

Structural Evolution of PGA Nascent Fiber during Single Low-Temperature and Segmented High-Temperature Hot Stretching

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Electronic Supplementary Information

Abstract Polyglycolide (PGA) fibers applied as surgical sutures strongly depend on their microstructure. The structural evolution of PGA nascent fibers during single low-temperature stretching and segmented high-temperature stretching was analyzed based on a combination of *in situ* WAXD/SAXS and DSC measurements. The results indicated that the hot stretching was conducive to the crystal perfection and the local fragmentation and recrystallization of the lamellar crystals may occur under stress induction. The single low-temperature stretching of PGA nascent fibers could be divided into three stages: the stretching of amorphous regions, stretch-induced crystallization and the stretching of crystalline regions. The elongation at break of the fibers can be substantially increased by adopting a segmented stretching method, and the high-temperature stretching can also significantly increase the crystallinity and orientation. The amorphous orientation peak appearing in the low-temperature stretching was gradually converted to crystallization peak during the heating process, which greatly improved the crystallinity and orientation of the fibers. High-temperature stretching compared with low-temperature stretching was more favorable for crystal perfection and structural evolution, where lamellar crystals underwent stress-induced fragmentation recrystallization to transform to fibrous crystals as the strain increased.

Keywords PGA fiber; Structural evolution; Hot stretching

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INTRODUCTION

In recent years, the increasingly serious white pollution has brought great damage to the environment, the use of biodegradable materials to replace these polymer materials that are difficult to degrade has become the focus of worldwide attention.^[1–10] Biodegradable polymers with excellent biocompatibility and biodegradability have attracted keen interest not only in daily necessities but also in medical applications, such as artificial organs, medical plastics and medicinal materials.^[11–15] Among the biomedical polymers developed thus far, aliphatic polyesters are of interest for their good melt processability, mechanical strength and excellent degradability.^[16,17] Polyglycolide (PGA) is the simplest linear aliphatic polyester and the first commercial biodegradable polymer material *in vivo*,^[18] which is also widely used in the fields of surgical suture, orthopedic materials and drug

controlled release system because of its good biocompatibility and biodegradability. PGA as surgical sutures in clinical application can overcome the disadvantages of traditional intestinal sutures, such as uneven composition, unstable absorption and prone to rejection effect leading to inflammation.^[19] However, despite the tremendous advantages of PGA surgical sutures, the current industrialized products are still limited by theoretical and technical issues, and the key properties such as mechanical and *in vivo* degradation properties still need further improvement.

It is well known that the application requires materials with well-defined properties and the mechanical and degradation properties of polymer sutures are the decisive factors for preparing high-quality surgical sutures.^[20,21] The desired mechanical properties of surgical sutures involve not only adequate initial tensile strength and modulus, but also sufficient retention of tensile strength during *in vitro* or *in vivo* degradation. The tensile strength of surgical suture determines the binding ability of wound tissue, whereas the degradation rate of sutures determines the maintenance of its breaking strength, which is particularly important for the application of

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such medical materials. However, the properties of polymer fibers depend largely on their structure, which varies with processing technology. Currently, two typical processing techniques are mainly adopted to manipulate the properties of fibers,^[22] one involves the hot-stretching process and the other involves the heat-setting process. The hot-stretching process imposes a mechanical stretching of the polymer chains and crystallites, resulting in an increase of crystalline orientation and crystallinity. These changes in structure usually yield an increase in tensile strength but a decrease in elongation.^[23–27] It seems that identical materials can behave differently with regards to their mechanical and degradation properties if they display different aggregation structure. Therefore, it is of great significance to link the relationship between aggregation structure and macroscopic properties, particularly the crystal structure of PGA fibers with the hot-stretching and heat-setting process.

The spinning and stretching processes are important factors that determine the aggregation structure and mechanical properties of fibers.^[28–30] Stretching temperature, stretching ratio and stretching rate all affect the structure and final properties. Generally, the amorphous distribution in the semi-crystalline polymers plays an important role in the retention time of tensile strength, whereby a higher degree of crystallinity and molecular orientation tend to result in higher values of the tensile strength and longer degradation times. Li *et al.*^[31,32] investigated the relationship among temperature, stretching ratio and structural changes and properties of PGA fibers during hot-stretching process, and found that the crystallinity, orientation of amorphous regions and mechanical properties of fibers increased with increasing stretching ratio, while the elongation at break decreased significantly. When the stretching ratio was higher than 7, the obvious phenomenon of stretch-induced crystallization occurred. Huang *et al.*^[33] found that poly(glycolide-co-lactide) (P(GA-co-LA)) nascent fibers were essentially amorphous, with a slight increase in crystallinity with increasing stretching ratio and a decrease in crystallinity with increasing stretching temperature during the stretching process. Mu *et al.*^[34] investigated the structure-property relationships of PGA fibers during hot-stretching process, and found that increasing the stretching temperature was conducive to the mutual sliding of macromolecular chains, which can increase the stretching multiplicity, but at the same time increased the disorientation, and therefore the final orientation cannot reach a higher value. Fu *et al.*^[21,22] investigated the relationship between the aggregation structure, processing and properties of PGA fibers by WAXD and DSC. It was found that higher hot-stretching temperatures increased the crystallite size, glass transition temperature and tensile strength, but decreased the elongation at break and the thermal shrinkage close to the glass transition temperature. However, although the research on the hot-stretching process of PGA fibers has been investigated, the previous studies have basically dealt with the relationship between processing and properties, and seldom addressed the effects of structural changes and structural evolution on subsequent performance. Deviating from the structure to investigate the relationship between processing and properties can only make a preliminary judgment on the performance, which not only lacks strong support but also cannot effectively adopt the structural evolution to reasonably design the performance of PGA fibers.

Our group has previously systematically investigated the structural evolution of PGA and P(GA-co-LA) fibers during heat setting process *via in situ* WAXD/SAXS and DSC techniques,^[35] and found the discharge of the LA unit of P(GA-co-LA) fibers occurred in the temperature interval of 60–80 °C, and the heat-setting temperature of 120 °C was more conducive to the formation and perfection of crystals, thus improving the properties of the fibers. However, there is still a lack of systematic understanding of the structural evolution in the hot-stretching process. Therefore, based on the above analysis, the structural evolution of PGA fibers during hot-stretching process is in-depth studied by synchrotron radiation WAXD /SAXS in this study.

EXPERIMENTAL

Materials

In our experiments, the PGA raw materials with an intrinsic viscosity of 1.2 dL/g were purchased from Purac company of the Netherlands. PGA raw materials were added into the screw extruder and extruded at 250 °C for melt spinning, ejected from the spinneret after metering, and the nascent fibers with a fineness of 275 dtex were made by winding with a drafting roller, the drafting multiple was 4.7 times, and the winding speed was 150 m/min. The PGA nascent fibers were then stored in a vacuum glove box.

Measurements of WAXD and SAXS during Hot Stretching

In situ wide-angle X-ray diffraction (WAXD) and small-angle X-ray diffraction (SAXS) measurements were performed at the BL16B1 beamline in Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of X-ray radiation was 0.1239 nm. The sample-to-detector distance was 206 mm for WAXD and 2150 mm for SAXS, respectively, and the image acquisition time of each data was 5 s. Two-dimensional (2D) WAXD and SAXS patterns were collected *via* X-ray detector of Pilatus 1M and Pilatus 2M, respectively.

The single low-temperature stretching of PGA nascent fibers was performed by using a tensile testing device (TST 350, Linkam, U.K.) at varying temperatures of 45, 50, 55, 60 °C with the stretching velocity of 50 μm/s. The *in situ* WAXD and SAXS tracked the corresponding structural evolution. In addition, the stretching temperature at the beginning of the segmented high-temperature stretching was 50 °C, and when a certain strain was reached, the stretching temperature was increased to 120, 130, 140 and 150 °C at the rate of 30 °C/min, respectively, and continued to stretch with the stretching velocity of 50 μm/s. The specific stretching processes are shown in the Fig. 1. The gauge length of fiber for stretching was 15 mm. The stretching data and WAXD / SAXS data were collected simultaneously during stretching. All X-ray images were corrected for background scattering, air scattering, and beam fluctuations and normalized.

