Scalable Reaction-spinning of Rigid-rod Upilex-S® Type Polyimide Fiber with an Ultrahigh $T_g$

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Abstract  In the family of polyimide (PI) materials, Upilex-S® film has been a shining star through the research PI materials due to its appealing merits. Unfortunately, the wholly rigid-rod backbone and easily formed skin-core micromorphology and microvoids of Upilex-S® type PI lead to the high difficulty in melt- and wet-spinning fabrication. Herein, we propose a facile and scalable method, reaction-spinning, to fabricate the Upilex-S® type PI fiber, in which the rapid solidification of spinning dope and partial imidization take place simultaneously. Thus, the stability and mechanical strength of as-spun fibers can be improved, and the microvoids in fibers can be greatly reduced in relative to the wet-spun fibers. The resultant Upilex-S® type PI fiber shows higher tensile strength and modulus than most commercial thermal-oxidative polymeric fibers with an ultrahigh glass transition temperature $T_g$ of 478 °C. Moreover, the WAXS and SAXS results indicate that orthorhombic crystals are formed for Upilex-S® type PI fiber in the post hot-drawing process. Increasing the hot-drawing temperature results in a continuous crystallization and high orientation of PI chains in amorphous phase and perfects the existing lamellar structure, which make a great contribution to the improved mechanical property.

Keywords  Polyimide fiber; Reaction-spinning; Ultrahigh $T_g$; Crystal structure

INTRODUCTION

Since the first successful commercialization of Nomex® and Kevlar® fibers by DuPont during 1960s and 1970s,[1] there has been steady progress and significant advances in developing high performance polymeric fibers for various applications, such as poly(p-phenylene benzobisoxazole) (PBO) fiber (Zylon, Toyobo Co. (Japan)), polybenzimidazole (PBI) fiber (Celanese Co. (USA)), poly(2,6-diimidazo[4,5-b:4,5′-e]pyridinylene-1,4-(2,5-di-hydroxy)phenylene) (PIPD) fiber (M5®, Magellan Systems International (USA)), and polyarylate fiber (Vectran®, Kuraray Co. (Japan)). Their rigid rod-like backbones are characteristic, and distinguish them with exceptional thermal and chemical resistances, outstanding flame retardancy and excellent mechanical property. Unfortunately, some of them exhibit common drawbacks, for instance, Kevlar® and Zylon® have low axial compressive strength,[5] while Kevlar®, Zylon® and Vectran® are all faced with poor resistance to ultraviolet and visible radiation,[5–3] which limit their practical applications in some harsh conditions. Accordingly, developing novel high-performance polymeric fibers with excellent compressive properties toward commercial application becomes an urgent topic in this field.

As a new member in the aromatic rigid-rod polymeric fibers, PI fibers possess a high comprehensive performance, including excellent thermal stability, good mechanical property, chemical and radiation resistance, and atomic oxygen resistance as well as intrinsic flame retardancy.[5–9] When annealed at 380 °C for 250 h, the tensile strength retention for PI fiber maintains over 80%, approximately 7-folds higher than those of the poly(p-phenylene terephthalamide) (PPTA) and PBO fibers. As exposed to UV radiation for 500 h, the PI fiber can keep a strength retention as high as 90%, while the PPTA and PBO fiber can only maintain 55% and 45% of their strengths, respectively, indicating a promising application for PI fibers in the area of space environment and harsh conditions.[10] In the past few decades, all-aromatic PIs have been always regarded as the highest performing engineering polymers. Typical commercial available all-aromatic PI is the Upilex-S® (Ube (Japan), Ltd.) derived from the 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and $p$-phenylenediamine (PDA), which exhibits a glass transition temper-
to fiber processing. For example, the non-observed melting temperature and insolvibility impede the conventional melt-spinning manufacturing process, while the easily formed skin-core micromorphology and micropores deeply hinder the fiber manufacturing by a “two-step” wet-spinning process.[13] Alternatively, dry-spinning is more convenient and environmentally friendly, with more ease of operation and relatively lower cost. Specifically, a prominent advantage for preparing PI fibers by the dry-spinning is that the soluble precursor poly(amic acid) (PAA) will be partially thermally imidized to PI in the high-temperature column, which means that the solidification of spinning dope and partial imidization take place simultaneously, which can be called a “reaction-pinning” method. Apparently, the reaction-spinning can avoid the internal microvoid formation during the wet-spinning, and the mechanical property and stability of the as-spun precursor fiber will be improved due to the partial imidization in the high temperature heating column. Moreover, the volatile solvent can be directly cooled and recycled in the spinning process. Thus, this method is more environmentally friendly and less costly compared to the traditional wet-spinning method, which retrenches the cost of fiber processing and makes them more applicable in large-scale practical application.

