



Preparation of high-performance polyimide fibers via a partial pre-imidization process

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Received: 22 June 2018

Accepted: 24 October 2018

Published online:

5 November 2018

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ABSTRACT

In this work, a series of polyimide fibers (PI) based on 3,3',4,4'-biphenyltetracarboxylic anhydride (BPDA)/*p*-phenylenediamine (PDA) were prepared through a partial pre-imidization process, and the properties of these fibers were investigated in detail. The pre-imidization degree (pre-ID) was successfully controlled by adjusting the amount of dehydration reagents, which was confirmed by Fourier Transform Infrared. The scanning electron microscope images show that the addition of dehydration reagents in the poly(amic acid) spinning dope improves the shaping of the precursor fibers, which is related to the thermodynamic phase separation in the coagulation bath. The WAXD patterns indicate that the formed partial rigid-rod and oriented PI chains in the pre-imidization process are beneficial for forming a more ordered and regular crystalline structure in the post-heat-drawing process, thus improving their mechanical properties, which exhibit an optimum tensile strength and modulus of 1.7 GPa and 95.0 GPa, respectively. Meanwhile, the prepared PI fibers exhibit excellent thermal stabilities with the 5 wt% ($T_{5\%}$) weight loss temperature ranging from 530 to 568 °C depending on the pre-imidization degree. This work provides a simple and facile approach to preparing high-performance PI fibers through the partial pre-imidization process.

Introduction

There is a growing interest in the next generation of materials to meet the requirements by aerospace, information technology, military hardware and so on. Aromatic polyimide (PI) fibers as one of the heterocyclic polymeric fibers have attracted tremendous attention from academia to industry because of its superb thermal stability, good chemical and radiation

resistance and excellent dielectric performance, which make PI fibers widely applied in many fields such as protective garments, high-temperature filtration, and ballistic vests and helmets [1–4].

However, the properties of current PI fibers are hardly satisfactory under some specific conditions; thus, researchers have devoted great efforts to improving the overall performances (particularly in mechanical properties) of PI fibers to expand their

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applications. Generally, the chemical structure design of PIs has been considered as an effective approach to modifying the properties [5, 6], such as the introduction of specific groups into the polymer backbone [7]. Cheng et al. [8] introduced a novel benzobisoxazole unit into the flexible polyimide backbone and fabricated a series of fibers. The plank-shaped benzobisoxazole rings greatly improved the molecular orientation and crystallinity of the prepared PI fibers, thus resulting in a maximum improvement of 153% in tensile strength and 282% in modulus of the fibers. Additionally, the enhancement of the interchain interaction is proved to be an effective way to improve the performance of PI fibers. A case in point is that Yin et al. [9] prepared a copolyimide fiber containing benzimidazole and amide units based on 4-amino-*N*-(4-aminophenyl) benzamide (DABA), 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and dianhydride BPDA, which introduced the H-bonding interaction and greatly improved the final mechanical properties of the fibers. In addition, rigid heterocyclic moieties have been used to fabricate high-performance PI fibers, and their tensile strength and modulus can reach over 2.5 GPa and 110 GPa, respectively [10, 11]. Moreover, incorporation of nanofillers (graphene oxide, carbon nanotube, clay, etc.) has also been regarded as a promising way to prepare high-performance PI fibers. Dong et al. [12] utilized amine-functionalized carbon nanotubes to reinforce the PI fiber by the method of in situ polymerization, and the resulted composite fibers possessed an optimum tensile strength of 2.41 GPa (approximately a 47% increase over that of the neat PI fiber) and a modulus of 99 GPa (27% increase compared with the neat PI fiber).

Besides the above-mentioned factors, the microstructures of polymer fibers formed in the spinning process also significantly affect their final mechanical properties. In the wet-spinning process, the spinning dope is gradually solidified via the phase separation as a result of the dual diffusion of the solvent and the coagulant. Thus, the coagulation process is a key process to control the microstructure and the mechanical properties of nascent fibers. The microvoid defects in the nascent fibers may severely damage the ultimate mechanical properties of final fibers [13–15]. Because of the poor solubilities and infusible characters of polyimides, a typical two-step method is mainly adopted to prepare PI fibers. The precursor poly(amic acid) (PAA) fibers are always

obtained by extruding PAA dopes into a coagulation bath and subsequently converted to the corresponding PI fibers through thermal or chemical imidization. In the coagulation bath, microvoids are easily generated during the dual diffusion process and these defects will be further amplified in the thermal imidization process. To obtain PAA fibers with a relatively dense inner structure, Park et al. [16] added acetic anhydride or acetic anhydride/pyridine into the PAA spinning dope to make the PAA solution slightly gelled before the spinning dope entered coagulant bath, and the diffusion rate became slower due to the conversion of partial PAA to polyimide. The ultimate stress and initial modulus of the obtained fiber increased by 49% and 27%, respectively. Wang et al. [17] prepared a series of polyimide films through a partial *pre*-imidization process, and those obtained PI films possessed improved mechanical properties, consistent with the increase in *pre*-imidization degree. Chang et al. [18] also demonstrated that the partial *pre*-imidization of the PAA spinning solution could obtain an ordered molecular packing arrangement of the polymer chains and gradually form homogeneous structures in the final fibers, which effectively enhanced the mechanical properties of PI fibers. They focused on the aggregation structure and mechanical properties of the resulted fibers. Therefore, it is speculated that the partial *pre*-imidization treatment of the PAA spinning dope can effectively modify its solidification process and result in a dense inner structure for the precursor fibers, thus greatly improving the performance of the final PI fibers. However, the modification mechanism of pre-partial imidization of PAA on the final PI materials has been rarely reported.

The polyimide (PI) derived from BPDA/PDA (Upilex-s type) is well known to show several excellent properties including a high thermal stability, a low coefficient of thermal expansion (CTE) and excellent mechanical properties [19, 20]. The Upilex-s polyimide film made by UBE industries (Japan) exhibits outstanding comprehensive properties (a tensile strength of 520 MPa and a tensile modulus of 9.1 GPa) compared to other types of polyimide films. Comparatively speaking, BPDA/PDA polyimide integrates the advantages of rigid linear chains and highly oriented molecular structures [21] that have been widely utilized in a variety of microelectronic applications, such as the substrates for flexible printed circuits (FPCs) and tape automated bonding

(TAB). Currently, there are few studies reporting the BPDA/PDA PI fiber due to the easily formed microvoids in the nascent BPDA/PDA PAA fiber, which is attributed to the very fast diffusion rate of the solvent and the coagulant, and the final Upilex-s type PI fibers always show disappointing mechanical behaviors. If the dual diffusion process for the BPDA/PDA PAA spinning dope can be effectively controlled, there is a great prospect to prepare polyimide fibers with a compact structure and high mechanical properties.

