

RESEARCH ARTICLE

Preparation of high-strength, high-modulus PVA fiber by synthesis of syndiotacticity-rich high molecular weight PVA polymers with VAc and VBz via emulsifier-free emulsion polymerization

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Funding information

National Key Research and Development Program of China, Grant/Award Number: 2016YFB0303200

Abstract

Different vinyl acetate (VAc) and vinyl benzoate (VBz) monomer ratios have been chosen as monomers to create high polymerization degree (P_n) and high syndiotacticity-diad content (*S-diad*) poly(vinyl alcohol) (PVA) polymers via emulsifier-free polymerization in order to address the problem of limited mechanical capabilities of PVA fibers prepared with low P_n and low *S-diad* polymer. The variations in hydrogen bonding, P_n , *S-diad*, and viscosity of different PVA polymers were investigated and evaluated using Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, gel permeation chromatography, and a viscosity tester. Moreover, various PVA fibers with high strength and modulus have been manufactured using a synthetic polymer as the raw material for dry-wet spinning. The effect of P_n and *S-diad* on the mechanical and thermal characteristics of PVA fibers is evaluated using a variety of characterization techniques, such as the scanning electron microscope, differential scanning calorimetry, thermogravimetric analyzer, X-ray diffraction, and tensile tester. As the ratio of VBz monomer increased, the results suggested that VBz may have a considerable impact on the P_n and *S-diad* of PVA polymers, the —OH vibration absorption peak reduced from 3491 to 3442 cm^{-1} ; the P_n increased from 2112 to 17,704; and the *S-diad* rose from 51.2% to 60.1%. In addition to the fact that P_n and *S-diad* significantly increased the fibers' strength and modulus, the crystallinity increased from 41.8% to 51.7%, and the orientation degree rose from 87.5% to 91.7%, as P_n and *S-diad* increased; the tensile strength and highest elastic modulus increased from 9.71 ± 0.3 cN/dtex to 12.74 ± 0.5 cN/dtex (increased of 31.2%) and 264.52 ± 9.3 cN/dtex to 338.41 ± 8.6 cN/dtex (increased of 27.9%); the elongation at break decreased from $5.63 \pm 0.3\%$ to $2.92 \pm 0.2\%$.

KEYWORDS

high-strength high-modulus PVA fiber, polymerization degree, polyvinyl alcohol polymer, syndiotacticity-diad content

1 | INTRODUCTION

High-performance poly(vinyl alcohol) (PVA) fibers have a high elastic modulus and tensile strength, making them potentially high-

performance fiber materials. Combined with concrete, it does not experience the same shrinkage and corrosion resistance concerns as steel reinforcement.^{1–9} Additionally, the PVA fiber exhibits excellent cement affinity, alkali resistance, and weather resistance.^{10,11} When

the cement mortar was mixed, relatively few high-mechanical qualities were added. PVA fibers significantly improve bending toughness, impact resistance, freezing–thawing stability, and splitting strength. Consequently, it can be applied in several applications, such as the reinforcement of dams, road surfaces, bridges, tunnels, and civil construction walls.^{1,12,13}

It is essential to synthesize polymers with a high polymerization degree (P_n) and syndiotacticity diad content (S -diad) PVA polymer to produce PVA fibers with superior mechanical properties.^{9,13} Since high P_n polymers have long macromolecule chains with a low proportion of defects, and high S -diad polymers have an ordered regularly regular macromolecular structure and a high proportion of intermolecular hydrogen bonds,^{14–17} and the strong hydrogen bond of PVA molecules induces a high-crystallization rate during the period of drawing process at high temperature.¹⁶ When employed to create PVA fiber, it can lessen intramolecular entanglement, improving the stretch ratio and stretch effectiveness,¹⁸ potentially strengthening the strength, modulus, and heat resistance of spinning fibers.^{19,20}

The three tactic variations of PVA molecules isotactic, syndiotactic, and atactic are well known. For the first, the OH groups are arranged on the same side as the molecular chains; for the second, they are arranged on the other side; and for the third, some OH groups are arranged on the same side while others are arranged on the opposite side. However, synthesizing the PVA polymer with a high P_n and high S -diad is problematic because vinyl acetate (VAc) has a small steric barrier and a growing radical chain with high reactivity.^{21,22} There have been various attempts to raise the PVA' P_n and S -diad. One of them is VPi/VAc, which has been described multiple times as a monomer made from PVA polymers with high P_n (1700–16,500) and high S -diad (52.8%–61.5%) contents.^{18,23–25} However, none of the synthetic polymers were spun. Using VAc/VPa as the monomers, we have presented a method for producing high P_n and high S -diad PVA polymer. This method has been employed successfully to produce PVA fiber with a tensile strength of 11.49 cN/dtex and an elastic modulus of 316.43 cN/dtex.²⁶ The strength and modulus were enhanced by 18.3% and 19.6%, respectively, compared to the fibers spun by the PVA polymer synthesized from a single VAc monomer, which was still insufficient.

For the reasons above, we anticipate that by enhancing the P_n and S -dia of PVA polymer, we will be able to manufacture PVA fibers with high strength and high modulus. Therefore, it is substantial to synthesize PVA polymers with high P_n and S -diad. To synthesize PVA polymer with higher P_n and S -diad than polymer synthesized using VAc/VPa monomer, the monomer with the unique molecular structure should be chosen for copolymerization with VAc.

Significantly, the phenyl ring in the vinyl benzoate (VBz) macromolecule has increased steric hindrance, which can encourage the interposition arrangement of structural units during polymerization.²⁷ Due to the monomers' low reactivity and high-steric hindrance, free radical polymerization can form longer chains with ordered structural units.^{23,24,28} The interposition arrangement structure of the —OH on the molecular chain can be efficiently kept following the alcoholysis of the prepolymer in VBz because it has a greater molecular mass and less active reactivity than VAc, VPa, and VPi. In order to create high

P_n and high S -diad PVA polymers, it is, therefore, more appropriate to think of it as a monomer and copolymerize with VAc monomer. The PVA polymer produced via emulsifier-free emulsion polymerization has a purer and more constrained distribution, which may enhance the properties of PVA fibers.²² Additionally, it has been demonstrated that using the dry-wet spinning method along with two stages of mechanical and thermal stretching can provide PVA fibers with outstanding mechanical properties.⁴ In other words, it is anticipated that the manufactured fiber made utilizing the synthesized PVA polymer as a raw material by dry-wet spinning will have higher mechanical and thermal properties. Moreover, the PVA polymer produced with VAc/VBz as monomers by emulsifier-free emulsion polymerization will have a high P_n and high S -diad.