Differential Scanning Calorimetry (DSC) Measurements

DSC measurements were performed with Pekin Elmer DSC8000 under nitrogen atmosphere. The PGA fibers were cut into pieces, and about 5 mg of the samples were heated at a rate of 10 °C/min from room temperature to 250 °C. The ΔH can be

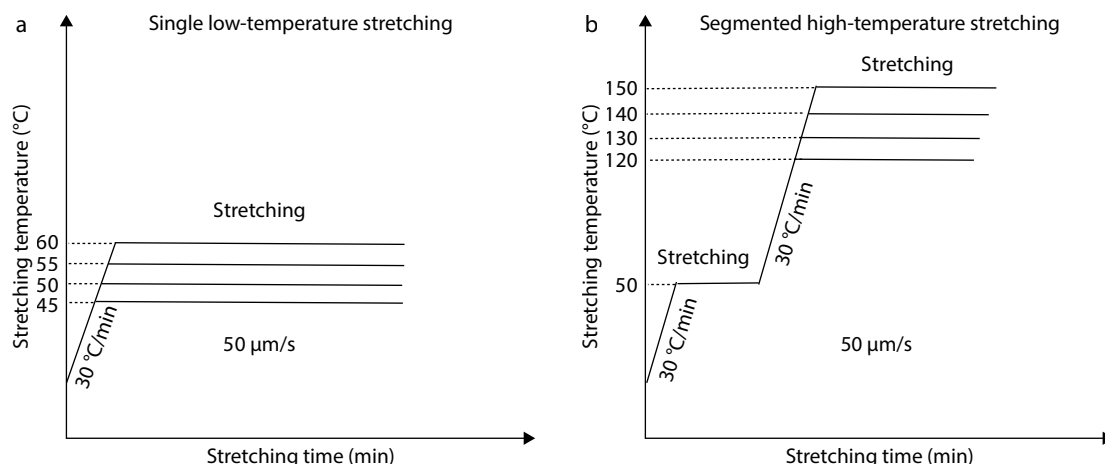


Fig. 1 The specific stretching processes: (a) single low-temperature stretching, (b) segmented high-temperature stretching.

obtained by extrapolating the post-melting baseline. The intersection point between the tangent line of the peak front and the scanning baseline was taken as the T_m .

Birefringence Measurements

The measurement of fiber birefringence was performed with a polarizing microscope. The sample to be tested was placed flat on a slide and placed on a polarizing microscope stage that had been orthogonalized. The polarizing and examining mirrors were orthogonal to the fiber axis at 45°, and the optical path difference between parallel and perpendicular fiber axes was measured by fiber interference color compensation, while the birefringence of the fiber was calculated from the fiber thickness measured in the microscope.

Analysis of WAXD and SAXS Data

WAXD and SAXS data analysis were performed out by the Fit2d software package.^[36] In WAXD analysis, the degree of crystalline orientation was obtained by using the Hermans' method.^[37] For a set of (hkl) planes, the average orientation, expressed as $\langle \cos^2\Phi \rangle_{hkl}$, can be calculated mathematically using the equation:

$$\langle \cos^2\Phi \rangle_{hkl} = \frac{\int_0^{\pi/2} I(\Phi) \cos^2\Phi \sin\Phi d\Phi}{\int_0^{\pi/2} I(\Phi) \sin\Phi d\Phi} \quad (1)$$

where Φ is the azimuthal angle, $I(\Phi)$ is the scattered intensity along the angle Φ . Hermans' orientation function f is defined as:

$$f = \frac{3\langle \cos^2\Phi \rangle - 1}{2} \quad (2)$$

where $f = -0.5$, when the normal of the reflection plane is perpendicular to the reference direction ($\Phi = 90^\circ$ or crystals are oriented parallel to the fiber axial direction). The degree of orientation, f_{020} , was calculated from the azimuthal intensity distribution of the (020) crystal reflection.

The crystallinity was performed with MDI Jade software, which calculated according to the diffraction intensity of crystalline phase and amorphous phase. By dividing the total intensities of the crystalline reflections, I_c over the overall intensity I_{total} is a measure of the mass fraction of the crystalline phase in the sample that can be obtained.

The orthorhombic unit cell parameters a and b were evalu-

ated in terms of the following equation by using the crystallographic plane analysis:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (3)$$

where h , k , l are the Miller indices and d_{hkl} is the interplanar spacing, defined by Bragg's law:

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \quad (4)$$

where λ is the X-ray wavelength and θ is the diffraction angle.

The (110) and (020) reflection peaks were used to determine the crystallite sizes, and the measurement was performed using the Scherrer equation:

$$D_{hkl} = \frac{K\lambda}{\beta\cos\theta} \quad (5)$$

where K is the shape factor (0.89), β is the experimental breadth at the maximum intensity.

The lamellar and amorphous thicknesses were hidden in the SAXS curve, in which only an apparent peak presented. This peak only indicated the apparent long period: the sum of the crystalline phase (L_c) and amorphous phase (L_a) stacking. In our study, the one-dimensional electron density correlation function $K(z)$ provided a practical approach to quantify the lamellar and amorphous thickness.^[38–39] The intensity peak of Lorentz-corrected SAXS curves can be divided into two correlation peaks which corresponding to two kinds of periodic structures by Gaussian functions, and the long period (L), lamellar thickness (L_c), and amorphous thickness (L_a) were obtained. $K(z)$ can be defined as:

$$K(z) = \frac{\int_0^\infty i(s) s^2 \cos(2\pi sz) ds}{\int_0^\infty i(s) s^2 ds} \quad (6)$$

where s is the reciprocal space coordinate, defined as $s = 2\sin\theta/\lambda$.

The average length, $\langle L_{\text{shish}} \rangle$, and misorientation, B_ϕ , of shish were calculated from the SAXS meridional streak feature with the Ruland streak method.^[40–42] The observed azimuthal width, B_{obs} , can be related to the $\langle L_{\text{shish}} \rangle$ and B_ϕ , obtained by Eq. (5) if all azimuthal distributions can be modeled by Lorentz functions:

$$B_{\text{obs}} = \frac{1}{\langle L_{\text{shish}} \rangle s} + B_\phi \quad (7)$$

RESULTS AND DISCUSSION

Structural Evolution during Single Low-Temperature Stretching Process

Before studying the crystal structural evolution of PGA fibers during hot-stretching process, the structural characteristics and properties of PGA nascent fibers before and after stretching were investigated and the DSC curves are presented in Fig. 2. The thermal properties obtained from the DSC curves are summarized in Table 1. It can be clearly seen from the curves that PGA nascent fibers possessed an obvious sharp cold crystallization peak before stretching. As is known to all that a polymer capable of cold crystallization requires two conditions: first, the polymer melt is capable of crystallizing during cooling; second, the crystallization rate of the polymer is relatively slow, whereupon the polymer melt is not able to complete crystallization at the specified cooling rate due to kinetic factors, and part of the chain segments are frozen in an intermediate state with an order degree higher than that of completely amorphous and lower than crystal structure. When the material was heated, a transformation to a crystalline structure occurred, manifesting as an exothermic cold crystallization. The PGA nascent fibers used in the experiment were able to appear such a sharp cold crystallization peak, indicating that the crystallinity of the PGA nascent fibers was relatively low. However, the cold crystallization enthalpy of PGA fibers after single low-temperature stretching decreased from 31.3 J/g to 19.6 J/g, the cold crystallization peak widened, and the cold crystallization temperature shifted to the lower temperature, indicating that stretching increased the orientation of molecular chains that have not yet completed the transformation to crystallization, and reduced the potential barrier in the transformation to

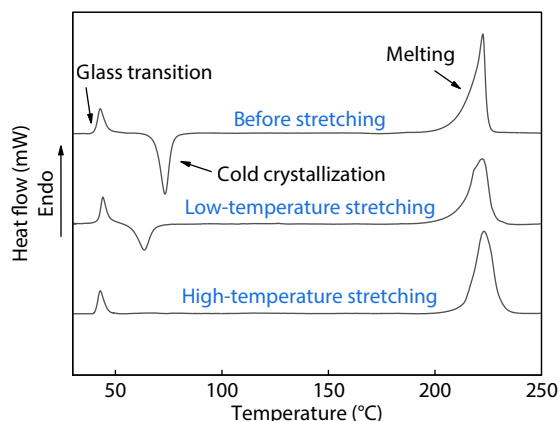


Fig. 2 DSC curves of PGA nascent fibers unstretched and after single low-temperature stretching and segmented high-temperature stretching at the heating rate of 10 °C/min.

Table 1 DSC thermal data of PGA nascent fiber unstretched and after single low-temperature stretching and segmented high-temperature stretching.

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PGA-before stretching	222.5	72.4	73.3	47.3
PGA-after low-temperature stretching	222.1	75.6	63.5	25.8
PGA-after high-temperature stretching	222.6	77.1	—	—

crystallization of molecular chains in amorphous regions, therefore, the crystals could be generated at a lower energy state. In addition, the DSC curves were also characterized by a sharp endothermic peak at the tail end of the glass transition, a phenomenon that has been occurred in many polymers, including P(GA-co-LA) nascent fibers, and was referred to as physical aging.^[31] The peak became more pronounced and sharper as it aged. However, it was also reported that this peak was a kind of physical entanglement,^[43,44] that was, an entanglement caused by local segment condensation. When the material underwent a glass transition, the chain segments moved cooperatively and the obtained heat energy allowed the physical entanglement to be unentangled, so the process was endothermic.

To investigate the structural evolution of PGA fibers during single low-temperature stretching process, PGA nascent fibers were selected for hot-stretching tests at 45, 50, 55 and 60 °C, and *in situ* WAXD and SAXS were used to detect the fiber structural changes. Fig. 3 shows the stress-strain curves of PGA nascent fibers stretched at different temperatures. Clearly, the strains of the fibers could reach more than 400% at all the selected stretching temperatures, and the strains were able to further increased without fiber fracture at lower stretching temperatures. There was a long plateau period in the early stage of stretching when the stretching temperature was 45, 50 and 55 °C, respectively. However, when the stretching temperature further increased to 60 °C, the plateau period shortened or even disappeared, the tensile stress increased significantly, and the fibers began to partially fracture at the later stage of stretching, which appeared as a sudden decrease in stress on the stress-strain curves.

