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Dissolution and Re-emergence of Flow-Induced Shish in Polyethylene with a Broad Molecular Weight Distribution

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ABSTRACT: Flow-induced shish formation in semicrystalline polymers is an important phenomenon since shish can strongly influence final material properties. The formation, dissolution, and re-emergence of flow-induced shish were studied for a polyethylene system with a broad molecular weight distribution using time-resolved synchrotron small-angle X-ray scattering (SAXS). The results show that shish are generated for a critical strain of 100 at various shear rates, ranging from 25 to 200 s−1. The shish formed at 140 °C are not stable and decay during a subsequent isothermal process. The specific shish dissolution dynamics is in contrast with the shish formation, affected by the shear rate applied. Unexpectedly, when the polymer melt with dissolved shish was cooled down, shish re-emerges. It demonstrates that the shish created did not dissolve completely into relaxed random coils but relaxed only partially into some ordered precursors that are below the limit of SAXS detection. Moreover, shish dissolution dynamics was significantly slowed down by lowering the isothermal annealing temperature from 140 to 138 or 135 °C, indicating that the shish dissolution involves more than chain mobility at low temperatures.

INTRODUCTION

Semicrystalline polymers are the most widely used class of polymeric materials. Representative examples include polyethylene (PE), isotactic polypropylene (iPP), and isotactic poly(1-butene) (iPBu-1), to name just a few. The widespread application of these polymers is due to the fact that their crystalline structures can be tailored via controlling the processing conditions. In this way a variety of desirable properties can be achieved. Flow, as an unavoidable processing factor, can have significant influences on the crystallites formed, i.e., raising nucleation density and inducing the appearance of oriented structure. Shish kebab is the typical oriented morphology, which consists of the fibrous cores (shish) and lamellar crystals (kebab) periodically spaced along shish. The shish cores are induced by flow first, providing nucleation sites as well as orientation templates for lamellar growth. Therefore, the features of flow-induced shish are a key factor to understand flow-induced crystallization. This understanding can be utilized to control the crystallite structure as created during processing.

Flow-induced shish-kebab structures were observed first in polymer solutions in the 1960s.† One of the most important pioneering works on flow-induced shish kebab, using polyethylene, was done by Pennings et al., which clearly shows lamellar crystallites of kebab located on the shish core and kebab diameters are about 100–300 nm with a roughly 100 nm space interval between the neighboring lamellae along shish.‡ Interestingly, it was found, using polarized light microscopy, that polyethylene shish can survive up to an unexpectedly high temperature of 151 °C, suggesting that shish consists of extended chains. To reveal the mechanism of shish formation in solution, the key question is how to extend polymer chains in solution. De Gennes predicted a flow-induced coil−stretch transition using hydrodynamics of polymer dilute solutions.‡ Keller et al. used birefringence combined with an opposed jets technique to demonstrate experimentally the coil−stretch transition and proposed that the stretched chains form shish and coiled chains fold into kebab.§ It has been realized that a dilute solution of polymer is a relatively simple system, and shish formation in the melt is more complicated because chain segments interact with each other and, consequently, build up entanglements. Recent studies of flow-induced shish formation focus on polymer bulk.§−∥ It was found that the addition of high molecular weight (HWM) chains enables the creation of shish, even at content as low as the critical overlap concentration of these long chains.§−⊥ Based on this experimental observation, it was thought for quite some time that shish was composed of the combined high molecular weight molecules. However, in 2007, Kimata et al. ingeniously made use of special polypropylene blend systems with deuterated molecules of various lengths and small-angle...
neutron scattering, demonstrating that shish has the same fraction of high molecular weight as the bulk melt.\textsuperscript{8} After determining which chains make the shish, the next question concerns how the chains aggregate into shish. For the appearance of shish kebab in the entangled solution system with paraffin as the solvent, Hashimoto et al. found a multistep formation mechanism, of which liquid—liquid phase separation occurs first. The resulting domains possess concentrated polymer chains aligned into string-like assemblies oriented along the flow direction. Bundles of stretched chain connecting neighboring domains grow into these domain interiors and, in this way, forming shish.\textsuperscript{10} For the bulk system, it was often thought that shish results from growth from dormant or flow-induced nuclei. Janeschitz-Kriegl et al.\textsuperscript{11} and Peters et al.\textsuperscript{12,13} envisaged that shish directly grows from nuclei along the flow direction. Besides, Seki et al. proposed a shish formation process, where the point-like precursor absorbs the HMW chains, leading to easier stretch of these absorbed molecules and consequently more point nuclei form; in the meantime, the point nuclei align along the flow direction and form shish.\textsuperscript{8} Moreover, Cui et al. emphasized that movement of point nuclei in the melt may cause a surface effect, which generate new nuclei along the trail of initial nuclei.\textsuperscript{9}

