

Shear-induced Precursors of Fibrillar Crystals of Poly(butene-1): A Rheological Study

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Electronic Supplementary Information

Abstract Strong preshear flow stretches poly(butene-1) chains to form flow-induced precursors of fibrillar crystals. The formation leads to further growth of shear/normal stress after the stress reaches the steady state. In this study, stress relaxation measurements are performed after intervals of a strong flow during which the precursors form. The small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measurements are conducted to characterize the crystalline structure formed after the preshear and relaxation processes, each of different periods. A combination of the stress relaxation and scattering results reveal that for the precursors formed within 5 s, the stress can fully relax and the orientation of the subsequent crystals (formed upon quenching the sample at different stress levels) decays gradually with the relaxation. In comparison, for those precursors formed after 5 s, the stress hardly relaxes during $\sim 10^4$ s, and the orientation of the subsequent crystals hardly decays, suggesting that the precursors have been somehow stabilized during the shear. These features have been discussed with respect to the percolation of the precursors to form a reversible network.

Keywords PB-1; Rheology; Precursor; Fibrillar crystal

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INTRODUCTION

Shear-induced crystallization is a common and important phenomenon in polymer processing operations including extrusion and injection molding where the shear flow is dominant. The shear flow can greatly align and stretch the polymer chains, to reduce the barrier of nucleation, resulting in a higher density of nuclei.

To quantify the effect of shear flow, it is possible to define two Weissenberg numbers, *i.e.*, $Wi = \tau_d \dot{\gamma}$ and $Wi_R = \tau_R \dot{\gamma}$, where τ_d and τ_R are the disentanglement time and the Rouse time, respectively.^[1] $Wi > 1$ and $Wi_R > 1$ are usually regarded as the criterions for orienting and stretching the polymer chains, respectively. Nevertheless, these criterions may only be qualitatively valid because both τ_d and τ_R may change with $\dot{\gamma}$. On the one hand, the disentanglement time τ_d relies on the topological interaction among the neighboring chains, and this multi-chain interaction changes during the shear flow, through the mechanism like the convective constraint release,^[2] *i.e.*, the retraction of the chains transiently stretched by the flow field would allow disentanglement to the certain

extent thereby shortening the relaxation time.^[3,4] On the other hand, the interchain friction may also reduce when all chains are commonly oriented/stretched to the same direction.^[5–8]

For many semicrystalline polymers, the memories of chain orientation and stretch have a much longer lifetime than the chain relaxation time. Namely, to erase the shear memory usually requires prolonged annealing time at elevated temperatures.^[9] It has been proposed that this memory is due to the formation of flow-induced precursors with a long lifetime. The lifetime (of the precursor) is usually reflected from the following crystallization kinetics. For example, Binsbergen examined the stability of the flow-induced precursors of isotactic polypropylene (*i*PP) by observing the evolution of orientation of the fibrillar crystals formed after different annealing periods and temperatures.^[10] They found that to fully erase the orientational memory within an annealing time of 60 s required an annealing temperature as high as the equilibrium melting temperature.

The direct characterization of the precursor structure is challenging owing to its low density and less ordered structure compared with the crystals. Janeschitz-Kriegl *et al.* characterized decay of the birefringence of pre-stretched *i*PP^[11] to determine the lifetime of precursor. They found that the decay accelerated with increasing the annealing temperature, and the lifetime determined from this decay exhibited the

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Arrhenius-type temperature dependence. Nevertheless, the lifetime thus-determined was much shorter than that detected (indirectly) from the following crystallization kinetics. In other words, it seems that removing the shear-induced nuclei requires a much longer time than removing the birefringence that reflects the chain orientation. This difference raises new questions regarding the molecular details of the so-called precursor.