In this work, a series of BPDA/PDA polyimide fibers were prepared through a partial *pre*-imidization method, and the effect of the pre-imidization degree on fiber morphologies formed in the wet-spinning process has been discussed in detail. WAXD was carried out to investigate the relationship between the aggregation structure and the *pre*-imidization degree. Meanwhile, the mechanical properties and thermal stabilities of the PI fibers with different pre-imidization degrees were also studied.

Experiment section

Materials

p-Phenylenediamine (PDA) was obtained from Zhejiang Dragon Chemical Co., Ltd (Hangzhou, China). 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA, 99.5%) was purchased from Hebei Haili Chemical Company (Shijia Zhuang, China). *N*-methyl-2-pyrrolidone (NMP) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China) and purified by distillation prior to use. Triethylamine and acetic anhydride were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Synthesis of partial pre-imidization (PAI) spinning dopes

PAI spinning dopes with different pre-imidization degrees were synthesized by the following procedure, as shown in Scheme 1a. A representative polymerization is as follows: A 250 mL three-necked flask equipped with a nitrogen inlet and a mechanical stirrer was charged with NMP (141 mL) and PDA (0.04 mol). Equimolar BPDA (0.04 mol) was added as the diamine was dissolved. The solution was stirred

at a low temperature ($-5 \sim 0$ °C) for 12 h, and the viscous PAA solution with a 10 wt% solid content was obtained. Then, different mole amounts of dehydration reagents (mole ratio of Triethylamine/Acetic anhydride = 1/1) were added into the synthesized PAA solutions to obtain partially imidized PAI spinning dopes with theoretical pre-imidization degrees of 0, 10, 15 and 20 mol%, and the corresponding samples were named 0%-PAA, 5%-PAA, 10%-PAA, 15%-PAA and 20%-PAA, respectively. Approximately 6 h later, viscous and homogeneous PAI solutions with different pre-imidization degrees (pre-IDs) were obtained and kept in the freezer until use.

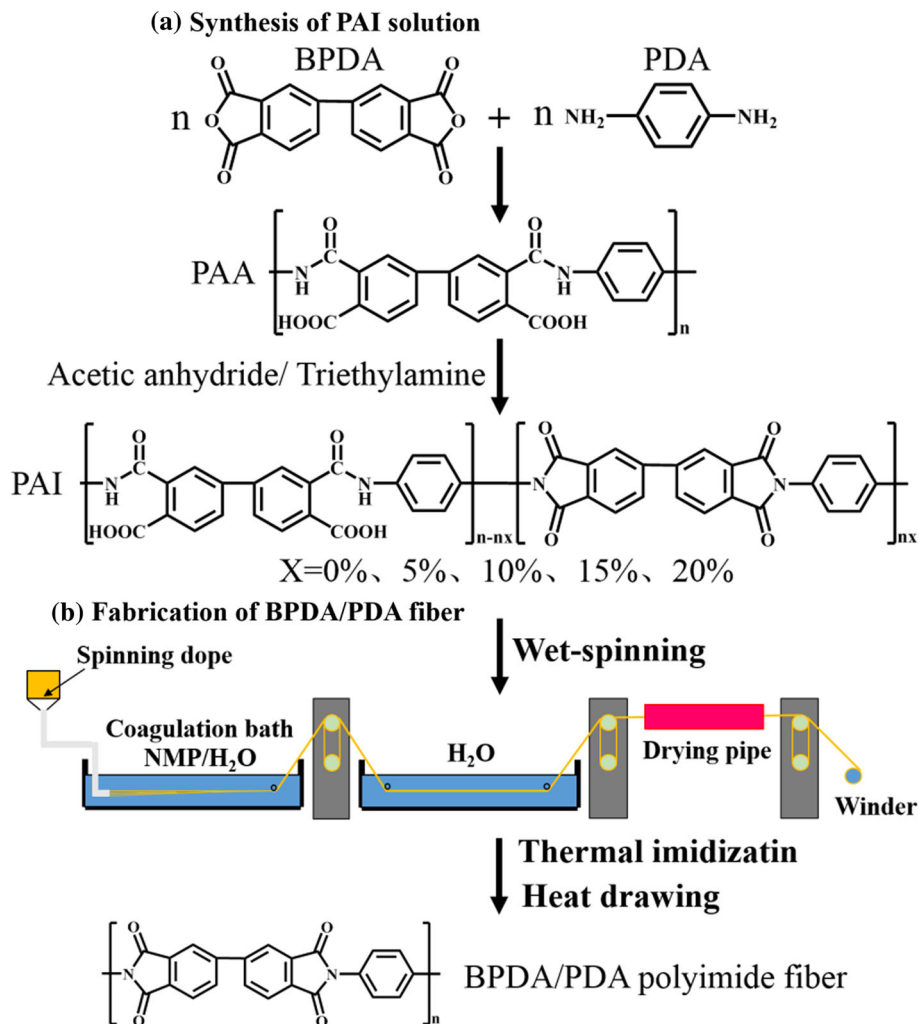
Preparation of PI fibers

The spinning solutions with different pre-IDs were degassed for approximately 12 h at room temperature prior to spinning and extruded into a coagulation bath through a spinneret (50 holes, 80 μ m in diameter), as shown in Scheme 1b. Then, the solidified filaments entered the following washing bath and heating tube. The obtained nascent fibers were dried under vacuum at 60 °C for 24 h to yield the PAI fibers, and then, the as-imidized PI fibers were obtained by heating the precursor fiber at 100, 200 and 220 °C for 30 min at each temperature. Finally, the PI fibers were obtained by drawing the as-imidized fibers with various ratios at 450–480 °C in a heating tube.