Herein, we reported the preparation of Upilex-S® type PI fiber by the reaction-spinning method. The correlation between the mechanical property and microstructure formed in the post-processing of the resultant Upilex-S® type PI fiber was analyzed in detail by the wide- and small-angle X-ray scattering (WAXS/SAXS). It is hoped that the methods and results reported herein can become an effective guidepost for preparing other novel high-performance polymeric fibers.

**EXPERIMENTAL**

**Materials**

Para-phenylenediamine (PDA, ≥99.5%) was purchased from Zhejiang Dragon Chemical Co., Ltd. (Hangzhou, China). 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA, ≥99.5%) was obtained from Hebei Haill Chemical Company (Shijiazhuang, China). Dimethylacetamide (DMAc) was provided by Shanghai Jinshan Jingwei Chemical Co., Ltd., and dried by 0.4 nm molecular sieve for 14 days prior to use.

**Synthesis of Poly(amic acid) (PAA) and Preparation of Upilex-S® Type PI Fiber**

As shown in Scheme 1, first, the spinning dope poly(amic acid) (PAA) was synthesized by mixing equimolar diamines PDA and dianhydride BPDA in DMAc under a dried nitrogen atmosphere at 0 °C for 24 h and controlling the solid weight fraction of 15 wt%. The synthesized PAA solution was vacuum degassed at 50 °C for 12 h prior spinning. Then, the PAA solution was transported by a metering pump under a high pressure and through a spinneret with 50 holes into the hot column, and the solvent was evaporated immediately and the spinning viscous flow solidified and was rolled up on a winding machine. The mixture of solvent steam and hot nitrogen was continuously...

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**Scheme 1** Synthesis of the BPDA-PDA PAA spinning dope and fabrication of PI fiber by a reaction-spinning approach.

https://doi.org/10.1007/s10118-021-2508-0
taken away by suction fan, and the solvent was cooled and recycled after the mixing steam derived through a heat exchanger. Consequently, partially imidized poly(amic acid-imide) precursor fibers were fabricated, which would be further thermally imidized at 300 °C. For further enhancing the mechanical properties, a hot-drawing treatment for the as-imidized fibers was performed under different temperatures. The resultant fibers were abbreviated as PI-x, where x means the hot-drawing temperature.

Characterization

The linear density of fibres was measured by the XD-1 Vibration Fibre Finesseness Tester developed by the Shanghai New Fibre Instrument Co., Ltd. Mechanical properties were measured by the XQ-1 tensile testing instrument with a gauge length of 20 mm at a strain rate of 50%·min⁻¹, and one specimen was measured at least ten times. The thermomechanical analysis of fibers was conducted on a TA Q400EM equipment under a custom mode with a pretension force of 0.1 N at a heating rate of 3 °C·min⁻¹ from 50 °C to 200 °C. The 10% weight loss temperature (Td,10%) and the temperature at the maximum degradation rate (Td,max) were obtained from a Netzsch 209F3 thermal gravimetric analyser at a heating rate of 10 °C·min⁻¹ to 950 °C in a nitrogen atmosphere. Two-dimensional wide- and small angle X-ray scattering (WAXS and SAXS) patterns were acquired at 16B1 Beamline in Shanghai Synchrotron Radiation Facility (SSRF). In detail, the wavelength was 0.124 nm, and the distances between the CCD X-ray detector (MAR CCD165) and samples were 208.7 and 1800 mm, respectively, for WAXS and SAXS measurements. The obtained data were analysed using the X-polar software (Precision Works Inc., NY, USA).

