



High-performance copolyimide fibers containing quinazolinone moiety: Preparation, structure and properties

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ABSTRACT

Copolyimide (co-PI) fibers with superior mechanical properties and high thermal stability were developed via a two-step polymerization/imidization process based on a new design of introducing an aromatic heterocyclic diamine monomer, 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone (AAQ) into rigid homopolyimide backbones of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine (p-PDA). Effects of the incorporated AAQ moieties on the micro-structure and properties of the prepared fibers were investigated. Fourier transform infrared (FTIR) results indicated that hydrogen bonding is formed between the AAQ and cyclic imide units that effectively strengthens the inter-molecular interactions. This has been considered to be the key factor responsible for the significantly enhanced mechanical properties of the co-PI fibers. Two-dimensional wide angle X-ray diffraction (2D WAXD) spectra showed that the co-PI fibers are highly oriented with well-ordered 2D structures along both the fiber and transverse directions. The co-PI fibers reached the optimum tensile strength and modulus of 2.8 GPa and 115 GPa, respectively, at the AAQ/p-PDA molar ratio of 5/5. The fiber also exhibited high thermal stability, with a 5%-weight-loss temperature of 599 °C under N₂ and 564 °C in air.

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1. Introduction

High-performance polymeric fibers with outstanding mechanical behaviors such as high strength and modulus have undergone significant developments in the past half century for various engineering applications. The driving force of developing these fibers has been of scientific and commercial interests [1,2]. Aromatic polyimides (PI) and copolyimides (co-PI) have been well-known as a class of high-performance polymers possessing valuable properties, of which in particular, they exhibit high mechanical properties, outstanding thermal stability, good chemical resistance as well as good electrical and dielectric properties [3–6]. These combined properties have also made PI and co-PI fibers as one of the important members in the high-performance polymeric fibers.

Since it was initially carried out by Japanese [7–9] and Soviet researchers [10] in 1980's, preparation and fabrication of high-performance aromatic PI fibers have made significant progresses in the past three decades. Currently, two fiber-formation paths

have been well-developed. One is referred to as one-step method [11–15], which produces PI and co-PI fibers directly from organo-soluble PIs obtained in a one-step polycondensation reaction of dianhydride with diamine in phenol solvents such as p-chlorophenol [13,14]. Several series of PI and co-PI fibers with good mechanical properties were prepared with this technique. For PI fibers, e.g., 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA)/2,2'-dimethyl-4,4'-diaminobiphenyl (DMB) fibers with a tensile strength of 3.3 GPa and an initial modulus of 130 GPa prepared by Cheng et al. [11–13,16,17]. The limitation of monomer selection for organo-soluble PI and co-PI and the toxicity of the employed phenol solvents during the fiber spinning severely restrict in utilizing the one-step method, making the large-scale production and application of PI fibers be difficult.

As an alternative approach, many researchers turned their focus to the two-step method [18,19], that is first spinning a poly(amic acid) (PAA) into the PI precursor fibers and then followed by the subsequent thermal or chemical cyclimidization to convert the PAA into final PI fibers. This method has been considered to be promising for realizing industrial level production of PI fibers since it possesses the advantages of the extensive selection of monomers, utilization of low toxic solvents such as dimethylacetamide (DMAc),

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dimethylformamide (DMF) and N-methyl-2-ketopyrrolidone (NMP), and the retention of the excellent thermal stability, chemical and irradiation resistance of PI. However, the mechanical properties of the prepared PI fibers so far have not been in comparison with those produced fibers in the one-step spinning method. For example, the tensile strength and initial modulus of the pyromellitic dianhydride (PMDA)/4,4'-oxydianiline (ODA) PI fibers prepared by Park et al. were 0.4 GPa and 5.2 GPa respectively [20], and another PI fiber based on 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)/ODA reported by Jr et al. showed a tensile strength of 0.2 GPa and initial modulus of 3.5 GPa [18,21]. Therefore, the improvement of performances of the PI fibers prepared from this two-step spinning method becomes an urgent and challenging task.

To improve the mechanical properties of polymeric fibers, generally speaking, many methods have been employed. Among them, incorporating rigid aromatic heterocyclic units to increase the rigidity of the polymer backbone and introducing additional intermolecular associations such as hydrogen bonding and/or chemical cross-linking have been reported to be two of the most efficient approaches. They have been demonstrated in the commercially available high-performance aromatic polymer fibers such as poly(p-phenylene benzobisthiazole) (PBT) [22], poly(p-phenylene benzobisoxazole) (PBO) [23], poly(p-phenylene benzo-bisimidazol) (PBI) [24], and polypyridobisimidazole (PIPD, M5) [25,26]. Take M5 fibers as an example, by incorporating both the aromatic heterocyclic rigid-rod units and intermolecular hydrogen bonding interactions, the fibers were reported to achieve a tensile strength of 4.0 GPa and a modulus up to 360 GPa [25].