The *in situ* 2D WAXD patterns of PGA nascent fibers at different strains and different stretching temperatures are displayed in Fig. 4. It could be clearly observed that PGA nascent fibers exhibited the characteristics of dispersion rings, indicating that the nascent fibers were initially amorphous. The scattering intensity of the two-dimensional diagram in the initial state increased significantly with the increasing stretching temperature, and the diffraction ring became clear. The diffraction patterns showed an obvious diffraction spot in the meridian direction as the strains increased during stretching when the stretching temperature was relatively low, and however, diffraction arcs instead of diffraction spots ap-

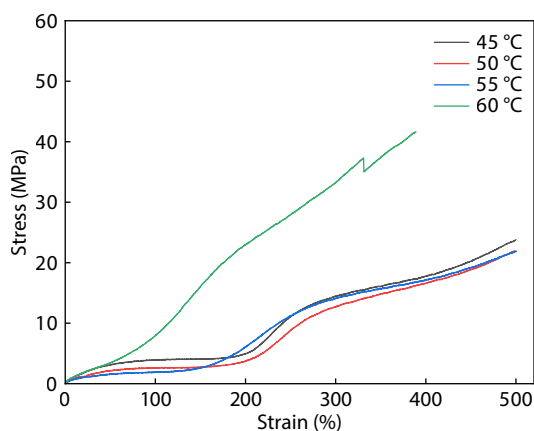


Fig. 3 The stress-strain curves of PGA nascent fibers stretched at different stretching temperatures.

peared in the later stage of stretching as the stretching temperature was further increased to 60 °C. In order to display the characteristics of diffraction results more clearly, the representative 1D WAXD curves of PGA nascent fibers extracted from the 2D WAXD patterns at different strains and stretching temperatures are presented in Fig. 5. Two characteristic diffraction peaks were clearly observed, which corresponded

to two diffraction spots or diffraction arcs in the 2D WAXD patterns, and the diffraction peak of $2\theta=17.8^\circ$ corresponded to the (110) crystalline plane, while the diffraction peak of $2\theta=22.9^\circ$ corresponded to the (020) crystalline plane. The PGA fibers showed an amorphous state in the early stage of stretching, and the diffraction peaks appeared gradually as the stretching proceeded, and became narrowed in the later

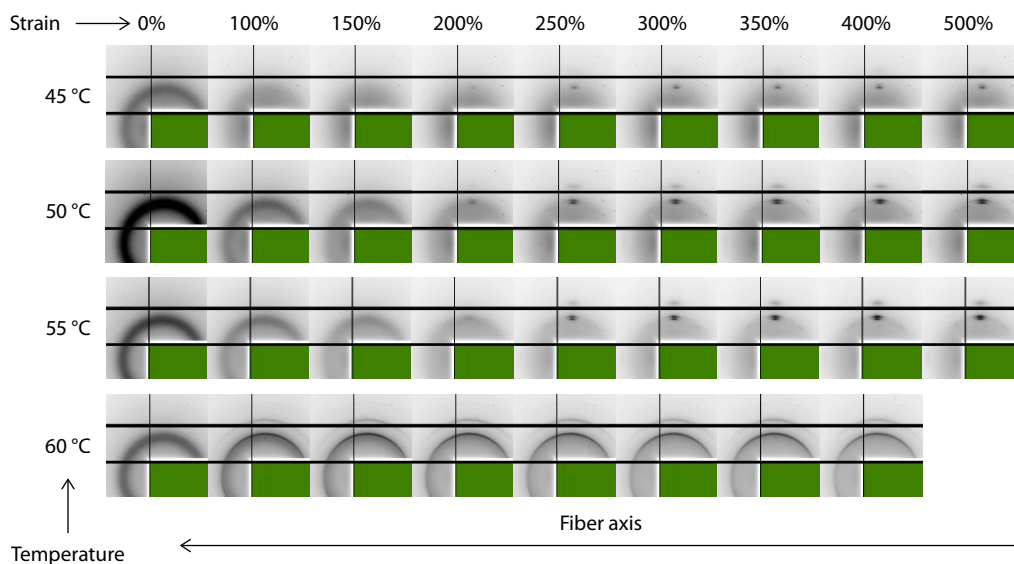


Fig. 4 The *in situ* 2D WAXD patterns of PGA nascent fibers at different stretching temperatures and strains.

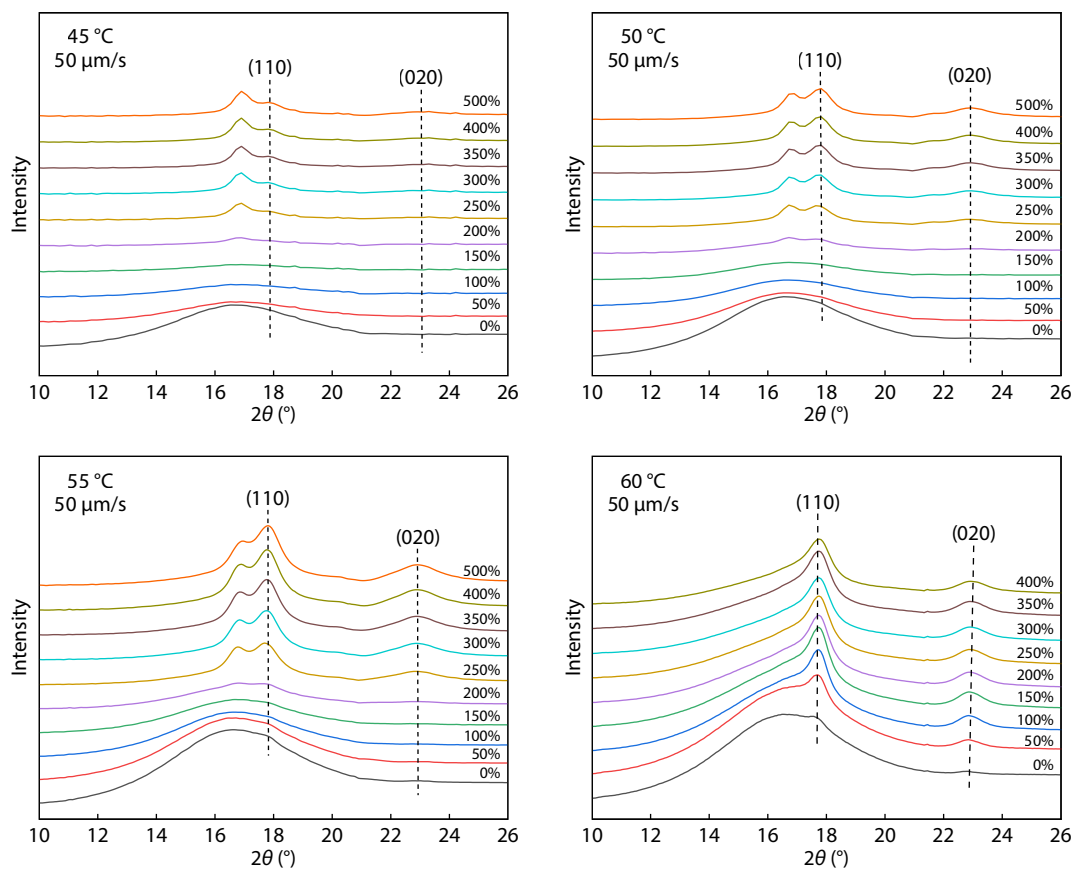


Fig. 5 The 1D WAXD curves of PGA nascent fibers at different stretching temperatures and strains.

stage. It was noteworthy that a strong diffraction peak located at $2\theta=16.9^\circ$ appeared with stretching at 45, 50 and 55 °C, respectively, which has not been reported in previous studies on PGA. The intensity of the diffraction peak showed a gradual decrease with the increasing stretching temperature, and gradually disappeared with the further increase of the stretching temperature to 60 °C. It was considered that the diffraction peak on the left side of the (110) crystalline plane was probably attributed to the orientation of the amorphous chains.^[45] In addition, the diffraction peak appeared gradually during the stretching process, which corresponded to the DSC results, indicating that stretching could increase the orientation of molecular chains in the amorphous region that have not yet completed the transition to crystallization. However, some crystallization would occur during the isothermal process before stretching. When the stretching temperature was relatively low, the initial crystallinity of the sample was low and the stretch-induced crystallization was slow at this temperature, resulting in an obvious amorphous orientation peak during stretching. When the stretching temperature was 60 °C, PGA fiber was already partially crystallized in the isothermal stage, so no obvious amorphous orientation peak appeared during the stretching process. We have verified the phenomenon and also calculated the percentage of this amorphous orientation peak in the overall crystallinity, the relevant results were placed in Figs. S1 and S2 in the electronic supplementary information (ESI).