In addition to monitoring shish appearance from the melt, the decay behavior of shish upon cessation of flow gives new insights into shish features and formation, as it does for other flow-induced objects. On the segmental level, the formation and decay of flow-induced helical conformation in isotactic polyethylene were explored by An et al. using the Fourier transform infrared spectrometry (FTIR).\textsuperscript{14} Two distinct relaxation behaviors were found at different temperature regimes, of which the kinetics follow first- and second-order exponential functions, respectively. The dual relaxation behaviors indicate that the helices are very likely to form compact helical bundles, and the corresponding interaction between helices influences the helical stability. Concerning the flow-induced nucleation precursors, the resulting orientation and crystallization kinetics were investigated to unveil their dissolution kinetics.\textsuperscript{15} It was found that the dissolution kinetics is much slower than the recovery of the unperturbed coil conformation of polymer chains, implying that the dissolution of flow-induced nucleation precursors is in fact more than reptation of polymer chains. Moreover, Balzano et al. studied the dissolution kinetics of the unstable mechanism of flow-induced shish in polyethylene at 140 °C.\textsuperscript{16} Interestingly, it was also found that the initial part of dissolution evolution can be described well by the modified Doi—Edwards memory function, and the characteristic dissolution time agrees well with the reptation time of the HMW part of the distribution of polymer system employed. They concluded that dissolution of (unstable) flow-induced shish involves reptation of stretched HWM chains which compose the backbones of shish. All chains in the molecular weight distribution aggregate into shish, while the stretched HMW chains form a scaffold for shish and determine the kinetics of shish dissolution. Actually, the experimental studies on revealing the dissolution behavior of flow-induced shish are rare; therefore, the present work focuses on this topic.

Moreover, another crucial question is in what flow-induced shish decays into—into complete random coils or into another intermediate state possessing certain degree of ordering. The disappearance of the equatorial SAXS signal, the fingerprint of shish, cannot answer this question because a too low concentration or an insufficient density contrast between (partially) relaxed structures and the amorphous melt may cause invisibility of flow-induced structures. However, these SAXS undetectable precursors, if any, can be reflected indirectly by the features (orientation or/and kinetics) of subsequent crystallization triggered by the cooling\textsuperscript{5,17} or by a pressure quench.\textsuperscript{18} Therefore, following these ideas, we explored the process of (partially) relaxed polymer melt to reveal the long-standing question on the final destiny of flow-induced shish.

**EXPERIMENTAL SECTION**

**Material.** A commercial high-density polyethylene (HDPE, BG10050E), kindly provided by Dow Chemical, is used in this work. Molecular weights are summarized in Table 1. The molecular weight distribution $M_w/M_n$ is rather broad.

<table>
<thead>
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<th>Table 1. Molecular Parameters of the HDPE Used in This Work</th>
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<td>Material</td>
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**Flow Device.** The flow device used in this work is a modified Linkam CSS450 shear cell with a plate—plate geometry, which has been described elsewhere.\textsuperscript{19,20} In this modified device, the quartz windows, which are originally designed for the optical microscope, were replaced by a pair of diamond windows for the in situ X-ray characterizations. The measurement of sample temperature was carefully calibrated using a calibrated chromel—alumel $\mu$-thermocouple composing of 50 μm diameter wires embedded in the polymer melt. A short-term shearing protocol was employed (see Figure 1). The HDPE sample was first heated to 190 °C and kept at this temperature for 10 min to erase all previous thermal and mechanical history. Next, the relaxed melt was cooled at 20 °C/min down to the chosen temperatures (140, 138, and 135 °C), where the shear was imposed. A strain of 100 was imposed, and based on previous exploratory experimental work,\textsuperscript{21,22} shear rates were varied from 25 to 200 s$^{-1}$. The isothermal process was monitored for 10 min, after which the sample was cooled with a cooling rate of 10 °C/min in order to explore whether oriented nuclei survived after the 10 min annealing, by observing the cooling crystallization morphology.

