

Preparation and Properties of High-performance Polyimide Copolymer Fibers Derived from 5-Amino-2-(2-hydroxy-5-aminobenzene)-benzoxazole

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Electronic Supplementary Information

Abstract A series of polyamic acid copolymers (co-PAA) with *para*-hydroxyl groups was synthesized using two diamine monomers, namely *p*-phenylenediamine (*p*-PDA) and 5-amino-2-(2-hydroxy-5-aminobenzene)-benzoxazole (*m*-pHBOA), of different molar ratios through copolymerization with 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) in *N,N*-dimethylacetamide (DMAc). The co-PAA solutions were used to fabricate fibers by dry-jet wet spinning, and thermal imidization was conducted to obtain polyimide copolymer (co-PI) fibers. The effects of the *m*-pHBOA moiety on molecular packing and physical properties of the prepared fibers were investigated. Fourier transform infrared (FTIR) spectroscopic results confirmed that intra/intermolecular hydrogen bonds originated from the hydroxyl group and the nitrogen atom of the benzoxazole group and/or the hydroxyl group and the oxygen atom of the carbonyl group of cyclic imide. As-prepared PI fibers displayed homogenous and smooth surface and uniform diameter. The glass transition temperatures (T_g s) of PI fibers were within 311–337 °C. The polyimide fibers showed 5% weight loss temperature ($T_5\%$) at above 510 °C in air. Two-dimensional wide-angle X-ray diffraction (WXR) patterns indicated that the homo-PI and co-PI fibers presented regularly arranged polymer chains along the fiber axial direction. The ordered molecular packing along the transversal direction was destroyed by introducing the *m*-pHBOA moiety. Moreover, the crystallinity and orientation factors increased with increasing draw ratio. Small-angle X-ray scattering (SAXS) results showed that it is beneficial to reduce defects in the fibers by increasing the draw ratio. The resultant PI fibers exhibited excellent mechanical properties with fracture strength and initial modulus of 2.48 and 89.73 GPa, respectively, when the molar ratio of *p*-PDA/*m*-pHBOA was 5/5 and the draw ratio was 3.0.

Keywords Polyimide fiber; Phenylenebenzoxazole; Hydroxyl group; Hydrogen bonding

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INTRODUCTION

Aromatic polyimide (PI) fibers are high-performance organic fibers that exhibit excellent thermal stability, chemical resistance, electrical insulation, and radiation-resistant properties.^[1–4] With their outstanding performance, aromatic PI fibers have been widely applied to high-temperature dusting, special protection, aerospace industries, and composite material. However, the mechanical properties of commercial PI fibers, such as, P84[®], Suplon[®], and Yilun[®] are inferior to those of rigid polymer fibers, such as Kevlar,^[5,6] PBO,^[7] and M5,^[8,9] which limit the application of PI fibers in high-technology field. Therefore, fabricating PI

fibers with high strength and modulus has become an urgent and challenging task.

Two methods have been well developed to fabricate PI fibers. First, the one-step method is that PI fibers are directly spun from PI solutions. These solutions are prepared through one-step polymerization of dianhydride and diamine in high-boiling point organic solvents, such as *p*-chlorophenol and *m*-cresol. Cheng and co-workers^[10] reported that a series of PI solutions was prepared by one-step polymerization of 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) and 2,2'-dimethy-4,4'-diaminobiphenyl (DMB) in *p*-chlorophenol, and the fibers were prepared by dry-jet wet spinning. The highly drawn fibers with a draw ratio of seven showed excellent mechanical properties with fracture strength of 3.3 GPa and initial modulus of 130 GPa. PI fibers prepared by one-step method typically possess high fracture strength and initial modulus.^[10–12] However, highly toxic solvents might be involved in one-step fabrication of limited PI fibers. Hence,

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this method is unsuitable for large-scale production of industry. Second, the two-step method is that PAA fibers are first spun from PAA solutions and then converted into PI fibers through chemical or thermal imidization. The typical solvents employed in this method are *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMAc), which have low toxicity. This method overcomes the problem of inherent solubility of PIs but produces numerous defects in the fibers due to the dual-diffusion and thermal-imidization processes, which result in poor mechanical properties of the ultimate PI fibers.^[13,14] Dorogy and Clair^[14] reported that the fracture strength and initial modulus of PI fibers derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (4,4'-ODA) by two-step method were 0.194 and 3.6 GPa, respectively.

Numerous studies have been focused on the fabrication of PI fibers with excellent mechanical properties. Some researchers attempted to optimize spinning parameters, such as spinning solution,^[13,15] spinning technology,^[14,16] and conditions of thermal imidization and drawing.^[17–22] Park and Farris^[13] reported that slight gelling was obtained by adding acetic anhydride and pyridine or only acetic anhydride to the PAA solution, and such gelling was conducive to the high drawing of the PAA fibers during spinning. The ultimate fracture strength and initial modulus of the PAA fibers were approximately 0.268 and 4.1 GPa, respectively. Yang *et al.*^[17] found that the mechanical properties of BPDA/*p*-PDA (*p*-phenylenediamine) fibers depended highly on the treatment temperature rather than the treatment time. The fibers treated at 400 °C for 60 s without tension under nitrogen atmosphere exhibited fracture strength and initial modulus of 1.4 and 70.0 GPa, respectively. Scholars have also focused on modifying the chemical structure of PI fibers. The most common approach is to copolymerize at least two kinds of diamines and/or dianhydrides into the polymer backbone.^[23–27] In particular, some rigid aromatic heterocyclic diamines, such as 2,5-bis(4-aminophenyl)-pyrimidine (2,5-PMR), 2,6-bis(4-aminophenyl)benzo[1,2-d:5,4-d']bisoxazole (PBOA), 2-(4-aminophenyl)-5-aminobenzoxazole (BOA), and 2-(4,4-aminophenyl)-5-aminobenzimidazole (BIA), have been introduced into the PI backbones and proven effective in improving the mechanical properties of fibers. Sukhanova and co-workers^[23] reported that high-performance co-PI fibers were prepared by copolymerization of 4,4'-oxybis(phthalic anhydride) with two diamines, namely, *p*-PDA and 2,5-PMR; the co-PI fibers fabricated exhibited optimal mechanical properties with fracture strength and initial modulus of 3.0 and 130 GPa, respectively, when the 2,5-PMR/*p*-PDA molar ratio was 5/5. Zhang *et al.*^[26] reported that as PBOA was incorporated into the main chains of BPDA and 4,4'-ODA, the fracture strength and initial modulus of the co-PI fiber reached 2.51 and 70.2 GPa, respectively, when the diamine ratio of PBOA/4,4'-ODA was 5/5. The common reason is that copolymerization is beneficial to improving the micro-block structure and providing a specific morphology for co-PI fibers.

Hydrogen bonding (H-bonding) plays an important role in

the mechanical properties of rigid polymer fibers. However, common PI structures cannot form intra/intermolecular H-bonding. In the past decade, rigid units bearing functional groups have been extensively investigated, and such units can form H-bonding to improve intermolecular interaction. For example, Wu *et al.*^[28] prepared a new type of polyimide fiber by introducing 2-(4-aminophenyl)-6-amino-4(3*H*)-quinazolinone (AAQ) into the rigid polyimide backbones of BPDA and *p*-PDA. When the AAQ/*p*-PDA molar ratio was 5/5, the fracture strength and the initial modulus of the co-PI fiber reached 2.8 and 115 GPa, respectively. This finding could be attributed to the strong H-bonding of —NH— in quinazolinone units to the oxygen atom of carbonyl group in the imide rings. In recent years, several diamine monomers containing *ortho*-hydroxyl groups have been synthesized and adopted to prepare PI. However, the rearrangement of corresponding macromolecule structures occurred during heat treatment (350–450 °C), resulting in the reduction of intermolecular interactions.^[29–31] Our previous studies^[32] indicated that PIs with *meta*-hydroxyl groups could form intra/intermolecular H-bonding among the rigid polymer chains and remarkably enhance the mechanical properties of the fibers. To investigate the effect of PIs with *para*-hydroxyl groups on the intermolecular H-bonding and the mechanical properties of fibers, we design and synthesize a diamine monomer of 5-amino-2-(2-hydroxy-5-aminobenzene)-benzoxazole (*m*-pHBOA) in this study. Then a series of co-PI fibers is fabricated through a two-step method based on the copolymerization of BPDA, *p*-PDA, and *m*-pHBOA. Homo-BPDA/*p*-PDA and homo-BPDA/*m*-pHBOA PI fibers are also prepared for comparison with co-PI fibers. The effects of *m*-pHBOA moiety and draw ratios on the microstructure and the thermal and mechanical properties of co-PI fibers are systematically investigated.

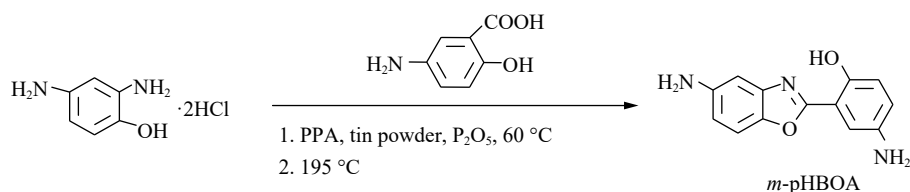
EXPERIMENTAL

Materials

2,4-Diaminophenol dihydrochloride (> 98%) and 5-aminosalicylic acid (> 99%) were obtained from Jiaxing Isenchem Co. Ltd. (Zhejiang, China) and used as received. Phosphorus (V) oxide (P₂O₅, ≥ 98%), polyphosphoric acid (PPA, including 80% of P₂O₅), tin powder (> 99%), and *N,N*-dimethylacetamide (DMAc) were purchased from Xilong Chemical Co. Ltd. (Guangdong, China) and used directly. BPDA and *p*-PDA were purchased from Changzhou Sunlight Medical Raw Material Co. Ltd. (Jiangsu, China) and purified by sublimation before use.