In order to fabricate high-strength and high-modulus PVA fibers. Using VAc and VBz as monomers, this article first synthesizes high P_n and high S -diad PVA polymers that can be used to make high-quality products without the need for emulsifiers. Through the dry-wet spinning method, using the synthesized polymers as the starting point, preparing a variety of PVA fibers with a high-strength and high modulus. Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (¹H-NMR), gel permeation chromatography (GPC), and viscosity measurements would be used to determine the VAc/VBz monomer ratios (100/0, 90/10, 80/20, 70/30, and 60/40 vol/vol) affected the PVA polymers. Using the scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), X-ray diffraction (XRD), and tensile tester, the impact of P_n and S -diad on the thermal and mechanical performance of PVA fibers will be evaluated.

2 | EXPERIMENTAL

2.1 | Materials

Aladdin, China supplied the monomers vinyl acetate (VAc, ≥99%), vinyl benzoate (VBz, ≥99%), sodium bisulfite (NaHSO₃, ≥99%), and potassium persulfate (KPS, ≥99%). The solvents dimethyl sulfoxide (DMSO, ≥99%) and sodium hydroxide (NaOH, ≥99%) were provided by Sinopharm Chemical Reagent Co. Ltd., and anhydrous methanol (CH₃OH, ≥99%) and ethanol (CH₃CH₂OH, ≥99%) were acquired from Lingfeng Chemical Reagent Co. Ltd., China.

2.2 | Synthesis of PVA polymer

The following illustrates the PVA polymer synthesis process. Five groups of 40 mL distilled water and 40 mL monomer was weighed. The amounts of VAc (density of 0.93 g/mL) and VBz (density of 1.07 g/mL) contained in the five groups were 40 mL and 0 mL, 36 mL and 4 mL, 32 mL and 8 mL, 28 mL and 12 mL, 24 mL and 16 mL, respectively. Distilled water monomers were added to a 500 mL three-neck round-bottom container with a reflux condenser and a nitrogen atmosphere (the volume ratio of VAc/VBz were 100/0, 90/10, 80/20, 70/30, and 60/40). Under the polymerization

temperature of 50°C, 1.5 wt% initiators KPS/NaHSO₃ (mass ratio of 2:1, 0.36 g and 0.18 g, respectively) were applied after degassing and stirring. A 4 hour time limit was set for the reaction to start, following the conclusion of the synthesis reaction. The obtained copolymer of vinyl acetate and vinyl benzoate (PVAc-co-PVBz) was then dried to constant weight in a drying oven at a temperature of 60°C; To make the 10 wt% CH₃OH solution, 15.0 grams of the finished copolymer and 170 milliliters of CH₃OH were dissolved in a 500 milliliters round-bottom flask with a stirring mechanism. To make the 20 wt% alkali solution of NaOH/CH₃OH, 3.0 g of sodium hydroxide and 15.2 milliliters of CH₃OH were combined. The alkali solution was added to the copolymer solution at 60°C with a flow rate of 5 mL/min while stirring the mixture for 30 minutes. The reaction was then stopped in cooling water, and the resulting PVA polymers were washed repeatedly for three times with 25°C deionized water to remove non-reactive small molecules, sodium ions, and other materials, so as to reduce the adverse effect of impurities on the performance of PVA fiber. After that, the PVA polymers were dried in a vacuum drying oven at about 60°C for 12 h. Besides, the weight of the finished product was used to compute the alcoholysis (AD) of PVAc-co-PVBz to PVA. Scheme 1 depicts the PVA polymer synthesis processes including synthesis and alcoholysis of copolymer.

2.3 | Properties of high strength and high modulus PVA fibers

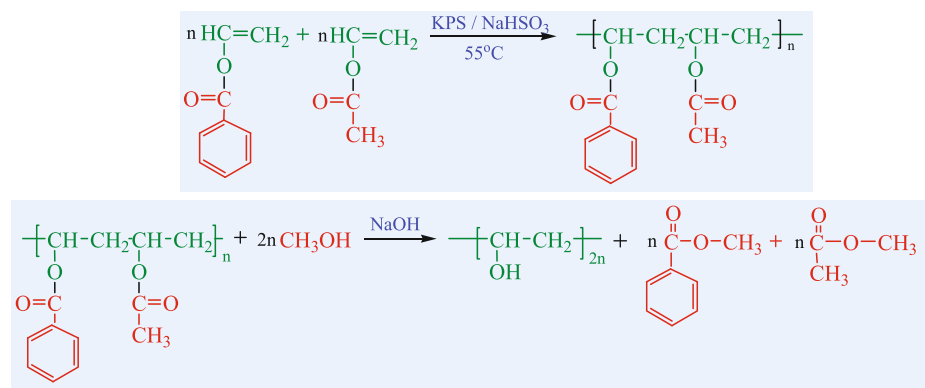
The manufactured PVA polymer (5.0 g) containing various P_n and S -diad was combined with 15.2 mL DMSO solution in a 250 mL flask at constant stirring temperatures of 55°C for 15 min to partially dissolve the polymer and 95°C for 60 min to completely dissolve the polymer. The ultimate concentration of the PVA spinning dopes was 23.0 wt%. The spinning dopes were deaerated in a drying oven at 60°C for around 5 h after the procedure was finished to dissolve any air bubbles.

In a steel high-pressure syringe with a spinneret aperture, 10 mL PVA spinning dopes were produced using the extrusion technique. The syringe was heated to 80°C before extruding spinning dopes through a metal spinneret with a 0.12 mm hole. A propulsion pump that was inverter-controlled operated at a frequency of 30 Hz and maintained a constant temperature of 80°C was also included in the

syringe. After that, a coagulation bath at 20°C was used to gel the pumped spinning dopes for 3 min. The coagulation bath was 8 cm distant from the spinneret aperture. After coagulating, the as-spun PVA fibers were pre-stretched with a stretching ratio of 2.2 times in the air. The gelled as-spun PVA fibers were collected using the rotating winder and then immersed in the 1000 mL ethanol coagulation solution for 12 h at 20°C to remove the DMSO agent. Fibers were drawn in two stages at 180 and 200°C in a heat pipe. The initial hot-drawing ratio, determined by the primary winding roller to driven roller ratio, was 2.8 times. The maximal fiber elongation, continuous collection without breaking, served as the ultimate hot-drawing value. The drawing ratio (R) at each stage was calculated using V_2/V_1 , where V_2 is the velocity of the take-up winder and V_1 is the velocity of the feeding winder. The equipment flowsheet for the dry-wet spinning process is shown in Figure 1.