**X-ray Characterization.** Small-angle X-ray scattering (SAXS) was employed to characterize formation and evolution of shish. All SAXS experiments were carried out at the Dutch-Belgian (DUBBLE) beamline BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.\textsuperscript{21,22} The wavelength used for this work was 1.24 Å. SAXS measurements were carried out with a detector with resolution of 512 × 512 pixels (260 μm × 260 μm) placed at a distance of 6.10 m. The exposure time for each SAXS pattern was 10 s.
RESULTS AND DISCUSSION

Flow has a significant influence on the ultimate morphology of the formed crystallites via generating oriented nuclei, which offer the orientation template for lamellar growth. First, it should be noted that the meaning of “oriented nuclei” is rather general, and it may include all potential objects that are capable of inducing oriented morphology. In previous work we attempted to divide oriented nuclei into several groups: shish, threadlike nuclei, and needlelike nuclei, according to how they can be detected using a combination of birefringence and SAXS.23 In that nomenclature, “shish” are those nuclei that can be detected by SAXS, “thread-like nuclei” are those that cannot be detected by SAXS but can be observed with birefringence, and, finally, “needle-like nuclei” are those under detection limits of both SAXS and birefringence. This work focuses on shish, a fibrillar structure possessing a higher density than the surrounding melt and consequently can be identified by the characteristic SAXS streak signal appearing in equator direction.

Formation of Shish. Figure 2 shows the SAXS patterns obtained at 140 °C immediately after all imposed flows with an identical strain 100 at shear rates varying from 25 to 200 s⁻¹. It is evident that clear SAXS streaks appear in all flow conditions, demonstrating shish formation at all flow conditions applied. For the specific polyethylene used here, the imposed strain of 100 is high enough to stretch the molecular chains sufficiently such that they are able to form shish at 140 °C. Molecular stretch is a prerequisite for shish formation.24–26

Shish is a typical class of oriented nuclei that can nucleate lateral growth of lamellae spaced periodically along them. The mechanism of shish formation is a fundamental part in understanding flow-induced crystallization. First, from a classical thermodynamic point of view, occurrence of nucleation requires a reduction of the Gibbs free energy, i.e., \( \Delta G < 0 \), the difference between the free energies of the initial state of the random coil chains and the ultimate stable nuclei. Flow enhances crystallization by introducing an additional change \( \Delta G_{\text{f}} \) to the total change in Gibbs free energy, \( \Delta G = \Delta G_{e} + \Delta G_{\text{f}} \) of which the first term on the right side, \( \Delta G_{e} \), is the driving force of quiescent crystallization provided by thermal fluctuations. Many works are devoted to finding macroscopic flow parameters responsible for the reduction of aforementioned nucleation barrier and their quantitative correlation in order to ultimately reveal mechanism of shear-induced nucleation. In this work, shish appear for all flow conditions applied, i.e., strain = 100 and shear rate = 25–200 s⁻¹. The appearance of shish in our results indicates a strain-dominant mechanism for shish formation, consistent with prior works presented in the literature. A strain-dominating mechanism has been related to the nucleation kinetic path by Cui et al.27 It was suggested that the two essential transitions of nucleation—stretch-induced conformation order and alignment of these ordered structures—are both driven by the extension of chains. Therefore, shish formation is controlled by the strain. The specific values of critical strains from different works are not compared, since they strongly depend on molecular parameters (molecular weight, molecular weight distribution, etc.) of the polymer investigated, which may be very different for the various works.