Cloud point titration

The PAI solutions with concentrations of 2.0, 3.0, 4.0 and 5.0 wt% in NMP were first prepared. Then, deionized water was slowly added into the PAI solutions by a microburette under magnetic stirring, and the temperature of the PAI solutions was kept at 28 °C. At the first sight of turbidity during the titration, the addition of water was stopped, and more water was added if the solution turned clear again after another 1 min of stirring; otherwise, it was considered as the cloud point. The cloud points of PAI solutions with high concentrations were calculated based on Boom's LCP correlation for the non-solvent/solvent/polymer ternary system [14].

Scheme 1 Fabrication of BPDA/PDA PI fibers by the wet-spinning process.



Measurement of the coagulation power

The synthesized spinning dope was dropped onto a clean glass slide and covered with another clean slide. Then, a coagulant was gradually dropped on the edge of the top slide. The diffusion of the coagulant fronts and the solidification of spinning dope with time were monitored by a microscope.

Characterization

FTIR spectroscopy was recorded on a Nicolet 8700 spectrometer in the range of 4000–400 cm^{-1} . The imidization degree (ID) of PAI fibers was determined according to previous works [22–24]. The band at 1376 cm^{-1} for the C–N stretching of the imide ring was selected for quantifying the ID, and the aromatic band at 1512 cm^{-1} for the C–C stretching of the *p*-substituted benzene backbone was utilized as the

internal standard. The corresponding ID was calculated using the following equation:

$$\text{ID} = \frac{(S_{1376}/S_{1512})_{T=60^\circ\text{C}}}{(S_{1376}/S_{1512})_{T=300^\circ\text{C}}} \times 100\% \quad (1)$$

where S is the area of the absorption band, $T = 60^\circ\text{C}$ is the treatment temperature, and $T = 300^\circ\text{C}$ is taken as the temperature of full imidization.

The molecular weights of polymers were measured on a PE series 200 permeation chromatography (GPC) instrument with a PL mixed-B10 m column. Polystyrene was used as the standard, and DMAc was used as the eluent at a flow rate of 1 mL/min. The morphologies of the fibers were observed on a SEM (HITACHI SU8010). The diffusion rates of the PAI solutions were obtained by a microscope (Leica DM750P, Germany). An appropriate amount of the polymer solution was placed on a glass slide and covered with a cover glass (as shown in Fig. 3). The

diffusion of the waterfronts with time was monitored by the microscope. The thickness of the solidified layer was proportional to the square root of time according to the following equation [16]:

$$\Xi = 1/4 \lim_{t \rightarrow 0} (d\xi^2/dt) \tag{2}$$

where Ξ was the initial boundary growth rate, ξ was the thickness of the solidified layer, and t is the time.

The mechanical properties of the prepared fibers were measured using an XQ-1 tensile testing instrument with a drawing rate of 10 mm/min and a gauge length of 20 mm. The thermal dynamic mechanical analysis (DMA) was carried out on a Q800 thermo-mechanical analyzer in an air atmosphere at a heating rate of 3 °C/min from 50 to 400 °C. The 5% weight loss temperature (T_{d-5}) and the temperature at the maximum degradation rate (T_{d-max}) were obtained from a Netzsch 209F3 thermal gravimetric analyzer at a heating rate of 10 °C/min to 800 °C.

Two-dimensional wide-angle X-ray diffraction (2D WAXD) O were obtained at Beamline 16 B1 in the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength is 1.24 Å, and a CCD X-ray detector (MAR CCD 165) was employed at a distance of 187 mm from the sample for WAXD measurements. The data were processed using the software package x-Polar (Precision Works Inc., NY, USA) and Peak-fit (version 4.12, Seasolve Co., San, CA). The crystallinity (X_c) of PI fibers was calculated by the following equation:

$$X_c = \frac{A_c}{A_c + A_a} \times 100\% \tag{3}$$

where A_c is the crystallization peak area, and A_a is the amorphous peak area. The crystal orientation along the fiber axis was calculated according to Hermans' orientation function:

$$f_c = \frac{1}{2} (3\langle \cos^2 \varphi \rangle - 1) \tag{4}$$

$$\langle \cos^2 \varphi \rangle = \frac{\int_0^{\frac{\pi}{2}} \cos^2 \varphi \sin \varphi d\varphi}{\int_0^{\frac{\pi}{2}} I(\varphi) \sin \varphi d\varphi} \tag{5}$$

where φ is the azimuthal angle of the (00*l*) plane, and $I(\varphi)$ is the intensity variation of the azimuthal angle of the (00*l*) reflection.

Results and discussion

Preparation of partially imidized nascent fibers

Molecular weights of polymers have a great effect on the final mechanical properties of polymers. Here, molecular weights of the pre-imidized PAAs were measured by GPC using DMAc as the eluent. The detailed molecular weights are listed in Table 1. It is seen that the M_n for PAA without the addition of dehydration reagents is approximately 92.8×10^4 g/mol with a PDI of 1.82. However, for the partially pre-imidized samples, the M_n ranges from 58.8×10^4 to 31.3×10^4 g/mol, and the addition of more dehydration reagents results in lower molecular weight. It is speculated that the decreased M_n value is due to the formation of water by-products produced in the process of the imidization reaction, which leads to the partial degradation of the PAA backbone.

The structures of poly(amic acid) and chemically partial imidization of poly(amic acid) have been monitored by FTIR. As shown in Fig. 1, the typical absorption band at 1654 cm^{-1} for the carbonyl from poly(amic acid) gradually decreases with increasing cyclization agent. In addition, the characteristic peaks at 1780, 1721, 1376 and 725 cm^{-1} (1780 cm^{-1} and 1721 cm^{-1} for C=O asymmetrical and symmetrical stretching, respectively, 1376 cm^{-1} for C–N stretching and 725 cm^{-1} for C=O bending of the imide ring) can be observed by adding the cyclization agent, suggesting the successful formation of the imide group. Meanwhile, the intensities of the characteristic absorption bands of polyimide increase markedly with the continually increasing chemical cyclizing agent, revealing that the pre-imidization degree can be adjusted by the amount of the cyclizing reagent.