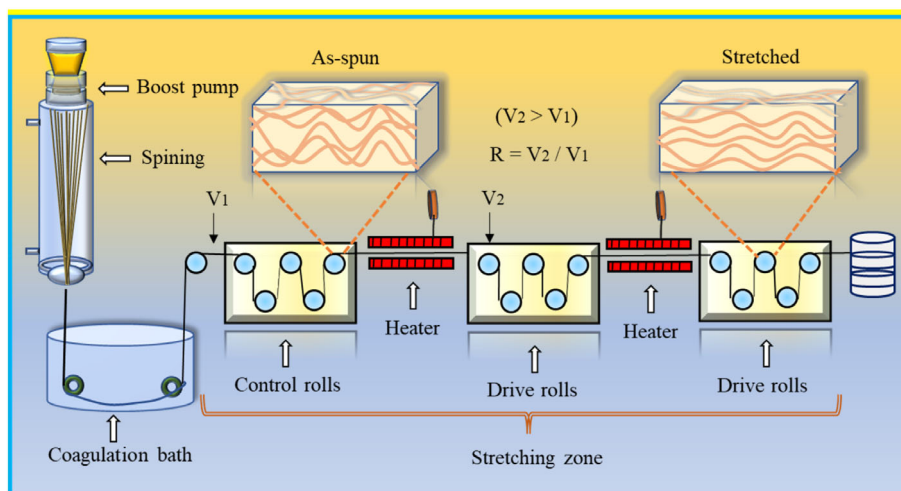
2.4 | Characterization

The P_n and PDI of the PVA polymers were determined using GPC (BIC, Bi-MwA) with hexafluoroisopropanol as the mobile solvent. The calibration method used a narrow distribution standard sample, and the MW served as a relative value to the calibration. The structures and PVA's S -diad were identified using proton nuclear magnetic resonance (¹H-NMR, Bruker, Avance3HD600 NMR). The functional hydroxyl groups (—OH) structure of PVA polymer was studied using FTIR in the 500–4000 cm^{−1} range (Nicolet, NEXUS-670). Benzene was used as the solvent to evaluate the viscosity of PVA polymers at a temperature of 25°C (±0.1°C) using a viscosity tester (Dongzhixun, China; model: WS-2-300). The inner capillary diameter of the viscometer was 0.54 mm. In order to assess the temperature transition behavior of PVA fibers in a nitrogen-constant atmosphere, the differential scanning calorimeter (DSC) (Netsch, 204) was utilized. The heating rate was 10°C min^{−1} from room temperature up to 260°C. Thermal breakdown curves for the test substances were produced using a TGA (Netsch, 209 F1). The heating rate up to 550°C was 20°C min^{−1}, and the nitrogen gas flow velocity was 30 mL/min. Cu K α radiation ($\lambda = 1.5418$ nm, 40 kV, 40 mA) was fitted to the Powder X-ray diffractometer (Bruker, Germany) employed for the crystallinities and orientation. PVA fibers' cross-sectional and surface morphology were



SCHEME 1 Synthesis processes of poly(vinyl alcohol) (PVA) polymer

FIGURE 1 Equipment flowsheet of dry-wet spinning process.



investigated using SEM (Phenon-World, Phenom G2 Pro) at an acceleration voltage of 5 kV. The elongation-strength connection of fibers was studied using a yarn tensile tester (Shanghai Lippe Institute of Applied Science and Technology Co, XL-2) fitted with fixtures and a fiber specimen length of 10 cm at a stretching speed of 20 mm/min, and 20 groups of each fiber were tested for average.

3 | RESULTS AND DISCUSSION

3.1 | FTIR characterization of PVA polymers

Several polymer characteristics were tested by FTIR spectroscopy in order to find out whether PVA polymers were successfully prepared using VBz and VAc monomers, and the effect of different volume ratio of VBz and VAc monomer on the hydrogen bond of PVA polymer, further, to predict the features of high-mechanical fiber. Figure 2A shows the formation of the hydrogen-bonding network of PVA polymers generated with different VAc and VBz monomers. There was a significant vibrational peak associated with —OH stretching in the 3491–3442 cm^{-1} range and absorption bands associated with —CH₂ and C—O stretching vibrations at around 2975 and 1062 cm^{-1} , respectively.^{29,30} If the intermolecular hydrogen bonding is larger than the strength of the intramolecular hydrogen bonding, and vice versa, the associated hydroxyl band will shift toward a lower wavenumber.^{31,32} With increasing VBz ratios, it was revealed that the peak of the —OH stretching vibration absorption shifted from 3491 cm^{-1} to a lower wavenumber of 3442 cm^{-1} . This is mainly due to the special structure of the benzene ring on the side group of VBz has a great steric hindrance effect,²⁷ during the polymerization, the arrangement structure of the side groups of the original prepolymer was changed, and more hydrogen bonds were formed between the —OH groups after alcoholysis. In addition, the stretching vibration absorption peaks of —CH₂ and C—O groups did not change much in all PVA spectral curves, indicating that the ratio of VBz monomers had little influence on these groups.

3.2 | ¹H NMR characterization of PVA polymers

The ¹H NMR was used to compute the *S-diad* and understand the effect of VBz and VAc monomer ratio on the *S-diad* of the obtained PVA polymer. And the ¹H NMR spectra are shown in Figure 2B. All the identified peaks are consistent with the appropriate protons; 1.44 ppm corresponds to the methylene group (—CH₂), 3.42 ppm to the water peak, and 3.83 ppm to the methine group (—CH—). The syndiotactic stereochemical isomer of the —OH vibration peak was observed at 4.34 ppm, while the atactic and isotactic stereochemical isomers were observed at 4.59 and 4.73 ppm, respectively.^{20,33} The chemical shifts and peak integrals of 4.29 ~ 4.81 ppm were used to describe the activities of the PVA polymers, and the *S-diad* of the PVA polymer was calculated by Equation (1).^{20,22} Syndiotactic, atactic, and isotactic content for each peak area is denoted by the letters *rr*, *mr*, and *mm*, respectively. According to the results of the peak area integration of the ¹H NMR spectra (Table S1), the *S-diad* of the synthesized PVA polymers increased from 51.2% to 60.1% as the VBz monomer concentration increased. This could be due to the steric hindrance structure of the benzoic group on VBz macromolecules, which may enhance the orderly —OH organization of molecular units.²⁷ The steric effect becomes stronger as the amount of VBz monomer increases, and the —OH on the PVA molecular chain generated by alcoholysis can retain its ordered radial arrangement structure. At the same time, high *S-diad* PVA polymers were suitable for the fabrication of PVA fibers with high mechanical properties.^{16,18}

$$S-diad = \frac{rr + \frac{1}{2}mr}{mm + mr + rr} \times 100\%. \quad (1)$$

3.3 | GPC characterization of the PVA polymers

The effect of VBz and VAc volume monomer ratio on the *P_n* of the produced PVA polymers has been evaluate by GPC, which are shown

