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Kinetics of the Polymorphic Transition in Isotactic Poly(1-butene) under Uniaxial Extension. New Insights From Designed Mechanical histories.

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Supporting Information

ABSTRACT: Isotactic poly(1-butene) (i-PBu) crystallizes upon cooling from the melt in a metastable tetragonal structure (form II), which slowly evolves toward the state of ultimate stability, i.e., the trigonal form I. It is well-known that this polymorphic transformation, which typically requires few weeks at room temperature, can be greatly accelerated by the application of mechanical stresses and/or deformation. However, the exact mechanism of this kinetics enhancement is not completely understood. In this work, the polymorphic transformation of i-PBu under tensile deformation is investigated in details. Thanks to properly designed mechanical histories—including experiments at different true strain and true stress rates—and to in situ wide-angle X-ray diffraction experiments, the role of the various deformation parameters is elucidated. The use of different time scales during the experiments enabled us to gain kinetics data on the transition, information which is disregarded in current literature. The set of experiments performed permit to highlight a stress-driven mechanism, active up to a fraction of transformed form I of about 0.4–0.5. After this value is reached, the stress-transformation time superposition principle does not hold anymore and the transition kinetics slows down, since a major part of the total applied stress is carried by the mechanically stronger form I lamellae.

INTRODUCTION

The mechanical properties of semicrystalline polymers are strongly dependent on their nanoscale morphology, constituted by crystalline lamellae and amorphous layers strongly interconnected. Moreover, for what concerns the crystalline part, the issue of polymorphism might arise. Indeed most of the polymers can crystallize in more than one structure, depending on the solidification conditions. The various modifications can present different packing of the same motif or even different chain conformation in the solid state, e.g., helix vs zigzag etc.^{1–3}

Obviously, each structure will respond in a different way to the application of stresses, thus imparting different mechanical properties. On the other hand, it is frequently observed that the initial crystalline structure can evolve and transform in another one during plastic deformation.^{4,5} Typically the polymorph possessing the more extended chain conformation is favored against the more compact one in tensile deformation or drawing.⁴ A well-known example of stretch induced phase transition is represented by isotactic polypropylene (i-PP) in its trigonal modification (β -phase). The trigonal to monoclinic (α -phase) transition occurring upon deformation is considered to be responsible of the improved toughness of β -phase i-PP.^{6,7} Another interesting case is that of syndiotactic polypropylene,

in which a reversible martensitic transformation from form II to form III at high strains produces an enthalpic elasticity, thanks to a “molecular spring” mechanism.^{8,9}

Isotactic poly(1-butene) (i-PBu) exhibits an interesting polymorphic behavior. Three structures, characterized by different chain conformation and packing mode have been identified. The chain segments in the crystals adopt a 3/1, 11/3, and 4/1 helical conformation in form I, form II and form III, respectively.^{10–12} Melt crystallization invariably leads to the formation of the tetragonal structure, form II.^{13–15} However, form II is metastable and evolves toward the ultimately stable trigonal form I upon storage at room temperature. The transition requires few weeks at ambient temperature.^{13–15} It is well-known that stretching largely accelerates this polymorphic transformation. This particular issue has been tackled several times throughout the last decades.^{16–22}

Asada et al. performed stress-relaxation experiments and noticed that time–temperature superposition is no longer valid at long times because of crystal transformation.^{16,17} Goldback

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explored the effect of a constant engineering stress and found a measurable acceleration of the kinetics of phase transition only at stresses above the yield stress. The author attributed the enhancement of the kinetics to the resulting shear and/or normal stresses.^{18,19} In the early 1980s, a model for the transformation of form II spherulites under tension was proposed.²⁰ The transformation begins in the equatorial region of the spherulite, while the lamellae in diagonal position undergo alignment and shear deformation before conversion to form I. Geil et al. studied the tensile behavior of form II at different rates of deformation. They noticed a double stage strain hardening, with a slope that decreases with increasing strain rate. The behavior was linked to the form II to form I phase transition.²¹ Recently, Liu et al. measured the phase transition in i-PBu via synchrotron X-ray diffraction.²² The experimental stress–strain curve was interpreted as a three stage mechanism, including incubation, nucleation and gelation of form I crystals. The strain hardening corresponds to the last stage and is due to an increased connectivity caused by the newly formed crystals.²² The polymorphic transformation was described as strain-dependent in these latter works.^{20–22}

Despite this extensive investigation some open questions still remains. For instance, it is still debated whether the polymorphic transition during tensile deformation is strain or stress controlled. In this work we focus on the kinetics of stretch induced form II-to-form I phase transition, by employing wide angle X-ray diffraction (WAXD) and purposely designed mechanical histories. Contrary to most of the previous studies, a wide range of time scales is explored by tuning either the deformation rate or the rate of stress increase. The results are critically compared with literature on i-PBu deformation, revealing that the transition is essentially driven by stress up to a fraction of form I of about 0.5.