In this study, we attempt to develop a rheological protocol to characterize the kinetics of precursor formation during preshear using poly(butene-1) (PB-1) as a model system.^[12–14] PB-1 is well known for its high mechanical performance and strong resistance to creep and has been widely used for manufacturing pipes through extrusion, during which the shear flow is dominant. As a result, studying the shear-induced crystallization of PB-1 is of practical importance.^[15] Chen and coworkers examined systematically the shear-induced crystallization behavior of PB-1.^[16–20] For a relatively low- M PB sample (commercial name PB0400, weight, and number average molecular weights of $M_w=238$ kg/mol and $M_n=96$ kg/mol, respectively), they found that shearing the sample at $Wi>1$ accelerated the crystallization kinetics, and to fully smear the shear memory within 300 s required an annealing temperature as high as 140 °C, which was close to the equilibrium crystallization temperature of 146 °C. This result is in accordance with the observation of Binsbergen.^[10] For another PB-1 sample with relatively high M (commercial name PB0110, with $M_w=742$ kg/mol and $M_n=227$ kg/mol), Chen and coworkers examined the shear-induced crystallization of fibrillar crystals. Considering the inverse of an average Rouse time is $1/\tau_R=5.5$ s^{−1} at 125 °C, they examined the shear-induced crystallization at high shear rates of 5–50 s^{−1} where a large fraction of chains was stretched. They found that the critical work for obtaining the fibrillar crystal decreased with increasing the shear rate, probably because the larger the shear rate (within 5–50 s^{−1}), the higher fraction of chains were stretched. They also found that the transformation from shear-induced form II crystals, with an 11/3 helix, to thermodynamically more stable form I crystals, with a 3/1 helix, was greatly accelerated and the acceleration enhanced with the preshear rate. They argued that the acceleration was owing to the elastic tension sustained by the tethered interlamellar chains along the shear direction: the tension would facilitate the formation of form I nuclei.^[21–29] Chen and coworkers also found that the formation of precursor led to further growth of shear/normal stress after the stress reached steady state during the preshear, which was assigned to formation of gel-like structure.^[30] After the preshear, a much slower relaxation process than the chain reptation manifested in the linear viscoelasticity (LVE). This feature enabled them to characterize the lifetime of precursor through tracing the evolution of LVE with time. They found that the intensity of the slow process decayed with annealing, and the characteristic time for this

decay is ~7000 s at an annealing temperature of 125 °C. Nevertheless, the slow process did not vanish completely even after annealing for 14 h at 125 °C, but vanished immediately upon raising the temperature to 180 °C. To explain these results, Chen *et al.* proposed that the precursors may have a non-uniform structure: those with low stability dissolved with time while those with high stability transformed into crystals during the annealing.^[2]

This study is a follow-up study of the previous studies of Chen *et al.*^[19,20] with the purpose of investigating the formation kinetics of the precursors of the fibrillar crystals of PB-1. To this end, we characterize the relaxation of shear stress immediately after the preshear of different periods and correlate the stress growth and relaxation with the structural evolution of the precursors. We also find further growth of shear/normal stress after the stress reaches steady state and attribute it to the percolation of the precursors in space, leading to a gel-like structure, which enables the stronger chain stretch thereby facilitating further growth of the precursors. Details are explained below.

EXPERIMENTAL

Materials

The sample we used in this experiment is PB0110 (PB-1), which is a Ziegler-Natta-based linear polybutene-1 product provided by Lyondellbasell. The molecular weight and distribution were characterized by high temperature gel permeation chromatography (GPC) equipped with a refractive index (DRI) monitor, a two-angle laser light scattering (TALLS) monitor (Agilent), and a continuous viscometer (CV), as explained in the previous study of Chen *et al.* And the tacticity of 0.970 was obtained by ¹³C-nuclear magnetic resonance (¹³C-NMR).^[18] The important parameters are summarized in Table 1.

Rheological Measurements

All rheological measurements were conducted on a strain-controlled rheometer ARES-G2 (TA Instruments). The samples were protected by the N₂ atmosphere to eliminate the degradation. An 8 mm cone-and-plate geometry with the cone angle of 0.0402 rad and truncation gap of 0.0558 mm was chosen. In our previous study, we found that the onset time for formation of shear-induced precursors was essentially the same upon conducting startup shear at 125 and 130 °C. We choose to study the stress growth and relaxation at 125 °C in this study because the precursors are more stable therein.

