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High strength electrospun polymer nanofibers made from BPDA–PDA polyimide

Chaobo Huang, Suqing Wang, Hean Zhang, Tingting Li, Shuiliang Chen, Chuilin Lai, Haoqing Hou *

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330027, China
Department of Pharmacology, Jiangxi Medicine College, Nanchang 330006, China

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Abstract

A series of high molecular weight PI precursors, poly(*p*-phenylene biphenyltetracarboxamide acid), were synthesized from 3,4,3′,4′-biphenyltetracarboxylic dianhydride (BPDA) and *p*-phenylenediamine (PDA) by using intense mechanical stirring at −15 to 0 °C for 48–72 h. The as-synthesized PI precursor solution was used to make BPDA/PDA polyimide thin films and electrospun nanofibers. IR, Ostward Viscometer, CMT-8102 Electromechanical Universal Testing Machine and scanning electron microscope (SEM) were used for the characterizations of the as-synthesized PI precursor, PI films and nanofiber sheets. The high molecular weight BPDA/PDA PI thin films and electrospun nanofiber sheets possess excellent mechanical properties of up to 900 MPa tensile strength with up to 18.0 GPa E-modulus and up to 210 MPa tensile strength with up to 2.5 GPa E-modulus, respectively.

Keywords: High strength; Polyimide; Nanofiber; Electrospinning

1. Introduction

Aromatic polyimides have been extensively investigated for their excellent thermal stability and high mechanical properties, along with their good chemical resistance and electrical properties [1–6]. Because of these outstanding properties, their application in fibers, films, coatings, and composites has been studied for many years. Typical examples were DU Pont PI2611 films developed by Du Pont and Upilex© S developed by Ube (Japan). They were made from BPDA/PDA polyimide. The tensile strength of those films was up to 550 MPa (6 μm) and 400 MPa (25 μm), respectively [7,8].

Generally, the mechanical properties of the polymer material were determined by polymer molecular structure, weight, and chain packing morphology. For a given polyimide, its mechanical properties rely heavily on its molecular weight and imidization temperature and time [9–12]. In the work reported here, polyimide (PI), poly(*p*-phenylene biphenyltetracarboximide) (BPDA/PDA), with ultra-high molecular weight was formed from its precursor, poly(*p*-phenylene biphenyltetracarboxamide acid) (BP-PAA),

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[*] Corresponding author. Fax: +86 791 8517500.
E-mail address: haoqing@jxnu.edu.cn (H. Hou).

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which was synthesized from BPDA and PDA at low temperature. Mechanical property measurements showed that the BPDA/PDA PI derived from the high molecular weight precursor, BP-PAA with an inherent viscosity of 7.63 dL/g, possessed a tensile strength of 900 MPa and an E-modulus of 18.0 GPa for a thin film of 6 μm thickness. The electrospun non-aligned PI nanofiber sheets made from BP-PAA with an inherent viscosity of 5.38 dL/g possessed a tensile strength of above 200 MPa and an E-modulus of about 2.5 GPa.

2. Experimental

2.1. Materials and measurements

N,*N*-dimethylacetamide (DMPAc) (Shanghai Jinwei Chem. Co.) was distilled over P_2O_5 under reduced pressure. 3,4,3′,4′-Biphenyltetracarboxylic dianhydride (BPDA) (Hebei Jida Plastic Products Co.) and *p*-phenylenediamine (PDA) (Quzhou Kaiyuan Fine Chem. Company) were purified by sublimation before use.

Inherent viscosity of PI precursor BP-PAA was measured using an Ostward Viscometer and the polymer solution in DMAc at 25 °C. The viscosity, electrical conductivity and surface tension of the concentrated PI precursor solution in DMAc were measured using NDJ-8S digital viscometer, DDS-11D conductivity meter, and a self-made tensiometer using maximum bubble pressure method [13,14], respectively. IR spectra of PI thin film and nanofiber sheet samples were recorded on a Perkin Elmer 781 spectrophotometer. SEM images were taken using a Quanta 200 scanning electron microscope. The mechanical properties were measured using SANS CMT-8102 stretching tester at a speed of 5 mm/min using thin films of about 6 μm thickness and nanofiber sheets of about 1 μm thickness.

