Polymorphic Transition of Pre-oriented Polybutene-1 under Tensile Deformation: In Situ FTIR Study

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Abstract  Deformation-induced phase transition of Form II to Form I in polybutene-1 (PB-1) has been investigated by time-resolved Fourier transform infrared (FTIR) spectroscopy over a wide temperature range from 25 °C to 105 °C. The initial film sample containing orientated lamellae is prepared by pre-stretching of PB-1 melt followed by solidification. This is to realize a homogeneity of subsequent deformation at the mesoscale of lamellar stacks by avoiding large-scale spherulites. The deformation induced phase transition is recognized to occur with two stages: first, Form II undergoes the lamellar fragmentation, slipping or local melting after yielding to activate its transition to Form I, which may be realized by releasing the restrictions on chains translational movements in crystalline phase; second, the phase transition proceeds with a continuous dissipation of external work and determines the tensile mechanical response of film. To quantify the relationship between crystalline transition of Form II to Form I and external tensile field, a simple kinetic equation is well established based on FTIR measurement. The equation can describe not only the dependence of crystal transitional degree on applied specific work, but also the retardation effect of elevating temperature on phase transition.

Keywords  Polybutene-1; Tensile deformation; FTIR; Crystalline transition; External work

INTRODUCTION

Tensile deformation is a common technical approach for industrial processing of semicrystalline polymers like film fabrication and fiber spinning, which is also encountered in the actual application of polymeric products a lot. Due to the stress sensitive polymorphism, deformation-induced phase transition of semicrystalline polymers has been an issue of great concern in both polymer academia and industry. The crystalline transition under deformation is suggested to proceed by two main protocols, including a direct chain conformational adjustment of solid-solid process and melting-recrystallization mediated by amorphous phase. Experiments in polyolefin have demonstrated that the crystalline transition for one polymer system is changeable between the two modes, depending on the specific deformation conditions like strain rate, temperature, crystal stability, etc. On the other hand, the crystal-crystal transition in return may lead to unique mechanical properties of polymer material, ascribed to the incorporation of new phase or the energy dissipation in the transitional process. Typical example can be found in β-IPP where deformation-induced β to α phase transition has been reported to be responsible for the improved toughness. Thus investigating the deformation-induced phase transition of semicrystalline polymers is of not only scientific importance but also great practice significance.

Polybutene-1 (PB-1) is a commercially valuable semicrystalline polyolefin with remarkable physical and mechanical properties, including good abrasion resistance, temperature resistance, low creep, and durableness with non-toxic. It presents four different crystal forms relying on crystallization condition, namely, I, I', II, and III. Directly cooling PB-1 melt under atmospheric pressure, Form II is generally formed but remains metastable and transforms into thermodynamically stable Form I after keeping at room temperature. Depending on the environmental condition, this transition may take several weeks to finish, during which the material properties are changed profoundly. By imposing tensile deformation, the transition of Form II to Form I can be significantly accelerated. Considering that deformation-induced Form II to Form I transition is able to occur far...
below vitrification temperature,[37] the related molecular mechanism should be different from that of the quiescent condition. By applying shear deformation perpendicular or parallel to the lamellar axis and tracking the lattice orientation with X-ray diffraction, Fujiwara proposed that the formation of Form I mainly results from the inter-lamellar slipping of Form II.[38] With imposing constant engineering stress to Form II, Goldbach found that the kinetics acceleration of phase transition occurs only at stress above the yield stress.[29,30] Then, the author directly attributes the kinetics enhancement to shear stress. Recently, with designing experiments of constant stress, constant strain rate, and constant stress rate, Cavallo et al. investigated the polymorphic transition of PB-1 in detail.[39] The stress-driven phase transition was found to slow down at later stage, which was ascribed to the massive formation of mechanically stronger Form I lamellae carrying the major part of applied stress. With using time-resolved synchrotron X-ray diffraction, our previous work has connected the phase transition process of Form II to Form I to the tensile stress-strain curve precisely, where three-stage mechanical deformation is recognized in terms of incubation, nucleation, and gelation of Form I crystal.[35] The strain hardening corresponding to the last stage is suggested to result from an increased connectivity of newly formed Form I crystallites. In view of the molecular dynamics, Miyoshi et al. demonstrated that Form II is a conformationally disordered crystal and performs extremely fast chain dynamics with uniaxial rotational diffusion of crystalline stems accompanying side-chain conformational transitions by nuclear magnetic resonance (NMR), while Form I does not undergo any overall or side-chains dynamics up to the melting point.[40,41] The huge chains dynamic contrasts lead to much higher mechanical strength of PB-1 with Form I than its counterpart with Form II.