Small-angle X-ray Scattering and Wide-angle X-ray Diffraction

The WAXD measurements were conducted using a custom-designed microfocus WAXD system (Xenocs SA, France) with a focused Cu K α X-ray source (GeniX3D, Xenocs SA, France) at a position of a radius of $R=3$ mm of the PB-1 sample disks of a diameter of 8 mm (unloaded from the rheometer). This position

Table 1 Important parameters of the PB-1 sample.

Name	M_n (g/mol)	M_w (g/mol)	M_w/M_n	M_e^a (g/mol)	T_g (°C)	T_m^b (°C)	τ_d^c (s)	τ_R^d (s)
PB0110	2.27×10^5	7.42×10^5	3.3	7.5×10^3	−22	115.9	62.5	0.179

Reported in Refs. [16,18,19]. ^a Determined from the double reptation model of the LVE master curve; ^b Melting temperature of form II; ^{c,d} Entanglement relaxation time and rouse relaxation time at reference temperature 125 °C.

was chosen because it was hardly affected by either the edge fracture or the truncation of the cone. The X-ray beam was generated at 50 kV and 0.6 mA, and its wavelength was 0.154 nm. The beam was focused on the sample position with a size of $40\ \mu\text{m} \times 60\ \mu\text{m}$, WAXD images were recorded using a semiconductor detector with a resolution of $487\ \text{pixel} \times 195\ \text{pixel}$, the pixel size was $172\ \mu\text{m} \times 172\ \mu\text{m}$, and the sample-to-detector distance was 37 mm (Pilatus 100 K, Dectris, Swiss). Each pattern was collected for 120 s.

The SAXS measurements were carried out on the 1W2A small-angle X-ray scattering station at Beijing Synchrotron Radiation Facility (BSRF). The wavelength of the X-ray was 1.54 Å, and the distance between the sample and the detector was 3500 mm. Two-dimensional (2D) scattering patterns were collected using a two-dimensional image plate detector, MAR165, with a pixel size of $79.1\ \mu\text{m} \times 79.1\ \mu\text{m}$ ($2048\ \text{pixel} \times 2048\ \text{pixel}$). The exposure time for each sample was 10 s. The 2D patterns were analyzed with Fit2D software.

Both WAXD and SAXS measurements were conducted for the crystallized samples annealed at room temperature (T) for more than two weeks. This choice was made because we found in our previous study that the strong preshear ($\geq 10\ \text{s}^{-1}$) led initially to the formation of the form II crystals, and the following form II to I transformation was greatly accelerated. Therefore, it was difficult to characterize the pure form II crystals and thus we conducted the scattering measurements on the fully annealed samples for which the form II to I transformation had been completed.

RESULTS AND DISCUSSION

Experimental Protocol

In the previous study of Chen *et al.*, they determined several important dynamic-related parameters from the linear viscoelasticity of PB-1, including the disentanglement time τ_d and Rouse time τ_R at $125\ ^\circ\text{C}$, as summarized in Table 1. From these values, we choose to apply preshear of $\dot{\gamma}=10\ \text{s}^{-1}$ in this study, considering that the criterion of chain stretch is $\dot{\gamma} > 1/\tau_R=5.5\ \text{s}^{-1}$ at $125\ ^\circ\text{C}$.^[19,31]

Fig. 1 illustrates the experimental protocol of this study. The PB-1 sample is heated to $180\ ^\circ\text{C}$ and annealed there for 10 min to remove the thermal and flow histories, and cooled down to $125\ ^\circ\text{C}$ at a rate of $10\ ^\circ\text{C}/\text{min}$, and then subjected to a shear flow of $\dot{\gamma}=10\ \text{s}^{-1}$ for different periods (3, 5, 8, 10, and 14 s). After the cessation of shear flow, the sample is relaxed for $\sim 10^4\ \text{s}$, and cooled down to $35\ ^\circ\text{C}$ for crystallization. After that, the sample disk is unloaded from the rheometer carefully and stored at room temperature for a sufficient period (more than two weeks) for the form II to I transition. After that, the sample disks are subjected to SAXS and WAXD measurements to characterize the crystalline structure of the PB-1 sample.