The peak at 1376 cm^{-1} is always regarded as the character of polyimides, which is always utilized to quantify the degree of imidization, and the peak at

Table 1 Molecular weights and experimental pre-IDs of partially imidized PAAs with various theoretical imidization degrees

Theoretical pre-ID (%)	0	5	10	15	20
M_n (g/mol $\times 10^4$)	92.8	58.8	41.7	35.9	31.3
PDI	1.82	1.63	1.57	1.79	1.74
Experimental pre-ID (%)	0	5.23	10.74	14.85	21.22

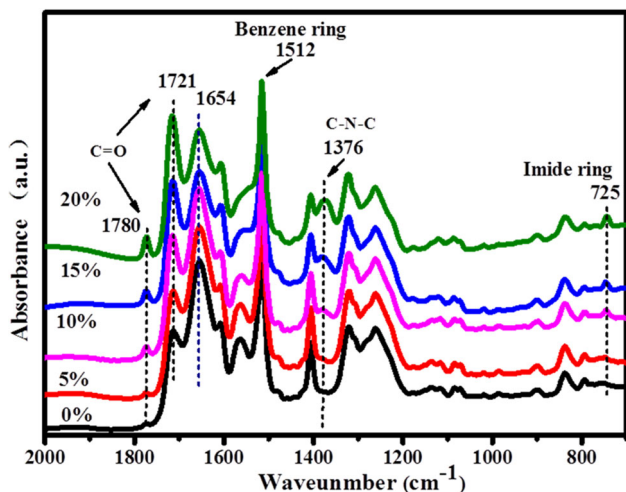


Figure 1 FTIR spectrums of the BPDA-PDA PAI fibers with different *pre*-imidization degrees.

1512 cm^{-1} can be used as an internal standard. The *pre*-imidization degree based on Eq (1) is calculated and summarized in Table 1. Apparently, the experimental data approach to the theoretical one and the *pre*-imidization degree show an upward trend with increasing chemical cyclizing agent. However, further increasing the cyclizing agent content will result in precipitation due to the poor solubility of the formed rigid-rod imide rings.

The fractured cross section (a_1 – e_1 , a_2 – e_2) and the surface (a_3 – e_3) morphologies of wet-spun nascent PAI fibers with different *pre*-imidization degrees are

depicted in Fig. 2. It is obvious that the un-*pre*-treated PAA fibers possess a noncircular cross section (Fig. 2 a_1 , a_2) and exhibit a typical skin–core structure with a cortical thickness of approximately $1.5\text{ }\mu\text{m}$, in which the loose core with many microvoids is surrounded by the thin dense layer. On the bright side, all partially *pre*-imidized nascent PAI fibers exhibit circular, more compact and homogeneous cross sections and inner structures, revealing that the partial *pre*-imidization treatment of the spinning solution can greatly modify the microstructure and the morphology of nascent fibers.

In the fiber-forming process, the phase separation process plays a dominant role in determining the final structure of wet-spun fibers. During the wet-spinning process, the solidification of fibers is realized by the dual diffusion of the solvent and the nonsolvent [25]. Namely, the removal of solvent from the coagulating filament and the solidification of the dissolved polymer occur simultaneously, and thus, the diffusion rate is a decisive factor in determining the internal morphology of the resulted filament. In general, a high rate of coagulation leads to a porous cross-sectional morphology, whereas a slow rate is beneficial for yielding a denser material [26]. In our case, for the un-*pre*-treated spinning dope, the solvent NMP shows an intense interaction with poly(amic acid) due to the existence of abundant polar amic acid groups, which seriously fetters the rapid diffusion of the solvent. As the spinning dope is extruded

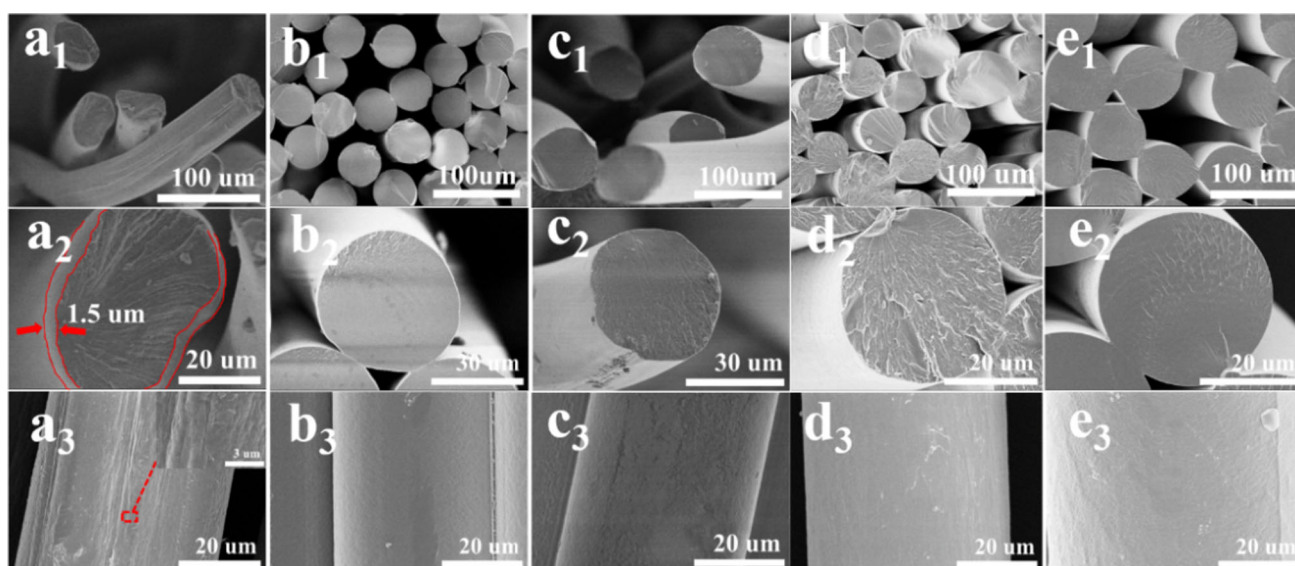


Figure 2 Fractured cross section and the surface morphologies of nascent PAI fibers with different *pre*-imidization degrees by wet spinning. Theoretical imidization degree: **a** 0%, **b** 5%, **c** 10%, **d** 15% and **e** 20%.

from the spinneret, the solidification boundary begins at the solution surface and moves inward with time until this reaches the center of the coagulated fiber. However, the initially formed compact “skin” and the relatively slow diffusion rate of the solvent simultaneously baffle the diffusion of the solvent out of the core of the filament, resulting in a typical “skin–core” and irregular cross-sectional morphology of the nascent PAA fiber. More seriously, the non-circular and “skin–core” nascent fiber could not bear a high drawing ratio during the sequent spinning and post-high-temperature drawing treatment due to the stress concentration and microporous defects, which would be detrimental to obtaining high-performance polyimide fibers [27]. As the chemical cyclization agent is added, partial amic acid groups transform into imide rings, leading to the decreased interactions between the polymer chains and the solvent as well as the coagulant due to the reduced polarity of the imide rings, which dramatically moderate the dual diffusion process of the solvent and the coagulant. Thus, the diffusion takes place in approximately equal volumes across the fiber surface, which results in a soft skin layer when the viscous spinning dope is extruded into the coagulation bath. Then, the transfiguration of skin layer would follow on the heels of the core shrinking, leading to a circular cross section and a uniform and dense internal structure. Given the morphology differences between untreated PAA and PAI fibers, it is believed that the partial pre-imidization treatment has a positive effect on adjusting the diffusion behavior of the solvent and the coagulant and is helpful to modify the microstructure of the nascent PAI fibers.