2.2. Synthesis of PI precursor BP-PAA

The typical example of polymerization is as follows: equimolar amounts of BPDA (2.9421 g, 0.01 mol) and P-DA (1.0814 g, 0.01 mol) and 36.0 g solvent DMAc were mixed in a 250 mL four-necked flask equipped with a mechanical stirrer, thermometer, nitrogen inlet and outlet, mechanically intense stirred at −15 °C for 72 h to give a highly sticky polymer solution. The inherent viscosity of the polymer product was measured to be 5.38 dL/g by diluting a bit precisely weighted amount of the as-synthesized highly sticky solution into diluted DMAc solution. The as-synthesized sticky PI precursor BP-PAA solution was kept in a freezer for the uses in making PI films and electrospun nanofibers. The inherent viscosities and synthesis conditions of other products were listed in Table 1.

Table 1
Inherent viscosity of BP-PAA

Name of products	[η] (dL/g)	Reaction time (h)/ temperature (°C)
PAA-1	4.24	48/0
PAA-2	5.17	72/0
PAA-3	5.38	72/−15
PAA-4	6.33	72/−10
PAA-5	7.63	72/−5

2.3. Preparation of BPDA–PDA PI film

The PI precursor BP-PAA solution was diluted using DMAc to give a 5 wt.% solution. The diluted solution was cast onto clean glass plates with a surface size of $35 \times 100\,\mathrm{mm}^2$, followed by drying at 80 °C for 20 min to form PI precursor BP-PAA thin film. The imidization of PI precursor films on glass plates were accomplished in a tubular glass reactor with an inner diameter of 55 mm at temperature from 100 to 450 °C under vacuum. The PI films were collected from the glass plates soaked in water at room temperature for a couple of days.

2.4. Electrospinning and preparation of PI nanofiber sheet

The electrospinning process was performed by using the above precursor solution in DMAc. Dodecyl ethyldimethylammonium bromide (DEDAB) of 0.118 wt.% compared to the precursor solution was used to increase the electrical conductivity of the solution for electrospinning processes. The electric fields were on the order of 200 kV/m, from a 50 kV electrical potential applied to a 25 cm gap between a spinneret and a 0.28 m diameter collector rotated at a controlled speed. The as-electrospun BP-PAA nanofibers were collected in a form of non-woven nanofiber sheet from the rotated collector. The nanofiber sheet was attached to a copper foil of 0.5 mm thickness. The copper foil with nanofiber sheet was rolled into a cylindrical tube with a diameter of about 50 mm. The imidization of nanofiber sheet was finished by using the above mentioned tubular glass reactor from 100 to 450 °C in vacuum.

3. Results and discussion

3.1. Preparation of PI precursor BP-PAA

Generally, the polycondensation between an aromatic dianhydride BPDA and an aromatic diamine PDA can be easily accomplished in an aprotic solvent such as DMAc to produce aromatic polyamic acid BP-PAA. The molecular weight of the as-formed BP-PAA heavily depends on the reaction temperature and reaction time as well as a stirring condition. In order to get high molecular weight polymer, intense mechanical stirring, low temperature of −15 to 0 °C, long reaction time of 48–72 h were used for the polymerization. The inherent viscosities of the as-synthesized polyamic acids were listed in Table 1. Here, the inherent viscosity, usually used to express molecular weight of polycondensation product, is used to characterize the molecular weight of BP-PAA products. The low reaction temperature was reported to be propitious for suppressing the by-product and producing high molecular weight product in a condensation between a diacyl chloride and a diamine [15]. However, the data in Table 1 show that too low temperature is not suitable to make a high molecular weight polymer. The high molecular weight polymer, BP-PAA with the highest inherent viscosity of 7.63 dL/g, was obtained at reaction temperature of −5 °C but at −15 °C. This can be explained that the reaction activity between BPDA and PDA is not enough or the movement of the formed polymer in reaction system is too slow at low temperature to form enough effective collisions between the reaction active sites.