To further analyze the structural changes of PGA fibers during the single low-temperature stretching process, the crystallinity and orientation calculated from the WAXD results were shown in Fig. 6. It was worth noting that a lower f_{020} value signified a higher degree of orientation. It can be found that the hot stretching process conducive to improve the crystallinity and orientation of PGA nascent fibers, and the increasing trend of crystallinity and orientation was roughly similar, which can be divided into three stages. In the first stage (*i.e.*, from 0% to 150% strain), the crystallinity and orientation of the fibers were relatively low, especially the crystallinity was almost close to 0, and the crystallinity as well as orientation increased slowly. In the second stage (*i.e.*, from about 150% to 350% strain), the crystallinity and orientation of the fibers showed a rapid increase. In the third stage of stretching (*i.e.*, from 350% to 500% strain), the crystallinity and degree of crystal orientation still increased, but the trend

slowed down. It should be pointed out that when the stretching temperature was 60 °C, the law was slightly different from other selected stretching temperatures, since the fibers has already partially crystallized in the isothermal stage before stretching, therefore the crystallinity was relatively higher at the later stages of stretching. In addition, the amorphous orientation peak gradually decreased with stretching when the stretching temperature was 60 °C, while the amorphous orientation peak gradually increased under other stretching conditions, which was more easily transformed into highly oriented crystals during the stretching process, resulting in a higher degree of orientation compared to 60 °C. Combined with the stress-strain curves, the single low-temperature stretching process of PGA nascent fibers can be divided into three stages, the plateau period with lower crystallinity and orientation corresponded to the stretching of amorphous regions, while the interval with rapid increase of tensile stress, crystallinity and orientation corresponded to the stretch-induced crystallization stage, and the final stage with slow increase of tensile stress, crystallinity and orientation corresponded to the stretching of crystalline regions. However, when the stretching temperature increased, the plateau period in the early stage of stretching was shorten or disappeared, and stretch-induced crystallization also occurred as the stretching progressed, but some crystals would be broken in the later stage of stretching.

All changes in structural parameters (orthorhombic unit cell parameters a and b ; lateral crystallite sizes, L_{110} and L_{020}) during single low-temperature stretching, calculated from the (110) and (020) crystalline planes of the WAXD data are summarized in Fig. 7. However, it should be noted that when the stretching temperature was 45 °C, the intensity of the amorphous orientation peak generated at the latter stage of stretching was much stronger than that of the (110) crystalline plane, and therefore, the corresponding unit cell parameters and crystallite sizes cannot be calculated. The unit cell parameters showed an overall decreasing trend with the increasing strains, indicating that stretching promoted crystal perfection. In addition, the value of unit cell parameters and crystallite sizes were generally larger at higher stretching temperatures, which was related to the thermal expansion. The unit cell parameters decreased significantly in the stretch-induced crystallization stage and slowly in the stretch-

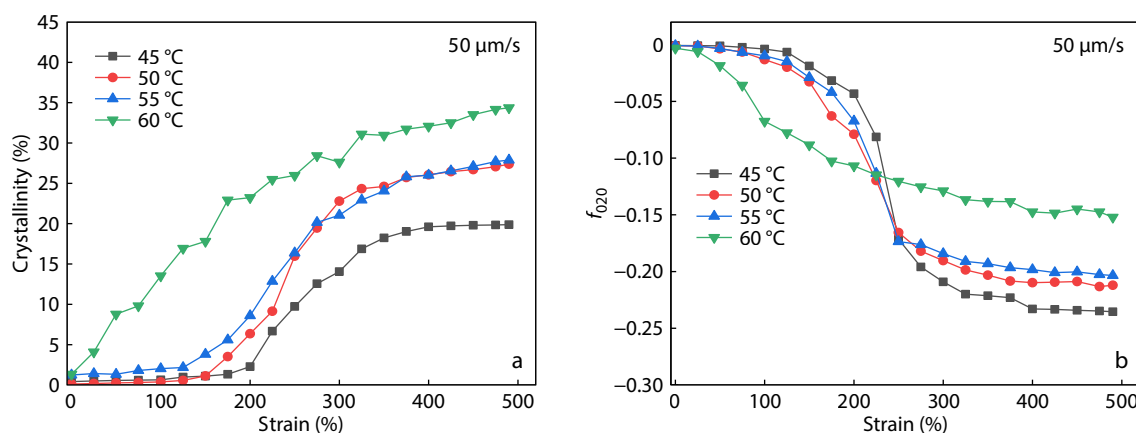


Fig. 6 The (a) crystallinity and (b) orientation of PGA nascent fibers at different stretching temperatures and strains.

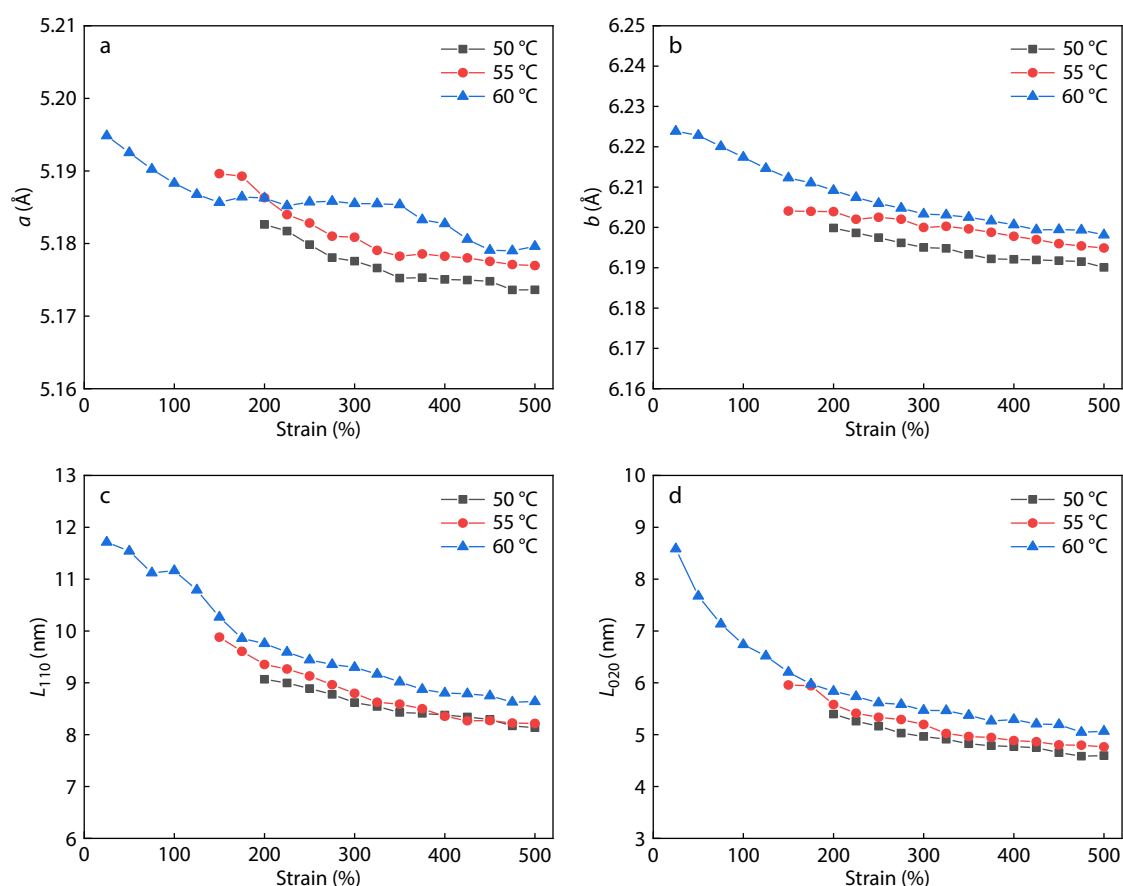


Fig. 7 The unit cell parameters (a) a , (b) b and crystallite sizes (c) L_{110} , (d) L_{020} of PGA nascent fibers at different stretching temperatures and strains.

ing of crystalline regions stage when the stretching temperature was lower, whereas when the stretching temperature further increased to 60 °C, the unit cell parameters decreased rapidly in this stage and further decreased during the subsequent stretching process since a number of crystals were generated in the stretching of amorphous regions. Meanwhile, the crystallite sizes also showed a gradual decrease as the stretching proceeded, which indicated that low-temperature stretching was more conducive to the formation of small crystals, resulting in the decrease of average crystallite sizes.

