tail in the distribution on phenomena related to flow induced crystallization has been well established,[5,15] and it has been confirmed by Hsiao et al. in their recent examination of the shear-induced formation of crystallization precursors in diluted blends of an high molecular weight polyethylene homopolymer in low molecular weight polyethylene copolymers.[51]

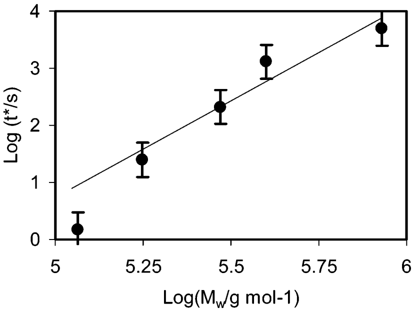

Figure 5. Dependence of the lifetime of flow-induced nucleation precursors at 130 °C on weight-average molar mass.

Conclusions

The lifetime of shear-induced nucleation precursors has been qualitatively and quantitatively investigated using transcrystallinity as morphological marker for residual perturbation in the crystallizing system. The information acquired on flow memory effects through this simple and inexpensive experimental approach corroborate the emerging evidence that flow produces ordered nanodomains that can linger in the superheated melt for long times after cessation of flow.

The data obtained with a series of isotactic poly(1-butene) samples reveal that, depending on molecular weight and temperature, the lifetime of the flow-induced nucleation precursors can be of the order of several hours. The temperature dependence of the survival time of the flow-induced nucleation precursors is described by an Arrhenius-type equation with an apparent activation energy of around 180 kcal/mol, independent of the average molecular weight of the polymer. On the other hand, the longer are the chains, the larger is the time needed to fully erase from the system the ordered structures generated under flow.

These results are consistent with a model of flow-induced structures in which macromolecular chains are engaged in local networks of aligned and ordered clusters, whose sizes are independent of weight-average molar mass and whose number is dependent on chain length.

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