To evaluate the effects of pre-imidization on the thermodynamics of the fiber formation, the Flory–Huggins theory is used to construct the ternary phase diagram containing binodal and spinodal curves. In the ternary phase diagram, the boundary of the homogeneous region and the metastable region or the unstable zone is the binodal curve, showing the composition of the polymer solution when it begins to split [28]. Figure 3 shows the binodal curves of the water/NMP/PAI ternary system with different pre-imidization degrees based on the experimental and theoretical cloud points. Apparently, the binodal curves of this ternary system are close to the polymer–NMP axis. The approaching tendency goes up with the increase in PAI fractions, while the amount of nonsolvent water decreases. Moreover, when the

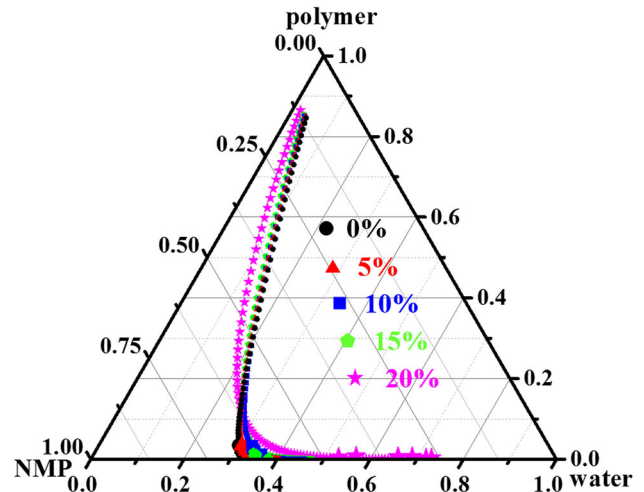


Figure 3 Cloud point curve with the experimental cloud point data and theoretical cloud point curve according to the LCP correlation for water/NMP/polymer ternary system with different pre-imidization degrees.

content of PAI is above 0.2 wt%, the binodal point curve approaches polymer–NMP axis closer with increasing pre-imidization degree, suggesting that the compatibility of the polymer and NMP becomes poor at high partial pre-imidization degrees and high concentrations of PAI, revealing that the PAI/NMP and PAI/H₂O interactions are retarded by the partial imidization treatment, which greatly affects the dual diffusion rate in the spinning process. Actually, the polymer content of the spinning dope reaches approximately 10 wt% that is in this concentration region. The results of the ternary phase diagram further demonstrate that the partial pre-imidization of the poly(amic acid) spinning dope is meaningful for improving its spinnability.

To further investigate the effect of pre-imidization on the fiber morphology, the diffusion rate of NMP into water is investigated. The diffusion rate of NMP in the spinning solution is investigated by the method reported in the previous work [16]. As shown in Fig. 4a, the specific growth rate of the solid layer forming on the surface of the spinning solution treated with water is measured, and the thickness of the solidified layer is proportional to the square root of time according to Eq (2). It has been illustrated that the initial boundary growth rate, Ξ , only depends on the rate of mass transfer and phase separation in the dual diffusion process. Obviously, the transfer rate of NMP out of the PAA-PI solution becomes lower as the pre-imidization degree increases according to the

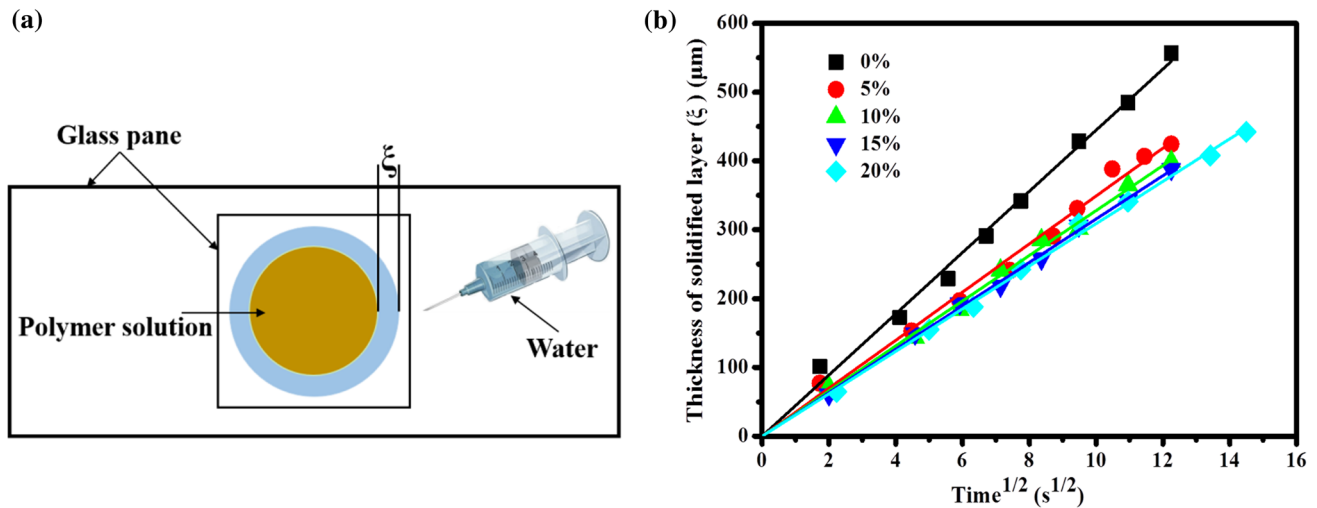


Figure 4 **a** Measurement of the coagulation power and **b** diffusion rate of NMP in PAA solution into water with different *pre*-imidization degrees.

gradually decreasing slope of the fitting curves, as shown in Fig. 4b. For instance, the ξ value for PAA-0% spinning solution is approximately 180 μm at $t^{1/2} = 4 \text{ s}^{1/2}$, while the corresponding value decreases to 124 μm for the PAA with a 20% pre-imidization degree, indicating that the solidification of the surface becomes slower for these *pre*-imidized spinning solutions, which is beneficial for forming a uniform and dense morphology.