3.2. Elctrospun PI precursor nanofiber sheets

The electrospinning process is a nanoprocess driven by a high electrical voltage power in a strong electrostatic field. Fig. 1 is a schematic of electrospinning device using polymer solution to produce nanofibers. Many process parameters, such as polymer concentration, electrical conductivity, surface tension of the used solution, molecular weight of the used polymer and the like, were reported to influence the diameter size and the surface morphology of the electrospun nanofibers [16–18]. The process parameters used for making BP-PAA electrospun nanofibers were listed in Table 2. SEM observation showed that the BP-PAA nanofibers made by using these process parameters in Table 2 were fine. The diameters of the nanofibers ranged from 50 to 250 nm with a main distribution of about 120 nm.

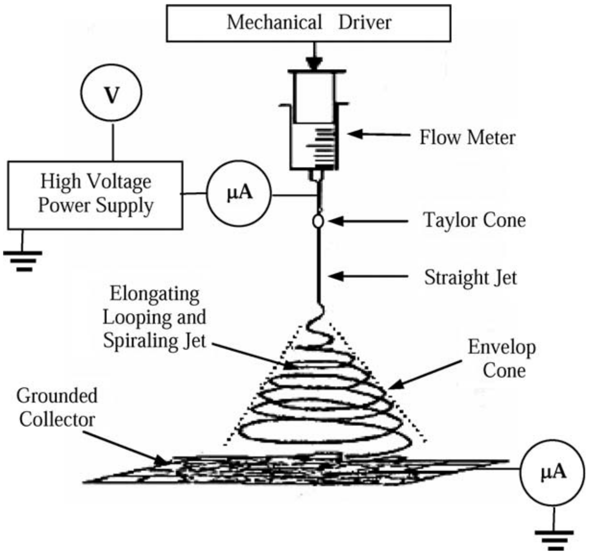

Fig. 1. Schematic of electrospinning set-up using polymer solution.

DEDAB is a kind of organic salt, which is electrical conductive. The electrical conductivity of the BP-PAA concentrated solution contained a small amount of DEDAB is much higher than that of the pristine solution. The small amount of DEDAB in the solution did not make obvious change on the viscosity and surface tension of the BP-PAA solution but electrical conductivity (see the data in Table 2). In the course of electrospinning process, an appropriate electrical conductivity of the polymer solution should make the Taylor cone and the solution jet endure more uniform electrical driven

Table 2
The solution parameters of electrospinning process

No.	$[\eta]_{25\,^\circ\mathrm{C}}$ (dL/g)	BP-PAA concen. (wt.%)	DEDAB concen. (wt.%)	Solution viscosity (Pa S)	Conductivity (μS/cm)	Surface tension (N/m)
1	5.38	5.0	0	4.789	1.1	76.14×10^{-3}
2	5.38	5.0	0.118	4.755	39.0	75.68×10^{-3}