MATERIALS AND METHODS

Materials. A commercial Ziegler–Natta isotactic poly(1-butene) (PBu 0200), kindly provided by Lyondell-Basell, was used in this study. The polymer is characterized by a weight-average molecular weight of 525 kg/mol and a polydispersity index of 4.9. Films with thickness around 500 μm were obtained by compression molding the supplied pellets between aluminum plates in a hydraulic press. A melt temperature of 180 $^{\circ}\text{C}$ for 5 min was chosen and the hot plates were subsequently quenched in air. Dog-bone samples with sizes of 22 $\times$ 5 $\times$ 0.5 mm (length $\times$ width $\times$ thickness), according to ISO527, were punched out the compression molded plate and tested in tension.

Mechanical Properties. Tensile tests were performed on the dog-bone samples by means of a Zwick-Roell testing machine type Z5.0 TN, equipped with a 100 N force cell. Since the samples deform homogeneously, the experiments could be true stress or true strain controlled, under the assumption that the material is incompressible. Different mechanical tests were performed by custom-built modules in the TestXpert II software, including constant true strain rate, constant true stress and constant true stress rate experiments. The true strain rates were ranging from 3×10^{-5} up to 10^{-2} . The constant true stresses were ranging from 2.5 to 3.5 MPa. The constant stress rates were chosen in such way that the rates would result in equally divided values on a log scale.

In Situ X-ray Diffraction during Tensile Deformation. Wide angle X-ray diffraction (WAXD) measurements during tensile deformation were performed at the beamline BM26B-DUBBLE of the ESRF,²³ focusing on the structural evolution of crystalline form II samples during the deformation. The sample clamps were properly aligned as such that the wider surface of the sample was oriented perpendicular to the X-ray beam.

An X-ray radiation with a wavelength of 1.033 $\text{\AA}$ was used, focused on the sample with a spot size of approximately 300 μm . WAXD

images were collected in transmission mode using a 2D Frelon detector, positioned at a sample-to-detector distance of about 220 mm. 2θ scale calibration was performed using $\alpha\text{-Al}_2\text{O}_3$ standard. The diffractograms were azimuthally averaged and radially integrated, resulting in scattered intensity vs 2θ curves.

The frame rate was adjusted according to the requirements of the particular experiment.

The structural evolution during the test was followed by monitoring the intensities of the peaks at 2θ values of 7.2° and 8.5° , characteristic of the 110 plane of form I and of the 200 plane of form II, respectively.²⁴

RESULTS AND DISCUSSION

Mechanical properties. The polymorphic transformation occurring in i-PBu upon storage fresh (form II) samples at room temperature is associated with profound changes in the mechanical response of the material. Figure 1 summarizes the

Figure 1. (a) True stress–true strain curves of form II samples stored at room temperature for the indicated times. A true strain rate of 10^{-3} s^{-1} was applied. (b) Haward–Thackray plot²⁵ of the curves in part a.

true stress–true strain curves of samples with different degree of transformation, i.e., different aging time and therefore composition in terms of the two polymorphs.

In parallel to the evolution to form I we can notice a remarkable overall increase in the stress, although the shape of the curves at larger strains do not differ markedly. From the mechanical point of view the transformation can be considered completed after about 3 weeks, since after 475 h the mechanical response hardly changes. In the Haward–Thackray plot²⁵ of Figure 1b, it can be observed that only the completely transformed samples display a neo-hookean behavior, i.e. a constant strain hardening modulus over a large strain interval. The other samples approach the slope of the completely transformed ones only at large strains.

The deformation kinetics of i-PBu after completion of the polymorphic transition to form I can be appreciated from

Figure 2, which shows true stress-true strain curves of form I samples collected at different deformation rates.