Synthesis of 5-Amino-2-(2-hydroxy-5-aminobenzene)-benzoxazole (*m*-pHBOA)

According to the previous literature,^[33] *m*-pHBOA was synthesized by condensation of 5-aminosalicylic acid and 2,4-diaminophenol dihydrochloride in PPA solution as shown in Scheme 1. PPA (2.0 kg), 2,4-diaminophenol dihydrochloride (197.06 g, 1.0 mol), 5-aminosalicylic acid (153.14 g, 1.0 mol), and tin powder (2.37 g, 0.02 mol) were added to a three-necked flask under a nitrogen atmosphere. The mixture was heated to 60 °C with stirring and the



Scheme 1 Synthetic route to 5-amino-2-(2-hydroxy-5-aminobenzene)-benzoxazole (*m*-pHBOA)

doughy mass was homogenized for 3 h. Then, P_2O_5 (70.97 g, 0.5 mol) was added, and the mixture was heated to 195 °C and maintained for 6 h. The solution was slowly cooled to 100 °C and poured into an ice water mixture under vigorous stirring. The precipitate was filtered and soaked overnight in a saturated sodium bicarbonate aqueous solution. The precipitate was collected, washed with water thoroughly, and dried at 80 °C in a vacuum oven. The crude product was purified by sublimation and light yellow crystals with a yield of 76.4% were obtained. The melting point was measured to be 221–222 °C. ^1H -NMR (400 MHz, $DMSO-d_6$, δ , ppm): 10.58 (s, 1H, OH), 7.45–7.47 (d, J = 8.4 Hz, 1H, Ar–H), 7.21 (s, 1H, Ar–H), 6.89 (s, 1H, Ar–H), 6.83–6.85 (d, J = 8.8 Hz, 1H, Ar–H), 6.79–6.81 (d, J = 8.4 Hz, 1H, Ar–H), 6.70–6.72 (d, J = 8.8 Hz, 1H, Ar–H), 5.19 (s, 2H, NH_2), 4.88 (s, 2H, NH_2) (Fig. S1a in electronic supplementary information, ESI). ^{13}C -NMR (100 MHz, $DMSO-d_6$, δ , ppm): 162.5, 149.1, 147.0, 141.5, 140.9, 140.4, 120.8, 117.3, 113.0, 110.5, 110.1, 109.9, 101.7 (Fig. S1b in ESI). FTIR (powder, ν , cm^{-1}): 3418, 3344, 3216 (N–H stretching), 1626 (benzoxazole C=N– stretching), 1501, 1489 (benzoxazole typical band), 1272 (benzoxazole Ar–O–C asymmetric stretching), 1243 (Ar–OH stretching), 918 (oxazole typical band) (Fig. S2 in ESI). Theoretical elemental analysis, calculated for $C_{13}H_{11}N_3O_2$: C, 64.72%, H, 4.60%, N, 17.42%, found: C, 64.73%, H, 4.58%, N, 17.34%.

Preparation of PAA Solution

A series of PAA solutions was successfully synthesized by copolymerization of different molar ratios of *m*-pHBOA/*p*-PDA with an equimolar amount of BPDA in DMAc to 10 wt% solid concentration and *m*-pHBOA/*p*-PDA molar ratios of 0/10, 1/9, 3/7, 5/5, 7/3, and 10/0. For example, the molar ratio of *m*-pHBOA/*p*-PDA was 5/5. In brief, 96.50 g (0.40 mol) of *m*-pHBOA, and 43.26 g (0.40 mol) of *p*-PDA were dissolved in 3590 mL of DMAc in a three-necked flask under a nitrogen atmosphere. Afterwards, 235.28 g (0.80 mol) of BPDA was gradually added into the solution. The reaction was carried out at 25 °C for 24 h. Polymeri-

zation was similarly conducted using the other ratios of *m*-pHBOA/*p*-PDA. The corresponding inherent viscosities of PAA solutions are listed in Table 1.

Table 1 Inherent viscosity of the PAA solutions of corresponding PI fibers

Sample	<i>m</i> -pHBOA/ <i>p</i> -PDA (molar ratio)	η_{inh} (dL/g)
Homo-PI-0	0/10	2.78
Co-PI-1	1/9	2.91
Co-PI-2	3/7	3.07
Co-PI-3	5/5	3.13
Co-PI-4	7/3	3.24
Homo-PI-0'	10/0	3.43

Fabrication of PAA Fibers and PI Fibers

PAA fibers were produced through dry-jet wet spinning, as shown in Fig. 1. In detail, the above-mentioned PAA solutions were filtered and degassed at room temperature. Subsequently, these solutions were extruded through a spinneret (100 orifices, 0.12 mm in diameter) *via* a short air gap into a H_2O /DMAc coagulation bath with a draft ratio of 2.3. The PAA fibers were washed by deionized water to remove the residual solvent, and the obtained fibers were dried at 50 °C for 12 h.

As-produced PAA fibers were converted to PI fibers by successive heating from room temperature to 350 °C at a heating rate of 7 °C/min under vacuum, and maintained at 350 °C for 30 min. The imidized fibers were drawn at different ratios to obtain the final PI fibers. Scheme 2 shows the synthetic process and chemical structure of the co-PI fibers.

Characterization

Melting point was determined through a Thomas Hoover capillary melting point apparatus. ^1H - and ^{13}C -nuclear magnetic resonance (NMR) spectra were recorded using a Mercury Plus 400 MHz spectrometer with tetramethylsilane as internal standard. Elemental analysis was carried out using a Perkin-Elmer model 2400 CHN analyzer. Inherent viscosity (η_{inh}) of the PAA solutions was measured using an

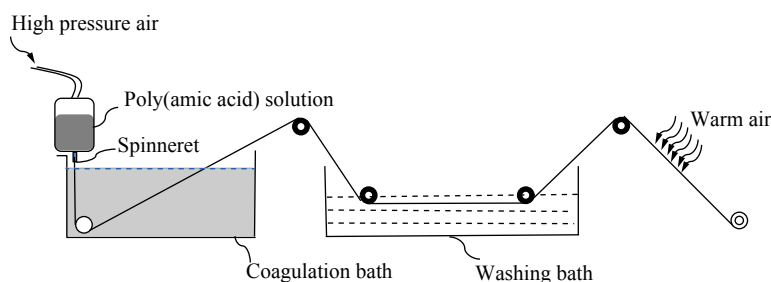
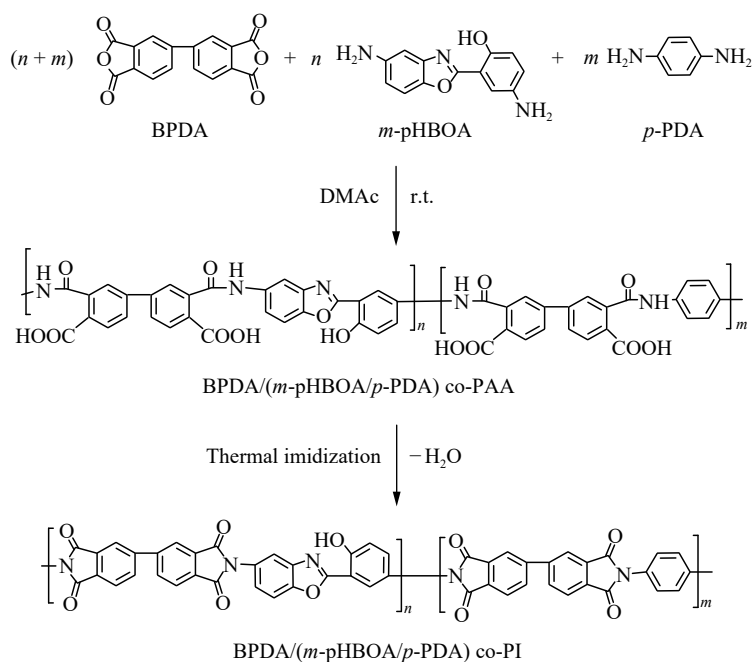


Fig. 1 The dry-jet wet spinning process of PAA fibers



Scheme 2 Two-step procedure for the preparation of homo-PI and co-PI fibers ($n/m = 0/10, 1/9, 3/7, 5/5, 7/3$ and $10/0$)

Ubbelohde viscometer at a concentration of 0.5 g/dL in DMAc at 30 °C. Fourier transform infrared (FTIR) spectra were recorded with a VERTEX 70 spectrometer within 4000–400 cm^{-1} . Curve-fitting deconvolution of the FTIR spectra was performed using the Origin 9.0 Software with Gaussian function to separate individual absorption contributions in the spectral region of 1750–1650 cm^{-1} . The surface morphology of PI fibers was obtained by an XL-30 ESEM FEG scanning electron microscope operated at 10.0 kV. Dynamic mechanical thermal analysis (DMTA) was performed on a Rheometric scientific DMTA-V at a heating rate of 10 °C/min and a load frequency of 1 Hz in the fiber tension geometry within 50–400 °C. The glass transition temperature (T_g) was regarded as the peak temperature in the $\tan\delta$ curve.

