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Molecular orientation in aligned electrospun polyimide nanofibers by polarized FT-IR spectroscopy

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ABSTRACT

Quantitative explanation on the improved mechanical properties of aligned electrospun polyimide (PI) nanofibers as the increased imidization temperatures is highly required. In this work, polarized FT-IR spectroscopy is applied to solve this problem. Based on the polarized FT-IR spectroscopy and the molecular model in the fibers, the length of the repeat unit of PI molecule, the angle between the fiber axis and the symmetric stretching direction of carbonyl group on the imide ring, and the angle between the PI molecular axis and fiber axis are all investigated. The Mark-Howink equation is used to calculate the number-average molar mass of PI molecules. The orientation states of PI molecules in the electrospun nanofibers are studied from the number-average molar mass of PI molecules and the average fiber diameter. Quantitative analysis of the orientation factor of PI molecules in the electrospun nanofibers is performed by polarized FT-IR spectroscopy.

1. Introduction

Polyimides (PIs) are well known as high performance materials with excellent mechanical properties, thermal stabilities and chemical resistance, and have applications as thermally and electrically conductive composites materials, high temperature filters, aerogels, sponges, battery separators, gas separators, and so on [1–9]. PI nanofibers could be prepared by electrospinning even from water soluble precursors and have been proved with superior mechanical properties [3,10,11]. Previous studies have revealed that imidization temperatures played an important role in the mechanical properties of the aligned electrospun PI nanofiber belts (A-PI-NFB) [12–14]. Huang et al. found that A-A-PI-NFB based on 3, 3′, 4, 4′-biphenyltetracarboxylic dianhydride (BPDA) and *p*-phenylenediamine (PDA) imidized at 430 °C for 30 min showed tensile strength of 664 MPa and modulus of 15.3 GPa, which were 81% and 68% higher than those of the A-PI-NFB imidized at 300 °C for 60 min [12]. Recently, similar tendency was found on A-PI-NFB based on BPDA and 4,4′-diaminobiphenyl (BPA) by our group [13]. The A-PI-NFB showed enhanced mechanical properties as the increasee of imidization temperatures, specifically, the A-PI-NFB imidized at 330 °C exhibited the smallest tensile strength of 326 MPa and modulus of 5.0 GPa while the A-PI-NFB imidized at 450 °C possessed the highest tensile strength of 689 MPa and modulus of 13.2 GPa, respectively. There is no differences on the chemical structures of the samples from the infrared spectroscopy of A-PI-NFB. The imidization temperature has significant effect on the mechanical properties of A-PI-NFB which was investigated by X-ray diffraction (XRD) [12,13,15,16]. The XRD results showed that the increasing imidization temperatures led to the increase of the crystalline degree, which qualitatively explain the effect of imidization temperature on the mechanical properties. However, there are still no reports regarding the quantitative investigation on the molecular orientation in A-PI-NFB induced by the imidization temperatures.

Compared to the XRD and transmission electron microscopy (TEM), polarized infrared spectroscopy is a straightforward, convenient and inexpensive technique to quantitatively determine the molecular orientation in uniaxially aligned fibers and films [17–27]. According to the Fraser's work, the degree of polymer molecular orientation (f) in fibers could be calculated from the following formulas: [28].

$$D = \frac{A_{\parallel}}{A_{\perp}} \tag{1}$$

$$D_0 = \frac{A_{\parallel}}{A_{\perp}} = 2\ cot^2\alpha \tag{2}$$

$$\frac{D = f\ cos^2\alpha + \frac{1}{3}(1-f)}{\frac{1}{2}f\ sin^2\alpha + \frac{1}{3}(1-f)} \tag{3}$$

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$$f = \frac{D-1}{D+2} \times \frac{2}{3\ cos^2\alpha - 1} = \frac{(D-1)(D_0+2)}{(D+2)(D_0-1)} \quad (4)$$

$$D>1, f = \frac{D-1}{D+2} \quad (5)$$

$$D<1, f = \frac{2(1-D)}{D+2} \quad (6)$$

where $A_{\parallel}$ = the absorbance for light polarized parallel to fiber axis; $A_{\perp}$ = the absorbance for light polarized perpendicular to fiber axis; D = Dichroic ratio; D_0 = Dichroic ratio for a perfectly oriented specimen; f = perfect orientation; 1 - f = perfectly random orientation; α = angle between transition moment direction from the polarized FT-IR and molecular axis. In the above equations, the angle α between transition moment direction and molecular axis is important to determine the molecular orientation degree in fibers. However, there are no reports regarding the measurement and the determination of the angle between the transition moment direction and PI molecular axis, which led to the insufficient studies on the relationships between the PI molecular orientation degree and the mechanical properties of electrospun PI nanofibers.

In this work, the highly aligned PI nanofibers with different imidization temperatures were prepared, and the angle α between transition moment direction and PI molecular axis was estimated. Based on the angle α, we quantitatively investigate the effect of imidization temperatures on the molecular orientation and mechanical properties via polarized FT-IR and tensile tests. At last, a model which described the PI molecular orientation in electrospun PI nanofibers was proposed.