The selected *in situ* 2D SAXS patterns of PGA nascent fibers at different stretching temperatures and strains are provided in Fig. 8. The longitudinal streak across the beam stop was corresponded to the signal of the fibrillar crystals, whereas the two scattering patterns along the horizontal direction on both sides of the beam stop corresponded to the signal of the lamellar crystals. As depicted in Fig. 8, there was no lamellar signal of PGA nascent fibers in the early stage of stretching at lower stretching temperature, but the lamellar signal gradually appeared after stretch-induced crystallization, and gradually increased after the stretching of the crystalline regions. However, when the stretching temperature was 45 °C, there was no lamellar signal in the whole stretching process due to the weak scattering intensity. In addition, when the stretching temperature was further raised to 60 °C, corresponding to the WAXD results, the PGA fibers began to partially crystallize at the isothermal stage before stretching, and the lamellar

signal appeared and became more obvious in the subsequent stretching process. The morphology parameters at the lamellar level could be extracted from these SAXS profiles using the method of correlation function. The long period of PGA fibers during the low-temperature stretching process are presented in Fig. 9. It can be drawn from the figure that when the stretching temperature was low, the long period showed a rapid decline in the stretch-induced crystallization stage and a slow decreasing trend in the stretching of crystalline regions, which was mainly considered to be due to the fact that the progressive formation of new small crystals during stretch-induced crystallization, thus resulting in a decrease in the average long period. However, when the stretching temperature was further raised to 60 °C, the long period showed a slight increase and then a rapid decrease, and the decrease of long period basically occurred in the early stage of stretching. The increase of long period at the beginning of stretching was mainly considered to the elongation of the amorphous layer between the lamellar crystals as the stress acted on them during the stretching process. Since some crystals were formed in the isotherm stage before stretching, the stretching law at 60 °C was different from the other three stretching temperatures selected.

Fig. 10 presents the average length of shish crystals and the misorientation of PGA nascent fibers at different temperatures and strains, which was calculated by using the Ruland method. The shish lengths of PGA nascent fibers at all stretch-

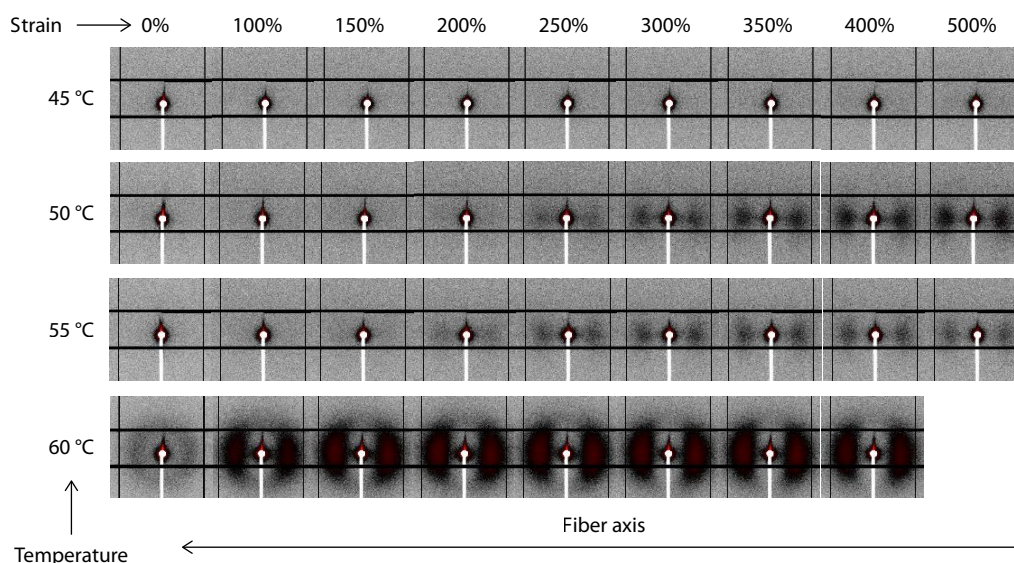


Fig. 8 The *in situ* 2D SAXS patterns of PGA nascent fibers at different stretching temperatures and strains.

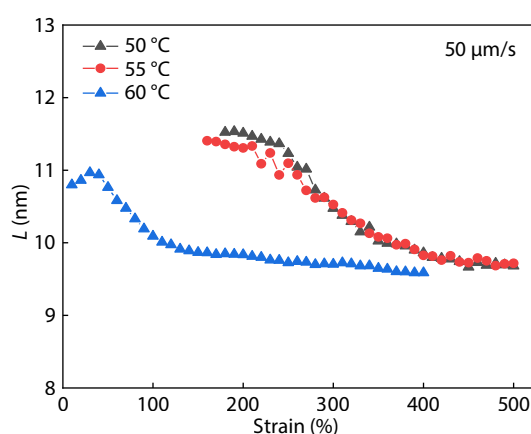


Fig. 9 The long period changes of PGA nascent fibers at different stretching temperatures and strains.

ing temperatures increased firstly and then decreased with the strain. The initial increase in shish length was due to the fact that the shish crystals formed at earlier stage of hot-stretching were longer but fewer comparing with those formed at later stage, while the decrease in shish length at later stages of stretching was attributed to the chain entanglement. As the hot stretching proceeded toward higher strains, the untangling of chain entanglement became increasingly difficult, so a large number of short shish crystals were formed in the later stage, resulting in a decrease in the average length of shish crystals. Moreover, it can also be drawn from the figure that the misorientation of shish crystals at all hot stretching temperatures showed a gradual decrease with increasing stretching strains, which indicated the shish crystals formed were increasingly well oriented.

Structural Evolution during Segmented Hot-Stretching Process

From the results of single low-temperature stretching study, it was concluded that the hot-stretching process of PGA nascent fibers at lower stretching temperature could be divided into

three stages: the stretching of the amorphous regions, stretch-induced crystallization and the stretching of the crystalline regions. However, since it was difficult to destroy the original crystals when the stretching temperature was relatively low, the stretching of the crystalline regions in the third stage would limit the structural evolution during the hot-stretching process. Therefore, on the basis of single stretching, a segmented stretching test was carried out, that was, selecting a suitable low stretching temperature (50 °C), conducted the stretching of amorphous regions and stretch-induced crystallization, and then increasing the stretching temperature to 120, 130, 140 and 150 °C for high temperature stretching after the formation of a large number of crystals, respectively. It should be pointed out that from the previous results, when the stretching temperature was 60 °C, part of the crystals could be formed in the isotherm stage before stretching, which would affect the subsequent stretching process and made the stretching law different from the other three temperatures. Therefore, we did not choose 60 °C as the initial stretching temperature for segmented stretching. Fig. 11 compared the stress-strain curves of PGA nascent fibers recorded during segmented stretching at various temperatures. Since the first stage (*i.e.*, the stretching of amorphous regions and stretch-induced crystallization) has always adopted the same approach, which was consistent with the single low-temperature stretching, only the subsequent high-temperature stretching curves were provided. It can be observed that the elongation at break obtained in this way by segmented stretching can reach more than 1200%, which was much larger than that of low-temperature stretching, and therefore, enabling further structural evolution of the fibers during the stretching process. In addition, it can also be seen from Fig. 2 that both the PGA nascent fibers and the fibers after single low-temperature stretching showed an obvious cold crystallization peak in the DSC curves, while the cold crystallization peak did not appear after high-temperature stretching, indicating that high-temperature stretching could significantly increase the orientation of the molecular chains that have not yet completed the transformation to

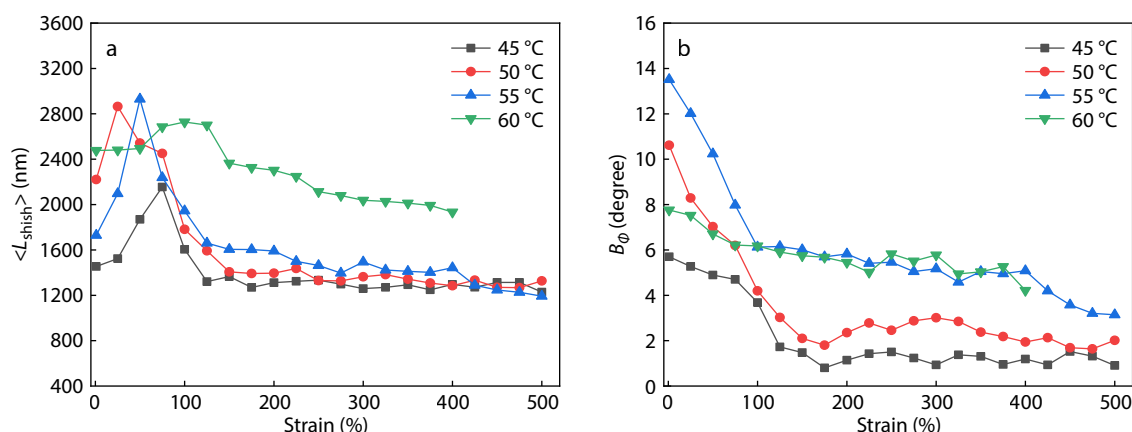


Fig. 10 The average length (a) and misorientation (b) of shish crystals of PGA nascent fibers at different stretching temperatures and strains.