The crystallinity (Xc) of fibres was calculated using the following equation:

\[ X_c = \frac{A_c}{A_c + A_a + A_m} \times 100\% \]  

where \( A_c \), \( A_a \) and \( A_m \) represent the crystalline, amorphous and mesomorphic fraction areas, respectively. The crystal orientation along the fiber axis was evaluated by Herman’s orientation factor (\( f_c \)) as shown in the following equation:

\[ f_c = \frac{3(\cos^2 \varphi) - 1}{2} \]  

\( \langle \cos^2 \varphi \rangle \) is the orientation parameter, which is determined by the Wilchinsky’s model[14] and can be calculated by following equation:

\[ \langle \cos^2 \varphi \rangle = \frac{\int_0^\theta \int_0^1 \rho(\beta) \cos^2 \beta \sin \beta \cos \beta \cos \beta \d \beta}{\int_0^\theta \int_0^1 \rho(\beta) \cos \beta \cos \beta \d \beta} \]  

where \( \theta \) is the Bragg angle, \( \beta \) is the azimuthal angle of crystal plane, and \( \rho(\beta) \) represents the diffraction intensity. The apparent crystal size of different fibers was calculated by using the Scherrer function:

\[ D_c = \frac{k\lambda}{\beta_\theta \cos \theta} \]  

where \( D_c \) is the crystal size, \( \lambda \) represents the radiation wavelength, \( k \) means a constant equal to 1, and \( \beta_\theta \) is the integral breadth (IB) of crystal peak.

Typical 2D SAXS patterns from semicrystalline polymers display an equatorial streak and two lobes along the meridian. This suggests the existence of stacks of lamellae, i.e. stacks of alternating crystalline, mesomorphic and amorphous layers. The characteristic longitudinal dimension of the lamellar stack, i.e. the long period (L), was analyzed by calculating a correlation function \( \gamma(r) \)[15,16] by a 1D Fourier transformation:

\[ \gamma(r) = \frac{\int_0^\infty I_1(q) \cos(qr) dq}{\int_0^\infty I_1(q) dq} \]  

where \( r \) is the distance of the electron density distribution, \( q_3 \) is the scattering vector along the meridional direction (Fig. 1), and \( I_1(q_3) \) is the integrated intensity on the meridian by a projection operation using the following formalism:

\[ I_1(q_3) = \int_0^\infty I(q_{12}, q_3)q_{12} dq_{12} \]  

\( \theta \) is the Bragg angle and \( \lambda \) is the radiation wavelength.

Besides, the long period \( L \) also can be calculated by the Bragg equation:

\[ L = \frac{\lambda}{2 \sin \theta} \frac{2\pi}{q} \]  

The lateral width of the lamellae can be obtained from IB of crystalline peaks fitted with the Lorentzian function in the maximum lamellar reflections by using the Scherrer equation (Eq. 4).

**RESULTS AND DISCUSSION**

A schematic illustration of Uplex-S® type PI fiber preparation via the reaction-spinning is shown in **Scheme 1**. The synthesized organo-soluble PAA spinning dope was extruded from a spinneret into a hot column, where the solvent was evaporated immediately and partial amic acid moieties were thermally cyclized to imide rings revealed by the characteristic bands at 1774, 1708 and 1363 cm⁻¹ of imide rings as shown in ATR-FTIR (Fig. 51 in the electronic supplementary information, ES1). At a winding speed of 220 m-min⁻¹, the imidization degree of the as-spun precursor fiber reaches 30% calculated by a previously reported method[17]. The precursor fiber will be thermally imidized by passing through a high temperature oven over 300 °C, and further treated by hot-drawing in a hot tube. In this
way, Upilex-S® type PI fiber with a dark yellow appearance can be prepared on a large scale.

Mechanical properties of the as-imidized and hot-drawn PI fiber are shown in Fig. 2. The as-imidized PI fiber has an initial modulus of 12.7 GPa, a tensile strength of 0.47 GPa, and reaches 16% elongation before failure. The improvement of mechanical properties of the PI fiber after postdrawing can be observed. It is clear that the fiber becomes stronger with rising hot-drawing temperature. For example, after postdrawing under 460 °C, the fiber shows considerably high breaking strength and modulus (1.72 and 74.4 GPa, respectively), 260% and 485% higher than those of the as-imidized PI fiber. Moreover, the use of our industrial-type spinning device with continuous mechanized in-line drawing endows fibers with highly consistent mechanical properties evidenced by low standard deviations. The thermomechanical analysis (TMA) reveals that the PI-460 fiber has a glass transition temperature Tg as high as 478 °C (Fig. S2 in ESI), comparable to that of the Upilex-S® film. The thermal stability of the prepared PI fiber was analyzed by the TGA in air (Fig. S3 in ESI). Little weight loss occurs until the onset of decomposition above 500 °C, and the maximum decomposition rate is found at about Tmax=618 °C, indicating the extraordinary high-temperature resistance. We also compare the tensile strength and Tg of prepared PI fiber with the properties of some commercial thermal-oxidative polymeric fibers. The tensile strength of the Upilex-S® type PI fiber in current study is higher than those of PBI,[19] Nomex,[18] polyetheretherketone (PEEK),[20] polysulfonamide (PSA)[21] aromatic polyester fibers[22] and previously reported PI fiber[23] as well as the commercial PI fiber[24] (P84®, Evonik, Germany). Moreover, the current fiber exhibits the highest Tg, indicating it is an ideal candidate used for fire fighters clothing, felt in industry, high temperature cut resistant gloves and aircraft engine fragment barrier, etc.