Figure 2. (a) True stress-true strain curves of form I samples deformed at the indicated rates. (b) Haward–Thackray plot of the curves in part a.

Noticeably the different curves almost collapse to a single one; i.e., the mechanical properties of the trigonal modification (form I) do not show any rate dependence. At higher strain rates viscous heating is observed and the strain hardening response decreases due to the increased temperature (not shown here). Figure 2b allows us to evaluate the average strain hardening modulus, which yields a value of 7.4 MPa. This value is in reasonable agreement with previous results in the literature of about 5 MPa.²⁶ The differences may be related to differences in molecular weight. In particular, the sample of this study possess an higher molecular weight, i.e., $M_w = 525$ vs 399 kg/mol,¹⁴ which was shown to lead to an increase in strain hardening of HDPE,²⁷ giving the increase in the number of entanglements per chain. It is instructive to compare these results with the mechanical behavior of the tetragonal structure (form II), shown in Figure 3.

The elastic modulus and the yield stress show a slight increase with increasing rate of deformation, in agreement with what observed for other polymeric materials (see Figure 3a, inset). The true stress-true strain curves of samples in form II present a much more interesting picture. In contrast to what is commonly observed in semicrystalline and amorphous polymers,^{28–30} the strain hardening response appears much more pronounced at lower strain rates (see Figure 3a). This, rather unusual, trend in the strain hardening response persists over the entire range of deformation rates experimentally covered. It should be noted, however, that, for the lowest strain rates, the stress at large strains reaches a response identical to the one of form I in that strain interval. This becomes much clearer in Figure 3b, which shows a Haward–Thackray plot of the samples in tetragonal modification (form II), compared to

Figure 3. (a) True stress-true strain curves of form II samples deformed at the indicated rates. Dashed gray line: stress–strain response of form I deformed at 10^{-3} s^{-1} . Inset: enlargement at low strains. (b) Haward–Thackray plot of the curves in part a.

that of the stable trigonal structure (form I). It can be seen that the stress is not linear with $(\lambda^2 - \lambda^{-1})$ for the samples in form II, but it changes with increasing strain until the strain hardening modulus approaches that of the aged form I sample.

The strain hardening in the tensile curve of i-PBu form II has been previously linked to the polymorphic transformation.^{21,22} In particular Liu et al. interpreted the strain hardening as originated by the formation of a new mechanical network with form I crystals acting as physical cross-links, a process called gelation.²² It should be noted that, contrary to the present study, a single strain rate was explored in their work. On the basis of the measured deformation kinetics of form II and of the mechanical properties of form I, we might give an alternative explanation. Given the much higher stresses required to maintain the plastic flow of form I compared to form II, it is clear that the replacement of tetragonal crystals by trigonal ones naturally provokes an increase in stress, which is necessary to continue the plastic deformation at the imposed rate.

In Situ Wide Angle X-ray Diffraction. The evolution of the content of the two polymorphs during deformation can be conveniently followed by X-ray diffraction. The actual content of the two modifications is calculated from the areas of two diagnostic diffraction peaks after subtraction of the amorphous halo, according to

$$f(I) = \frac{A(110)_I}{A(110)_I + RA(200)_{II}} \quad (1)$$

where $A(110)_I$ and $A(200)_{II}$ are the areas below the 110 peak of form I and the 200 peak of form II, respectively. The parameter R takes into account the differences in the diffraction power of the two families of planes, and it has been estimated equal to 0.36.²⁴ The amorphous halo has been determined from

Figure 4. Evolution of WAXD patterns during deformation at the indicated strain rates.

Figure 5. Examples of the evolution of phase contents during time in experiments performed (a) at constant stress (3 MPa), (b) constant strain rate (10^{-3} s^{-1}), and (c) constant stress rate ($10^{-2} \text{ MPa s}^{-1}$).

WAXD pattern of an atactic poly(1-butene) sample. The resulting weight fraction of form I is considered in the following discussion on transformation kinetics.

Figure 4 shows an example of the 2D-WAXD patterns evolution during stretching PBU samples at different rates. In the undeformed state the samples are predominantly in form II. With the progress of deformation the crystals become oriented and the diagnostic 110 peak of form I grows in intensity. It can be appreciated that, for a given value of deformation, a higher content of form I is achieved for the slower strain rate.