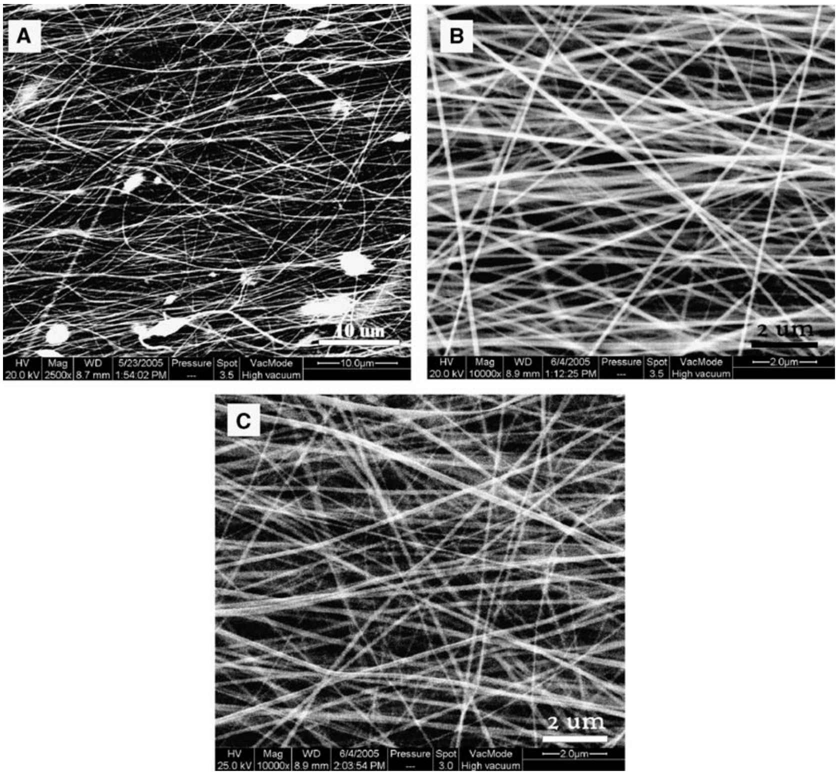

Fig. 2. Scanning electron microscopic images of the electrospun BPDA–PDA PI nanofibers collected using a rotated collector at a surface speed of 0.3 m/s. (A) Non-aligned nanofiber sheet of PI precursor BP-PAA containing a part of beaded nanofibers; (B) PI precursor BP-PAA nanofiber with a small amount of organic salt DEDAB; (C) BPDA–PDA PI nanofiber sheet.

force. As a result, no beaded solution jet was formed from the beginning or in the course of the rapid jet movement from the spinneret to the grounded collector. Therefore, a small amount of DEDAB in the BP-PAA solution was helpful for eliminating polymer beads on nanofibers to make the nanofibers smooth. SEM images (Fig. 2A) showed that the nanofibers formed using BP-PAA solution without DEDAB contained lots of beads on the fibers.

3.3. Imidization of BP-PAA films and nanofiber sheets

The imidization of the PI precursor BP-PAA thin films and electrospun nanofiber sheets were performed in a high temperature furnace, by the following steps: (1) 100 °C in vacuum for 1 h to remove the residue solvent; (2) heating up to 200 °C at a rate of 10 °C/min in vacuum and annealing for 30 min; (3) heating up to 250 °C at a rate of 5 °C/min and stayed for 30 min, then up to 300 °C at a rate of 5 °C/min and annealing for 30 min in vacuum to finish the imidization process of the precursor nanofiber sheets or films; (4) heating up to 450 °C at a rate of 2 °C/min in vacuum and annealing for 20 min for a heat-reduced self-ordering of PI molecules [19,20] in the PI thin film and nanofibers. The SEM images showed that there was no obvious difference between the PI precursor nanofibers and PI nanofibers (Fig. 2B and C).

Although the curing temperature was up to 450 °C, the IR spectra showed that the imidization of film sample was not perfect. As shown in Fig. 3B, the absorption band at around 3261 cm^{-1} indicated that there was still a part of N–H and O–H bondings in the macromolecular structure. However, the imidization of nanofiber sample was almost completed. The absorption peak attributed to N–H and O–H bondings did not appear in the range from 3000 and 4000 cm^{-1} on the IR spectrum of Fig. 3A. What resulted in the imidization difference between film sample and nanofiber sample keeps unknown for the time being.

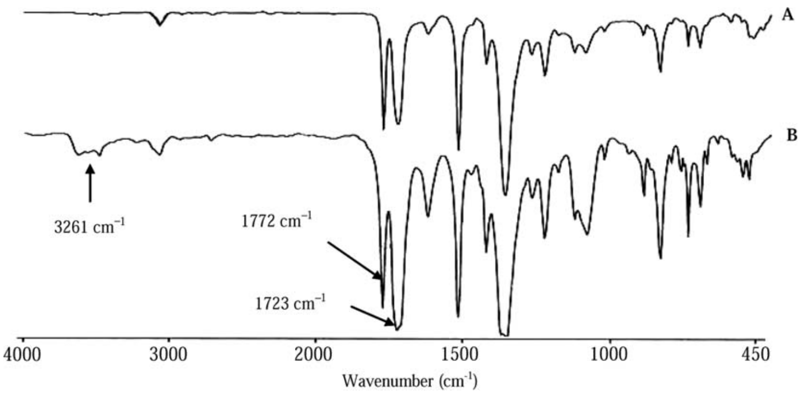

Fig. 3. FT-IR spectra of BPDA–PDA PI: (A) PI nanofiber sheet; (B) PI film.