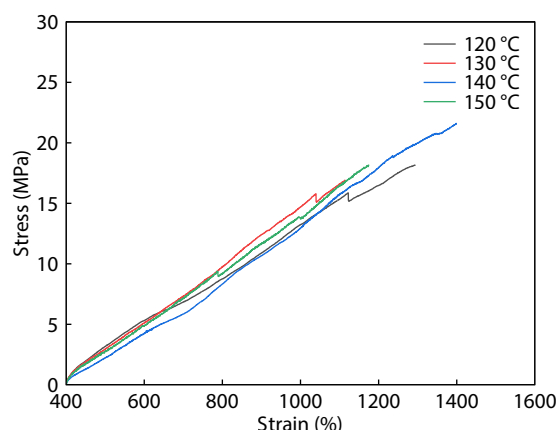


Fig. 11 The stress-strain curves of PGA nascent fiber during the stretching of high temperature.

crystallization and increase the orientation of the fibers.

To further investigate the structural evolution of PGA nascent fibers during segmented stretching, the *in situ* WAXD patterns and one-dimensional WAXD intensity distribution

curves of PGA fibers are presented in Figs. 12 and 13 (the 1D WAXD curves during the heating process are presented in Fig. S3 in ESI). Since the stretching of amorphous regions and stretch-induced crystallization stage were the same as that of single low-temperature stretching, only the experimental results of high-temperature stretching were investigated later. Similarly, the 1D curves at different hot stretching temperatures were roughly similar, only the 1D WAXD curves variation plots at 120 °C were presented, but the subsequent discussion was valid for all samples. Apparently, the intensity of the amorphous orientation peak appeared in the latter stage of low-temperature stretch-induced crystallization was high, but when the stretching temperature was raised to the selected hot-stretching temperature for isotherm, the orientation of the amorphous chains gradually weakened due to the violent movement of the molecular chains, so the amorphous orientation peak gradually disappeared. However, the diffraction peaks of the (110) and (020) crystalline planes with low intensity became sharp and the diffraction intensity increased significantly after isotherm. A reasonable interpretation was that the temperature raised to the selected hot

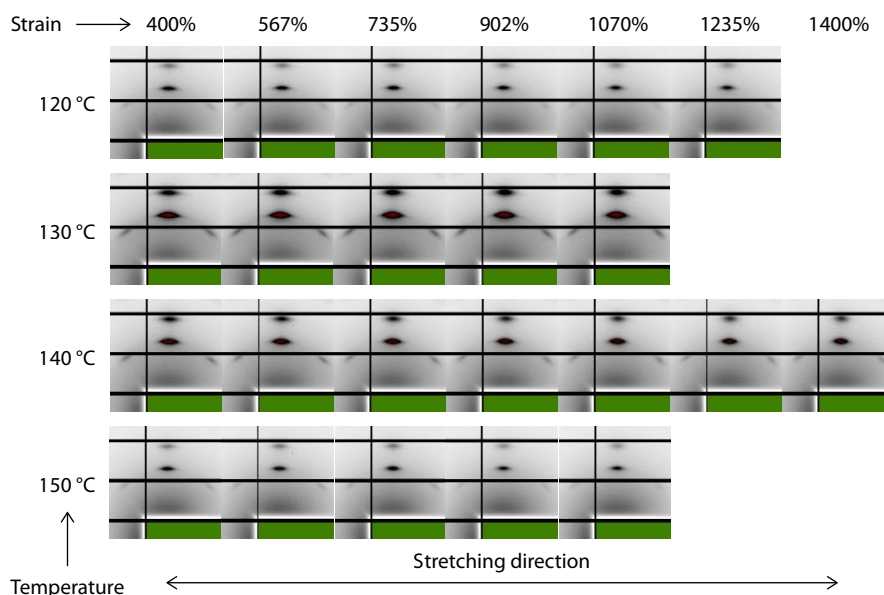


Fig. 12 The *in situ* WAXD patterns of PGA nascent fibers at different temperatures and strains during the stretching of high temperature.

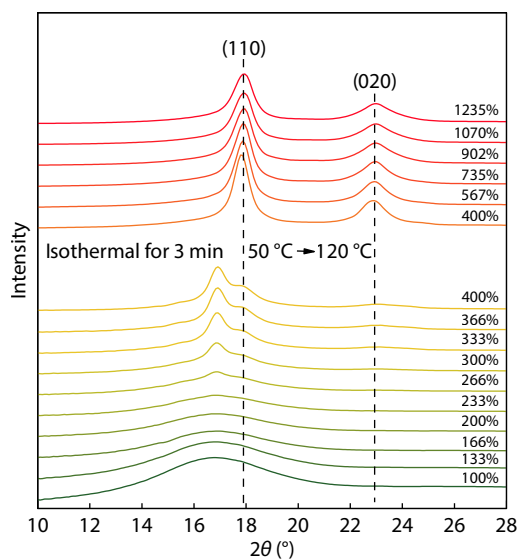


Fig. 13 The 1D WAXD curves of PGA nascent fibers at different strains under segmented stretching.

stretching temperature and isothermed was conducive to the conversion of the oriented amorphous chains to crystallization.

The crystallinity and orientation calculated from WAXD results for all stretching temperatures during the high-temperature stretching are depicted in Fig. 14. During the heating process, the crystallinity and orientation showed a rapid increase with the increasing temperature, as the oriented amorphous chains gradually transformed to crystallization (Fig. S4 in ESI). The orientation increased in a stable trend, while the crystallinity increased at a faster rate during the high-temperature stretching as the stretching proceeded. However, in contrast, the crystallinity and orientation were basically remained unchanged or increased slowly in the stretching of the crystallization regions during the previous low-temperature stretching. In addition, in order to investig-

ate the effect of the stretching on the whole fiber including amorphous and crystal part, the orientation of fibers was also measured by optical birefringence method, and the results are shown in Table 2. Similar to the previous results, the fibers showed a low birefringence before stretching, while the orientation of the fibers increased after low-temperature stretching and the birefringence increased, the higher birefringence after high-temperature stretching indicated a higher orientation of the fibers. Also, it can be seen from the table that the amorphous regions of the fibers with lower initial crystallinity during low-temperature stretching possessed higher orientation, which was consistent with the variation of the previous amorphous orientation peak as well. The value of crystallinity and orientation of the fibers increased to a certain extent after high-temperature stretching compared to low-temperature stretching, indicating that high-temperature stretching was more favorable to the evolution of the crystal structure.

The unit cell parameters and lateral crystallite sizes varying as a function of the strain of high-temperature stretching, which extracted from the WAXD data, are summarized in Fig. 15. During the heating process, the unit cell parameters and crystallite sizes increased with the temperature due to the thermal expansion (Fig. S5 in ESI). It can be drawn from Fig. 15 that with the stretching processed, the unit cell parameters at all selected temperatures showed a rapid decrease and then followed by a tendency to be essentially constant, which demonstrated that high-temperature stretching was advantageous to the crystal perfection. However, it was interesting to observe that the difference in the unit cell parameter a at different stretching temperatures was not significant, while the unit cell parameter b was more different and increased with the stretching temperatures, which was principally caused by the difference in the thermal expansion coefficients in the direction of different crystallographic axes.^[46] This phenomenon was previously observed by our group during the study of the structural evolution of PGA and P(GA-co-LA) fibers during heat-setting process, and a detailed explana-

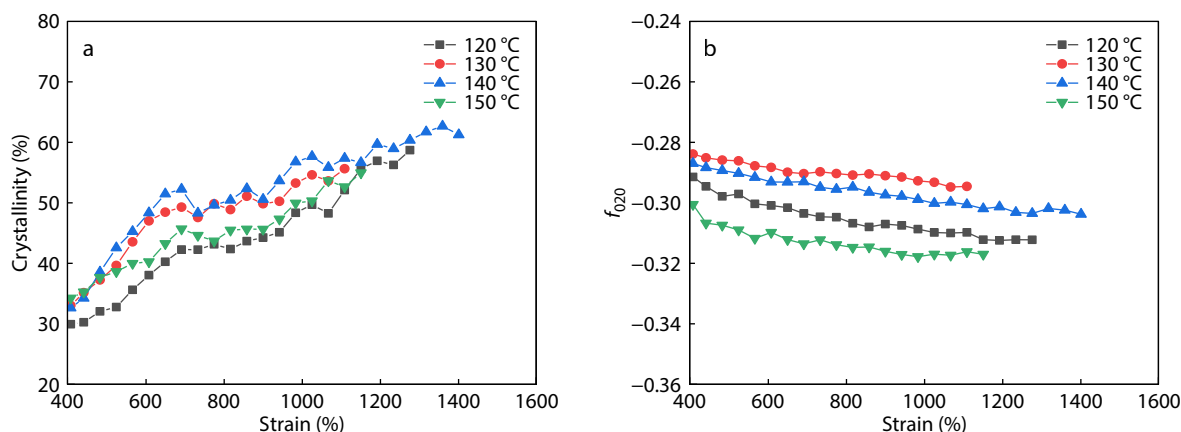


Fig. 14 The crystallinity (a) and orientation (b) of PGA nascent fibers during the stretching of high temperature.

Table 2 The birefringence of the stretched PGA fibers with different stretching temperatures based on the optical birefringence method.