The effects of flow on the polymer chains include orienting the macromolecular contour path and even stretching of segments.24 For a known shear strength of shear rate \( \dot{\gamma} \), these effects can be assessed by two Weissenberg numbers, \( W_{0} = \dot{\gamma} \times \tau_{\text{re}} \) and \( W_{1} = \dot{\gamma} \times \tau_{\text{Rouse}} \), which are based on the reptation time \( \tau_{\text{re}} \) and the Rouse time \( \tau_{\text{Rouse}} \), respectively. In principle, polymer chains will be oriented when \( W_{0} > 1 \) and stretched for \( W_{1} > 1 \). We will utilize these two Weissenberg numbers to quantitatively assess the possibility of the molecular deformation. For the material used in this work, the average weight molecular weight is 251.6 kg/mol, and using the molecular weight between entanglements \( M_{e} = 828 \text{ g/mol} \), the corresponding average number of entanglements per chain is \( Z \approx 303.28 \). According to the tube model, the reptation time and the Rouse times can be obtained from

\[
\tau_{\text{Rouse}} = \frac{\tau Z^2}{9} \quad \text{and} \quad \tau_{\text{re}} = 3\tau Z \left( 1 - \frac{1.51}{\sqrt{Z}} \right)^2
\]

with the entanglement equilibration time \( \tau_{\text{e}} (7 \times 10^{-9} \text{ s at 190 °C}) \).28 Using the Arrhenius type of temperature dependence \( (E_{a} = 36 \text{ kJ/mol}) \), the estimated \( W_{0} \) and \( W_{1} \) for the highest applied shear rate of 200 s⁻¹ are 300 and 0.4, respectively. The high reptation time-based \( W_{0} \) of 300 suggests average chains can be oriented by flow, but the value of 0.4 for the Rouse time-based \( W_{1} \) below the unit, implies that the flow cannot stretch a majority of polymer chains. However, experimental observation of shish formation in all flow conditions indicates the occurrence of molecular stretch. This shish appearance is due to the broad distribution of molecular weight of polymer chains. Above estimation of \( W_{1} \) is based on the Rouse time of average chains. However, in a polymer system with a broadly distributed molecular weight, the high molecular weight (HMW) part is playing a more important role in inducing formation of oriented nuclei because these chains are easier to be stretched due to their long relaxation time, and the stretched long chains recruit their neighboring chains to form nuclei.29–30 Therefore, to generate shish, it is not necessary to stretch all chains of various lengths in the melt, and it seems that only stretching of the high molecular weight (HMW) part is enough. This issue is discussed in more detail in the next section.

Dissolution of Shish. After formation, shish tend to nucleate crystallite growth when there is enough driving force (undercooling) for folded-chain lamellae. However, the experimental temperature of 140 °C employed in present work is quite high, i.e., above the nominal melting temperature of lamellar crystallites (typically around 134 °C) and even already very close to the equilibrium melting temperature of 141.5 °C (414.5 K).31 At this high temperature, shish do not trigger lamellar growth. The question is if these fibrillar structures of shish, themselves, may survive or relax, i.e., if they are stable at this specific temperature. The results present concern the evolution of shish at 140 °C after flow. Figure 3 shows the isothermal evolution of shish generated by shear rate of 100 s⁻¹. It is observed that the SAXS equatorial streak decay during the isothermal process. The equatorial streak cannot
even be seen anymore after 600 s. A first qualitative conclusion is that the shish dissolve at 140 °C. The stability of flow-induced structure has attracted attention because the relaxation might give an insight into the structural features of those flow-induced objects. For instance, An et al. explored stability of flow-induced helices in isotactic polypropylene and found that the helices appeared to have a dual relaxation behavior. These two relaxations were related to dissolution of helix bundles and recoiling of isolated sequences of 3/1 helical conformations, respectively.