Despite years of work on deformation-induced phase transition of PB-1, very few quantitative trends are known with confidence, such as the relationship between structural evolution and external deformation conditions like deformational work and temperature, which is important for understanding the processing and service characteristics of material. In this work, in situ Fourier transform infrared (FTIR) spectroscopy was performed to monitor the phase behaviors of pre-oriented PB-1 film under uniaxial deformation over various temperatures. Compared to conventional X-ray diffraction where the crystalline signal may be influenced by the sample or lattice orientation, non-polarized FTIR is more reliable to quantitatively characterize the actual content variation of crystal as well as its transition under deformation. Also, the pre-oriented PB-1 selected as the testing sample is conducive to acquiring the intrinsic structure-mechanics relationship of lamellae by eliminating the influence of large-scale spherulites. The onset of Form I is found to lag behind the decrease of Form II after yielding, indicating that lamellar fragmentation, slipping, or melting may be a prerequisite for Form I formation, which takes effect by a possible way of releasing the restrictions on chains’ translational movements in crystalline phase. On the basis of FTIR measurement, the deformation-induced Form II to Form I transition is quantitatively correlated to the specific work of applied tensile field, according to which the transitional kinetics and the temperature effect are discussed.

EXPERIMENTAL

Sample Preparation

Commercially available PB-1 (trade name PB0110M) was purchased from Lyondell Basell Industries with number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of 230 and 711 kg/mol, respectively. Its quiescent melting temperature was 127 °C for Form I and 117 °C for Form II measured by a differential scanning calorimeter (DSC, TA Instruments 2920) with a heating/cooling rate of 10 °C/min. Raw PB-1 granules were first molded into thin films by vacuum press at 180 °C under 10 MPa for 10 min, and then cooled rapidly down to room temperature for solidification. The thickness of PB-1 film was about 0.2 mm that ensured the effective light transmission of Fourier transform infrared (FTIR) spectroscopy. The prepared film was cut into rectangular pieces with a dimension of 26 mm × 8 mm × 0.2 mm for tensile experiment.

Experimental Procedure

A homemade two-drum tensile device is employed to impose well-defined deformation and thermal history on the sample, which is schematically drawn in Fig. 1(a). Its design is similar to Sentmanat-type rheometer, as detailedly described elsewhere.[42] The rectangular sample is secured to two geared drums by means of thin clamps. Tensile deformation is realized by servo motor driving two geared drums to synchronously rotate in the opposite direction. The sample length ($L_o$) of 16 mm subjected to deformation keeps unchanged in the whole process, allowing us to obtain the Hencky strain ($\varepsilon$) of sample. The strain rate is defined as $\varepsilon = 2V/L_o$ with a rotational

![Fig. 1](https://doi.org/10.1007/s10118-020-2409-7)
linear velocity $V$ of each drum. Tensile parts including clamps, drums, and the sample are located in a heating oven, which is sealed by two ZnSe plates to allow IR light passing through the sample center. It should be noted that the drum surface is fully roughed by abrasive blast in order to avoid the sample slipping under deformation.

Fig. 1(b) presents the experimental procedure in this work. Each film sample was first heated up to 180 °C at a rate of 15 °C/min and then held for 10 min to erase the preparation history. Thereafter, it was rapidly cooled down to room temperature (25 °C) at a rate of about 8 °C/min, during which a step-strain of 0.8 with strain rate of 1 s$^{-1}$ was applied to melt once the temperature reached 120 °C. Such a pre-stretching provided the molecular chains with a certain pre-orientation. By further lowering temperature, the oriented lamellar crystal was formed (see the X-ray diffraction measurement in the electronic supplementary information, ESI), which was fully completed by keeping sample at room temperature for 3 min. Note that without large-scale spherulites inside, the resulting oriented lamellae can make the subsequent deformation of sample relatively homogeneous at the mesoscale of lamellar stacks[43,44] which is of great benefit for extracting the intrinsic relationship of structural evolutions and mechanical behaviors. The pre-oriented film was then heated to the preset target temperature $T$ and held for 5 min followed immediately by stretching. Meanwhile, a slow nitrogen gas flow was used as heating/cooling medium to homogenize the sample temperature and realized a temperature fluctuation of ±0.5 °C. The tensile temperature $T$ covers a wide range from 25 °C to 105 °C with an interval of 20 °C. Torque was recorded by a torque sensor in real time to characterize the mechanical response of film. For all the experiments, the tensile speed of 112 μm/s corresponding to a strain rate of 0.007 s$^{-1}$ kept constant until the sample was finally fractured.