Characterization of thermally treated PI fibers

The partial pre-imidization treatment can remarkably modify the dual diffusion behavior of the solvent and the nonsolvent in the PAI fiber spinning process, which can eliminate the formation of the skin-core structure in the nascent fibers. It is well known that the formed aggregation structure including the orientation degree and the crystalline structure also has a great effect on the properties of final fibers. Thus, it is worthwhile to investigate the influence of pre-imidization on the molecule stacking of the resulted fibers. The typical 2D WAXD patterns of the thermally imidized and drawn PI fibers with different pre-IDs are shown in Fig. 5. All of the imidized fibers exhibit similar obscure equatorial arcs, named “amorphous halos,” and faint diffused diffraction streaks exist along the meridian direction of WAXD patterns, indicating a relatively low order of polymer chains stacking in the imidized fibers. The formed similar WAXD diffraction patterns for these samples

illustrate that the pre-chemical imidization treatment of the poly(amic acid) spinning solutions has little influence on the molecule packing of the final polyimide chains in the resulted as-imidized PI fibers.

However, after the hot-drawing process, these diffused diffraction streaks along the meridian become more distinct, and obvious arcs appear in the quadrants and off-axis, indicating that a high degree of orientation and a well-defined crystalline structure come into being in the PI fibers. As the pre-imidization degree increases, the diffraction streaks along the equator break into a plurality of isolated shorter arcs, indicating the enhancement of the regular lateral stacking of polyimide chains. Meanwhile, the diffraction streak becomes shorter and more intense for the pre-imidized PI fibers, which further illustrates that the pre-imidization treatment can enhance the formation of crystalline structure in the drawn PI fibers. To the best of our knowledge, it can be explained that the formed rigid-rod and oriented polyimide chains in the spinning solution are inclined to align regularly due to the reduced interaction with the solvent and the mutual exclusion of polyimide chains. Under the effect of external loads and high temperatures, these aligned polymer chains easily form a highly ordered crystalline structure.

The one-dimensional slices of the equatorial and meridional profiles of drawn PI fibers derived from Fig. 5a2–e2 are shown in Fig. 6. It is obvious that well-defined crystalline structures successfully form in the drawn PI fibers, and the crystals are based on an orthorhombic unit cell (lattice parameters of

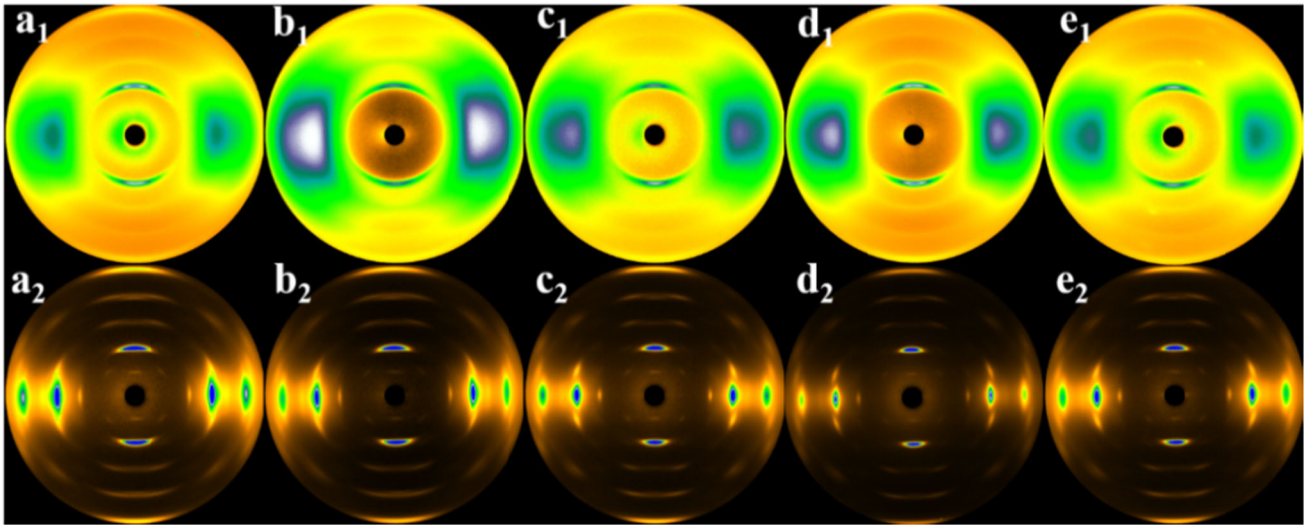


Figure 5 2D WAXD of the PI fibers with different pre-imidization degrees, (a1–e1): as-imidized fibers without the heat-drawing treatment; (a2–e2): drawn PI fibers with the same drawing

ratio of 1.5. Theoretical pre-imidization degrees: **a** 0%, **b** 5%, **c** 10%, **d** 15% and **e** 20%.

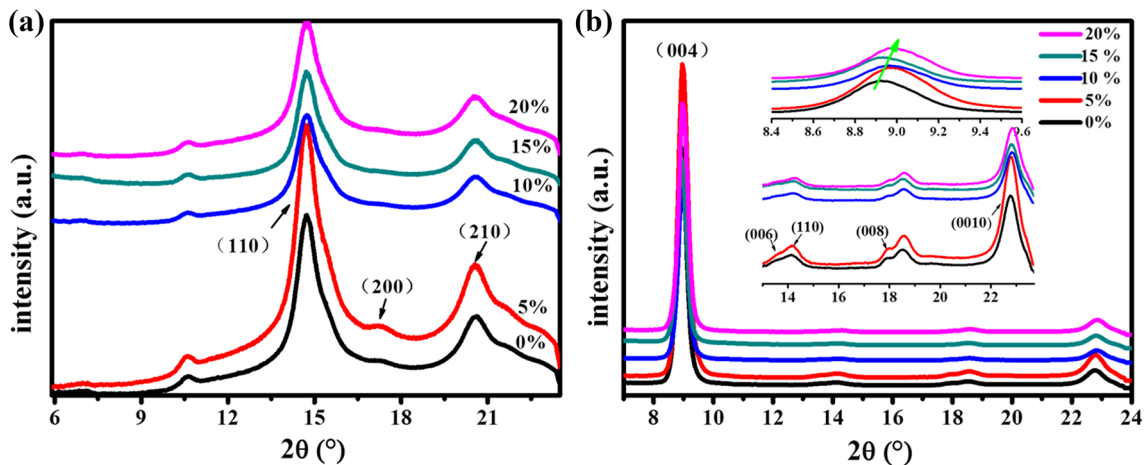


Figure 6 **a** 1D WAXD equatorial and **b** meridional profiles of the drawn PI fibers derived from Fig. 5(a2–e2).