It is well known that as the basic structure parameters, orientation and crystallinity in the fibers play an important role in their mechanical properties. The rigid-rod BPDA-PDA polyimide chains tend to form crystals based on the orthorhombic crystal unit cell with a space group of Pba21.[23,24] The crystal structures of as-imidized and hot-drawn Upilex-S® type PI fibers were analyzed by wide- and small-angle X-ray scattering (WAXS and SAXS). The WAXS intensity profiles, acquired every 30 °C when hot-drawing the sample from 370 °C to 460 °C, reveal that this PI fiber presents a semi-crystalline structure (Fig. 3a). Dramatic changes in the 2D WAXS patterns occur as increasing the drawing temperature. The equatorial and meridional scattering intensities become much more intense, indicating the formation of well-defined crystalline regions in the fibers. For detail, 1D integrated intensity profiles around the equator and meridian obtained from the WAXS patterns were used for evaluating the positions of diffraction peaks. A well-defined strain-induced crystallization and highly oriented crystalline structure subsequently form in the hot-drawing process (Figs. 3b and 3c). The appearance of intensive (00l) peaks, such as (004), (006), (008) and (0010), indicates the polyimide chains being highly aligned in the fiber axis and the presence of periodic lamellar structure.

The hot-drawn PI fiber has orthogonal geometry in a lattice parameter a=8.40 Å, b=5.80 Å and c=30.5 Å, with (00l) diffractions appearing on the meridian, and (hk0) diffractions appearing on the h0 layer line as well as the positions of the (hk0) planes on the equator (Fig. 3a). A typical deconvolution of the WAXS intensity profile of PI-460 fiber is shown in Fig. 4(a), in which several diffraction peaks relating to the crystal phase, mesomorphic phase and amorphous phase can be distinguished. The temperature dependence of the degree of crystallinity estimated from the 1D WAXS scans is shown in Fig. 4(b). Clearly, the postdrawing causes the following changes in phase composition. With increasing the hot-drawing temperature, the amount of the rigid fraction composed of orthorhombic crystals increases from ~18.7% for the as-imidized fiber to 41.9% for the PI-460 at the expense of amorphous fraction (decreasing from 69.8% for the as-imidized fiber to 46.3% for the PI-460). It is interesting to find that the mesomorphic phase fraction hardly changes with the hot-drawing temperature and equals 11.5%–14.0%. It can be speculated that an increase in temperature can provide the needed kinetic energy that facilitates the reorganization of
Fig. 3 (a) WAXS patterns of PI fibers treated under different hot-drawing temperatures, and temperature-dependent 1D integrated WAXS intensities for PI fibers along (b) equator and (c) meridian.

Fig. 4 (a) Typical one-dimensional integrated WAXS intensity profile of the PI-460 and the corresponding peak separation analysis to estimate the crystallinity, (b) temperature dependence of amorphous, mesomorphic and crystal phases fractions in different PI fibers, (c) azimuthal profiles of the (004) diffraction with hot-drawing temperature for prepared PI fibers and degrees of orientation factor calculated based on (004) and (0010) planes for different hot-drawn PI fibers, and (d) the relationship of $1/E$ and $\langle \sin^2 \phi \rangle$ for hot-drawn PI fibers.
the chains in amorphous phase for crystallization and perfection of the existing crystals in the fibers. Besides, the chain orientation, as expressed by the full width at half-maximum (FWHM) of the azimuthal intensity distribution of the (004) plane, increases very significantly with hot-drawing temperature supported by the decreased FWHM (Fig. 4c). The Herman’s orientation parameter estimated from the (00l) planes is plotted against the hot-drawing temperature, which exceeds 0.94 for the PI-460 based on the (004) diffraction, indicating a very high orientational order of crystals and a typical "orientation induced crystallization" effect in this fiber. As reported by Northolt et al.,[28] the relation between the modulus and the chain orientation can be given by

\[ \frac{1}{E} = \frac{1}{e_c} + \frac{\langle \sin^2 \phi \rangle}{2g} \]  