During tensile deformation, the structural evolution was monitored by in situ FTIR measurements which were carried out in a Bruker Tensor 27 FTIR spectrometer. The measured wavenumber covered a range of 700–3900 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Eight scans were taken to average the signals for one FTIR spectrum, corresponding to a time resolution of 3.5 s/frame or a strain resolution of 0.025/frame. The baseline of each spectrum was adjusted uniformly using OPUS 5.5 package.

**RESULTS AND DISCUSSION**

**Tensile Mechanical Behavior**

Engineering stress ($\sigma_2$)-strain curves of the tensile deformation with strain rate of 0.007 s$^{-1}$ at different temperatures of 25, 45, 65, 85, and 105 °C are plotted in Fig. 2. At the initial deformational stage within the small strain of around 0.1, the sample presents an elastic mechanical behavior followed by yielding. Note that no stress maximum is observed around the yielding point for each experiment, consistent with the almost no necking occurrence of film shown in Fig. 1(a). This is different from the situations of normal PE and iPP, where significant stress maximum is always observed. There are two possible reasons. One is that the initial film sample used in this work is pre-oriented, which does not tend to adopt a stress maximum as sharp as the un-oriented one containing isotropic spherulites, as reported in PE and iPP[45,46] The other is that the high mobility of crystalline stems in Form II is comparable to the amorphous phase[46-48] which avoids the stress maximum at the yielding point. Overall, the tensile deformation of pre-oriented film can be taken to be homogenous at the macroscale. By further increasing tensile strain, the stress shows an accelerated increase until the final fracture of sample, namely an enhancement of tensile modulus. Overall, high temperature always leads to a lower tensile stress and also a larger fracture strain than that of low temperature.

![Fig. 2 Engineering stress-strain curves of pre-oriented PB-1 film under tensile deformation with strain rate of 0.007 s$^{-1}$ at different temperatures from 25 °C to 105 °C.](https://doi.org/10.1007/s10118-020-2409-7)

**Polymeric Transition of PB-1**

FTIR measurement is synchronously implemented to follow the structural evolution of PB-1 film under deformation. Fig. 3 presents a representative experimental result at 25 °C to reflect the time or strain dependence of IR absorption spectra. According to previous literature reports, the bands at 1328, 1098, 1060, 1027, 1014, 1000, 923, 845, and 815 cm$^{-1}$ stem from the conformational vibrations of Form I crystal, while 1111, 1049, 1001, and 905 cm$^{-1}$ from Form II[46-48] For simplicity, we only focus on the two stronger characteristic bands at 923 and 905 cm$^{-1}$ to analyze the evolutions of Form I and Form II.
respectively, which are assigned to the CH$_2$ and CH$_3$ rocking vibration mode in their crystal lattices. It can be found that the absorption band at 905 cm$^{-1}$ weakens gradually along with increasing tensile strain, during which the band at 923 cm$^{-1}$ becomes increasingly strong. This trend indicates a deformation-induced crystalline transition of metastable Form II to stable Form I of PB-1. By multi-peak fitting with Gaussian function in Fig. 4(a), the absorbance curve between 870 and 950 cm$^{-1}$ is deconvoluted into two components for a quantitative analysis of crystalline content variation. In addition, the absorption intensity of the band at around 1152 cm$^{-1}$ that represents the backbone CH$_2$ bending and C$\equiv$C covalent-bond vibrations keeps decreasing in the whole deformational process, showing no correlation with that of 923 and 905 cm$^{-1}$. This indicates that it can be taken as the fingerprint of film thickness.