Crystallization Behavior After Stress Relaxation

Fig. 2 shows the transient shear stress σ^+ (filled square symbols) and primary normal stress N_1^+ (filled diamond symbols) responses upon the application of the steady shear of $10\ \text{s}^{-1}$ at $125\ ^\circ\text{C}$, and the transient stress σ^- during the stress relaxation after the preshear of different periods, $t_s=3, 5, 8, 10, 14\ \text{s}$ (unfilled sphere symbols). To trace the structural evolution of the

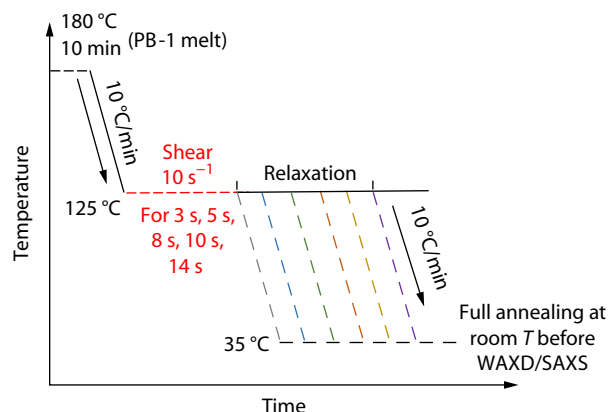


Fig. 1 Schematic illustration of the experimental protocol: relaxation of shear stress after the preshear of different periods of PB-1 and correlate the stress evolution with the structural change of the shear-induced precursors.

precursor, the sample is quenched before and during the stress relaxation process, where the time points of quenching are indicated by the larger unfilled sphere symbols.

In Fig. 2, the onset time of further growth of shear/normal stress is 5 s after the stress reaches steady state. Therefore, $t_s=3\ \text{s}$ and $t=8\ \text{s}$ or longer can be regarded as the measurements before and after the onset, respectively. The different stress relaxation behavior is indeed seen for these two cases. After preshear of $t_s=3\ \text{s}$, the stress relaxation can be achieved within $1 \times 10^4\ \text{s}$. In comparison, the stress cannot fully relax within $1 \times 10^4\ \text{s}$ after shearing of $t_s=5\ \text{s}$ or longer. This result indicates that the onset corresponds to the formation of a certain gel-like structure that cannot relax during the $1 \times 10^4\ \text{s}$.

To further check the different relaxation behavior, we normalize the stress during the relaxation $\sigma^-(t - t_s)$ with that at the starting point of the relaxation, i.e., $\sigma^-(t_s)$ at t_s , and plot the normalized stress against the relaxation time $t - t_s$ in Fig. 3

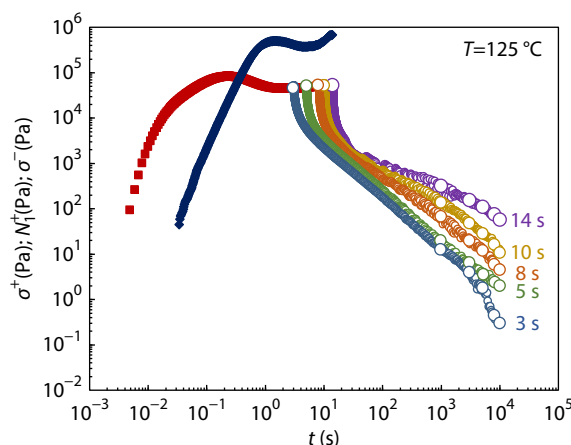


Fig. 2 Evolution of the transient shear stress σ^+ (filled squares) and primary normal stress N_1^+ (filled diamonds) during the startup measurements, and the transient stress σ^- during the stress relaxation measurements (unfilled small spheres) after preshear of different periods as indicated ($t_s=0, 3, 5, 8, 10$, and $14\ \text{s}$, see unfilled large spheres).