Concerning relaxation, the perturbed molecules, i.e., oriented and stretched by the flow, tend to recover their random coil conformation via retraction and reptation. Balzano et al. showed that the initial characteristic relaxation time of shish dissolution coincides with the reptation time of the HWM tail, based on the memory function for attaining the random coil conformation, suggesting that the early stage of shish relaxation is dominated by reptation of HMW chains. The dissolution behavior of shish structures is quantified by the evolution of the SAXS integrated intensity over the specific streak region, $I_{\text{eq}}^{\text{SAXS}} = \int_{0.018}^{0.5} \int_{-0.2}^{0.2} f(az, q) d_{az} d_{q}$, where $az$ is the azimuthal angle and $q$ is the norm of the scattering vector. These are summarized in Figure 4. It is evident that for all flow conditions flow-induced shish dissolve with time at 140 °C, and interestingly, the dissolution kinetics are affected by the imposed shear rate. The solid lines in Figure 4 refer to the data fitting using the modified Doi–Edwards model:

$$I_{\text{eq}}^{\text{SAXS}}(t) = S_{t} \mu(t, \tau_{D}^{\text{HWM}}) = S_{t} \pi \sum_{p \text{ odd}} \frac{1}{p} \left( \frac{-p^2(t - t_{0})}{\tau_{D}} \right)$$

with $S_{t}$ a vertical shift factor (used because of the arbitrariness of the intensity scale), $t_{0}$ the reference time when relaxation starts, and $\tau_{D}$ the characteristic relaxation time.

The very good correlation between experimental data of shish dissolution kinetics, and the theoretical relaxation model provides us with a characteristic relaxation time $\tau_{0}$ for each shear rate (see Figure 5). The characteristic relaxation time decreases with increasing shear rate.

As stated before, it is well recognized that the HMW chains are at the basis of shish formation. For a given flow strength, a certain part of HWM chains can be oriented and stretched, and these stretched HWM chains recruit neighboring (with low $M_{w}$) chains to form shish. The stretched HWM chains are the scaffold for shish. It seems therefore reasonable to link the shish stability to these stretched HWM chains. Actually, in a polymer system with a broad molecular weight distribution, the definition of HWM chains and the amount of stretched chains is determined by the specific shear rate imposed. For a shear rate $\dot{\gamma}$, the stretchable HWM chains are those macromolecules that should have the Rouse times larger than reciprocal shear rate to ensure $W_{i} = \dot{\gamma} \times \tau_{Rouse} > 1$. This implies that in a broadly distributed PE system the fraction of the HWM that dominates the formation of shish is actually determined by the shear rate and can be varied by changing the shear rate. Therefore, with increasing the shear rate the lower limit of molecular weight in HWM fraction that is stretched decreases, leading to a decrease of the average relaxation time of HWM chains and the dissolution of shish becomes faster.

**Re-emergence of Shish.** The above observations of shish relaxation are based on SAXS measurement. However, the extinguishing SAXS signal during annealing cannot exclude the possibility of survival of other ordered objects, and therefore the next question is into what do the shish evolve: completely relaxed chains with random coil conformation or another type of ordered structure that is not fully relaxed? The indirect means of visualizing this potentially ordered structures, which are below detection limits, is to measure the features after subsequent crystallization. This can be triggered by undercooling via temperature or pressure. Here, crystallization is triggered through cooling of the postrelaxation polymer melt. Figure 6 shows selected SAXS patterns during cooling. At beginning, at 136.7 °C, similar to the dissolved melt after isothermal process, no SAXS signal can be observed. As cooling proceeds down to 128.3 °C, SAXS equatorial streaks appear and the SAXS streaks becomes clearer with further cooling. Oriented lamellae (kebab) is nucleated as well; see the SAXS pattern at 125 °C. The reappearance of shish during cooling
clearly indicates that shish relaxes into partially ordered precursors, rather than into equilibrium random coils.