(9)

where \( E \) is the tensile modulus, \( e_c \) represents the crystalline or chain modulus, \( g \) means the shear modulus and \( \langle \sin^2 \phi \rangle \) is the second moment of the orientation distribution. As depicted in Fig. 4(d), the graph of \( 1/E \) versus \( \langle \sin^2 \phi \rangle \), the datapoints of fibers are positioned on a straight line with a slope of \( 1/2g \) and an intercept of \( 1/e_c \) on \( Y \)-axis. Accordingly, the theoretical crystalline modulus of this type PI fiber reaches 705 GPa, while the actual tensile modulus of PI-460 (74.4 GPa) is only 10% of what is calculated to be the theoretical limit, indicating that there is room for the improvement in tensile properties of the Upilex-S® type PI fibers.

The crystal structure parameters, including crystal and amorphous fractions, average crystal size parallel to the fiber axis, and orientation degree, are plotted against tensile strength and modulus of the resultant PI fibers as shown in Fig. 5. The mechanical property strongly depends on the crystalline structure, and the modulus/tensile strength increases linearly with crystal fraction and Herman’s orientation parameter, which is very often the case for most polymeric fibers. It is remarkable that the size of orthorhombic crystals in (004) direction parallel to the fiber axis increases with the hot-drawing temperature, resulting in an improvement of mechanical property of the fibers, which means that the growth of microcrystals in the hot-drawn PI fiber promotes the rapid increase in mechanical property.

2D SAXS patterns are shown for as-imidized and various hot-drawn PI fibers in Fig. 6(a). These patterns are typical for polymeric fibers containing microfibrils. Two spots on the meridian indicate the long period of fibrils, while the equatorial streaks in the direction perpendicular to the fiber axis are indicative of the internal fibrillar morphology. Clearly, the periodic lamellar structure gradually becomes more apparent as increasing the hot-drawing temperature. In order to estimate the lamellar structure parameters, SAXS data were analyzed by calculating the 1D correlation function \( \gamma(r) \) of the electron density distribution (Eqs. 5–7) (Fig. 6b), and the long period \( (L_z) \) and the lamellar thickness can be directly estimated. Especially, according to Strobl et al.,[15] the thickness of the mesomorphic phase zone \( d_{me} \) can be directly derived from the curvature of \( \gamma(r) \) (Fig. 6c). The temperature-dependent long period, thickness of crystalline zone, mesomorphic phase and amorphous region are obtained and listed in

![Graphs](https://doi.org/10.1007/s10118-021-2508-0)

*Fig. 5*  The correlations between tensile property (initial modulus (left) and tensile strength (right)) and microstructure parameters (e.g., crystal and amorphous fraction, crystal size and degree of orientation).
Table 1. Obviously, the values of $L_1$, $l_c$, $l_{me}$ and $l_a$ increase rapidly with the hot-drawing temperature. For example, the $L_1$ value increases from 17.3 nm to 34.9 nm (100% increase) as rising the hot-drawing temperature to 460 °C, whereas the $l_c$, $l_{me}$ and $l_a$ increase 100%, 528% and 50%, respectively. These results indicate that the increase in long period $L_1$ is mainly attributed to growth of crystal phase and transition zone (mesophase), implying that more chains in the amorphous phase are crystallized with increasing drawing temperature. The representative $Iq^2$ versus scattering factor $q$ curves along

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**Table 1.** Long period ($L_1$), thickness of crystal ($l_c$), mesomorphic ($l_{me}$) and amorphous phases ($l_a$), Scherer width of crystal phase ($D_c$) as well as crystal size as determined by WAXS and SAXS.