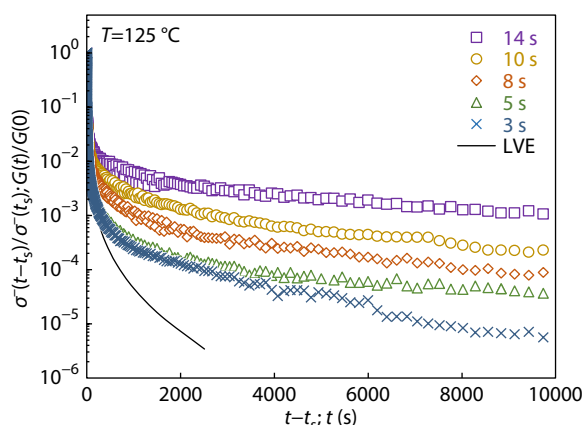


Fig. 3 Transient stress during the relaxation $\sigma^-(t-t_s)$ normalized by $\sigma^-(t_s)$ at t_s with t_s being the shearing time and plotted against the relaxation time $t-t_s$. For comparison, the linear relaxation modulus $G(t)$ is normalized by $G(0)$ at $t=0$ s and plotted against t in the solid curve.

(in unfilled symbols). For comparison, we also normalize the linear relaxation modulus $G(t)$ by $G(0)$ at $t=0$ s and plot $G(t)/G(0)$ against t in solid curve. Comparison between the plot of $\sigma^-(t-t_s)/\sigma^-(t_s)$ against $t-t_s$ with $t_s=3$ s and $G(t)/G(0)$ against t reveals that the relaxation of the former is still considerably slower than the disentanglement time determined from the linear viscoelasticity. For usual entangled polymer chains, the chain relaxation time after the nonlinear preshear should be similar to or even faster than the disentanglement time obtained in LVE owing to the mechanism like convective constrain release^[3,4] and the frictional reduction.^[5–8] Therefore, the slower relaxation after preshear unequivocally indicates that certain structures larger than the polymer chains have formed. The stress can fully relax after preshear with $t_s=3$ s probably because the precursors have formed but not stabilized, and thus the relaxation of stress can be more easily achieved through the thermal motion of the precursors. In contrast, stress relaxation cannot be achieved after the preshear of $t_s=5$ s even after a relaxation time of $\sim 10^4$ s, and σ^- at a long time ($\sim 1 \times 10^4$ s) increases with the shearing time. This trend may reflect that the percolated structure forms for the precursors, which grows with increasing t_s , leading to the

higher σ^- . One piece of evidence of this argument is that the further growth of both σ^+ and N_1^+ after the stress reaches steady state can be seen after $t_s=5$ s. Probably, the formation of the percolated network would strongly facilitate the chain stretch, particularly for those network strands, thereby in turn stabilizing the precursors.

The samples after preshear and relaxation, each of the different periods, were quenched and annealed for more than two weeks at room temperature to complete the form II to I transformation, and subjected to the SAXS and WAXD measurements. It should be noted that the preshear and relaxation processes affect not only the crystalline structure, but also the crystallization kinetics, e.g., application of a preshear of 10 s^{-1} for 5 s strongly increases the onset T of crystallization during cooling, as shown in Fig. S1 (in the electronic supplementary information, ESI). Nevertheless, the present focus is placed on the crystalline structure rather than the crystallization kinetics. Fig. 4(a) compares the two-dimensional WAXD profiles obtained for the sample quenched after representative shearing periods of $t_s=3, 5, 8$ and 14 s and the relaxation time $t-t_s=0, 1000, 3000, 5000, 8000, 10000$ s. Before the stress relaxation ($t_s=0$), the orientation of the form I crystals increases with t_s : The diffraction spots of (110), (300) and (220+211) crystallographic planes of the oriented crystals of form I manifest gradually with increasing t_s in the 2D scattering profiles. In particular, the diffraction spots of the (110) plane appear along the shear direction after the preshear of $t_s=3$ s,^[32] which fade away gradually with increasing the relaxation time up to $\sim 1 \times 10^4$ s, in accordance with the full stress relaxation seen earlier in Figs. 2 and 3. The diffraction spots intensify and fade away more slowly with increasing t_s to 5 s or longer: for the extreme case with $t_s=14$ s, the diffraction spots remain even after a relaxation period of 10^4 s.