Thermo-gravimetric analysis (TGA) was carried out with a TA-Q50 instrument in dynamic nitrogen and air environments at a heating rate of 10 °C/min. Two-dimensional wide-angle X-ray diffraction (2D WAXD) measurement was performed on a Nano-inXider system (Xenocs France) equipped with a semiconductor detector (Pilatus 100K, Dectris, Swiss) attached to a multilayer focused Cu $K\alpha$ X-ray source (GeniX^{3D} Cu ULD, Xenocs SA, France). The X-ray radiation wavelength was 0.154 nm, the distance between the sample and detector was 75.25 mm, the diffraction angle (2θ) was within 5°–32°, and the exposure time for each diffraction frame was 240 s. Two-dimensional small-angle X-ray scattering (2D SAXS) experiments were performed using a GeniX^{3D} Cu ULD (Xenocs SA, France) with Cu $K\alpha$ radiation (wavelength, $\lambda = 0.154$ nm). The generator was operated at 40 kV and 650 μA . 2D SAXS patterns were obtained using a Pilatus 100 K detector (Dectris, Swiss, 487 pixels $\times$ 198 pixels, pixel size = 172 μm). The sample-to-detector distance was set as 6558 mm. The effective scattering vector q

($q = (4\pi\sin\theta)/\lambda$, where 2θ is the scattering angle, and λ is the X-ray wavelength) at this distance ranged from 0.018 nm^{-1} to 0.42 nm^{-1} . The exposure time for each scattering frame was 300 s. 2D diffraction and scattering patterns were analyzed using FIT 2D software. Crystallinity (X_c) was calculated using Eq. (1):

$$X_c = \frac{A_c}{A_c + A_a} \times 100\% \quad (1)$$

where A_c and A_a are the total peak area of the crystalline and amorphous phases, respectively. Crystallization and amorphous contribution were separated by the curve-fitting deconvolution of the one-dimensional integrated WAXD intensity profiles performed using Origin 9.0 software. Orientation factor (f_c) was determined according to Hermans' orientation function:^[34]

$$f_c \times 100\% = [3 \langle \cos^2 \phi_c \rangle - 1] / 2 \quad (2)$$

where $\langle \cos^2 \phi_c \rangle$ is the orientation parameter of the molecular chain axis (c) along the fiber axis, and it was determined according to the Wilchinsky mode^[35] and the crystal symmetry of the prepared PI fibers with characteristic reflections in the equatorial direction. For the reflection plane (hkl), the orientation parameter $\langle \cos^2 \phi_c \rangle$ can be calculated using Eq. (3):^[34]

$$\cos^2 \phi_c = \frac{\int_0^{\pi/2} I(\phi_c) \cos^2 \phi_c \sin \phi_c d\phi_c}{\int_0^{\pi/2} I(\phi_c) \sin \phi_c d\phi_c} \quad (3)$$

where ϕ_c represents the angle between the fiber axis and the c axis of the crystal unit cell, and $I(\phi_c)$ is the intensity along the reflection plane (hkl). Ruland formula was chosen to

calculate the average length (L) of microvoids parallel to the fiber axis:^[36]

$$B_{\text{obs}} = \frac{2\pi}{Lq} + B_{\phi} \quad (4)$$

where B_{obs} and B_{ϕ} denote the integral breadth and misorientation of microvoids. The Guinier function was used to calculate the radius (R) of microvoids in the cross-section, as shown in Eq. (5):^[37]

$$I(q) = I(0) \exp \frac{-q^2 R^2}{5} \quad (5)$$

where $I(0)$ was the incident light intensity, and $I(q)$ is the scattering intensity in reciprocal. The average radius ($\bar{R}$) of microvoids was calculated through the Fankuchen successive tangent method using Eq. (6):^[38]

$$\bar{R} = \sum R_i \omega_i \quad (i = 1, 2, 3 \dots) \quad (6)$$

where R_i and ω_i are the radius of different sizes and the corresponding volume percentage of microvoids, respectively. Mechanical properties were measured with Textechno FAVIMAT instrument by using a gauge length of 20 mm and an extension rate of 5 mm/min. Initial modulus was obtained as the slope of the engineering stress-strain curve between 0.2% and 0.4 % elongation. At least 10 filaments were tested for each type of fibers.

RESULTS AND DISCUSSION

Synthesis of PAA Solutions

A series of PAA solutions were obtained after the reaction of BPDA with *m*-pHBOA/*p*-PDA of different molar ratios. As shown in Table 1, the inherent viscosities of PAA solutions are 2.78, 2.91, 3.07, 3.13, 3.24, and 3.43 dL/g, corresponding to the molar ratios of *m*-pHBOA/*p*-PDA of 0/10, 1/9, 3/7, 5/5, 7/3, and 10/0, respectively. The polymerization of dianhydride and diamine is the nucleophilic substitution reaction of amino group. Therefore, η_{inh} increased with the increasing *m*-pHBOA content possibly because of the strong electron-donating ability of the amino groups in the *m*-pHBOA monomer.

Structure Characterization of PI Fibers

The chemical structure of the PI fibers with different molar ratios of *m*-pHBOA/*p*-PDA was identified by ART-IR spectra. As shown in Fig. 2, four characteristic absorption bands at about 1772, 1701, 733, and 1353 cm^{-1} are attributed to C=O asymmetrical stretching, symmetrical stretching, and bending, and the C—N stretching of the cyclic imide, respectively. The characteristic absorption band near 1655 cm^{-1} for C=O asymmetrical stretching of the amide group disappears, which indicates the high imidization degree of PI fibers. Two apparent absorption bands at 1547 and 1251 cm^{-1} correspond to benzoxazole C=N— asymmetric stretching and benzoxazole Ar—O—C asymmetric stretching, respectively, and the intensities of these bands increase with the increasing *m*-pHBOA content. Although the characteristic absorption band at around 3400 cm^{-1} for —OH stretching cannot be detected due to the formation of intramolecular or/and intermolecular H-bond-

ing (Fig. 3), the apparent absorption band at about 1189 cm^{-1} for Ar—OH stretching can be observed. These results indicate that *m*-pHBOA moiety was successfully incorporated into the backbones of co-PI fibers.

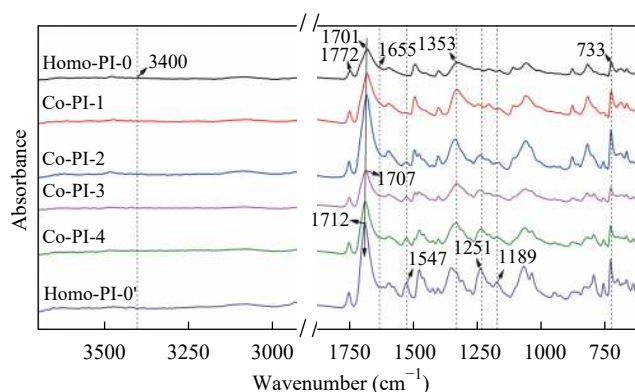


Fig. 2 FTIR spectra of the prepared PI fibers with different molar ratios of diamine monomer

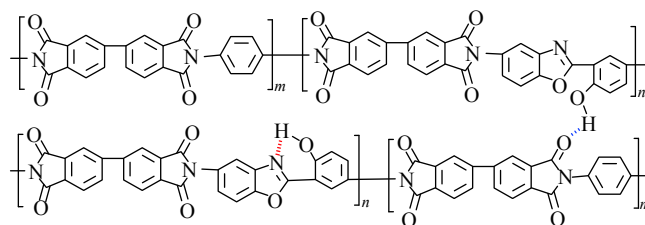


Fig. 3 Inter/intra molecular H-bonding in co-PI structure

Hydrogen Bonding Interaction in PI Fibers

FTIR spectroscopy is frequently used to detect the existence of H-bonding interactions because of its high sensitivity to the frequency shift of the proton donor and acceptor at H-bonding formation.^[39,40] As shown in Fig. 2, the band corresponding to C=O symmetrical stretching of the imide groups gradually moves towards higher frequency from 1701 cm^{-1} to 1712 cm^{-1} with the increasing content of *m*-pHBOA. It is due to the —OH group not only forming intermolecular H-bonding with the oxygen atom of C=O but also forming intramolecular H-bonding with the nitrogen atom of benzoxazole (Fig. 3). A conjugated system was formed by the intramolecular H-bonding, which greatly enhanced the ring tension of the imide rings and led to blue shift of the absorption band C=O symmetrical stretching of imide groups.

Fig. 4 shows the deconvoluted results of FTIR spectra within 1750–1650 cm^{-1} . Five bands are separately identified for co-PI and homo-PI-0' fibers. Band I (near 1687 cm^{-1}) and band V (near 1733 cm^{-1}) correspond to the C=O symmetric and asymmetric stretching of the intermolecular noncyclic imide mode, respectively.^[41,42] Band II (near 1702 cm^{-1}) and band IV (near 1721 cm^{-1}) are assigned to the effects of intermolecular and intramolecular H-bonding on C=O symmetric stretching of the cyclic imide mode,^[43] respectively. Band III (near 1711 cm^{-1}) is related to the “free” C=O symmetric stretching, which includes the effects of other interactions, such as van der Waals forces, except that of inter/intramolecular H-bonding on the C=O stretching.^[44]