Inspired by these known successes, with the purpose of obtaining high-performance PI and co-PI fibers, in the present work, an aromatic heterocyclic diamine, 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone (AAQ), which possesses a strong hydrogen-bonding formation capability [27], was designed as the third monomer and copolymerized with the rigid BPDA and p-phenylenediamine (p-PDA) system to enhance intermolecular interactions via hydrogen bonding and cross-linking. The effects of the incorporated AAQ moieties on orientation and crystallinity of the co-PI fibers and their correlations with mechanical and thermal properties of the co-PI fibers are systematically investigated.

2. Experimental

2.1. Materials

The monomer BPDA was obtained from Shi Jiazhuang Hai Li Chemical Company, and purified by sublimation before use. The monomer p-PDA was obtained from Shangyu Li Xing Chemical Company, and purified by recrystallization. DMAc (analytical pure, $\leq 0.1\%$ contained water) was purchased from Tianjin Fu Chen Chemicals Reagent Factory and used after distillation. Quinazolinone amine, AAQ, was synthesized according to the procedure published in Refs. [27], and dried thoroughly under vacuum prior to use.

2.2. Preparation of BPDA/(p-PDA/AAQ) co-PI fibers

The co-PI fibers were prepared according to the following procedure. First, the BPDA/(p-PDA/AAQ) copoly(amic acid) (co-PAA) in solution was synthesized by dissolving the two diamines, p-PDA and AAQ in DMAc followed by the addition of equimolar amount of dianhydride gradually. After stirring at 0 °C under nitrogen atmosphere for 14 h, a yellow viscous solution with 15 wt% solid content was obtained. With this procedure, co-PAA resins with different AAQ/p-PDA mole ratio (0:10, 1:9, 3:7, 5:5, 7:3 and 9:1) were

synthesized in the present work. The inherent viscosities of the resulting solution varied in the range of 1.63–2.05 dL g⁻¹, as shown in Table 1, which are all suitable precursor resins for fiber spinning. The co-PI fibers were then prepared through the previously-described wet spinning method. First, the co-PAA precursor fibers were produced by extruding the viscous co-PAA solutions through a spinneret (100 holes, 75 μ m in diameter) using high-pressure nitrogen into a H₂O/DMAc coagulation bath with the concomitant drawing on three sets of spinning rollers with an entire drawing ratio of 1.3. co-PI fibers were then obtained by heating the co-PAA precursors under a drawing ratio of 1.05 continuously through a high-temperature tube oven at 240 °C for 3.5 min and subsequently, through another high-temperature tube oven at 370 °C for 5 min. During the thermal treatment process, the co-PAA was cyclimidized into its final co-PI form with the simultaneous formation of crystallization and orientation along the fiber direction, yielding co-PI fibers with desirable properties. The chemical structures of the BPDA/(p-PDA/AAQ) co-PAA and co-PI fibers synthesized in the present work are illustrated in Scheme 1.

2.3. Characterization

Intrinsic viscosities of the synthesized co-PAA were measured at 35 °C using a Germany SCHOTT 52510 Ubbelohde viscometer with capillary inner diameter of 0.58 mm. co-PAA solutions in DMAc with concentrations of 0.5, 1.0, 1.5, 2.0 mg ml⁻¹ were measured and the intrinsic viscosity was determined by extrapolating the concentration of co-PAA solution to zero.

Single fiber tensile testing was performed on an YG001A-1 instrument at an extension rate of 10 mm min⁻¹. The length of the fiber samples was set as 20 mm. For each type of fiber, at least 20 monofilaments were tested and the average values were used as the representative.

Fourier transform infrared (FTIR) spectra were obtained at a resolution of 4 cm⁻¹ on Nexus 670 instrument made by Nicolet Company. The samples were prepared by pulverizing the fibers with KBr to obtain discs. All measurements were carried out under ambient atmosphere conditions. Curve-fitting deconvolution of the infrared spectra was performed using Origin 8.5 Software to separate individual absorption contributions in the spectral region of 1750–1700 cm⁻¹. They were identified by a second-derivative analysis. The nonlinear least squares fitting method was used to obtain the best fit of the sum of the calculated peaks to that of the measured peaks. The bands were fitted assuming that the absorption peaks are in Gaussian type.

Two-dimensional wide angle X-ray diffraction (2D WAXD) experiments were conducted on a Rigakua 18 kW rotating anode X-ray generator using Cu K α radiation (0.1542 nm) in a transmission mode. R-Axis-IV image plate system was attached as the detector. The peak positions were calibrated using the diffraction of silicon powder ($2\theta = 28.47^\circ$). A bundle of closely-packed parallel fibers

Table 1

The intrinsic viscosities of the synthesized BPDA/(p-PDA/AAQ) co-PAA with different AAQ/p-PDA molar ratios and the mechanical properties of the corresponding co-PI fibers.

co-PI fibers	AAQ: p-PDA (molar ratio)	$[\eta]$ /(dL g ⁻¹)	Tensile strength/(GPa)	Modulus/(GPa)	Elongation/(%)
co-PI-0	0	1.78	1.2	64.6	2.1
co-PI-1	1:9	1.72	1.3	67.2	2.3
co-PI-2	3:7	2.05	2.7	104.8	3.1
co-PI-3	5:5	1.83	2.8	115.2	3.1
co-PI-4	7:3	1.63	2.7	113.1	2.7
co-PI-5	9:1	1.99	1.9	104.3	2.0

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