The integral area of absorption band is calculated to reveal the content variation of corresponding structure. To characterize the film thickness, the area ($A_{1152}$) surrounded by the band between 1125 and 1165 cm$^{-1}$ and the horizontal baseline is integrated, as shown in Fig. 4(b). By eliminating the influence of film thickness on spectral intensity, the area ratios of $A_{923}/A_{1152}$ and $A_{905}/A_{1152}$ are employed to evaluate the contents of Form I (Fig. 4c) and Form II crystal (Fig. 4d), respectively. It can be seen that $A_{923}/A_{1152}$ starts at a value of around 0.3 rather than 0, indicating a small amount of Form I already existing in the initial film, which can be attributed to the induction of pre-deformation with strain of 0.8 imposed at 120 °C. By increasing tensile strain, Form I increases after undergoing a temporary plateau or weak decline. The calculated $A_{923}/A_{1152}$ reaches a final saturation value close to 3 for deformation at 25 and 45 °C, in contrast to the continuous increase until film fracture above 65 °C. Meanwhile, Form II ($A_{905}/A_{1152}$) keeps decreasing when the strain is beyond yielding. The lower the temperature, the faster the content variations of both Form I and Form II.

Due to the structural difference between hexagonal Form I with chain conformation of $\alpha$ helix and tetragonal Form II with $\beta$ helix and tetragonal Form II with $\beta$ helix and tetragonal Form II, the absolute absorption intensities of Form I at 923 cm$^{-1}$ ($A_{923}$) and Form II at 905 cm$^{-1}$ ($A_{905}$) per unit of mass is different. To count the total crystal content under deformation, establishing the numerical relationship between $A_{923}$ and $A_{905}$ is a required step, although some previous researches have employed an assumption of $A_{923} = A_{905}$. To solve this, the FTIR spectra of undeformed PB-1 film after keeping 0 and 7 days at room temperature (25 °C) are compared in Fig. 5(a). With an assumption of linear relation $A_{923} = \beta A_{905}$, the total crystal content $X_c$ can be expressed as

![Fig. 4](https://doi.org/10.1007/s10118-020-2409-7)
Deformation-induced melting or crystallization of PB-1 can be illustrated by calculating the variation of total crystal content in the subsequent process. Compared to the significant increase of average slope of absorbance (Fig. 4(c)), which further supports that Form I comes mainly from the transition of Form II rather than the crystallization of amorphous phase. Compared to the transition at the quiescent condition where several weeks may be taken to finish,[24,28] tensile deformation greatly accelerates this process. Besides, increasing deformational temperature would retard the crystalline transition of PB-1, as shown by a decrease of average slope of $D_t$ curves.

The Form II to Form I transition has been reported to be a nucleation and growth process at the quiescent condition,[32,34,35] where the nucleus of Form I is thought to be created by thermal stress or internal stress due to the existence of irregular stack of lamellae, local variation of lamellar thickness, and bending of lamellae.[27] In this work, the tensile deformation has shortened the phase transition period from

\[ D_t = \frac{\Delta a_{923}}{\Delta a_{923} + \beta a_{905}} \]  

Fig. 5(d) shows the calculated $D_t$ as a function of strain at different temperatures. $D_t$ develops with a similar trend to that of Form I in Fig. 4(c), which further supports that Form I comes mainly from the transition of Form II rather than the crystallization of amorphous phase. Compared to the transition at the quiescent condition where several weeks may be taken to finish,[24,28] tensile deformation greatly accelerates this process. Besides, increasing deformational temperature would retard the crystalline transition of PB-1, as shown by a decrease of average slope of $D_t$ curves.

To further clarify the effect of tensile deformation on crystalline transition, the transitional degree ($D_t$) of Form II to Form I is calculated with

\[ D_t = \frac{\Delta a_{923}}{\Delta a_{923} + \beta a_{905}} \]  

Relationship between Crystal Transitional Degree and External Work

The Form II to Form I transition has been reported to be a nucleation and growth process at the quiescent condition,[32,34,35] where the nucleus of Form I is thought to be created by thermal stress or internal stress due to the existence of irregular stack of lamellae, local variation of lamellar thickness, and bending of lamellae.[27] In this work, the tensile deformation has shortened the phase transition period from

\[ X_c = \beta \frac{a_{905}}{A_{1152}} + \frac{a_{923}}{A_{1152}} \]  

by equating the total crystal to Form I. With considering the constant $X_c$ due to no melting or crystallization of PB-1 expected at the quiescent condition at 25 °C, one can further obtain

\[ \beta \frac{a_{905}}{A_{1152}} + \frac{a_{923}}{A_{1152}} = \beta \frac{a_{905}}{A_{1152}} + \frac{a_{923}}{A_{1152}} \]