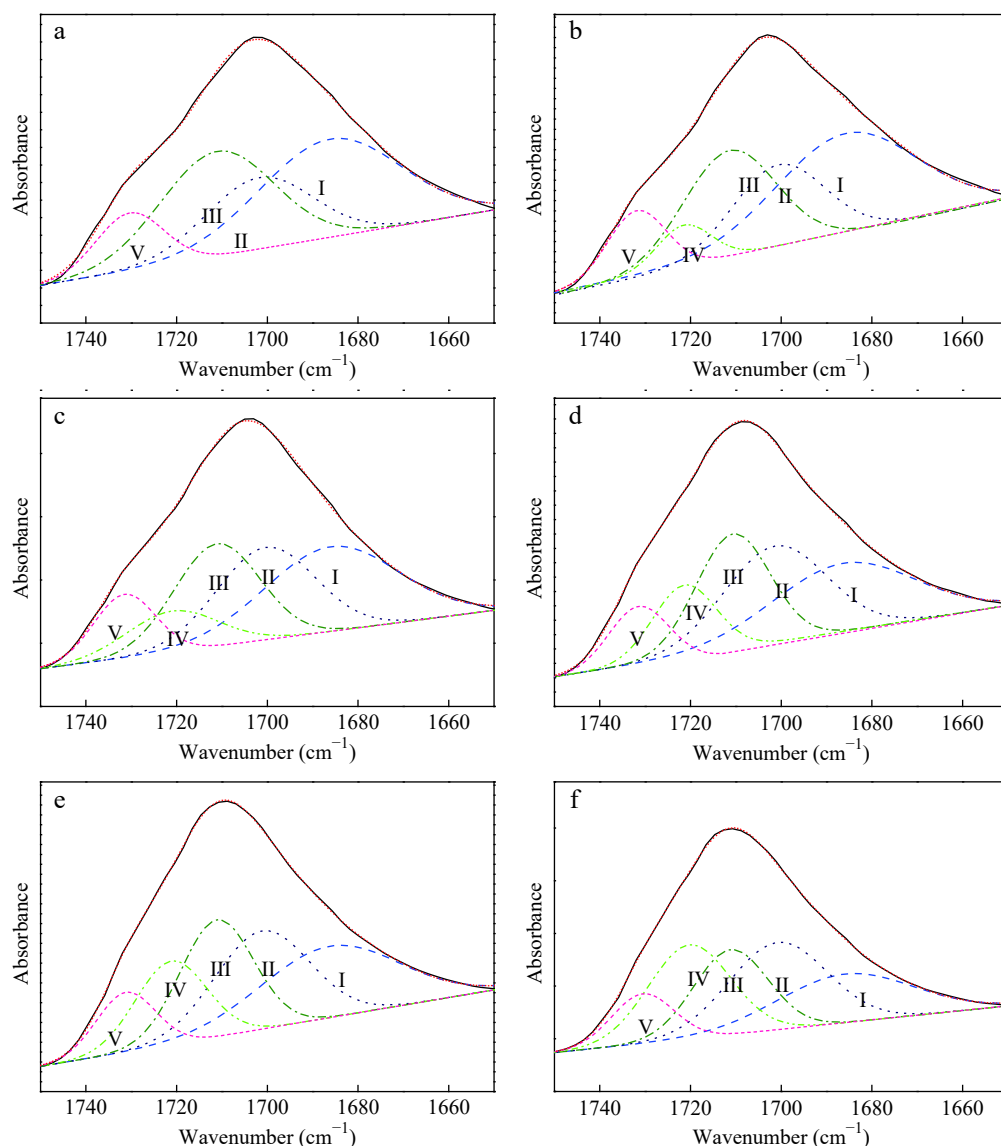


Fig. 4 Curve-fitting FTIR spectra in the range of 1750–1650 cm^{-1} for the prepared PI fibers: (a) homo-PI-0, (b) co-PI-1, (c) co-PI-2, (d) co-PI-3, (e) co-PI-4, and (f) homo-PI-0'

In the homo-PI-0 fiber, intermolecular H-bonding is formed between the $-\text{NH}-$ of the intermolecular noncyclic imide mode and the oxygen atom of the $\text{C}=\text{O}$ group, and intramolecular H-bonding is not formed due to the absence of the $-\text{OH}$ groups. The fitted results are summarized in Table 2. The percentage of inter/intramolecular H-bonding imides (H_{inter} and H_{intra}) can be calculated according to Eqs.

(7) and (8), respectively.

$$H_{\text{inter}} = \frac{A_{\text{II}}}{A_{\text{II}} + A_{\text{III}} + A_{\text{IV}}} \quad (7)$$

$$H_{\text{intra}} = \frac{A_{\text{IV}}}{A_{\text{II}} + A_{\text{III}} + A_{\text{IV}}} \quad (8)$$

Table 2 Curve-fitting results of FTIR spectra in the range of 1750–1650 cm^{-1} for the prepared PI fibers

Sample	Intermolecular imide				Cyclic imide						H_{inter} (%)	H_{intra} (%)
	Band I		Band V		Band II		Band III		Band IV			
	Freq. (cm ⁻¹)	Area (%)	Freq. (cm ⁻¹)	Area (%)	Freq. (cm ⁻¹)	Area (%)	Freq. (cm ⁻¹)	Area (%)	Freq. (cm ⁻¹)	Area (%)		
Homo-PI-0	1686	36.1	1730	10.5	1703	20.5	1711	32.9	—	—	38.4	—
Co-PI-1	1687	35.4	1733	10.2	1702	21.4	1711	27.2	1721	5.8	39.3	10.7
Co-PI-2	1687	30.4	1733	10.0	1702	24.5	1711	25.0	1721	10.1	41.1	16.9
Co-PI-3	1687	27.5	1733	9.7	1701	26.9	1711	23.6	1721	12.3	42.8	19.6
Co-PI-4	1687	25.8	1733	9.5	1701	26.3	1711	22.5	1721	15.9	40.7	24.6
Homo-PI-0'	1688	21.3	1734	9.0	1700	27.8	1711	20.0	1721	21.9	39.9	31.4

where A_{II} , A_{III} , and A_{IV} are the peak areas of bands II, III, and IV, respectively. The computing results are also listed in Table 2.

As shown in Table 2, the peaks corresponding to band II gradually move from 1703 cm^{-1} to 1700 cm^{-1} with the increasing *m*-pHBOA content. H_{inter} increases from 38.4% to 42.8% when the *m*-pHBOA content increases from 0% to 50%, which indicates the formation of strong intermolecular H-bonding. Nevertheless, a decrease in H_{inter} occurs with further increase in the *m*-pHBOA content, which may be attributed to the reduction of the intermolecular noncyclic imide mode and the increase in the —OH groups that forms additional intramolecular H-bonding. H_{intra} gradually increases from 10.7% to 31.4% with the increasing *m*-pHBOA content, which demonstrates the formation of the additional conjugated system. In addition, the percentages of the C=O symmetric (band I) and asymmetric stretching (band V) of the intermolecular noncyclic imide mode gradually decrease with the increasing *m*-pHBOA content, which suggests a decrease in side reactions during thermal cycloimidization with increasing *m*-pHBOA moiety.

Surface Morphology

The surface morphologies of the PI fibers are investigated by scanning electron microscopy (SEM) (Fig. 5). All the PI fibers show homogenous and smooth surface, uniform

morphology, and average diameter of about $15\text{ }\mu\text{m}$. These results are due to the balanced dual diffusion between the solvent and the coagulant, and the appropriate concentration of the coagulation bath for all fibers.

Glass Transition Temperature and Thermal Stability

The glass transition temperatures (T_g s) of the PI fibers are studied through dynamic mechanical analysis (DMA) (Fig. 6a). The detailed peak temperatures in $\tan\delta$ curves are listed in Table 3. The values of T_g s are 325, 317, 312, 311, 321, and 337 °C, which correspond to the *m*-pHBOA/*p*-PDA molar ratios of 0/10, 1/9, 3/7, 5/5, 7/3, and 10/0, respectively. The T_g s of the PI fibers first decrease from 325 °C to 311 °C with the increasing *m*-pHBOA content (from 0% to 50%) and then increase from 311 °C to 337 °C. The relationship between T_g s and the composition is non-linear, and this phenomenon is similar to that for poly(AN-*co*-St), as reported by Fan *et al.*^[45] The addition of *m*-pHBOA is beneficial to increasing the intermolecular interactions, but the regularity of the molecular chains decreases to facilitate the movement of molecular segments. Further increasing the content of *m*-pHBOA increases the regularity of the molecular chains and forms stronger inter/intramolecular H-bonding interaction, which can hinder the segmental motion of the polymer chains to some extent. Moreover, a thermal residual stress peak appears when the content of *m*-pHBOA

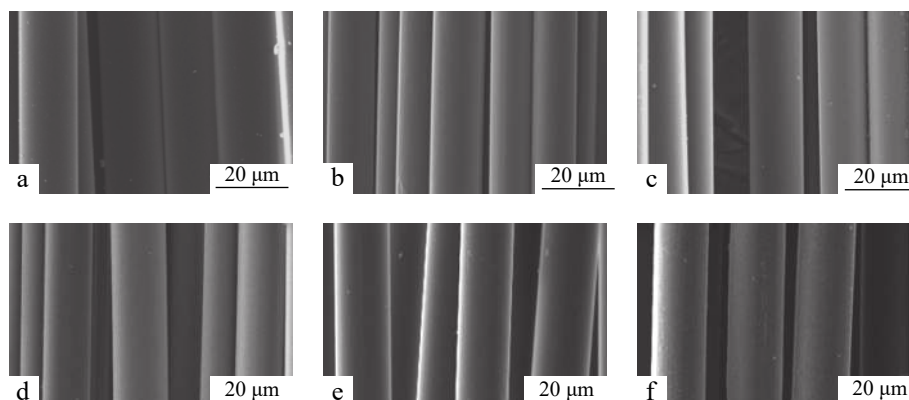


Fig. 5 Surface morphologies of the prepared PI fibers with different molar ratios of diamine monomer: (a) homo-PI-0, (b) co-PI-1, (c) co-PI-2, (d) co-PI-3, (e) co-PI-4, and (f) homo-PI-0'

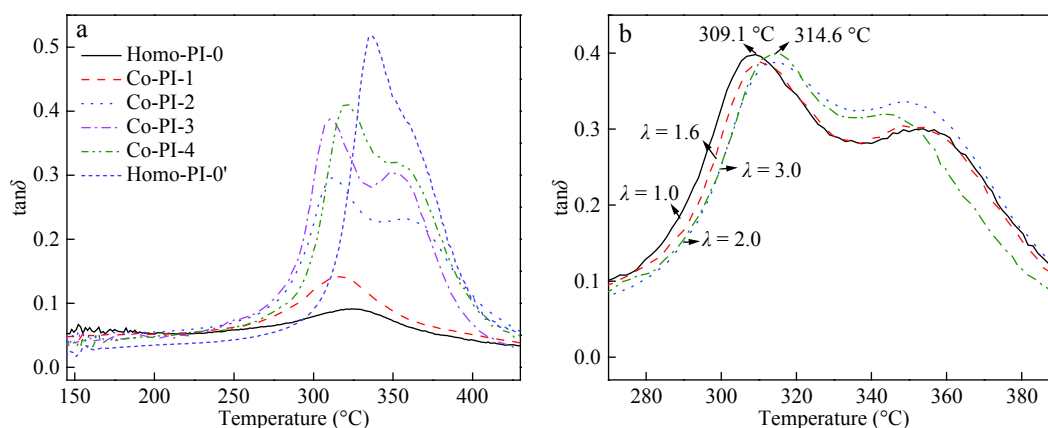


Fig. 6 DMA curves of (a) the prepared fibers with different molar ratios of diamine monomer and (b) the co-PI-3 fibers with different draw ratios