2. Experimental

2.1. Materials

3, 3′, 4, 4′-biphenyltetracarboxylic dianhydride (BPDA) (Jida Plastic Products Co. Hebei, China) and 4, 4′-diaminobiphenyl (BPA) (Kaiyuan Fine Chem. Co. Quzhou, China) were purified by sublimation before used. *N*, *N*′-dimethyl acetamide (DMAc) (Jingwei Chemical Co., Shanghai, China) was distilled over P_2O_5 under reduced pressure. Other materials were used as received.

2.2. Preparation of Aligned Polyimide Nanofibers

The PI precursor solution (10 wt%), polyamic acid (BPDA-BPA-PAA) was prepared by polycondensation from 5.8846 g of BPDA (0.0200 mol), 3.6848 g of BPA (0.0200 mol) and 86.0 g of DMAc with intense mechanical stirring at 0 °C for 24 h. The intrinsic viscosity of the PAA was 5.73 dl/g measured at a concentration of 0.25 g/dl at 25 °C. The as-synthesized PAA solution was diluted by DMAc to 4 wt%. Small amount cetyltrimethylammonium bromide (CTAB, 2 wt% respect to the PAA) was added to decrease the surface tension and increase the electrical conductivity of the electrospinning solution, respectively. The applied electric field was 100 kV/m, by imposing a 20 kV electrical potential to a 20 cm gap between a spinneret and a collector. The aligned nanofibers were collected by a disc (diameter: 0.15 m, disc rim: 3 cm) with high rotating speed of 1500 rpm. All the samples were first dried in an vacuum oven at 70 °C for 6 h to remove the residual solvent and then imidized in a high-temperature furnace using the following protocol: 1) heating up to 250 °C at a rate of 10 °C/min in N_2 and annealing for 30 min; 2) heating up to the final temperature (330, 370, 400, 430 and 450 °C) at a rate of 2 °C/min in N_2 and annealing for 60 min to complete the imidization process. The corresponding samples with different imidization temperatures were denoted as PI-330, PI-370, PI-400, PI-430 and PI-450, respectively.

2.3. Characterizations

Polarized FT-IR spectra were recorded by using a Bruker Tensor 27 spectrophotometer in the transmission mode with an accessory of Zn-Se polarizer. During measurement, the fiber alignment was parallel to the direction of 0° polarizer. The morphologies of PI nanofibers were characterized by a Quanta 200 scanning electron microscope (SEM) with an acceleration voltage of 20 kV. Before scanning, the specimens were sputter-coated with gold (2 nm) to avoid charge accumulations. The fiber alignment degree (d_{fa}) was calculated by the following equation: [29,30].

$$d_{fa} = \frac{3\ cos^2\theta - 1}{2} \quad (7)$$

where θ is the angle between the individual fiber alignment and the preferred direction along the rotation direction during the electrospinning.

3. Results and Discussion

3.1. Fiber Morphology and Orientation

Previous reports showed that no molecular orientation was observed in the randomly deposited nanofiber mats by polarized FT-IR due to the non-alignment of nanofibers, although the molecules were generally oriented along the fiber axis during electrospinning [19]. Therefore, it is important to prepare highly aligned electrospun nanofibers to rule out the effect of fiber alignment on the molecular orientation. As shown in Fig. 1, the obtained yellow PI nanofiber belt showed nearly perfect fiber alignment with fiber alignment degree (d_{fa}) >95%, which is a guarantee for the investigation of molecular orientation in electrospun nanofibers. It is well known that the fiber diameters play a significant role on the mechanical properties, that is the size effect on mechanical properties. Recently, Papkov et al. demonstrated that the reduction of electrospun fiber diameter from 2.8 μm to about 100 nm led to the great enhancement of elastic modules from 0.36 to 48 GPa, tensile strength from 15 to 1750 MPa and toughness from 0.25 to 605 MPa, respectively [31]. Similar size effects on mechanical properties of electrospun nanofibers were also observed by other research groups [32–34]. Therefore, in this study, to exclude the fiber size effect on the mechanical properties, all the samples, PI-330, PI-370, PI-400, PI-430 and PI-450 were obtained from the same original PAA belts to achieve the same fiber diameters. As shown in Fig. 1B and C, PI-330 and PI-450 showed average fiber diameters of 250 ± 39 nm and 252 ± 57 nm, respectively. The quite similar fiber diameters could be ascribed to the inheritance from the same PAA belts and the excellent thermal stabilities on diameter of BPDA-BPA-PI nanofibers, although the imidization temperatures are fairly different [13].

3.2. Angle between Fiber Axis and Molecular Axis

Fig. 2A presents the principle of polarized FT-IR measurement. When the transition moment (E) direction of polarized FT-IR is parallel to the vibration (M) of the functional group in molecules, the strongest IR peak could be observed. Otherwise smallest IR peak would be obtained when the E direction of polarized FT-IR is perpendicular to the M of molecular group. However, it is difficult to determine the preferred parallel or perpendicular direction by once or twice polarized FT-IR measurements. In this work, polarized FT-IR spectroscopy were recorded with every 5° polarized angle for the sample PI-330. Previous reports indicates that the signals at 1770 and 1719 cm^{-1} could be attributed to the symmetric and asymmetric stretching of the two carbonyl groups (C=O) on imide rings [35,36]. From the stretching style of C=O in Fig. 2A, it can be found that the directions of symmetric ($M_{s.str.(C=O)}$) and asymmetric ($M_{as.str.(C=O)}$) stretching are perpendicular. As shown in Fig. 2B and C, an increased signal intensity from 15° to 105° polarized angle and a