After formation, and depending on its stability, flow-induced shish can follow two different paths: (1) survive and further rearrange to trigger crystallization or (2) relax. The shish stability is closely related with structural features of shish formed and the temperature. Balzano et al. suggested that a geometry ratio (length over diameter) is the determining factor for shish stability. In this work, disappearance of shish characteristic SAXS streaks indicates that the shish formed is unstable and tends to relax. The isothermal dissolution process and the re-emergence of shish with cooling is schematically illustrated in Figure 7. Shish are often described as bundles of densely packed parallel chain stems. There should be some relatively free segments dangling from the shish ends or from the lateral surface, i.e., not included in shish but connected with their counterparts inside the shish. Upon cessation of flow, it is proposed that loosening of shish bundles starts from these relatively free chain ends. During flow, the disordered and free segments coming out from the two end surfaces of shish can be stretched and aligned along flow direction, lending to the free longitudinal growth of shish. Upon cessation of flow, the connected free segments tend to move to reduce the entropy as much as possible and, consequently, introduce mobility of their counterparts inside shish. The growth fronts of shish during flow now become dissolution fronts. The relatively free chains protruding from the shish into the melt can also be located along the lateral surface. These were termed as “hairs” by Keller et al., and they are thought to interact with the chains surrounding the shish and change the melt rheology during flow. This concept was used and successfully validated in a model by Roozemond et al., who introduced an effective radius related to the chains protruding from the shish. In this way, the initial relatively sharp boundary between shish and their surrounding melt vanishes. When the packing density of shish is lower than some critical threshold, shish cannot be detected anymore with SAXS.

The re-emergence of shish by cooling further demonstrates that shish relax into a still ordered precursors, less in volume than the initial shish. Segments belonging to these partially relaxed precursors still exhibit a certain degree of ordering. This survival of ordering may be due to thermodynamic stability or due to its slow relaxation dynamics. For the latter case, Cavallo et al. studied dissolution time of SAXS undetectable nucleation precursors and found dissolution times that were much larger than the reptation time. However, in the present work we applied a constant annealing time protocol, and therefore, the reason for precursor survival, thermodynamic stability, or long dissolution dynamics cannot be distinguished. Anyway, the residual ordered chains are activated again and tend to pack into shish when undercooling provides the driving force for these precursors to crystallize.

The shish reemergence with cooling implies an intermediate ordered state during the dissolution process, i.e., between a stable crystalline shish and the equilibrated conformation of random coils. A similar ordered state has been reported in other studies on flow-induced crystallization. The commonly accepted reasons why these ordering structures cannot be observed by SAXS are (a) a nonsufficient density contrast between ordering entities with the surrounding melt and (b) a too low concentration of these structures. Concerning the reemergence of shish with cooling these two possibilities are not equally likely. If density decrease is the main reason for shish dissolution, shish do not relax completely into the equilibrated random coil but evolves to some precursors. These precursors possess a certain extent of ordering, and when enough undercooling for these specific ordering is provided by cooling, the oriented and stretched chain segments of these precursors tend to pack more densely again. As dense packing must lead to an increase in density, SAXS equatorial streaks can be observed again. However, in the case that shish dissolution is only caused by the decrease of shish concentration, it is unlikely to observe shish with cooling. The reason is the following. In addition to sufficient undercooling, shish formation also requires effective molecular stretch. The requirement of molecular stretch can only be met by an external field, as for example shear. Cooling is not able to stretch molecules to generate new shish. Therefore, it is reasonable to infer that the formed shish gradually lose their densely packed chains during the isothermal process at 140 °C, resulting in a decrease in packing density and below certain threshold the disappearance of shish in SAXS detection.

Actually, whether the pathway of shish formation involves any type of intermediate ordering or mesophase is a long-standing question. It is not easy to reveal this question because these ordered states apparently are SAXS undetectable. However, the existence of an intermediate ordering state between random coil chain and shish was demonstrated in the process of shish dissolution in this work, and this in turn answers the question if shish formation also goes through this step of an intermediate state, i.e., a path from random coil via the intermediate ordering aggregates to the final shish structures.

**Temperature Dependency of Shish Dissolution.** Temperature is a major variable for crystallization; undercooling is the driving force for crystallization. Temperature also determines chain mobility, which is often quantified by the relaxation times. As temperature decreases, undercooling raises and chain mobility decreases. Both effects favor occurrence of flow-induced nucleation for identical shear rates. Figure 8...
show the shish formation and evolutions at various temperatures (140, 138, and 135 °C) for the same shear of 100 and shear rate 200 s⁻¹. First of all, SAXS equatorial streaks demonstrate that shish are formed at all of these three temperatures. Lowering the temperature provides a larger driving force for crystallization as well as it enhances the effect of identical shear. Therefore, it is obvious to observe stronger shish formation at lower temperatures as can be seen by the more intensive SAXS streak signal at 138 and 135 °C compared to 140 °C. This is due to a higher concentration of shish or a larger density contrast between shish and surrounding melt, or both.