Table 3 Thermal properties of the prepared PI fibers with different molar ratios of diamine monomer

Sample	T_g ^a (°C)	Temperatures at certain weight loss (°C)				Char yield ^b (%)
		In air		In N ₂		
		$T_{5\%}$	$T_{10\%}$	$T_{5\%}$	$T_{10\%}$	
Homo-PI-0	325	542	567	593	607	63.3
Co-PI-1	317	543	562	567	590	60.4
Co-PI-2	312	531	549	558	580	62.5
Co-PI-3	311	520	542	547	574	59.9
Co-PI-4	321	510	529	544	568	60.7
Homo-PI-0'	337	521	540	562	587	59.1

^a Peak temperature of $\tan\delta$ measured by DMA at a heating rate of 10 °C/min; ^b Percentage of carbon residue at 850 °C in nitrogen

is higher than 30%. The possible reason is that the asymmetry of *m*-pHBOA moiety leads to serious entanglement of macromolecular chains. When PI fibers pass through a drafting furnace with large temperature difference between the inside and outside, the generated thermal stress cannot be fully released. T_g s of co-PI-3 fibers with different draw ratios are also investigated (Fig. 6b), which increase from 309.1 °C to 314.6 °C with the increasing draw ratio from 1 to 3. The increased T_g at higher draw ratio is attributed to the increase in crystallinity (discussed in the molecular packing sections), thereby hindering the segmental motion of the polymer chains.

The thermal and thermo-oxidative stability of the fibers is characterized by TGA, as shown in Fig. 7. The temperature at 5% weight loss ($T_{5\%}$) and 10% weight loss ($T_{10\%}$) under nitrogen and air atmospheres and the percentage of residues at 850 °C under nitrogen atmosphere are summarized in Table 3. The $T_{5\%}$ values of copolymer fibers decrease with

the increasing *m*-pHBOA content from 567 °C to 544 °C under nitrogen atmosphere and from 543 °C to 510 °C in air. The $T_{10\%}$ values also decrease from 590 °C to 568 °C under nitrogen atmosphere and from 562 °C to 529 °C under air atmosphere, respectively. Further, the char yields at 850 °C in nitrogen atmosphere are within 59.9 wt%–62.5 wt%. These results indicated that the copolymer fibers maintained their excellent thermal and thermo-oxidative stabilities.

Molecular Packing in PI Fibers

The crystal parameters of the PI fibers with different molar ratios are analyzed according to 2D WAXD patterns as shown in Fig. 8. Several clear diffraction streaks can be observed along the meridian direction, which reveal the regularly arranged polymer chains along the fiber axial direction. In the equator direction, the 2D WAXD patterns of homo-PI-0 and co-PI-1 fibers in Figs. 8(a) and 8(b) show a few clear diffraction streaks, which demonstrate ordered molecular packing along the transversal direction of the fibers. Noticeable changes in the patterns can be observed in Figs. 8(c)–8(f) after further increasing the content of *m*-pHBOA. The equatorial diffraction streaks become more diffuse gradually, demonstrating the reduced order of packing along the transversal direction of the fibers.

1D WAXD patterns along the meridian and equator direc-

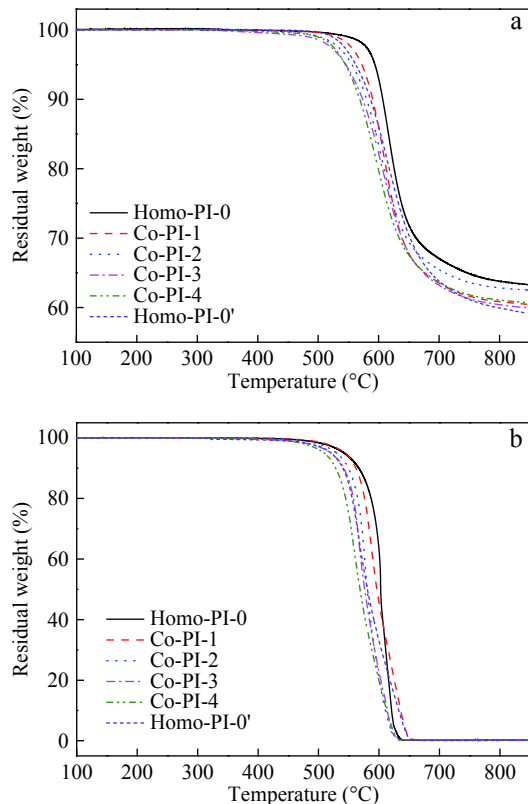


Fig. 7 TGA of the prepared fibers with different molar ratios of diamine monomer, in (a) N₂ and (b) air

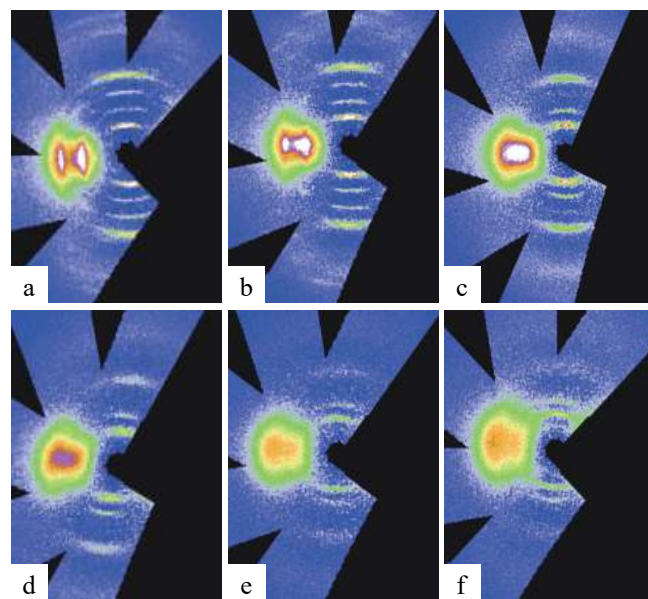


Fig. 8 2D WAXD patterns of the fibers prepared at different molar ratios of diamine monomer: (a) homo-PI-0, (b) co-PI-1, (c) co-PI-2, (d) co-PI-3, (e) co-PI-4, and (f) homo-PI-0'

tions are obtained (Figs. 9a and 9b) by integrating their 2D WAXD patterns to investigate the crystalline structure in PI fibers with different molar ratios. In the meridian direction (Fig. 9a), several diffraction peaks are observed for each fiber, and they reveal a regular arrangement of the polymer chains along the fiber axial direction. The diffraction peak positions of two homo-PI fibers are completely different, which reveals the difference in the crystal structures of these two polymer fibers. The diffraction peaks with relatively strong intensity for each fiber are observed at $2\theta = 11.2^\circ$, 11.3° , 11.5° , 12.4° , 12.8° , and 13.4° , which correspond to homo-PI-0, co-PI-1, co-PI-2, co-PI-3, co-PI-4, and homo-PI-0' fibers, respectively. The incorporation of *m*-pHBOA makes the diffraction peaks move to a high diffraction angle, indicating a decrease in *d*-spacing which is due to the asymmetric structure of *m*-pHBOA moiety and the formation of strong inter/intra molecular H-bonding. Moreover, a few peaks disappear in the co-PI fibers compared with the homo-PI-0 fiber, suggesting a decrease in the ordered structure along the fiber axis. On the equator direction (Fig. 9b), three diffraction peaks are observed at $2\theta = 13.1^\circ$, 18.2° , and 25.5° for the homo-PI-0 fiber. These diffraction peaks broaden or disappear gradually with the increasing *m*-pHBOA content, indicating a decrease in the lateral packing order from the random distribution of BPDA/*p*-PDA and BPDA/*m*-pHBOA units in the polymer chains.

Fig. 9(c) shows the one-dimensional integrated WAXD intensity profiles. Curve-fitting deconvolution is performed using Origin 9.0 software to separate the crystalline and amorphous contribution. According to the integrated pro-

files of the prepared PI fibers, several main diffraction peaks and two amorphous peaks are used to fit the experimental curves as illustrated in Figs. S3(a)–S3(f) (in ESI). Crystallinity (X_c) can be calculated according to Eq. (1), and the details are listed in Table 4. The crystallinities of homo-PI-0, co-PI-1, co-PI-2, co-PI-3, co-PI-4, and homo-PI-0' fibers are 45.8%, 29.9%, 10.1%, 6.0%, 4.5%, and 5.4%, respectively. Obviously, the crystallinity of the PI fibers decreases gradually with the increasing *m*-pHBOA content. This result indicated that the copolymerization reaction broke the ordered chain alignment to some extent.