| Sample     | Correlation function analysis | Bragg equation | SAXS | WAXS |
|------------|-------------------------------|----------------|------|------|
|            | $L_1$ (nm)        | $l_c$ (nm)     | $l_{me}$ (nm) | $l_a$ (nm) | $L_2$ (nm) | $D_c$ (nm) | $d_{004}$ (nm) | $d_{110}$ (nm) |
| As-imidized| 17.5                      | 5.1            | 0.7          | 10.8        | 15.3        | 6.9        | 9.6           | 3.2          |
| PI-370     | 23.4                      | 6.9            | 2.6          | 11.3        | 20.3        | 7.8        | 10.7          | 3.2          |
| PI-400     | 25.5                      | 7.9            | 2.8          | 12.0        | 24.2        | 8.4        | 12.6          | 4.1          |
| PI-430     | 30.6                      | 9.0            | 3.9          | 14.9        | 27.3        | 10.4       | 13.9          | 5.2          |
| PI-460     | 34.9                      | 10.5           | 4.4          | 15.6        | 31.4        | 10.5       | 18.8          | 5.3          |

$L_1$ is the long period obtained by correlation function analysis, $L_2$ is the long period calculated by Bragg equation; $l_c$, $l_{me}$ and $l_a$ are the thicknesses of crystal, mesomorphic and amorphous phases, respectively; $D_c$ is the lateral width of lamellae.

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**Fig. 6.** (a) SAXS patterns of PI fibers treated under different hot-drawing temperatures, (b) experimental correction function $\gamma(r)$ obtained for PI fibers treated under different hot-drawing temperatures, (c) representative plot of one-dimensional correlation function (Determinations of the electron density difference ($\eta_c - \eta_a$) in crystalline and amorphous regions, the mean crystallite and mesomorphic phase thickness $d_c$ and $d_{me}$ and the long period $L$ are demonstrated in the figure), (d) dependence of $Iq^2$ on $q$ for PI fibers treated under different hot-drawing temperatures, and (e) analysis of the longitudinal slices (a scan through the SAXS pattern parallel to the fiber axis).
the fiber axis is shown in Fig. 6(d). A peak maximum can be clearly observed and the peak position is gradually shifted to lower \( q \), indicating the increase in the long period. In detail, the long period \( L_2 \) can be further determined by the Bragg function \( L_2 = 2\pi/n_q \) (Eq. 8), and the results are listed in Table 1. The calculated values of \( L_2 \) range from 15.3 nm to 31.4 nm, which are comparable to the \( L_1 \) estimated from the \( y(r)-r \) curvatures. As suggested by Murthy et al.,\(^{[19]} \) an equatorial azimuthal scan along the \( q_{12} \) at \( q_1 \) corresponding to the maximum in the lamellar reflections can be used to estimate the lateral width of the lamellae (\( D_\parallel \)) using the Scherrer equation (Eq. 4) (Fig. 6e). The values in Table 1 show that the diameter of the lamellae calculated from this width increases with hot-drawing temperature. This observation further indicates that continuous crystallization of polyimide chains in amorphous phase perfects the existing lamellar structure. There is an interesting result that the crystal size \( D_{110} \) in the (110) diffraction is almost half of the \( D_\parallel \) for all of fibers as listed in Table 1. In our opinion, this is not a coincidence, and the deep-rooted reason will be further explored.

CONCLUSIONS

In summary, we presented a scalable reaction-spinning method for fabricating the Upilex-S® type PI fiber, in which the solidification of spinning dope and partial imidization take place simultaneously. The reaction-spinning approach removes the obstacles for fiber spinning of PI fibers with a wholly rigid rod-like chemical structure. The resultant Upilex-S® type PI fiber shows a better mechanical property than many reported commercial thermal-oxidative polymeric fibers (Nomex®, PEEK, PAS, P84®, etc.) with an ultrahigh \( T_g \) around 478 °C. The WAXS and SAXS results reveal that a perfect orthorhombic crystal structure forms during the postdrawing of as-imidized Upilex-S® type PI fiber. A higher drawing temperature facilitates the constant crystallization of polyimide chains in amorphous phase and perfects the existing lamellar structure, which ensure the gradual increase in mechanical behavior of PI fiber with hot-drawing temperature.

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/s10118-021-2508-0.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51903038, 21774019, and 21975040), the Program of Shanghai Academic Research Leader (No. 18XD1400100) and the Scientific Research Innovation Plan of Shanghai Education Commission (No. 2019-01-07-00-03-E00001).

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https://doi.org/10.1007/s10118-021-2508-0