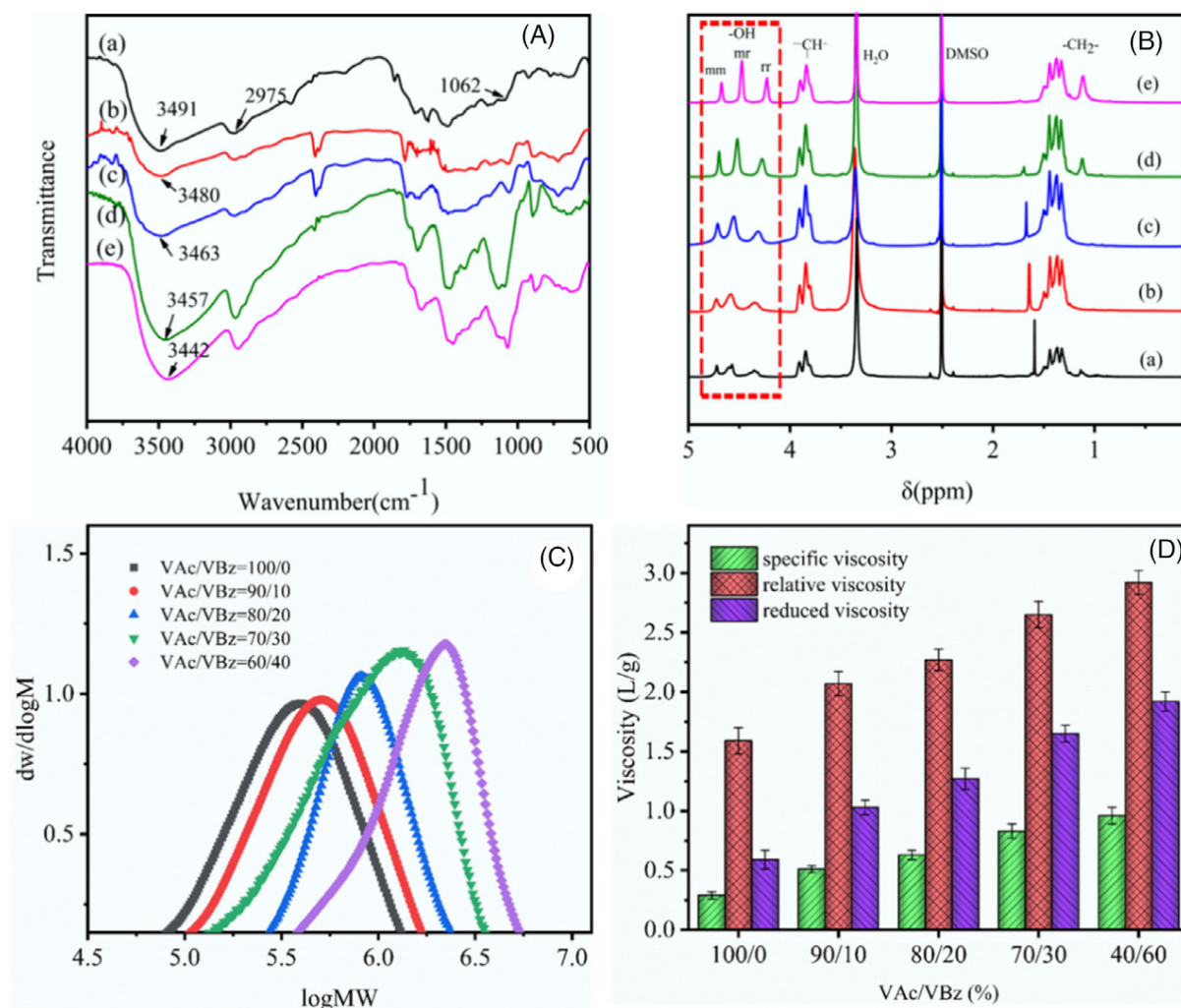


FIGURE 2 (A) Fourier transform infrared spectroscopy (FTIR) spectra of poly(vinyl alcohol) (PVA) polymer ([a] VAc/VBz = 100/0, [b] VAc/VBz = 90/10, [c] VAc/VBz = 80/20, [d] VAc/VBz = 70/30, [e] VAc/VBz = 60/40; (B) ¹H NMR curves of PVA polymer ([a] VAc/VBz = 100/0, [b] VAc/VBz = 90/10, [c] VAc/VBz = 80/20, [d] VAc/VBz = 70/30, [e] VAc/VBz = 60/40); (C) gel permeation chromatography (GPC) curves of PVA polymer; (D) viscosity values of PVA polymer.

in Figure 2C. According to GPC analysis, the P_n of the produced PVA polymers increased with the addition of VBz monomer from 2112 to 17,704, while the molecular weight distribution index (PDI) of each sample was kept to a maximum of 2.0. In addition, according to the weighing method, the alcoholysis (AD) of PVA polymers all reached 99% (Table 1). Therefore, compared to PDI and AD , the VBz monomer has a stronger impact on the P_n of PVA polymer. This was because the VBz monomer has a higher relative molecular weight and a lower reactivity than the VAc monomer under the same reaction conditions, so when it is utilized for polymerization, the PVA polymer may have a longer molecular chain.²¹ In addition, the reaction of emulsion polymerization using water as the emulsifier at a low-monomer concentration may limit the transfer of free radicals to the solvent, resulting in a narrower molecular weight range.²² For ease of expression, the names PVA-2199 (51), PVA-3199 (53), PVA-7499 (55), PVA-12499 (58), and PVA-17799 (60) were given to the synthesized polymers used in the subsequent experiment.