Representative examples of the evolution of phases and total crystalline content in time during deformation is reported in Figure 5. It can be noticed that, for any mechanical history, the decrease in form II content parallels the increase in form I, while the total crystalline fraction remains unchanged.

This scheme is valid for all the performed experiments, except in the case of the lowest constant strain rate experiment (10^{-4} s^{-1}). In the latter case a small decrease of the total crystalline content, from 45 to 40% is observed. We consider this variation negligible. The time evolution of phase contents

depicted in Figure 5 clearly indicates that form I develops at the expenses of pristine form II crystals—during the fragmentation and fibrils formation—rather than from the amorphous phase, whose amount keeps unaltered. Being assessed this transformation pathway, we proceed with the examination of the role of mechanical history.

In order to investigate the effect of stress, experiments at constant true stress were carried out. The mechanical history, i.e., true stress and true strain vs time, is reported in the Supporting Information (Figure S1, parts a and b, respectively). The target stress value is achieved in less than 45 s and kept constant afterward. To safely exclude the viscoelastic response of the materials, only data above 450 s were considered. Points before this limit time are shown in gray in the plots. The strain increases as a function of time with a decreasing slope due to the polymorphic transformation. Indeed the stresses applied (2.5–3.5 MPa) are much lower than the yield point of form I sample. The degree of transformation as a function of strain and time is reported in Figure 6.

Figure 6. Form I fraction vs strain (a) and time (b) for experiment performed at constant true stress.

Figure 6a clearly shows that the role of strain in the transformation is minimal. In fact, for all the explored stresses the transformation proceeds at almost constant and relatively small strains. A given transformation value is reached at higher strains the higher the stress applied, in agreement with the creep curves shown in the Supporting Information. The role of stress in accelerating the kinetics of transition can be appreciated from Figure 6b. The fraction of form I approximately follows a linear dependence on the logarithm of time, with a stress dependent slope. Considering the transformation half-time, we can see that it is reached at shorter times with increasing stresses. Goldback performed experiments of transformation kinetics in the condition of constant engineering stresses, i.e., the true stress was increasing in time due to the homogeneous deformation of the samples. He

showed that for very low stresses a stress–transformation time superposition holds, meaning that the curves of form I fraction against time were superposable by a simple horizontal shift on the time axis.¹⁹ However, for higher stresses a deviation from this behavior started to occur. Our results, obtained under constant true stress conditions, are consistent with and expand those of Goldback. Indeed the curves in Figure 5b are superposable by a horizontal shift for the two lower stress values, while the highest value is not. It is important to notice that for the highest stress value the transformation is slower than what expected by the simple stress–transformation time superposition. Indeed, if we would simply shift the curves obtained at lower stresses to match the value of half-transformation time of the one at higher stress, a steeper slope of the fraction of form I vs the logarithm of time would be expected. This indicates that, also under the simple condition of constant true stress, the description of form II-to-form I transformation kinetics is complicated and it probably consists of more than one process.

Figure 7 shows the evolution of form I in experiments performed at different constant (true) strain rates. Data are plotted against true strain, time and true stress in parts a–c of Figure 7, respectively.

As already deduced from the true stress–true strain curves in Figure 3, the data of conversion against strain and conversion against stress demonstrate that the transformation is not strain controlled. Indeed, while for strains lower than about 0.2 all the curves are very close, at higher strain levels a given value of conversion is reached at lower and lower strains with decreasing strain rate (see Figure 7a). From Figure 7b, it becomes clear that this behavior is due to the longer time available for the transformation at the lower imposed strain rates. The shape of the curve does not suggest a simple horizontal shift of the conversion curves with strain rate, i.e., transformation time–strain rate superposition does not hold. An “induction time”, during which transformation does not occur, is observed in Figure 7b. As a consequence of this latent period, transformation starts at deformation of about 10% for the higher strain rates (see Figure 7a), while for the much lower strain rate of 10^{-4} s^{-1} , the delay in terms of strain is negligible. The data of Figure 7c clearly show that all the different strain rates collapse in a single curves for stress values below 5 MPa (and transformed fractions lower than 0.4–0.5). Therefore, from the data of Figure 7 one deduces that, while strain is not controlling the form II-to-form I transformation under tensile deformation, a stress acceleration is the dominant process at low stresses. Deviations from the stress–transformation time superposition occur at high stress values.