In addition, the orientation factor along the fiber axis is also investigated by WAXD. Fig. 9(d) shows the azimuthal intensity distribution at about $2\theta = 25^\circ$ for the fibers prepared with different molar ratios of diamine monomers. Orientation factor (f_c) could be calculated by Eqs. (2) and (3), and the details are listed in Table 4. The orientation factors are 0.832, 0.871, 0.796, 0.767, 0.748, and 0.723, which correspond to homo-PI-0, co-PI-1, co-PI-2, co-PI-3, co-PI-4, and

Table 4 Crystallinity and orientation factors of the prepared PI fibers with different molar ratios of diamine monomer

Sample	WAXD	
	Crystallinity (%)	Orientation factor (f_c)
Homo-PI-0	45.8	0.832
Co-PI-1	29.9	0.871
Co-PI-2	10.1	0.796
Co-PI-3	6.0	0.767
Co-PI-4	4.5	0.748
Homo-PI-0'	5.4	0.723

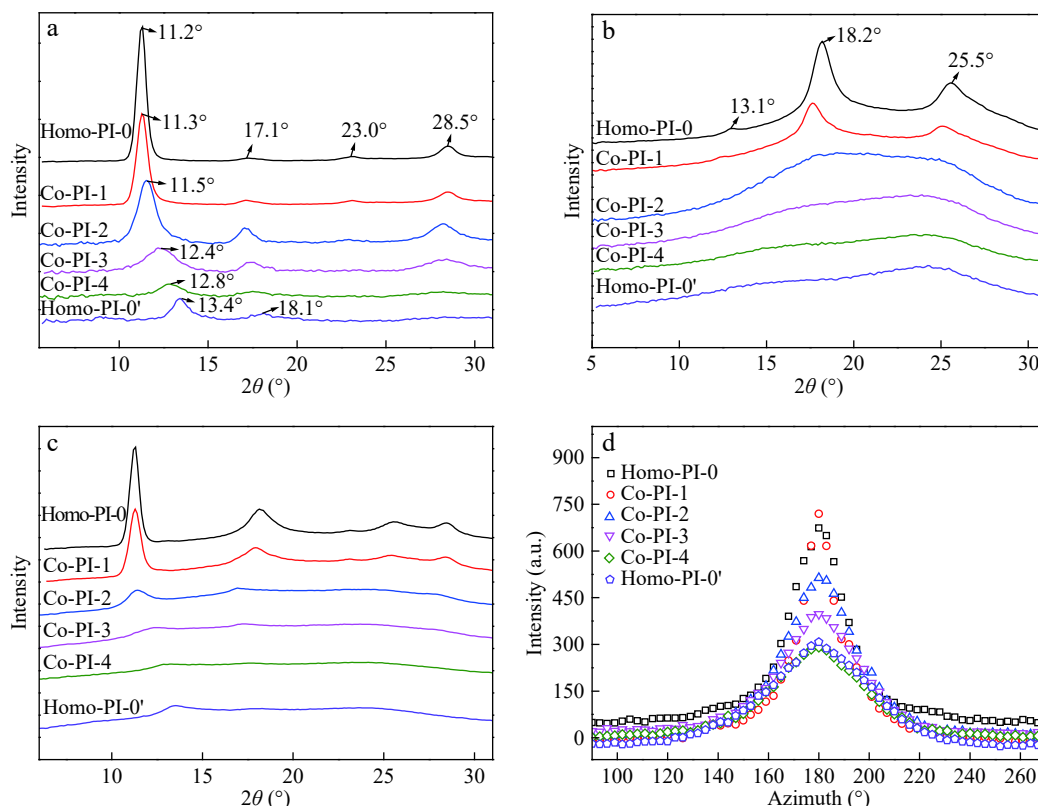


Fig. 9 1D WAXD patterns of the prepared fibers with different molar ratios of diamine monomer: (a) meridian direction, (b) equator direction, (c) integrated intensity, and (d) azimuthal intensity distribution at around $2\theta = 25^\circ$

and homo-PI-0' fibers, respectively. The orientation factor decreased with the increasing *m*-pHBOA content because of the asymmetric structure of the *m*-pHBOA moiety.

The co-PI-3 fibers prepared at different draw ratios were

studied by 2D WAXD, as shown in Fig. 10. The diffraction streaks become clear gradually, indicating that increasing the draw ratio causes higher crystal orientation in the axial direction. Fig. 11 illustrates the one-dimensional integrated WAXD

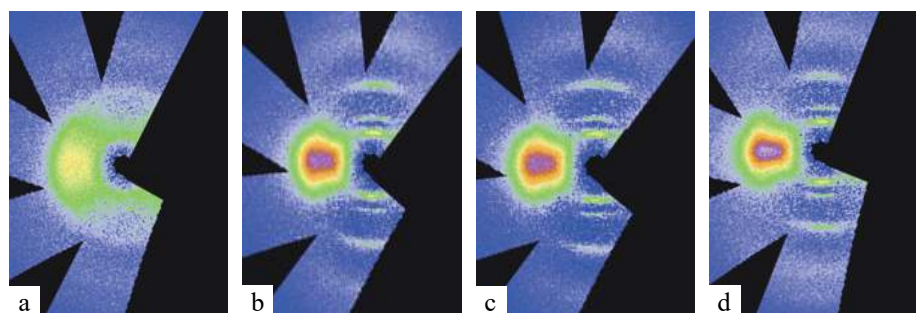


Fig. 10 2D WAXD patterns of the co-PI-3 fibers with different draw ratios: (a) $\lambda = 1.0$, (b) $\lambda = 1.6$, (c) $\lambda = 2.0$, and (d) $\lambda = 3.0$

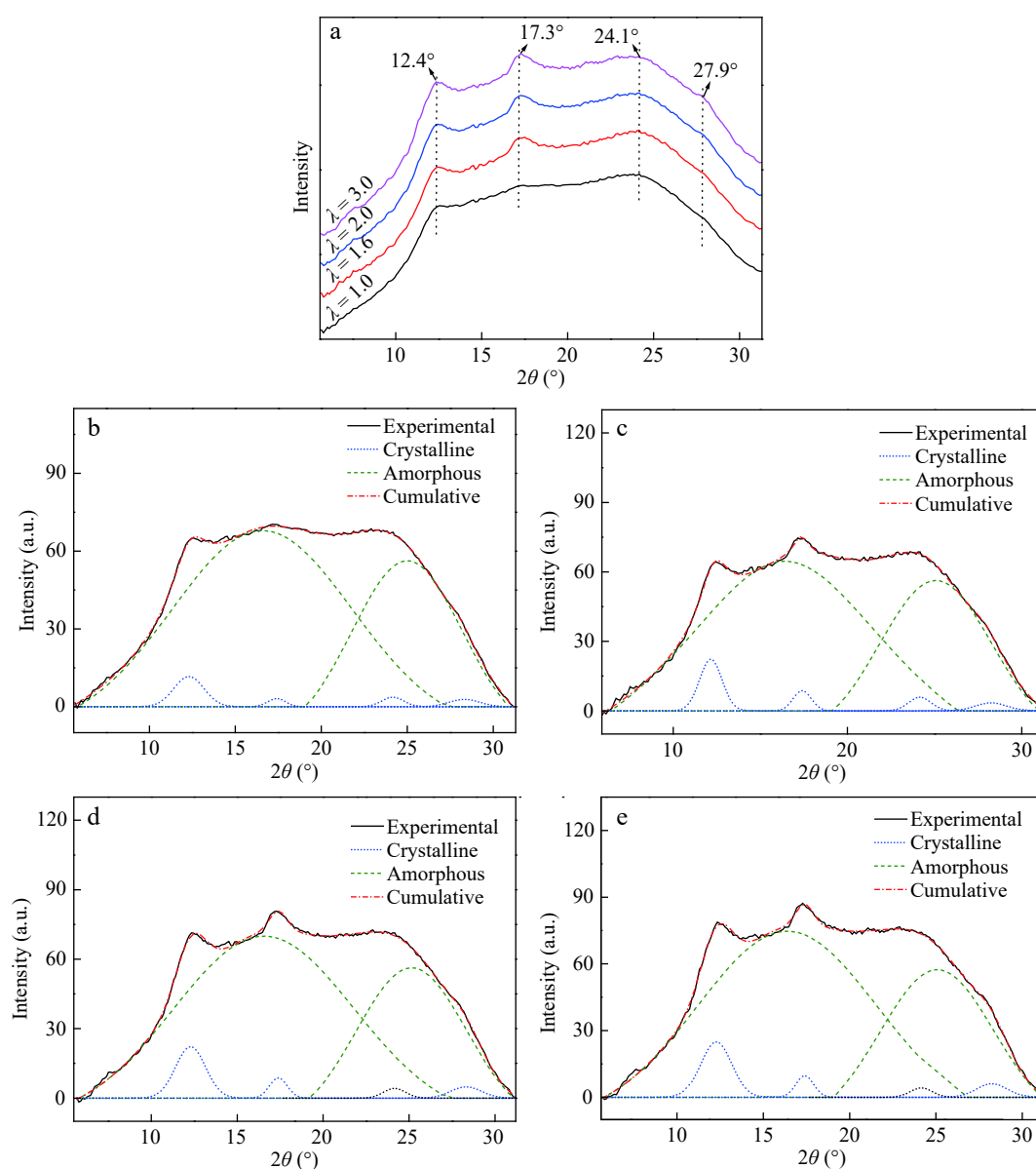


Fig. 11 (a) 1D integrated WAXD patterns for the co-PI-3 fibers with different draw ratios and their curve-fitting deconvolution: (b) $\lambda = 1.0$, (c) $\lambda = 1.6$, (d) $\lambda = 2.0$, and (e) $\lambda = 3.0$

intensity profiles of the co-PI-3 fibers with different draw ratios and their curve-fitting deconvolution. Crystallinity (X_c) and orientation factor are also calculated according to Eq. (1), and the details are listed in Table 5. The crystallinity increases from 3.4% to 6.8%. The orientation factor increases gradually from 0.576 to 0.767, 0.775, and 0.791, corresponding to draw ratios of 1.0, 1.6, 2.0, and 3.0, respectively. These results indicated that the hot-drawing process facilitated crystallization and crystal orientation, thereby contributing to the final mechanical property.