Sample	Nascent fiber	45 °C	50 °C	55 °C	60 °C	120 °C	130 °C	140 °C	150 °C
Δn	0.0678	0.0581	0.0548	0.0596	0.0353	0.0554	0.0655	0.0663	0.0678

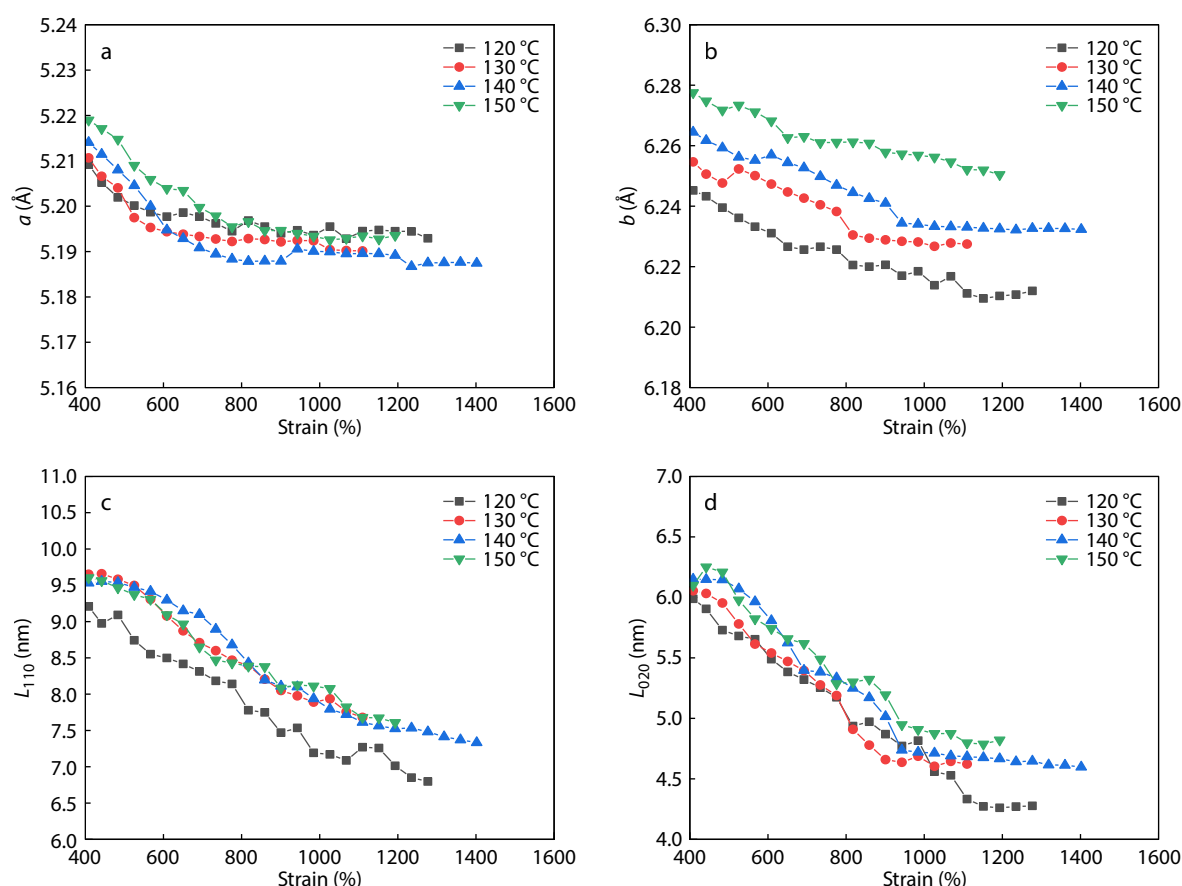


Fig. 15 The unit cell parameters (a) a , (b) b and crystallite sizes (c) L_{110} , (d) L_{020} of PGA nascent fibers at different strains during the stretching of high temperature.

tion of the trend was provided. That was, the intermolecular forces were related the coefficient of thermal expansion, and the greater the intermolecular forces, the smaller the thermal expansion coefficient.^[47] Due to the existence of a weak hydrogen bond on the (110) crystalline plane, the intermolecular force was larger than that of the (020) crystalline plane, and therefore, the thermal expansion coefficient of the (020) crystalline plane was higher than (110) crystalline plane, resulting in the increasing trend of the unit cell parameter b larger than unit cell parameter a . As can also be observed from Fig. 15, the crystallite sizes decreased gradually with the progress of high-temperature stretching, which was mainly considered as a change caused by stress-induced fragmentation recrystallization or lamellar slip during high-temperature stretching. In addition, the unit cell parameters and crystallite sizes of fibers stretched at high temperatures showed a more significant decrease than those stretched at low temperatures, and the value of the unit cell parameters and crystallite sizes stretched at high temperatures were also smaller compared with those stretched at low temperatures. In general, the unit cell parameters and crystallite sizes increased with the increasing stretching temperatures due to the occurrence of thermal expansion. However, the value after high-temperature stretching were still smaller than those after low-temperature stretching, indicating that high-temperature stretching was more conducive to the crystal perfection and structural evolution of fibers than low-temperature stretch-

ing, promoting the transformation of lamellar to fibrous crystals by stress-induced fragmentation recrystallization, resulting in fiber fibrillation.

Corresponding SAXS changes during high-temperature stretching were suitable for a complete understanding of the structural evolution. Fig. 16 presents the selected 2D SAXS patterns of PGA nascent fibers stretching at high temperature. The lamellar signal formed by stretch-induced crystallization was weak in the low-temperature stretching, while the lamellar signal was significantly enhanced when the temperature was raised to 120, 130, 140 and 150 °C. Combined with the previous WAXD results, it can be concluded that the amorphous orientation peak appearing in the low-temperature stretching was gradually converted to crystallization peak during the heating process. With the progress of high-temperature stretching, the lamellar signal gradually approached the center of the spot, indicating that the long period increased as the stretching proceeded. The one-dimensional SAXS profiles, extracted from the 2D SAXS patterns, were analyzed via the method of correlation function to estimate the lamellar morphological variables. The several morphological variables including the long period (L), the lamellar thickness (L_c) and the amorphous thickness (L_a) of PGA nascent fibers during high-temperature stretching are displayed in Fig. 17. The long period decreased gradually with the stretching process in the low-temperature stretching, while the value of long period showed a gradual increase

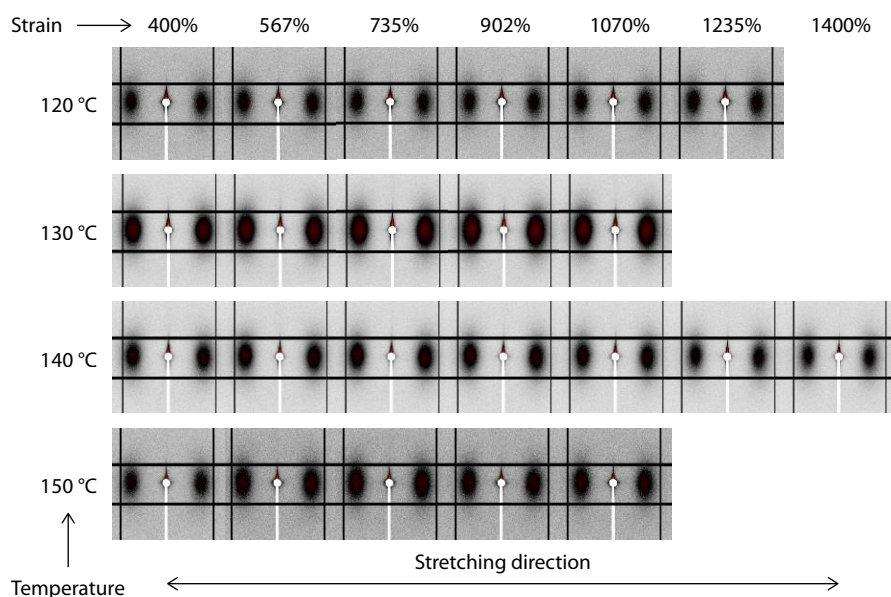


Fig. 16 The *in situ* SAXS images of PGA nascent fibers at different strains during the stretching of high temperature.

with the increasing strains during the high-temperature stretching. In addition, it could also be observed that the lamellar thickness and amorphous thickness also showed an upward trend during the high-temperature stretching, and the increasing trend of lamellar thickness was higher than that of amorphous thickness. Combined with the long period data, it was considered that some smaller crystals were formed in stretch-induced crystallization stage, which lead to the decrease of average long period, and upper temperature was more conducive to the growth of lamellar crystals, therefore, with the increase of temperature, the structure of lamellar crystals became more perfect, and new thicker lamellar crystals could be generated, resulting in an increasing of long period and lamellar thickness.

The average length and misorientation of shish during high-temperature stretching are depicted in Fig. 18. It could be observed that the average shish length at all hot stretching temperatures decreased with the increasing strains during high-temperature stretching, which was due to the fact that the formation of shish crystals in the later stages of

stretching mainly came from the chains with more chain entanglements, resulting in a decrease in the average length of shish crystals. However, the average shish length after high-temperature stretching was significantly smaller compared with low-temperature stretching, which was considered to be the fact that only a small number of long shish crystals were generated at the early stage of stretching, while a large number of short shish crystals were formed at the later stage of high-temperature stretching. Furthermore, the misorientation decreased with the increasing strains at all hot stretching temperatures, and the value after high-temperature stretching was significantly lower than that after low-temperature stretching, which was clearly visible in the image in Fig. 18, indicating that the shish crystals formed after high-temperature stretching were preferably oriented compared with low-temperature stretching.