To elucidate the role of stress in a different window, i.e., at higher stresses, a third mechanical test has been designed and applied. It consists of experiments carried out at different constant true stress rates. As reported in the Supporting Information, Figure S2, the stress increase is linear with time, while the strain shows a complex non linear dependence on the same variable. However, the true stress–true strain response of the material looks similar to that of constant strain rate experiments: it displays a yield stress, a stress plateau and a strain hardening region (see Figure S2c). The evolution of the trigonal modification during time and as a function of strain is reported in Figure 8a and 8b, respectively.

The time evolution of form I fraction immediately reveals the role of stress in enhancing the transformation kinetics. Indeed the time needed to reach a given degree of transformation

Figure 7. Form I fraction vs strain (a), time (b), and stress (c) for the experiment performed at constant strain rate.

Figure 8. Form I fraction vs time (a), strain (b), and stress (c) for experiments performed at a constant true stress rate.

decreases with increasing stress rate. It is necessary to note that the experiments with the higher stress rate are also the shorter ones, this notwithstanding, the possibility to spend some time at a high stress level permits to reach a higher degree of conversion. If we consider the strain dependence of the transformation, we see on the other hand that for a lower rate

of stress build-up the transition occurs at larger strain. The conversion is independent of the stress rate, up to a strain of around 0.3. Although this seems to indicate that, in apparent contrast with the data of Figure 6c, a strain-controlled mechanism is active at low deformations, it should be noted that in this strain interval also the stress–strain response is

independent of the stress rate (see Figures 8c and S2c). Indeed, the data of Figure 8c show again a perfect superposition of the different experiments for the low stress values. Remarkably, the stress-controlled acceleration seems to hold again up to 5 MPa, corresponding to a form I fraction of 0.4–0.5. It must be underlined that the existence of stress acceleration is unequivocally demonstrated, since the same results are obtained from different experiments (constant strain rate vs constant stress rate) and for different time windows. With respect to the transformation at stresses larger than 5 MPa, Figure 8b clearly states that stress is still an accelerating factor, but a simple stress-transformation time superposition rule does not hold anymore. The curves for different stress rates do not superpose with each other, and a higher degree of conversion is reached at lower strains for the samples deformed with a lower stress rate. An apparent deceleration in the stress dependence of the transformation kinetics can be grasped from Figure 6b, 7c, and 8c. This deviation starts when half of the original form II crystals have been replaced by the trigonal form I. It is therefore logical to link this deceleration with the fact that the residual form II crystals are submitted to a decreasing stress, as the major fraction of the total applied stress will be sustained by the mechanically stronger new form I lamellae.

On the basis of the mechanical and structural data collected we can refine the proposed mechanism of phase transition.^{20,22} It is evident that a two steps process is observed: first we encounter a purely stress dependent kinetics and later, at higher transformation levels, stress still has an accelerating effect, but less pronounced. According to the optical microscopy data of G'Sell et al.,²⁰ we can attribute the stress dependent process to a transformation of the lamellae already perpendicular to the deformation direction, i.e., those in the equatorial regions of the spherulites. The stress can act directly on the chains oriented in the drawing direction, causing the instantaneous transformation into form I, which possess a more extended helical conformation respect to form II. For what concerns the second part, it becomes the predominant one when plastic flow has set in and the mechanical network of form I lamellae bears the majority of the applied stress. The stress acceleration could be linked to an increased mobility of the chains, as usually described by the Eyring rate equation.³¹

In order to understand the reason for the measured stress activation of the phase transition we should recall some details on the mechanism of transformation in unstrained samples. It is well-known that the form II-to-form I transformation is controlled by primary nucleation: Form I nucleates in one lamellae and then rapidly spread over the full width of the crystals.^{18,19,32–35} The rate-determining step is the nucleation inside the lamella, and it occurs due to thermal stresses or internal stresses, such as those generated by irregular stacking of lamellae, lamellar bending etc. Fujiwara investigated the transformation on an oriented form II sample submitted to shear in directions perpendicular and parallel to the lamellar axis.³⁶ He reported that the transformation is enhanced in both directions and suggested that chain slip in the tetragonal modification is responsible for an increased form I nucleation rate. Indeed, from the molecular point of view, the form II-to-form I transformation involves an extension along the *c* axis, together with a crystallographic slip along the 110 planes of the tetragonal structure.