To quantify the relationship between the stress relaxation and the subsequent crystalline orientation, we evaluate the orientation order parameters S_{hkl} that represents the orientation of the normal vector of the lattice plane (hkl) to the reference direction (shear direction) using the Hermans orientation equation:^[33]

$$S_{hkl} = \frac{3 \langle \cos^2 \phi_{hkl} \rangle - 1}{2} \quad (1)$$

where ϕ_{hkl} denotes the angle between the stretching direction

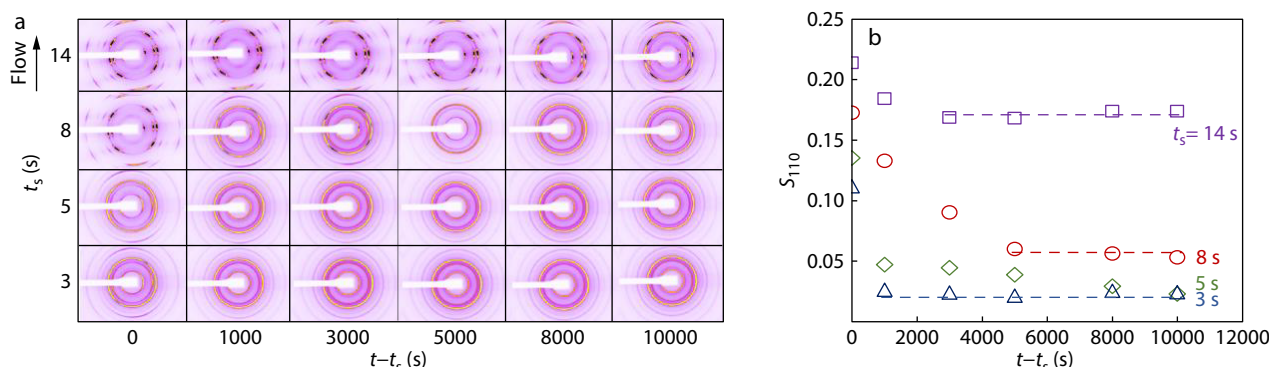


Fig. 4 (a) 2D WAXD scattering patterns of PB-1 samples obtained after preshear of different t_s and relaxation of different periods, $t-t_s$. The shear direction is indicated in the arrow. (b) The evolution of the degree of orientation of 110-reflection (S_{110}) associated with the 110-reflection with relaxation time $t-t_s$ for PB-1 samples after different shearing periods t_s .

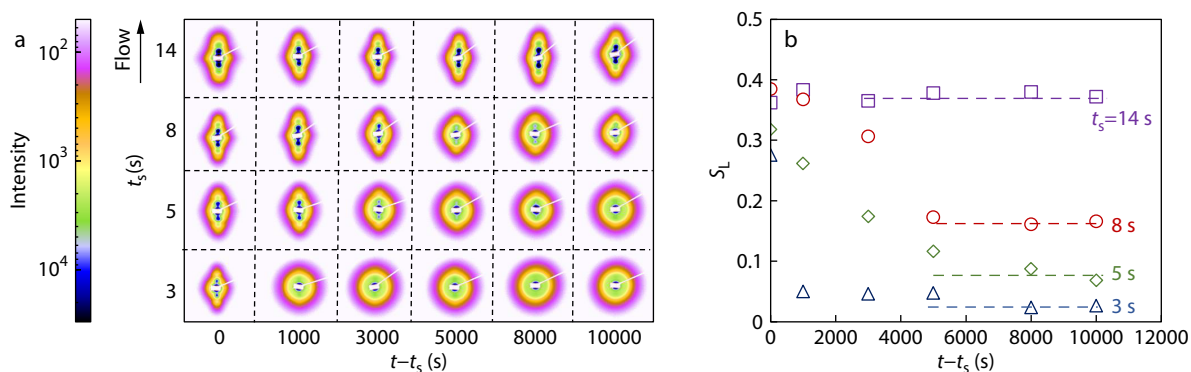


Fig. 5 (a) Evolution of scattering patterns of 2D SAXS with different shearing periods t_s and relaxation time $t - t_s$. The shear direction is indicated by the arrow. (b) Orientational parameter S_L plotted against $t - t_s$.