$a = 8.620 \text{ \AA}$, $b = 6.270 \text{ \AA}$, $c = 31.986 \text{ \AA}$, consistent with Yoon and Ree’s results [29, 30]. The repeat unit length of the BPDA-PDA dimer projected along the fiber axis is estimated to be 32.0 \AA . As shown in Fig. 6a, four diffraction peaks at $2\theta = 10.5^\circ$, 14.7° ([110]), 17.2° ([200]) and 20.6° ([210]) with d -spacing values of 6.77 , 4.85 , 4.15 and 3.47 \AA , respectively, appear in the equatorial direction, implying regularly well-ordered molecular chains in the transversal direction of these fibers. Four distinct diffraction peaks representing the $[00l]$ planes are detected on the meridian in addition to the $[hkl]$ planes, as shown in Fig. 6b, which are at $2\theta = 8.9^\circ$ ([004]), 13.5° ([006]),

17.93° ([008]) and 22.7° ([0010]) with d -spacings of 7.91 , 5.27 , 3.98 and 3.15 \AA , respectively, revealing the formation of a typical lamellar structure in the resulted PI fibers. Meanwhile, the streak at $2\theta = 8.9^\circ$ shifts to a larger 2θ value as the pre-imidization degree increases, indicating a decreased d -spacing value.

To analyze the crystallinity and orientation degree of the drawn PI fibers, the radical 2θ scan and the azimuthal φ scan were carried out, as illustrated in Fig. 7a. The obtained crystallinity X_c and Hermans’ orientation parameter f_c are shown in Fig. 7b. It is evident that the crystallinity of PI fibers enhances

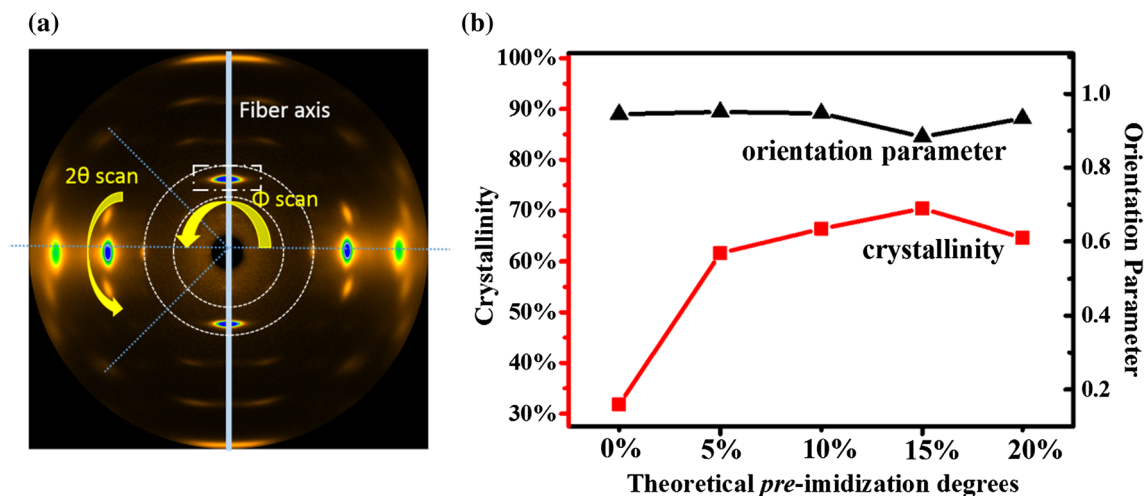


Figure 7 **a** Radical 2θ scan and azimuthal ϕ scan of WAXD patterns for the drawn PI fiber; **b** crystallinity and orientation degrees f_c of the PI fibers with the same drawing ratio of 1.5.

significantly with partial pre-chemical imidization degrees, which may be because the effect of the partial pre-imidization treatment allows polyimide chains to have a better rigid and pre-oriented structure to form a more ordered and regular crystalline structure in the post-heat-drawing process.

The mechanical properties of PI fibers obtained from different PAI fibers and their maximal drawing ratio are presented in Fig. 8, and we can find that the un-pre-treated PI fiber has the drawing ratio of 1.5 because the nascent fiber with the noncircular cross section and the “skin-core” structure cannot bear a high drawing ratio during heat-drawing [30], but the maximal drawing ratio of the PI fiber with 5% pre-ID increases to 2.3 due to the circular cross section alleviating the stress concentration. It is believed that the partial pre-imidization process can improve the

processability of the BPDA/PDA PI fiber. Meanwhile, the maximal drawing ratio shows a decrease trend with increasing pre-IDs. Similarly, the mechanical properties of the PI fibers are greatly improved by the partial pre-imidization treatment. The PI fibers with 5% pre-IDs reach the highest tensile strength and initial modulus of 1.71 GPa and 95 GPa, respectively, which increase by 70% and 48%, respectively, compared to the untreated PI fibers. For the other pretreated samples, the mechanical properties decrease with more dehydration agents.