Micro-morphological Evolution with Draw Ratio

Microvoids in the PI fibers prepared by two-step method are formed during the dual-diffusion and thermal-imidization processes.^[23,46] The length, radius, and orientation of the microvoids would change during the hot-drawing process. Micro-morphological evolution can be detected by SAXS technique. Fig. 12 shows the SAXS patterns of the co-PI-3 fibers with different draw ratios. Apparently, all the scattering patterns show a sharp and elongated streak along the equatorial direction, which could be attributed to the presence of the long and narrow microvoids that are preferably aligned parallel to the fiber axis direction. Moreover, the elongated shapes become sharper with the increasing draw ratio. These results illustrate that the micro-morphology of the co-PI-3 fibers has changed.

The average length and misorientation of microvoids parallel to the fiber axis are calculated based on the Ruland formula in Eq. (4). Fig. 13 shows the Ruland plot of the co-PI-3 fibers with different draw ratios, and the corresponding results are listed in Table 5. As the draw ratio of the co-PI-3 fibers increases from 1.0 to 1.6, 2.0, and 3.0, the average lengths of the microvoids change from 411 nm to 363, 358,

and 344 nm, and the misorientations from 5.93° to 2.39°, 0.75°, and 0.30°, respectively. The average length and misorientation of microvoids decrease with the draw ratio, indicating the breakage of microvoids and the increase in their orientation in the fibers. The Guinier function in Eq. (5) can be applied to calculate the radius of microvoids in the cross-section. The average radius of microvoids is calculated through the Fankuchen successive tangent method according to Eq. (6). Fig. 14 shows the Guinier plot of the co-PI-3 fibers with different draw ratios along the equator direction and the calculated results are listed in Table 5. The microvoids in the fibers present multi-order cross-section characteristics because of the coagulation conditions. In addition, the average radius of the microvoids decreases from 14.65 nm to 12.08 nm with the increasing draw ratio. These results indicated that higher draw ratio was beneficial to reducing defects in the fibers.

Mechanical Properties

Mechanical property is a significant parameter that should be considered for engineering applications of polymeric fibers. Fig. 15 illustrates the variations of mechanical properties with the increase of *m*-pHBOA content, and the details are listed in Table 6. The homo-PI-0 and homo-PI-0' fibers possess fracture strength of 1.15 and 1.32 GPa, and initial modulus of 82.05 and 21.63 GPa, respectively. The fracture strengths of co-PI-1 to co-PI-4 are 1.40, 1.87, 2.06, and 1.66 GPa, and their initial moduli are 86.43, 88.92, 74.77, and 42.58 GPa, respectively. Elongation at break gradually increases from 1.52% to 10.23% with the increasing *m*-pHBOA content. The highest fracture strength and initial modulus are observed in co-PI-3 and co-PI-2, respectively. The original order structure of the BPDA/*p*-PDA system is

Table 5 Crystallinity, orientation factor and microvoid parameters of co-PI-3 fibers with different draw ratios

	WAXD		SAXS								
	Crystallinity (%)	Orientation factor (f_c)	L (nm)	B_ϕ (°)	R_1 (nm)	R_2 (nm)	R_3 (nm)	ω_1 (%)	ω_2 (%)	ω_3 (%)	$\bar{R}$ (nm)
$\lambda = 1.0$	3.4	0.576	411	5.92	5.69	12.28	22.75	24.3	30.7	45.0	14.65
$\lambda = 1.6$	6.0	0.767	363	2.39	5.62	11.14	18.92	27.2	28.5	44.3	13.09
$\lambda = 2.0$	6.3	0.775	358	0.75	5.48	10.55	18.98	28.6	28.2	43.2	12.74
$\lambda = 3.0$	6.8	0.791	344	0.30	5.48	11.01	18.32	31.4	30.2	38.4	12.08

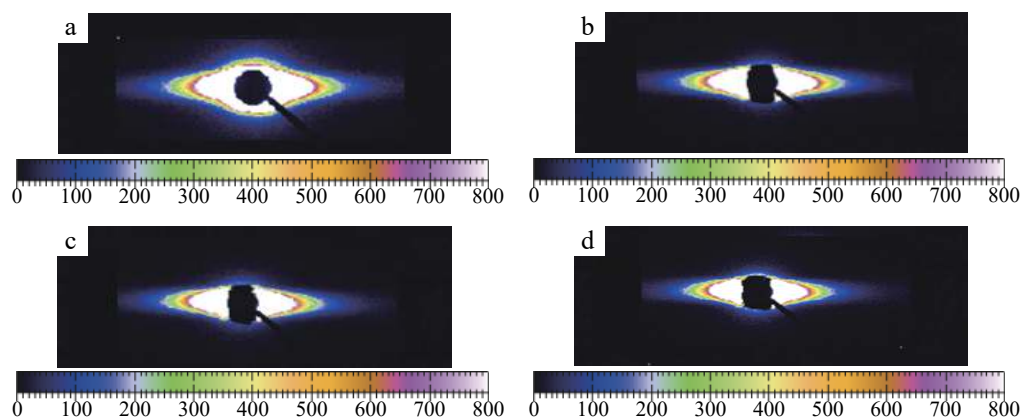


Fig. 12 2D SAXS patterns of the co-PI-3 fibers with different draw ratios: (a) $\lambda = 1.0$, (b) $\lambda = 1.6$, (c) $\lambda = 2.0$, and (d) $\lambda = 3.0$

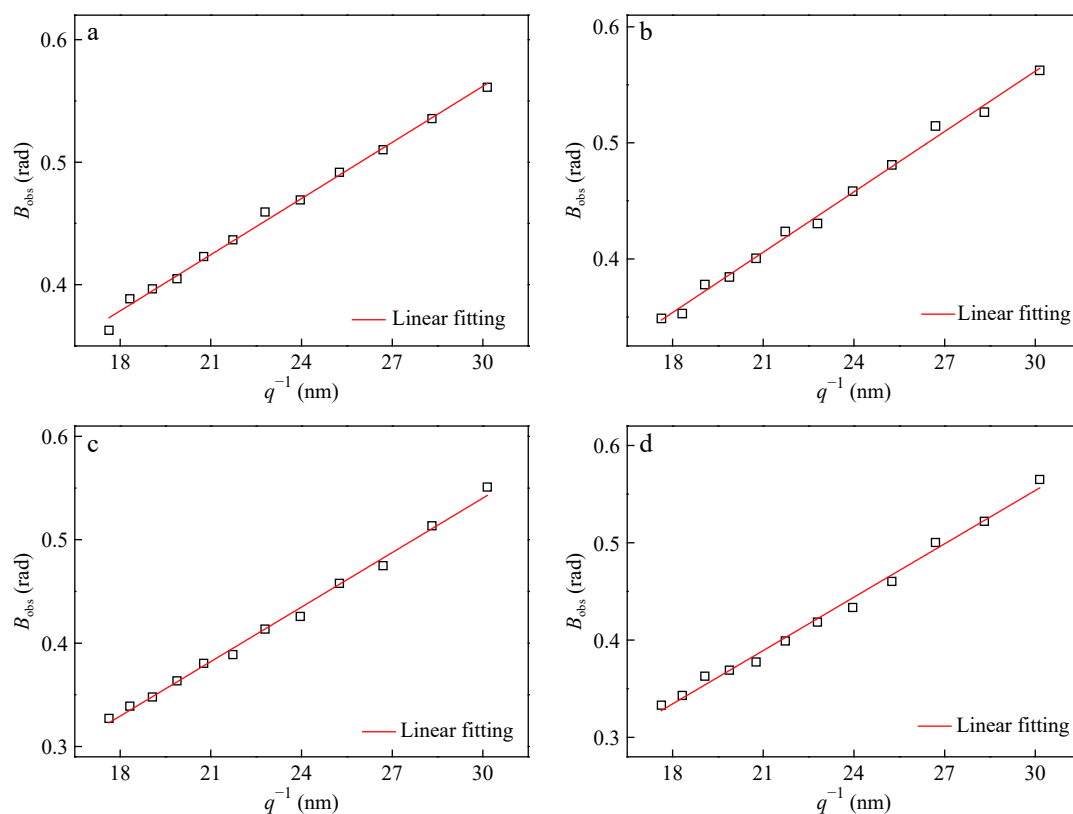


Fig. 13 Ruland plot of the co-PI-3 fiber with different draw ratios: (a) $\lambda = 1.0$, (b) $\lambda = 1.6$, (c) $\lambda = 2.0$, and (d) $\lambda = 3.0$