It is also necessary to note that the plastic deformation process includes the creation and propagation of defects, or “dislocations”, into and through the crystalline lamellae. The

generation and propagation rate of these conformational defects is enhanced by the application of stress. Therefore, we can suggest that the role of stress in accelerating the kinetics of phase transition is due to an increased nucleation of form I in form II lamellae, by injection of defect points or by creation of local stresses, for instance in the presence of tie-chains between lamellae.

Finally, the stress-induced polymorphic transformation in i-PBu can be compared to those occurring in other semicrystalline polymers. Auremma et al. investigated in details the polymorphic transformation during the uniaxial extension of sPP.^{8,9} The authors showed that the transition between form II and form III occurs with a change in the chain conformation: from helical to more extended trans conformers. Moreover, the stretching reversibly transforms a stable phase into a metastable one. Finally, they demonstrated that the transition is instantaneous and does not depend on the rate of straining, suggesting a strain control of the process. The sPP deformation-induced transformation is clearly different from the one of i-PBu. First of all the i-PBu transition is irreversible, since it involves the transformation from a metastable to a stable phase. Furthermore, as highlighted in this work, the polymorphic transformation is mostly controlled by stress, rather than by strain. The only feature in common with the transition observed during stretching sPP is the extension in the chain conformation, from a 11/3 to a 3/1 helix in i-PBu.

An irreversible transition between a metastable and a stable phase was also reported for i-PP, between trigonal β and monoclinic α -phase.^{6,7,37,38} However, in this case, the chain conformation is preserved, being always the characteristic 3/1 helix. It has been suggested that the stress-induced transition between β and α -phase involves a mechanical melting and recrystallization process, since the local arrangement of the 3/1 helical chain segments of different chirality, right- and left-handed, is much different in the two structures.^{37,38} This is in contrast to what happens for i-PBu, in which the transition is not mediated by the amorphous phase, but occurs directly as a solid–solid process (see Figure 5).

Another widely studied polymorphic stress-induced transformation is that regarding the orthorhombic and monoclinic phases of polyethylene.^{39–41} The mechanism of phase transformation has been described as a transverse shear process, with a slip direction normal to the chain axis.³⁹ The orthorhombic–monoclinic transformation is concomitant to the fragmentation of the crystalline lamellae, which results from the occurrence of localized crystal slip.^{40,41} In this respect the analogy of this process with the one of i-PBu is evident, since also the latter requires crystallographic slippage transverse to the chain direction, in particular along the 110 planes of the tetragonal form II.³⁶

■ CONCLUSIONS

Polymorphism has a double role in the mechanical properties of semicrystalline materials. On one hand the type of structure directly determines the final material properties; on the other hand the initial structure can completely change during deformation. The latter is the case of isotactic poly(1-butene), which crystallizes in a tetragonal modification (form II) that evolves to a trigonal structure (form I) during stretching.

The two polymorphs show a markedly different response to deformation. Form I presents a much higher modulus and yield stress, and the mechanical properties are not affected by the rate of deformation. On the contrary, the true stress–true strain

curves of form II are strongly deformation rate dependent. Indeed the signature of the polymorphic transition occurring during the tensile test is a remarkable strain hardening, which becomes more and more important the lower the strain rate.

The stretch induced transition has been followed by wide-angle X-ray diffraction during purposely designed mechanical test. Experiments at constant stress, at constant strain rate and at constant stress rate were carried out. The use of different time scales during the experiments enabled us to gain kinetics data on the transition, information which was overlooked in current literature.

By combining the results of the different mechanical protocols it is possible to elucidate the mechanism of transformation. At first a stress-driven process, which probably transforms directly the lamellae perpendicular to the drawing direction, is active. After a critical transformation value has been reached this process is exhausted and the effect of stress becomes less marked, since most of the applied stress is carried by form I crystals. In this latter stage the transformation is closely related to the process of plastic deformation: the stress enhanced nucleation of form I occurs while the form II lamellae undergo shear deformation, break up and transformation into fibrillar entities.

■ ASSOCIATED CONTENT

■ Supporting Information

True stress vs time and true strain vs time plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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