Here, $a_{905}$, $a_{923}$, and $A_{1152}$ are data from the film keeping for 0 day, and $A_{905}$, $A_{923}$, and $A_{1152}$ for 7 days. By deconvoluting the absorbance curves (Fig. 5b), the value of $\beta$ is calculated to be 1.27. This means that the IR absorption of CH$_2$ and CH$_3$ rocking vibration in crystal lattice is enhanced once Form II is transformed into Form I.
several weeks needed at the quiescent condition to less than 10 min, so it is reasonable to consider that the transition is mainly driven by applying large external stress while the spontaneous transition due to internal thermal stress is negligible. In addition, it is accepted that Form I has a lower free energy ($G_I$) than that of Form II ($G_{II}$), but Form II to Form I transition must overcome a free energy barrier $G^*$ no matter at the quiescent or deformational condition. Thus, the acceleration effect of deformation on phase transition can be ascribed thermodynamically to the decrease of $G^*$ due to the rise of $G_{II}$, analogous to flow-induced crystallization in supercooled polymer melts.\[56\] As a non-equilibrium process, the transition of Form II to Form I under deformation requires a continuous input and dissipation of external energy to maintain, which is actually provided by the deformation work.

Here, the specific tensile work $w$ is employed to tentatively correlate with the structural evolution, which is defined as the work applied to the sample per unit of volume (J/cm$^3$). Given the tensile mode by two drums rotation in the opposite direction in this work, the true stress is calculated by $\sigma_t(e) = \sigma_f(e)e^{\varepsilon}$ due to the approximately homogeneous deformation of film without necking. Then, $w$ is expressed as

\[ w(e) = \int_0^e \sigma_f(e)e^{\varepsilon} \, \varepsilon \, \text{d}\varepsilon \]  

which can be computed based on the engineering stress-strain curves in Fig. 2. Fig. 6(a) plots the crystal transitional degree $D_t$ as a function of $w$ in different experiments. In terms of reflecting the dependence of $D_t$ on deformational temperature, the $D_t-w$ curves are consistent with the $D_t-\varepsilon$ curves (Fig. 5d), that is, elevating temperature retards the transition. It needs to be emphasized that the retardation effect is not caused by the low tensile stress or low external work at high temperature, but the low transitional efficiency, which is the intrinsic property of PB-1 phase transition.

Fig. 6(a) shows that the phase transition starts from an initial value of $D_t = 0.08$, which results from the pre-stretching of PB-1 melt at 120 °C as mentioned above. However, the maximum $D_t$ is just close to 0.8 but not an ideal value of 1 under deformation, such as at 25 and 45 °C. This indicates that the tensile operation is unable to realize a thorough transition of Form II to Form I, agreeing with the report from Cavallo et al.\[39\] Very recently, Qiao et al. proposed a mechanism to explain the similar retardance of transition under the quiescent condition, where the internal stress responsible for phase transition is suggested to be shielded by already formed Form I lamellae.\[37\] Such a case may be also encountered during the tensile deformation, since the massive formation of highly ordered Form I would also influence the local stress or strain transmission, leading to low stress or even stress-free state of partial Form II until the fracture of sample.

**Theoretical Modeling**

The crystalline transition of Form II to Form I under deformation proceeds at the expense of external work thermodynamically. Referring to the Evans-Avrami equation that describes the isothermal crystallization kinetics with time as an independent variable,\[58,59\] the variation rate of $D_t$ with $w^\alpha$ is assumed to hold in a linear relation with the unconverted portion, that is,

\[ d D_t(w)/d w^\alpha = K[D_{t-max} - D_t(w)] \]  

where $D_{t-max}$ is the achievable maximum transitional degree, $n$ is a constant that will be discussed later, and $K$ is a coefficient that reflects the transitional efficiency driven by specific work. From Eq. (5), one can obtain

\[ D_t(w) = D_{t-max} - C e^{\alpha(-K w^n)} \]  

where $D_{t-max}$ is about 0.8 for pre-oriented PB-1 film in this work. Given a boundary condition that the initial $D_t$ is about 0.08 at $w = 0$ J/cm$^3$ before tensile deformation, $C$ is calculated to be 0.72. Then, Eq. (6) can be specified as $D_t(w) = 0.8 - 0.72 e^{\alpha(-K w^n)}$.