3.4 | Viscosity characterization of PVA polymers

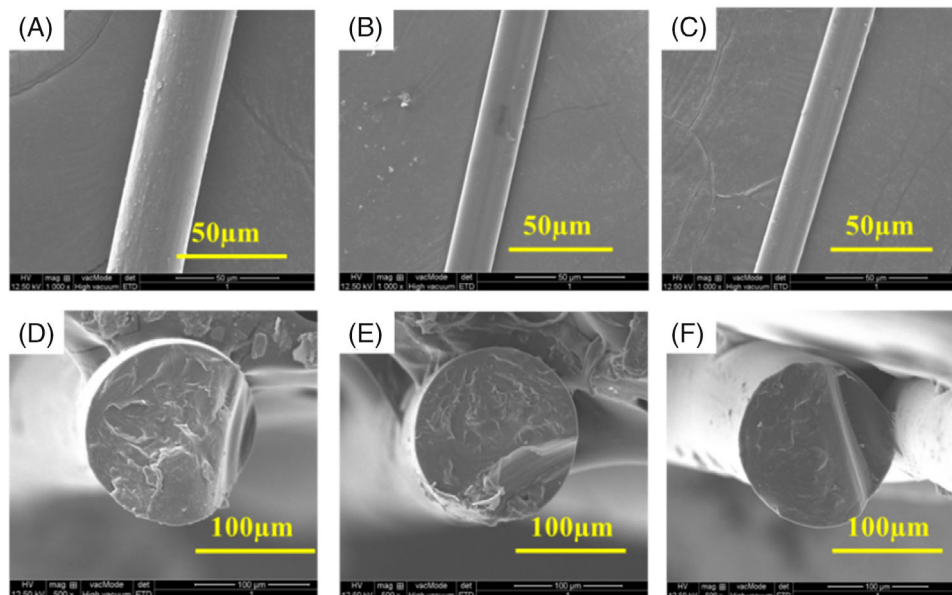
The viscosity measurement of polymer is mainly to characterize its solubility and spinnability. Figure 2D and Table S2 illustrate the viscosity values of PVA polymers. Viscosity measurements showed that the VBz monomer ratio has a significant impact on the relative viscosity (η_r), specific viscosity (η_{sp}), and reduces viscosity (η_{sp}/c) of PVA polymers. This is because PVA polymers with a high P_n have more structural units in their molecular chains and longer molecular chains. The movement of the PVA macromolecule chain is more constrained, resulting in decreased macromolecule mobility.³⁴ Simultaneously, as the S -diad of PVA polymers increases, it becomes easier to create strong hydrogen bond connections between PVA macromolecules in the spinning solution, causing the PVA molecular chains to come into closer contact,^{16,35} hence, increasing the viscosity of the polymer.

Due to the lengthy dissolution period of PVA polymer with high P_n and S -diad, and the produced spinning solution as an excessively

TABLE 1 The molecular weight distribution (*PDI*), polymerization degree (P_n), alcoholysis (*AD*), and syndiotacticity-diad content (*S-diad*)

Samples (VAc/VBz)	P_n	<i>PDI</i>	<i>AD</i> (%)	<i>S-diad</i> (%)
PVA (100/0)	2079 ± 42	1.68 ± 0.09	99.3 ± 0.2	51.2 ± 0.5
PVA (90/10)	3106 ± 50	1.86 ± 0.12	99.5 ± 0.1	52.7 ± 0.7
PVA (80/20)	7411 ± 69	1.61 ± 0.10	99.2 ± 0.3	55.3 ± 0.6
PVA (70/30)	12,373 ± 73	1.92 ± 0.13	99.6 ± 0.2	58.0 ± 0.8
PVA (60/40)	17,704 ± 98	1.77 ± 0.11	99.5 ± 0.1	60.1 ± 0.6

Abbreviation: PVA, poly(vinyl alcohol).

FIGURE 3 Scanning electron microscopy (SEM) pictures of poly(vinyl alcohol) (PVA) fiber (spun fiber: [A] PVA-2199 (51), [B] PVA-3199 (53), and [C] PVA-7499 (55); as-spun fiber: [D] PVA-2199 (51), [E] PVA-3199 (53), and [F] PVA-7499 (55)).

high viscosity. In this study, only three kinds of fibers, PVA-2199 (51), PVA-3199 (53), and PVA-7499 (55), were spun using the same spinning (the properties of their polymers are shown as Figures S1–S3). Before spinning, the polymers PVA-12499 (58) and PVA-17799 (60) need to be re-optimized. To study the impacts of P_n and *S-diad* on the mechanical properties and thermal stability of the fibers under identical spinning process circumstances, only three kinds of fibers, PVA-2199 (51), PVA-3199 (53), and PVA-7499 (55), were examined in depth.

3.5 | SEM of PVA fibers

Using SEM, the microstructure of PVA fibers with varying P_n and *S-diad* was investigated in more detail. Figure 3A–C illustrates the surface morphology of PVA fibers as captured by SEM. The newly designed PVA fibers are smooth and featureless. In addition, the diameter of the fibers shrunk when P_n and *S-diad* increased. This is because the high P_n PVA fiber has a low proportion of terminal defects on the macromolecular chains, which is conducive to enhancing the stretch ratio. The high *S-diad* PVA fiber is more likely to crystallize, which is conducive to enhancing stretch efficiency.^{26,36,37} And it is consistent with higher fiber hot-drawing ratios, which could improve mechanical qualities.³⁸

Figure 3D–F depicts the form of as-spun PVA fibers that have not undergone thermal stretching. As noted, the diameter of the fibers gradually lowers, the cross-sectional shape remains flat and round as P_n and *S-diad* levels increase, and the round morphology of PVA fibers produced using the dry-wet method made it simple to achieve high-expansion thermal stretching.^{34,38} It is advantageous to improve the mechanical properties of fibers.

3.6 | DSC analysis of PVA fibers

As depicted in Figure 4, DSC was performed to better understand how the thermal crystal behavior of PVA fibers fabricated with various P_n and *S-diad* polymers varied. The crystallinity (X_{c1}) was obtained using the following Equation (2).

$$X_{c1} = \frac{\Delta H_m}{\Delta H_m^0 \omega} \cdot 100\%, \quad (2)$$

where ω was the proportion mass of polymer in PVA fibers, the value was 100%; ΔH_m^0 corresponds to the fusion enthalpy of 100% crystallized PVA, the value was 161 J g^{-1} .^{39,40}

Table 2 lists the fibers' melting point (T_m), heat of fusion (ΔH_m), and crystallinity (X_{c1}) characteristics. With the rise in P_n and *S-diad*,

the PVA fiber's T_m , ΔH_m , and X_{c1} markedly improved. The changes in the PVA fiber's melting peak value showed that the crystalline area had become more developed. Semi-crystalline PVA fibers typically melt at a temperature between 229 and 237°C, and as the P_n and S -diad increased, the melting point of PVA fibers rose to higher temperatures. This is primarily because as the length of the chain of macromolecules increases and the hydrogen bond between macromolecules become stronger, the movement of the molecular chain becomes restricted. Consequently, more heat is required to break the hydrogen bond and release the PVA molecular chain from its