and the normal vector onto the lattice plane or onto the amorphous chain sequence, and $\cos\phi_{hkl}^2$ is defined as:

$$\langle \cos\phi_{hkl}^2 \rangle = \frac{\int_0^{\pi/2} I_{hkl}(\phi) \cos^2\phi \sin\phi d\phi}{\int_0^{\pi/2} I_{hkl}(\phi) \sin\phi d\phi} \quad (2)$$

The value of the order parameter can be derived from the azimuthal intensity distribution function $I(\phi)$ along the respective circle by using the Polanyi equation:^[34]

$$\cos\phi_{hkl} = \cos\theta_{hkl} \cos\psi \quad (3)$$

The equation relates the azimuthal angle ψ along the Debye circle and the Bragg scattering angle 2θ to ϕ .

Fig. 4(b) compares S_{110} obtained for the 2D profiles shown in Fig. 4(a), where S_{110} obtained after the preshear of t_s is plotted against the relaxation time $t - t_s$. S_{110} obtained after preshear of different t_s differs not only in the initial amplitude, but also in the decay behavior. The strong decay can be clearly observed for $t_s \leq 8$ s, but the remaining fraction of the crystalline orientation after the annealing of 10^4 s increases with increasing t_s , subsequently the crystalline orientation can hardly decay after preshear of $t_s = 14$ s.

Similar decay behavior of the crystalline orientation can be observed in the 2D SAXS patterns in Fig. 5. The SAXS patterns provide additional information regarding the formation of the shish-kebab structure. The patterns in Fig. 5(a) reveal a transition from highly oriented crystals after preshear of $t_s = 3$ s to almost anisotropic crystals after the stress relaxation of $t - t_s = 10^4$ s. Importantly, a bright-streak orthogonal to the flow direction appears for $t_s = 8$ or 14 s, reflecting the formation of the shish-kebab structure, where the streak position indicates a correlation spacing of the shish bundle chains. The streak vanishes after relaxation of 3000 s for preshear of $t_s = 8$ s but remains even after relaxation for 10^4 s for preshear of $t_s = 14$ s. In the right panel, we compare the orientation parameter S_L defined by the integrate of lamellar crystal, where the decay behavior is quite similar to that revealed in the Fig. 4(b), i.e., the orientational decay slows down with the increasing t_s and becomes very weak for $t_s = 14$ s, leading to a high degree of orientation therein. Comparison of the scattering and stress relaxation results suggests the strong correlation among (1) the hardening seen as a growth of σ^+ and N_1^+ after the stress reaches steady state, (2) the relaxation behavior of the stress sustained by the precursor, and (3) the formation of

the shish-kebab structure. All these features can be explained through considering the percolation of the shear-induced precursors in space, because the percolation leads to the formation of a transient network and accordingly stronger chain stretch during the continuous flow, which would in turn facilitate the formation or growth of precursors with the higher stability.

CONCLUSIONS

This study examines the structural evolution of shear-induced precursors of fibrillar PB-1 crystals during both the preshear and the following annealing processes. The experiment is carefully designed to cover a range before and after the onset of the growth of σ^+ and N_1^+ after the stress reaches steady state. We find that the stress cannot fully relax after the onset, and the remaining stress after the 1×10^4 s annealing increases greatly with extending the period of preshear longer than 5 s. In addition, we find that the shish-kebab structure manifests when the shear period is longer than 5 s, and the fraction of non-decayable orientation also increases significantly with the period of preshear longer than 5 s. We propose that the formation of the shish-kebab crystals is related to the formation of a reversible precursor network that is indicated by the onset. After the onset, the networks strands are strongly stretched by the subsequent shear flow, thereby in turn stabilizing the gel-like precursors.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2705-5>.

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