Comparing Figs. 4(c) and 4(d), Form I always requires a certain strain or work consumption before its onset, in contrast to the approximatively continuous decrease of Form II. Within small strain of 0.1 before yielding, both Form I and Form II adopt a constant content due to the elastic deformation of film without lamellar destruction. The lamellar fragmentation or slipping is expected to occur when entering into the yielding stage, which has been recognized to be the main feature of stress-induced structural instability of semicrystalline polymers.\[60-63\] According to the early report from Gohil et al.,\[37\] the Form I transformed from Form II is charac-

Fig. 6 (a) Crystal transitional degree of Form II to Form I as a function of specific work at different temperatures. The dotted lines show the fitting results. (b) $K$ values fitted by Eq. (7) as a function of deformational temperature. The solid curve drawn is a guide to the eyes.

![Graph showing the relationship between $D_t$ and $w$](https://doi.org/10.1007/s10118-020-2409-7)
terized by a separated fiber or lamellar texture with lateral size of several tens of angstroms under deformation, compared to several thousands of angstroms for thermal induction under the quiescent condition. Thus, sufficient fragmentation of Form II lamellae may be required to create smaller block units as precursors for Form I formation, which would benefit the force transmission and then accelerate the phase transition. On the other hand, the plastic behavior of lamellar fragmentation or slipping accompanied by local melting may be conducive to releasing the restrictions on chains’ translational movements in crystalline phase. According to the systematic investigations from Qiao et al., the intercrystalline links and entanglements play an essential role in determining the phase transition kinetics of Form II to Form I under the quiescent condition, which slow the transition down by regarding the chains translational motions in crystal.\[55,57,64,65\]

Under deformation, the enhanced crystalline chains mobility may be not realized by the direct removal of intercrystalline links or entanglements, but by the local crystalline destruction, slipping, or melting, which would facilitate the conformational adjustment of crystalline segments in the transition process. The physical picture mentioned above has been included in the schematic drawing of structural evolution of pre-oriented PB-1 under tensile deformation in Fig. 7. Note that the plotted chain folding number in one folded cluster is close to 2, as evidenced by Hong et al. from NMR measurement.[66,67]

![Fig. 7 Schematic drawing of the structural evolution of pre-oriented PB-1 under tensile deformation. The Form I with low content in the initial sample is omitted for brevity.](image)

Compared to the deformation at low temperature, high temperature always leads to stronger hysteresis of the onset strain for Form I formation (Fig. 5d). This may be because high temperature results in a faster stress relaxation, which counteracts the acceleration effect of deformation on crystalline transition. The specific work consumption \( w_o \) for lamellae fragmentation or slipping is 0.11 (25 °C), 0.14 (45 °C), 0.55 (65 °C), 0.76 (85 °C), and 0.82 J/cm\(^2\) (105 °C) at different temperatures. Then, the transitional degree \( D_1(w) \) can be rewritten as

\[
D_1(w) = 0.8 - 0.72\exp[-K(w - w_o)^{0.5}] 
\]

by deducting the work consumption at initial stage. With Eq. (7), the experimentally measured evolutions of \( D_1(w) \) with specific work are well fitted in Fig. 6(a), and the fitting parameters are listed in Table 1. It is found that \( K \) fitted decreases from 0.61 (J/cm\(^3\))\(^{-0.5} \) to 0.04 (J/cm\(^3\))\(^{-0.5} \) with increasing temperature from 25 °C to 105 °C (also shown in Fig. 6b). This indicates a higher acceleration efficiency of deformation on crystalline transition at low temperature, concurrent with the observed shorter incubation period in Fig. 5(d). In addition, the index \( n \) adopts a constant value of 0.5 for all the investigated temperatures.