Figure 9 shows the DMA curves of the prepared PI fibers with different pre-imidization degrees. An obvious relaxation process (α relaxation) can be identified between 290 and 320 °C, and the peak temperature corresponds to the glass transition temperature (T_g) of the fibers. The T_g values for the PI

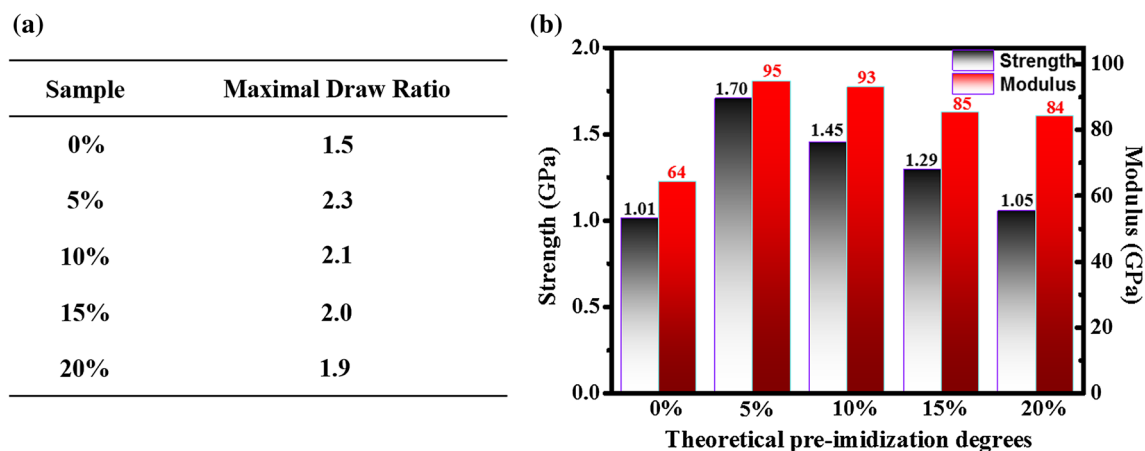


Figure 8 **a** Maximal drawing ratios and **b** mechanical properties of the PI fibers with different pre-imidization degrees.

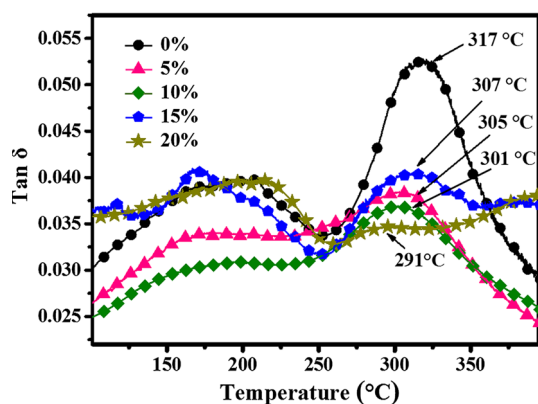


Figure 9 DMA results of the PI fibers with different pre-oxidation degrees.

fibers with 0, 5, 10, 15 and 20% pre-IDs are 317, 307, 305, 301 and 291 °C, respectively. Meanwhile, the intensities of the α relaxation decrease, which demonstrates a higher crystallinity with the increase in pre-oxidation degrees. The appeared secondary transition peaks between 150 and 200 °C are probably due to the rotation of molecular chains. The distinct α relaxation for the untreated BPDA-PDA PI fiber gradually becomes inconspicuous as evidenced by the decreased intensity of the relaxation peak, which demonstrates higher crystallinities for the pre-oxidized samples [31], as shown in Fig. 7. Another possible reason for the unclear T_g of the pre-oxidized PI fibers is the formation of strong hydrogen bonding interchain interactions in the amorphous regions, which may act as the crosslinks that reduce the mobility of molecule chains [21].

The thermal stabilities of the PI fibers have been evaluated by TGA measurement in a nitrogen atmosphere. Figure 10 illustrates the TGA traces and the

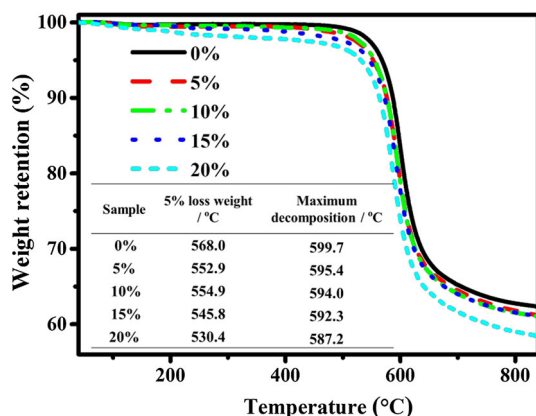


Figure 10 TGA thermograms of the PI fibers with different pre-oxidation degrees.

thermal analysis data for the fibers. The 5 wt% ($T_{5\%}$) weight loss temperature and the maximum decomposition temperature (T_{max}) can be observed in the range of 530–568 and 587–600 °C, respectively, indicating that the PI fibers exhibit excellent thermal stabilities. In addition, the $T_{5\%}$ and T_{max} of the PI fibers show a slight decrease with the increase in pre-oxidation degree, which was induced by the decomposition of residual dehydration reagents in fibers [18].

Conclusion

In summary, we demonstrated a facile method to improve the spinnability of the BPDA-PDA spinning dope through a partial pre-oxidation process by just adding some specific amounts of dehydrating agents in the spinning solution. The PAA molecule chains show a more intense interaction with the solvent NMP in the un-pre-treated PAA solution than in the partial pre-oxidized PAI solutions due to the existence of abundant polar amic acid groups, which seriously fetters the rapid diffusion of the solvent in the spinning process. The partial pre-oxidation treatment has a positive effect on adjusting the diffusion behavior of the solvent and the coagulant, which is helpful to modify the microstructure of the nascent PAI fibers. The WAXD patterns of the final PI fibers reveal the formation of partial rigid-rod and oriented PI chains in the spinning solution, which is favorable for crystallization during the heat-drawing process. Correspondingly, the pre-oxidized PAI fibers have a better mechanical property than the untreated ones, and the final PI fiber with the 5% pre-ID exhibits the best tensile strength (1.71 GPa) and modulus (95 GPa), which are increased by 70% and 48% compared to the untreated one, respectively. Meanwhile, the prepared Upilex-s-type PI fibers exhibit excellent thermal stabilities. In conclusion, this work provided a simple and facile approach to preparing high-performance PI fibers through the partial pre-oxidation process.

Acknowledgements

This study was funded by the Fundamental Research Funds for the Central Universities (2232017A-01), Shanghai Science and Technology Commission

“Yangfan” Program (17YF1400500), Shanghai Science and Technology Innovation Action Plan (16JC1403600) and the Opening Foundation of State Key Laboratory for Modification of Chemical Fibers and Polymer Materials (LK1604).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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