The postflow evolution of shish also varies with the isothermal temperature. At 140 °C, SAXS streak intensity completely fades after 600 s, whereas at 138 °C the signal only partially decays. At 135 °C the shish formed even grow for the first 70 s upon cessation of flow and then decays slowly. Evidently, shish generated by identical shear conditions shows distinct stability behavior at different temperatures, i.e., different relaxation behaviors.

The modified memory function was used to describe the relaxation behaviors at these various temperatures (see Figure 8). The 138 and 135 °C characteristic relaxation times determined with memory function are around 3300 and 8600 s, respectively, much larger than the 85 s at 140 °C, showing a remarkable increase for lowering temperature by only 5 °C. The temperature dependency of the relaxation can be described by the Arrhenius equation, which is written as \( \tau(T) = \tau_0 \exp(E_a/RT) \) with \( \tau_0 \) being a reference time constant dependent on the material, \( E_a \) the activation energy, and \( R \) the universal gas constant. The activation energy obtained is around 1200 kJ/mol. This seems rather high, since it is really 2 orders larger than that of chain mobility (36 kJ/mol). This indicates a significant slowing down of chain mobility in the precursors with temperature. Indeed, it has been reported that the dissolution of some flow-induced structures may exhibit much larger activation energy than that of the polymer melt.\(^{14,15}\) However, such substantial difference in activation energy between shish relaxation and chain mobility, by approximately 2 orders, is rare.

Cavallo et al. found that the activation energy for the flow-induced precursors is around 200 kJ/mol, roughly 1 order of magnitude larger than that of pure melt.\(^{15}\) The large activation energies indicate that the dissolution process is different from melt chain mobility. For flow-induced helices in isotactic polypropylene, An et al. also related the two observed relaxation behaviors to differences in aggregated and isolated flow-induced helices.\(^{14}\) It was stated that that interaction between helices influences their relaxation behavior. It seems that more factors than chain mobility can affect the relaxation kinetics. Flow-induced structures, no matter if they are precursors or shish, are ordered aggregates, and the ordered packing restricts the chain movement. This can explain that the activation energy of shish relaxation 1200 kJ/mol found in the present work is much larger than that of precursor dissolution, around 200 kJ/mol reported by Cavallo et al.\(^{15}\)

The shish of interest in the present work can be observed with X-rays. Their ultimate ordering structure after relaxation is quite similar to those SAXS undetectable nucleation precursors. Thus, we concluded that shish are more ordered than flow-induced precursors studied by Cavallo et al.\(^{15}\) This only results in the ordering degree of two objects: shish and nucleation precursors. Via the dependency of dissolution kinetics with temperature, it was revealed that their transitions, i.e., from shish to nucleation precursors and from nucleation precursors to equilibrium random coil, depend on temperature in different ways. The higher activation energy of flow-induced nucleation precursors indicates a process of detaching chain segments from the lateral surfaces. Following the same idea, it is reasonable to infer that looseness of chain segment inside shish is more difficult as indicated by the further larger activation energy of dissolution in flow-induced shish.

\[ \text{CONCLUSIONS} \]

The formation and dissolution of flow-induced shish are studied for a broad molecular weight distribution polyethylene. The SAXS results show that for this specific polyethylene system a strain of 100 is sufficient to induce shish at 140 °C, regardless of the shear rate within the range of 25–200 s⁻¹. Interestingly, the shish formed are unstable and decay during the isothermal process at 140 °C. The dissolution dynamics depends on the shear rate applied; the higher the shear rate, the faster the dissolution. Moreover, the (partially) dissolved shish can be observed again via cooling after the annealing process (10 min). This demonstrates that shish only relaxes into partially ordered precursors rather than a completely relaxed random coil.

Moreover, the dynamics of shish dissolution is also explored at various temperatures for a shear rate 200 s⁻¹. The dissolution dynamics slows down significantly with lowering the temperature.

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**Notes**
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