### Table 1 Fitting parameters of Eq. (7) for the \( D_1(w) \) curves.

| Temperature (°C) | Parameter | \( K \) (J/cm\(^3\))\(^{-0.5} \) | \( n \) |
|------------------|-----------|--------------------------------|-------|
| 25               |           | 0.61                          | 0.5   |
| 45               |           | 0.43                          | 0.5   |
| 65               |           | 0.23                          | 0.5   |
| 85               |           | 0.12                          | 0.5   |
| 105              |           | 0.04                          | 0.5   |

To further understand the physical meaning behind Eq. (7), the classic Avrami equation to describe isothermal crystallization kinetics is re-mentioned here. It has a general form of \( x = 1 - \exp[-kt^n] \) with crystallinity of \( x \), crystallization time of \( t \), and crystallization rate constant of \( k \), which is similar to Eq. (7) in form. The time \( t \) is chosen as a variable to associate with phase transition, different from the specific work \( w \) in this work. Under the quiescent condition, the transition of Form II to Form I needs several weeks to finish, compared to less than 10 min under deformation. Thus, it is reasonable to assume that the Form II to Form I transition is directly driven by deformational work, where the time-related thermal induction plays less important role under deformation. For the Avrami equation, the index \( n \) is related to the nucleation rate and growth morphology of new phase, where \( n = 0.5 \) corresponds to a diffusion-controlled growth over the pre-existing nuclei rather than interface-controlled growth over sporadic nuclei.[68,69] In this work, \( n = 0.5 \) is well fitted for all the investigated samples, which is actually in keeping with the stress-induced solid-to-solid transition. First, Form I initiates from the already existing Form II rather than randomly nucleating from the amorphous phase. Second, the growth of Form I from Form II matrix is determined mainly by the tensile stress transmission and distribution inside sample, instead of an interface-controlled process. In addition, the \( K-T \) curve in Fig. 6(b) presents a decreasing slop with elevating temperature. This may be related to a route change of crystalline transition from direct solid-solid to melting-recrystallization dominated process,[35] where the latter may dissipate more external work and lead to lower transitional efficiency.

At last, it is worth mentioning that the phase transition determines the mechanical response of PB-1 film. The decrease of tensile modulus with increasing temperature is not just caused by the conventional temperature effect where high-
her temperature leads to lower mechanical strengths or modulus of both lamellar crystal and amorphous phase. This is supported by the fact that the mechanical difference between different temperatures does not become significant until the film is stretched beyond yielding, which quite matches with the occurrence of Form II to Form I transition. First, high temperature always leads to a stronger hysteresis of the onset strain for crystalline transition (Fig. 5d), consistent with the onset of modulus enhancement or strain hardening after yielding. Second, the higher the Form I content, the stronger the tensile modulus, which is consistent no matter comparing one single tensile process at different strains or tensile experiments at different temperatures. It has been reported that the metastable Form II is a conformationally disordered crystal and performs extremely fast chain dynamics, while Form I possesses completely fixed crystalline stems and side-chain conformations up to the melting point. Thus, the newly formed hard network built by Form I crystallites to replace the relatively soft network of Form II is the intrinsic reason for mechanical enhancement of PB-1 at large strain.

CONCLUSIONS

Current work has studied the polymorphic transition of PB-1 under uniaxial tensile deformation by in situ FTIR technique. The pre-oriented PB-1 film is prepared as a model sample in order to realize relatively homogeneous deformation at the mesoscale of lamellar stacks by avoiding large-scale spherulites, which is conducive to achieving the intrinsic structure-mechanics relationship. Deformation-induced phase transition of metastable Form II to stable Form I is found to not occur until after yielding, that is, a pre-consumption of deformational work is required. At this stage, the lamellar fragmentation, slipping, or melting involved may release the restrictions on chains translational movements in crystalline phase, which would facilitate the conformational adjustment of crystalline segments and activate the transition of Form II to Form I. The crystalline transition proceeds drastically in the subsequent tensile process, where a kinetic equation of $D_0[w] = 0.8 - 0.72\exp\left[-K(w - w_0)^{0.5}\right]$ is well established by neglecting the contribution of spontaneous transition from thermal fluctuation and demonstrated to be suitable to describe the dependence of crystal transitional degree on applied specific work. It is also found that increasing temperature leads to not only a hysteresis of the onset strain for crystalline transition but also a lower transitional efficiency. The retardation effect of elevating temperature can be embodied in the decrease of calculated K value. In addition, along with the evolution from soft Form II to hard Form I crystalline network, the tensile modulus of PB-1 is greatly enhanced. By establishing the quantitative relationship between structural transition and external work, the current work is instructive to understand the complex phase and mechanical behaviors of PB-1 material.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2409-7.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51803189 and 51503186) and the Postdoctoral Science Foundation of China (No. 2018M630832).

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