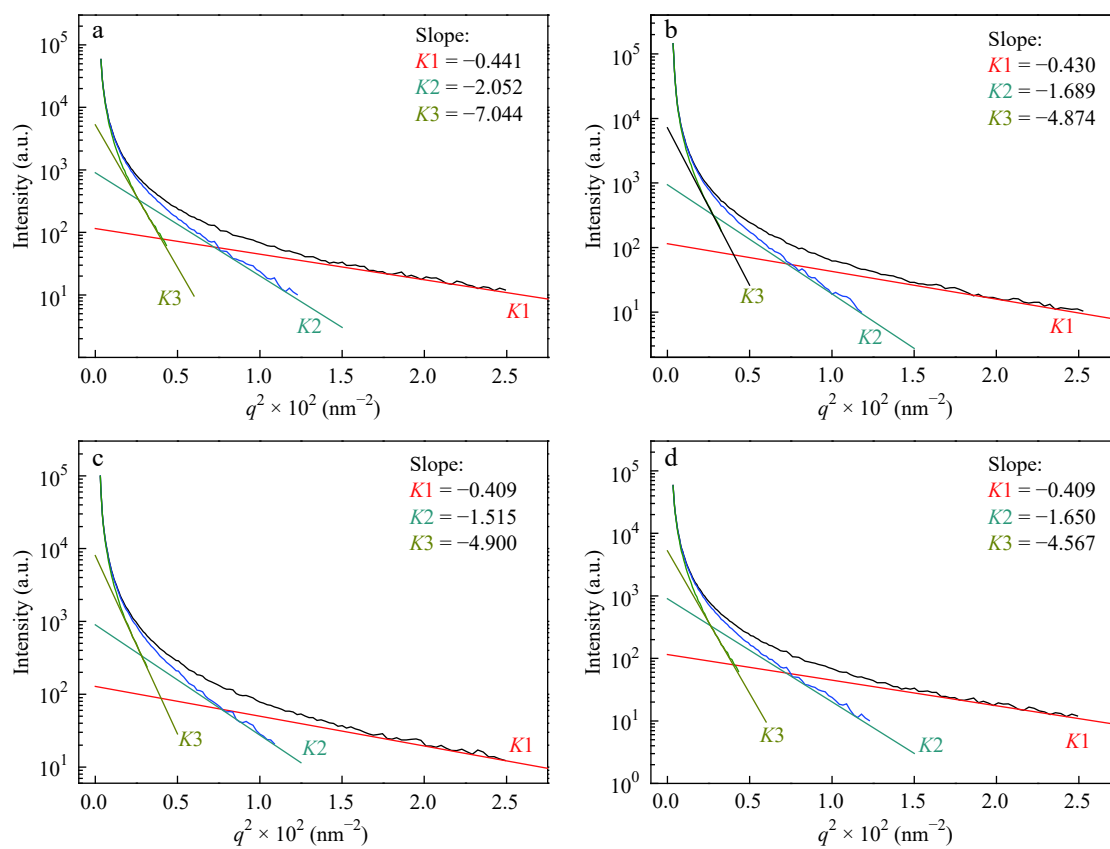


Fig. 14 Guinier plot of the co-PI-3 fibers with different draw ratios along the equator direction by Fankuchen successive tangent method: (a) $\lambda = 1.0$, (b) $\lambda = 1.6$, (c) $\lambda = 2.0$, and (d) $\lambda = 3.0$

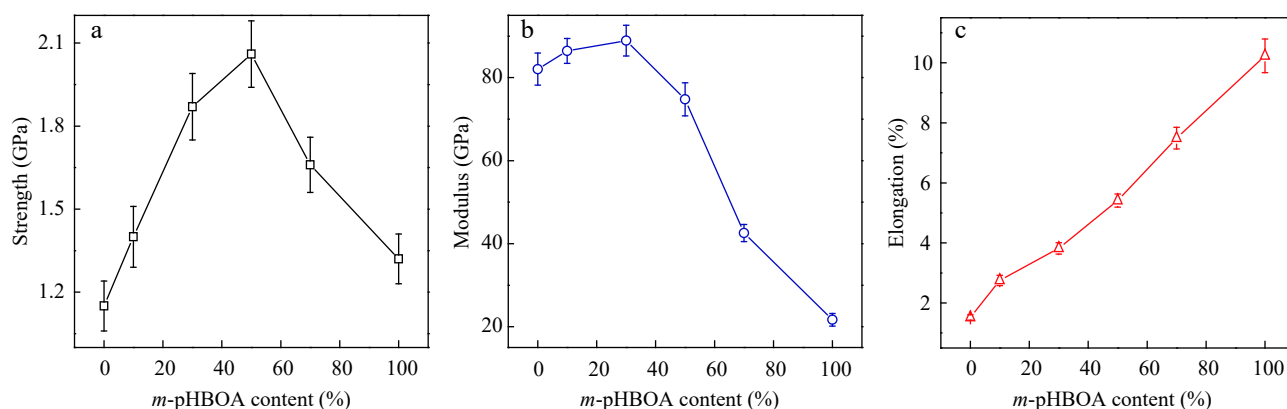


Fig. 15 Variations of mechanical properties with increasing *m*-pHBOA content in PI fibers prepared: (a) strength, (b) modulus, and (c) elongation

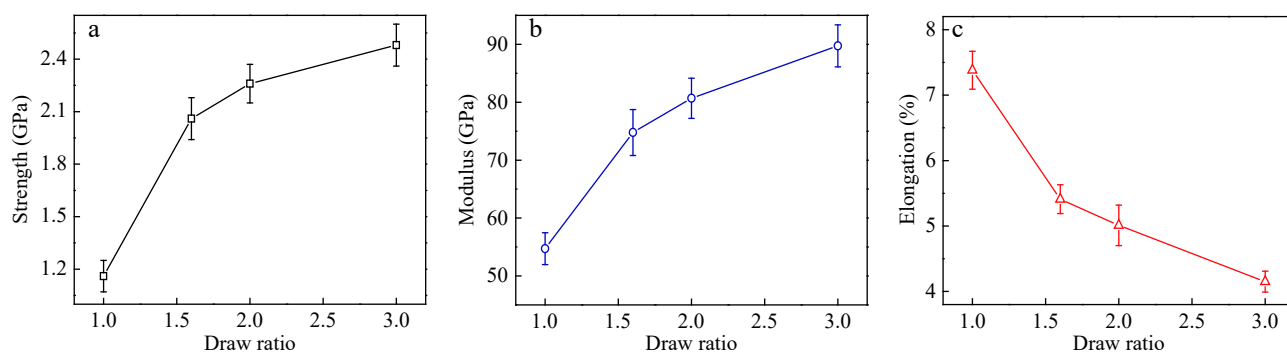


Fig. 16 Variations of mechanical properties with increasing draw ratio for the co-PI-3 fibers: (a) strength, (b) modulus, and (c) elongation

Table 6 Mechanical properties of the prepared PI fibers

Sample	<i>m</i> -pHBOA/ <i>p</i> -PDA (molar ratio)	Draft/draw ratio	Mechanical properties		
			Strength (GPa)	Modulus (GPa)	Elongation (%)
Homo-PI-0	0/10	2.3/1.3	1.15 ± 0.09	82.05 ± 3.87	1.52 ± 0.09
Co-PI-1	1/9	2.3/1.6	1.40 ± 0.11	86.43 ± 3.01	2.85 ± 0.17
Co-PI-2	3/7	2.3/1.6	1.87 ± 0.12	88.92 ± 3.70	3.82 ± 0.19
Co-PI-3	5/5	2.3/1.6	2.06 ± 0.12	74.77 ± 3.97	5.41 ± 0.22
Co-PI-4	7/3	2.3/1.6	1.66 ± 0.10	42.58 ± 2.05	7.49 ± 0.36
Homo-PI-0'	10/0	2.3/1.6	1.32 ± 0.09	21.69 ± 1.52	10.23 ± 0.56
Co-PI-3'	5/5	2.3/1.0	1.16 ± 0.09	54.71 ± 2.75	7.38 ± 0.29
Co-PI-3''	5/5	2.3/2.0	2.26 ± 0.11	80.68 ± 3.46	5.01 ± 0.31
Co-PI-3'''	5/5	2.3/3.0	2.48 ± 0.12	89.73 ± 3.63	4.15 ± 0.16

disturbed by the introduction of *m*-pHBOA moiety into the molecular structure. However, the intra/intermolecular H-bonds originated from the —OH group and the nitrogen atom of benzoxazole groups and/or the —OH group and the oxygen atom of carbonyl groups of cyclic imide. The above-mentioned H_{inter} in the co-PI-3 fiber occupies the highest percentage of 42.8%, which is the main reason for the highest fracture strength. Nevertheless, the low ordered packing and orientation factor (only 0.767) lead to a lower initial modulus.

Fig. 16 shows the variations on mechanical properties of the co-PI-3 fibers with different draw ratios, and the details are listed in Table 6. When the draw ratio of the co-PI-3 fibers varies from 1.0 to 1.6, 2.0 and 3.0, their fracture

strengths are 1.16, 2.06, 2.26, and 2.48 GPa, and their initial moduli are 54.71, 74.77, 80.68, and 89.73 GPa, respectively. Elongation at break gradually decreases from 7.38% to 4.15% with the increasing draw ratio. Apparently, the co-PI-3 fiber with higher draw ratio exhibits higher fracture strength, higher initial modulus, and lower elongation at break. The improvement on the fracture strength and initial modulus with the increasing draw ratio could be attributed to the increase in crystallinity and orientation factor and the decrease in the average length (L) and radius ($\bar{R}$) of microvoids.

CONCLUSIONS

A series of high-performance polyimide copolymer fibers

with *para*-hydroxyl groups is successfully prepared using copolymerization of BPDA, *p*-PDA, and *m*-pHBOA through the traditional two-step method. Intramolecular or intermolecular H-bonding has been demonstrated to be originated from the hydroxyl group and the nitrogen atom of benzoxazole group and/or the hydroxyl group and the oxygen atom of carbonyl group of cyclic imide, which are suggested to account for the enhanced mechanical properties. The prepared PI fibers show T_g s within 311–337 °C, and their $T_{5\%}$ values are within 529–593 °C and 510–542 °C in nitrogen and air atmospheres, respectively, indicating excellent thermal and thermo-oxidative stability. The ordered molecular packing along the transversal direction of fibers is damaged by introducing the *m*-pHBOA moiety, and the orientation factor of the co-PI fibers decreases with the increasing *m*-pHBOA content. The crystallinity and orientation factor increase with increasing draw ratio, which is also beneficial to reducing defects in the fibers. When the molar ratio of *m*-pHBOA/*p*-PDA is 5/5 and the draw ratio is 3.0, the fracture strength and initial modulus can reach 2.48 and 89.73 GPa, respectively. These results indicated that strong intermolecular interaction, high crystallinity and orientation factor, and minimal defects contribute to the final mechanical properties. Future work will focus on designing and synthesizing a diamine monomer containing two hydroxyl groups, which can form multiple intermolecular hydrogen bonding, to further improve the mechanical properties of PI fibers. This study provides useful insights for preparing PI fibers with excellent mechanical properties to meet the requirement of advanced composite materials in the fields of aeronautics, astronautics, military, and nuclear industries.

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/s10118-019-2205-4>.

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