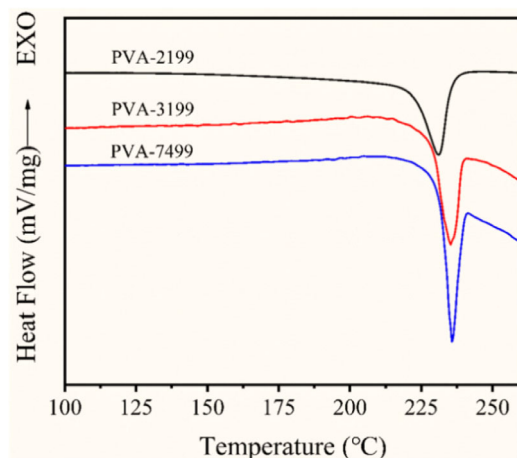


FIGURE 4 Differential scanning calorimetry (DSC) curves of poly(vinyl alcohol) (PVA) fibers.

TABLE 2 Parameters obtained from DSC curves of PVA fibers

Sample	T_m (°C)	ΔH_m (J/g)	X_{c1} (%)
PVA-2199 (51)	229 ± 0.5	70.4 ± 1.3	43.7 ± 0.8
PVA-3199 (53)	236 ± 0.4	74.4 ± 1.4	46.2 ± 0.6
PVA-7499 (55)	237 ± 0.5	86.5 ± 1.3	53.7 ± 0.8

Abbreviation: PVA, poly(vinyl alcohol).

restriction of movement and melting, thereby increasing the T_m and ΔH_m . The increased X_{c1} in PVA fibers was most likely a result of the strong hydrogen bond of S -diad, which generates a high-crystallization rate,^{9,12,16} and an ordered association of PVA molecules.²⁶ In addition, the orderly and tight arrangement of PVA molecules that results from the hot-drawing process can assist crystallization. The hydroxyl groups that were rebuilt during the hot-drawing process may have created intermolecular hydrogen bonds, contributing to enhanced crystallinity and producing highly regular molecular chains.^{11,41}

3.7 | TGA analysis of PVA fibers

TGA was employed to understand how P_n and S -diad influence the degradation of PVA fibers. The TGA (a) and DTG (b) graphs of the PVA-2199 (51), PVA-3199 (53), and PVA-7499 (55) fibers at a heating rate of 20°C min⁻¹ are shown in Figure 5, and the thermogram data are shown in Table 3. The TGA curves showed that the fibers undergo four distinct stages of degradation: the evaporation of plasticizer water from the fibers, the removal of the hydroxyl group on the side of the PVA molecule, the degradation of the PVA backbone molecule, and the decomposition and volatilization of the fibers.^{30,42–44} While the figure shows that the process of PVA degradation corresponds to three visible stages of heat decomposition, the temperature ranges associated with the removal of the —OH group at about 280 ~ 305°C, the breakdown of the PVA backbone molecule at roughly 340 ~ 400°C, and the decomposition and volatilization of fiber at

TABLE 3 The decomposition temperatures of PVA fibers

Samples	T_{d1} (°C)	T_{d2} (°C)	T_{d3} (°C)
PVA-2199 (51)	286.5 ± 2.5	367.4 ± 3.3	457.4 ± 3.4
PVA-3199 (53)	296.1 ± 2.5	380.1 ± 3.1	459.5 ± 3.0
PVA-7499 (55)	299.7 ± 2.4	386.2 ± 3.3	463.5 ± 2.6

Abbreviation: PVA, poly(vinyl alcohol).

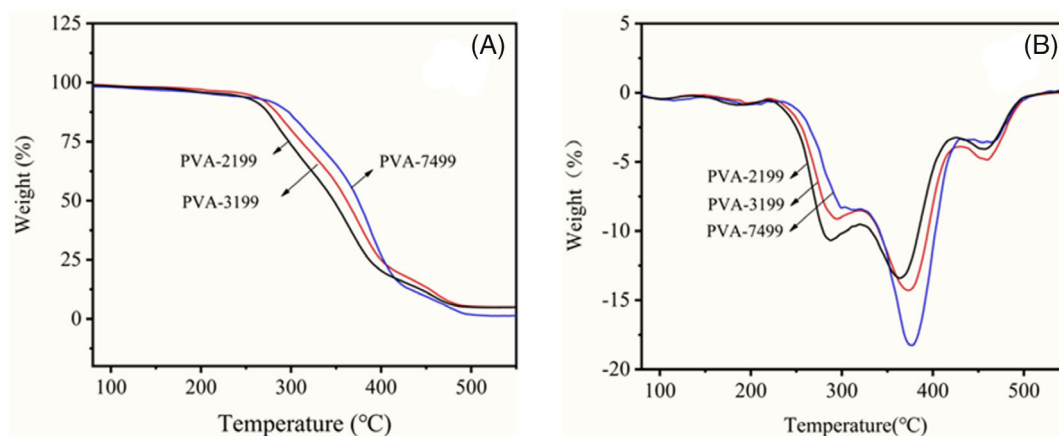


FIGURE 5 (A) Thermogravimetric analyzer (TGA) diagrams of the poly(vinyl alcohol) (PVA) fibers. (B) DTG diagrams of the PVA fibers.

440 ~ 480 °C were relatively clear. The maximum thermal decomposition temperature of the removal of —OH group (T_{d1}) of PVA fibers shifted from 286.5°C to a higher temperature of 299.7°C, the maximum thermal mass temperature of the degradation of the main chain (T_{d2}) was shifted from 367.4°C to a higher temperature of 386.2°C and the maximum thermal mass temperature of the decomposition and volatilization of fiber (T_{d3}) was shifted from 457.4°C to a higher temperature of 463.5°C, which suggests that P_n and $S\text{-diad}$ had a positive influence on PVA fibers' thermal stability. The higher thermal stability of —OH groups can be attributed to their higher chain compactness due to strong intermolecular hydrogen bonds and the higher stereoregularity of high $S\text{-diad}$ PVA.^{12,45} Additionally, the PVA fiber with high $S\text{-diad}$ has a more compact arrangement of macromolecular chains with higher crystallinity, which limits the thermal movement of macromolecular chains and raises the main chain's degradation temperature.^{25,46,47} The fiber decomposition volatilization temperature increased slightly, mainly because the hydrogen bond change only occurred between the hydroxyl groups. The degradation of the backbone mainly occurred in the amorphous region. In contrast, the decomposition in this temperature range occurred in the crystalline region,⁴⁶ which was only affected by the degree of crystallization, so the temperature change was not as pronounced as in the former case.