Combining the above DSC, WAXD, SAXS and stress-strain curve results, the structural evolution of PGA nascent fibers during single low-temperature stretching and segmented high-temperature stretching is depicted in Fig. 19. It was con-

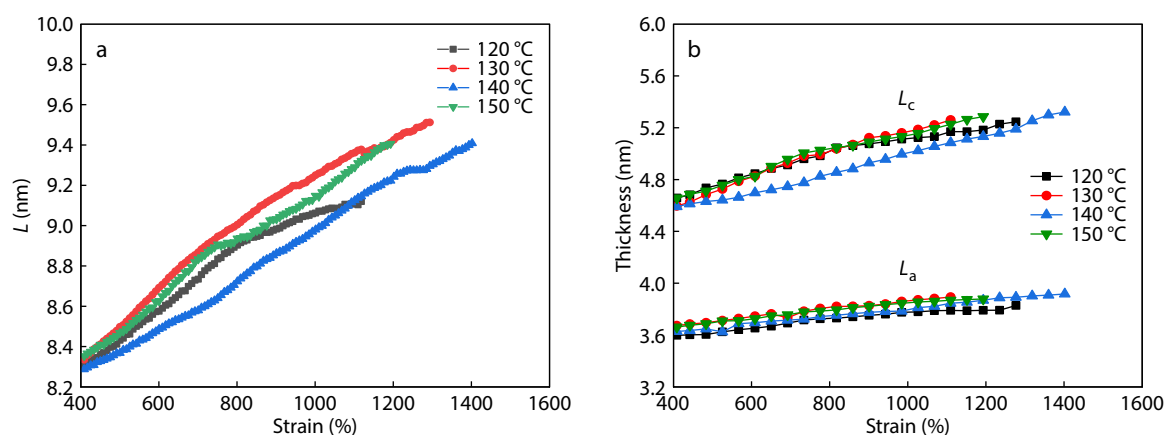


Fig. 17 The long period (a), lamellar thickness (L_c) and amorphous thickness (L_a) (b) changes of PGA nascent fibers during the stretching of high temperature.

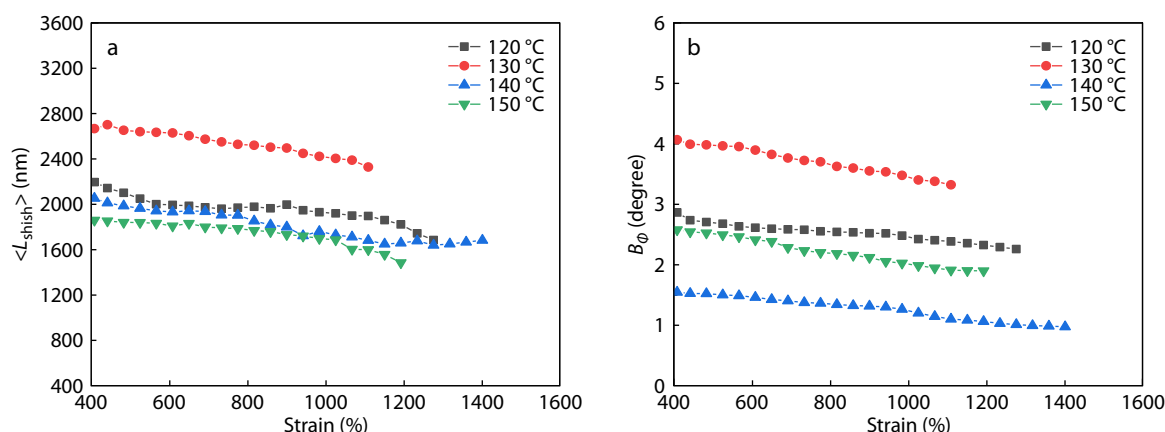


Fig. 18 The average length (a) and misorientation (b) of shish crystals of PGA nascent fibers during the stretching of high temperature.

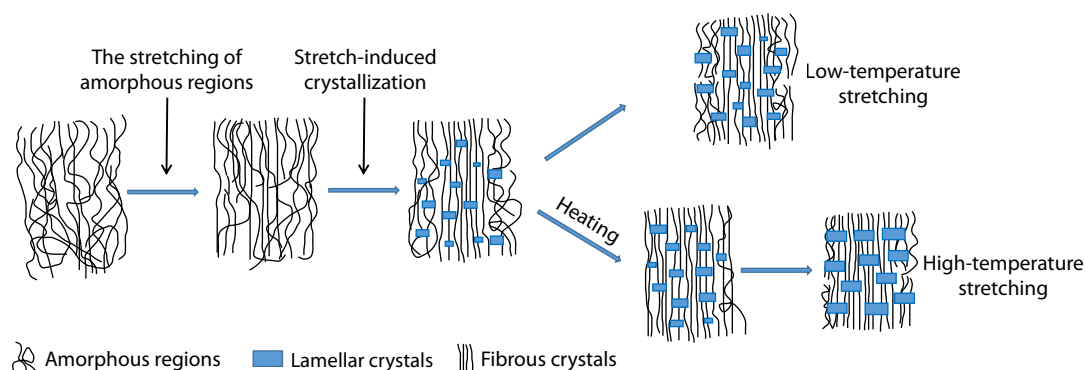


Fig. 19 The schematic diagram of the structural evolution of PGA nascent fibers during single low-temperature stretching and segmented high-temperature stretching.

cluded that the structural evolution of PGA nascent fibers during single low-temperature stretching process could be divided into three stages: the stretching in the amorphous regions, stretch-induced crystallization and the stretching in the crystalline regions. The unit cell parameters and crystallite sizes showed a gradual decrease during low-temperature stretching, indicating that stretching promoted the crystal perfection. The low-temperature stretching was more conducive to the formation of small crystals, resulting in the decrease of average crystallite sizes and long period. Meanwhile, only a small number of longer shish crystals were generated at the early stage of stretching, and as the hot stretching proceeded to higher strains, the untwisting of chain entanglement became difficult and a large number of short shish crystals were generated at a later stage, and therefore, the average length of shish crystals showed a tendency to increase and then decrease during low-temperature stretching. Furthermore, it was found that high-temperature stretching after the end of the stretch-induced crystallization stage in low-temperature stretching can promote the further evolution of the aggregate structure of PGA fibers. High-temperature stretching not only substantially increased the elongation at break of the fibers, but also improved the crystallinity and orientation. The amorphous orientation peak appearing in the low-temperature stretching was gradually converted to crystallization peak during the heating process, which greatly improved the crystallinity and orientation of the fibers. High-temperature stretching was more conducive to the growth of

lamellar crystals, and the structure of the lamellar crystals became more perfect and new thicker lamellar crystals could be generated as the temperature increased, contributing to a gradual increase of the long period and lamellar thickness during the high-temperature stretching process. The decreasing trend of unit cell parameters and crystallite sizes of fibers during high-temperature stretching was larger than that of low-temperature stretching, and the final values were also smaller than low-temperature stretching, indicating that lamellar crystals probably be transformed into fibrous crystals through stress-induced fragmentation recrystallization. Furthermore, the average shish length and misorientation stretched at high temperature were significantly lower than those stretched at low temperature, illustrating that shish crystals with preferable orientation could be formed after high-temperature stretching. In summary, high-temperature stretching was more conducive to the crystal perfection and structural evolution of fibers compared with low-temperature stretching, promoting the transformation of lamellar to fibrous crystals.

CONCLUSIONS

The structural evolution of PGA nascent fibers during single low-temperature stretching and segmented high-temperature stretching was investigated by WAXD/SAXS and DSC measurements. It was concluded that the single hot-stretching process of PGA fibers at lower stretching temperatures could be

divided into three stages: the stretching of amorphous regions, stretch-induced crystallization and the stretching of crystalline regions. Stretching promoted the crystal perfection, and low-temperature stretching was prone to the formation of small crystals, resulting in the decrease in average crystallite sizes and long period. The segmented high-temperature stretching could not only substantially increase the elongation at break of the fibers, but also increase the crystallinity and orientation. High-temperature stretching was more conducive to the growth of lamellar crystals and lamellar crystals with larger long period could be generated during the stretching process. Furthermore, it was also found that high-temperature stretching was more favorable than low-temperature stretching for crystal perfection and structural evolution of fibers, promoting the transformation of lamellar to fibrous crystals by stress-induced fragmentation recrystallization, resulting in fiber fibrillation. This research was not only important to understand the structural evolution of PGA fibers during stretching but also expected to be helpful to provide a theoretical basis for the preparation of the fibers with high performance in industrial production.

Conflict of Interests

The authors declare no interest conflict.



Electronic Supplementary Information

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