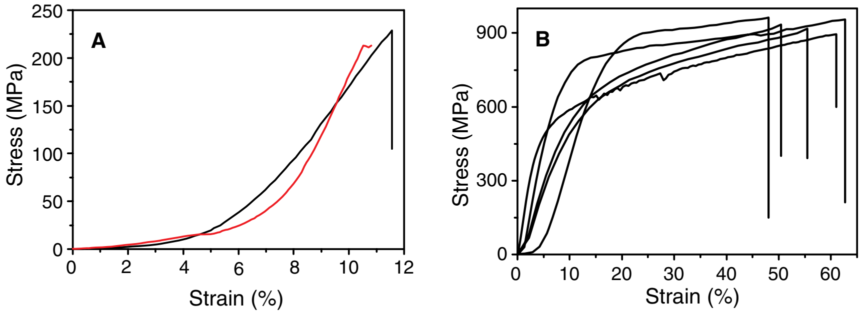

Fig. 4. Typical stress–strain curve of nanofiber sheets (A) of BPDA–PDA PI derived from precursor BP-PAA with high inherent viscosity of 5.38 dL/g and thin films (B) of BPDA–PDA PI derived from precursor BP-PAA with high inherent viscosity of 7.6 dL/g.

Table 3
Mechanical properties of BPDA–PDA PI thin film and nanofiber sheet

Name of the sample	PI precursor [η] (dL/g)	Film thickness (μm)	Tensile strength (MPa)	Young's modulus (GPa)	Strain (%)
PI-1(PAA-1)	4.24	5.9	450	7.6	50
PI-2(PAA-2)	5.17	6.0	610	10.3	50
PI-3(PAA-3)	5.38	6.0	720	12.5	52
PI-4(PAA-4)	6.33	6.1	870	16.0	45
PI-5(PAA-5)	7.63	6.3	900	18.0	55
Nanofiber sheet made by using PI-5 (PAA-5)	5.38	1.1	210	2.5	11

3.4. Mechanical property testing of BP-PAA PI thin films and nanofiber sheets

Mechanical property testing was performed using CMT-8102 Electromechanical Universal Testing Machine (SANS Company). The samples were prepared in 2 mm width and 60 mm length. The cross section of the nanofiber sheet sample was calculated via the sample weight and the BPDA–PDA PI density of 1.467 g/cm^3 [21]. The stress–strain curves in Fig. 4A shows that the tensile strength of the PI non-aligned nanofiber non-woven fabric is more than 200 MPa with an E-modulus of about 2.5 GPa, much higher compared to those previously reported tensile strength values (lower than 20 MPa) of electrospun nanofiber sheets [22–27]. BPDA–PDA PI thin film (6 μm) exhibited a tensile strength of more than 900 MPa and E-modulus of more than 18.0 GPa (Fig. 4B). The previously reported highest tensile strength of a thin film was 550 MPa (6 μm) and 400 MPa (25 μm), respectively [7,8]. The mechanical properties of BPDA–PDA PI thin film with different molecular weight were listed in Table 3. The data in Table 3 show that the mechanical property of the PI thin film relies on their molecular weight.

4. Conclusions

A series of PI precursors, poly(*p*-phenylene biphenyltetracarboxamide acid), were synthesized from BPDA and PDA using mechanically intense stirring at −15 to 0 °C for 48–72 h. The polyimide thin films and non-aligned nanofiber sheets, prepared by using the high molecular weight precursors, possess excellent mechanical properties of up to 900 MPa tensile strength with 18.0 GPa E-modulus and up to 210 MPa tensile strength with 2.5 GPa, respectively. One can expect that such excellent polymer will be used to make high performance electrospun nanofibers for uses in protective clothing, heat-resistance filter and so on.

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