3.8 | XRD of PVA fibers

We all know that one of the most important factors influencing the mechanical properties of a fiber is its potential to crystallize, hence, one-dimensional (1D) XRD was adopted to research how P_n and $S\text{-diad}$ influence the crystallinity of PVA fibers. Figure 6A shows the 1D XRD curves of PVA fibers with different P_n and $S\text{-diad}$ values. The major diffraction peaks of the fibers, which correspond to the (100), (101), and (200) planes and demonstrate the polycrystalline character of PVA fibers, were measured at $2\theta = 10.8^\circ$, 19.2° and 22.06° ,

respectively.^{30,36,48} The diffraction peak shows the regular lattice of the PVA fibers.⁴⁹ Table 4 displays the crystallinity of PVA fiber as evaluated by 1D XRD. The crystallinities increased from 41.8% to 51.7% when the P_n and $S\text{-diad}$ of PVA fibers increased. This may be due to the low proportion of terminal flaws in PVA fibers with high P_n , which enhances the stretch ratio.³⁴ While the high $S\text{-diad}$ PVA fibers have a higher proportion of hydrogen bonds between macromolecules and a more ordered chain arrangement of macromolecules, the crystallinity of the fiber may be enhanced.^{14,16} Additionally, the crystallinity values (X_{c2}), however, are lower than those of X_{c1} measured by DSC, which may be due to the heating technique used in DSC, which may have aided in the crystallization of the PVA macromolecule.⁴⁹ In general, a greater mechanical property may result from the higher crystallinity of PVA fiber.^{37,39}

Since the crystallinity of a fiber is boosted by the orientation behavior of the fiber's macromolecular chain during the hot-drawing process.⁵⁰ P_n and $S\text{-diad}$ were evaluated to see how they affected the overall chain orientation structure of PVA fibers during the hot drawing process. Figure 6B illustrates the integrated intensity distribution curve obtained after the 360° azimuth-scanning integration of different PVA fibers along the (101) crystal plane ($2\theta = 19.2^\circ$) by two-dimensional (2D) XRD, and $FWHM$ is the full-wide-at-half-maximum of the intensity distribution curve produced by the software of 2D XRD instrument, then, the orientation index (n) of PVA fiber can be calculated using Equation (3),³⁹ and the results were presented in Table 4.

TABLE 4 Crystallinity and orientation of the PVA fibers

Samples	X_{c2} (%)	n (%)
PVA-2199 (51)	41.8 ± 0.5	87.5 ± 0.6
PVA-3199 (53)	42.9 ± 0.4	89.1 ± 0.7
PVA-7499 (55)	51.7 ± 0.3	91.7 ± 0.6

Abbreviation: PVA, poly(vinyl alcohol).

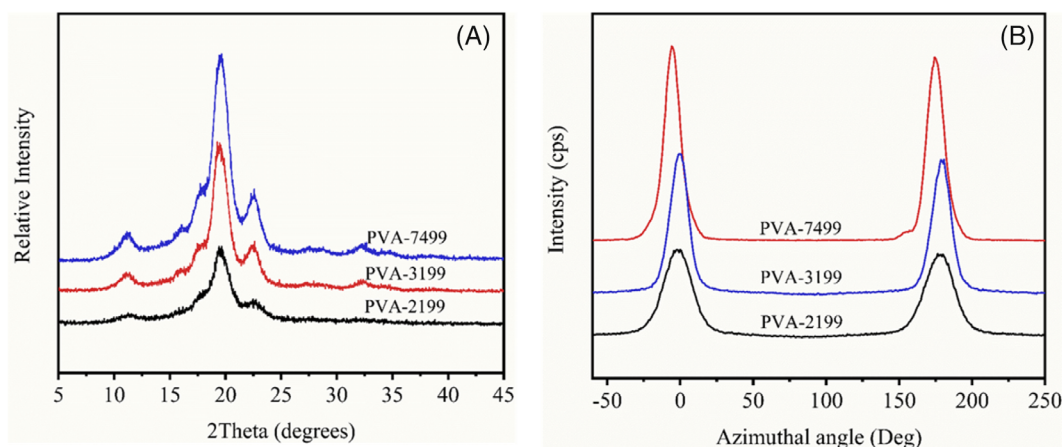


FIGURE 6 (A) X-ray diffraction curves of poly(vinyl alcohol) (PVA) fibers. (B) Intensity distribution curve along the (101) crystal plane of PVA fiber.

$$n = \frac{180^\circ - \text{FWHM}}{180^\circ} \quad (3)$$

According to the azimuthal integration data, the orientation degree increased as P_n and S -diad increased. The PVA-7499 fiber exhibits the highest n of 91.7% because it has longer chain and fewer intramolecular hydrogen bonds. The PVA macromolecules are forced to move and align along the fiber axis when subjected to stress and temperature⁵¹ thereby orienting the fiber's macromolecular chain. This is one of the most important factors for PVA fiber to obtain excellent mechanical properties.

3.9 | Mechanical properties of PVA fibers

The yarn tensile tester was used to test the mechanical properties of PVA fibers fabricated with various P_n and S -diad PVA polymers. Figure 7A depicts the tensile test technique and yarn tensile tester with fixtures and a fiber specimen length of 10 cm at a stretching speed of 20 mm/min, in 20 groups of each fiber were tested to determine the average tensile strength. Figure 7B depicts the stress-strain behavior of PVA fibers, whereas Table 5 summarizes the tensile properties of these produced fibers. Figure 7B shows how much the elastic modulus and tensile strength of PVA fibers created with synthetic polymer increased. The PVA-7499 (55) fiber has the highest tensile strength, at 12.74 ± 0.5 cN/dtex, which is approximately 31.2% higher than that of PVA-2199 fiber. It also has the highest elastic modulus at 338.41 ± 8.6 cN/dtex, which is approximately 27.9% higher than that

of PVA-2199 fiber, indicating that the PVA polymer's P_n and S -diad have a positive impact on fiber strength. This is because the high P_n PVA polymer has a lower proportion of molecular chain defects, which increases the drawing ratio of PVA fibers. At the same time, the PVA polymer with a high S -diad has a high hydrogen bond concentration between molecules. As the number of intermolecular hydrogen bonds increases, a robust and durable network connection structure is generated between macromolecular chains, preventing the entanglement of macromolecules themselves.^{37,52} PVA macromolecular chains with a low-entanglement degree are more effective at stretching and can be straightened more quickly. After better stretching, the macromolecules in the PVA fiber tended to align along the axial direction, and the PVA fiber's crystallinity, orientation, and mechanical properties were subsequently enhanced.^{4,39} In addition, when the P_n and S -diad of the polymer increased, so did the PVA polymer dissolution time, indicating that the sample exhibited low solubility. For instance, the dissolution time of PVA-7499 (55) polymer was 6.5 h, which was 96.9% longer than PVA-2199 (51) polymer. And this is consistent with the viscosity values of PVA polymers.

4 | CONCLUSIONS

(1) Using VAc and VBz as monomers and emulsifier-free polymerization, the high P_n and S -diad PVA polymer was successfully developed and fabricated in this study. Additionally, the impacts of VBz ratios on the P_n and S -diad of polymers were studied. According to the characterization analysis of FTIR, GPC, ^1H NMR, and viscosity tester, with

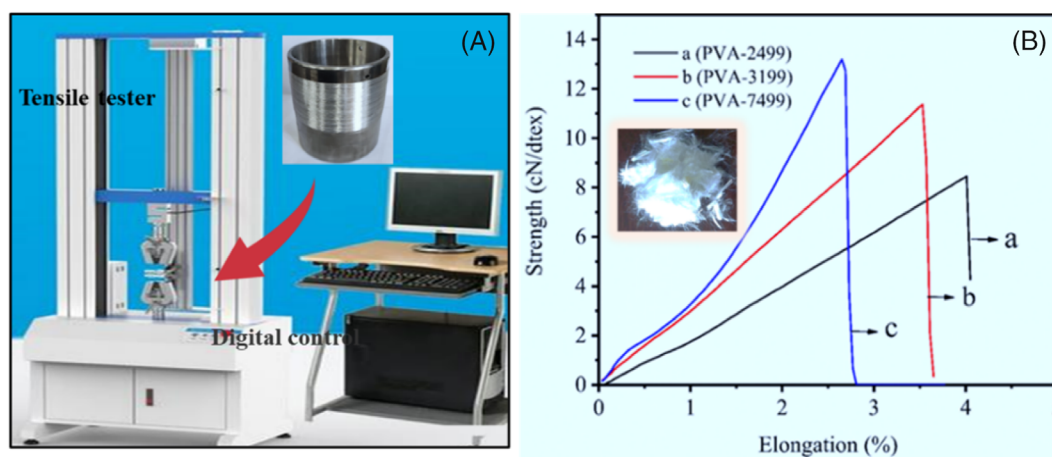


FIGURE 7 (A) The stress-strain tester. (B) Typical elongation-strength curves of the poly(vinyl alcohol) (PVA) fibers.

TABLE 5 The mechanical properties of PVA fibers

Samples	Dissolution time (h)	Drawing ratio	Denier (dtex)	Tensile strength (cN/dtex)	Elastic modulus (cN/dtex)	Elongation (%)
PVA-2199 (51)	3.3 ± 0.3	14.3 ± 0.4	9.8 ± 0.5	9.71 ± 0.3	264.52 ± 9.3	5.63 ± 0.3
PVA-3199 (53)	4.2 ± 0.4	18.1 ± 0.5	6.4 ± 0.4	11.87 ± 0.3	302.40 ± 8.1	3.79 ± 0.3
PVA-7499 (55)	6.5 ± 0.3	20.4 ± 0.5	5.5 ± 0.3	12.74 ± 0.5	338.41 ± 8.6	2.92 ± 0.2

Abbreviation: PVA, poly(vinyl alcohol).

the rise in VBz ratios, it was discovered that the peak of the —OH stretching vibration absorption moved from 3491 cm^{-1} to a lower wavenumber of 3442 cm^{-1} . The addition of VBz also caused an accelerated increase in P_n (from 2112 to 17,704) as well as an increase in $S\text{-diad}$ (from 51.2% to 60.1%), relative viscosity (from 1.59 $\text{L}\cdot\text{g}^{-1}$ to 2.92 $\text{L}\cdot\text{g}^{-1}$), specific viscosity (from 0.59 $\text{L}\cdot\text{g}^{-1}$ to 1.92 $\text{L}\cdot\text{g}^{-1}$) and reduces viscosity (from 0.29 $\text{L}\cdot\text{g}^{-1}$ to 0.96 $\text{L}\cdot\text{g}^{-1}$) of PVA polymers.

(2) PVA-2199 (51), PVA-3199 (53), and PVA-7499 (55) fibers with high strength and high modulus were successfully fabricated using the synthesized PVA polymers as raw materials by the dry-wet spinning method. The outcomes also demonstrated that not all synthesized PVA polymers are suitable for spinning due to poor solubility and spinnability as P_n and $S\text{-diad}$ were raised. PVA polymers with excessively high P_n and $S\text{-diad}$ are required to further optimize the spinning process before spinning.

(3) According to the findings of the mechanical tests, the fibers' tensile strength increased from 9.71 cN/dtex to 12.74 cN/dtex (an increase of 31.2%), and their elastic modulus increased from 264.52 cN/dtex to 338.41 cN/dtex (increased of 27.9%) when P_n and $S\text{-diad}$ increased. Additionally, according to the XRD results, the crystallinity of PVA fibers increased from 41.8% to 51.7% with an increase in P_n and $S\text{-diad}$ the orientation increased from 87.5% to 91.7%, the maximum thermal decomposition temperature of the elimination of the —OH group on the fiber increased from 286.5°C to 299.7°C, the maximum thermal decomposition temperature of the main chain increased from 367.4°C to 386.2°C. The maximum thermal decomposition temperature of the fiber decomposition volatilization increased from 457.4°C to 463.5°C.

With all of these qualities, VAc/VBz can be used as monomers in the synthesis of PVA polymers with high P_n and high $S\text{-diad}$. And they can be used to produce PVA fibers with high strength and high modulus as starting materials. Thus, a better method for creating PVA fibers with high mechanical performance was described in this research.

ACKNOWLEDGMENT

This work is supported by National Key Research and Development Program of China (2016YFB0303200).

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Wang H, He J, Zou L, Wang C, Li YV. Preparation of high-strength, high-modulus PVA fiber by synthesis of syndiotacticity-rich high molecular weight PVA polymers with VAc and VBz via emulsifier-free emulsion polymerization. *Polym Adv Technol*. 2023;34(6):1948-1958. doi:10.1002/pat.6022