Polymer 60 (2015) 221–227

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Intermolecular ordering as the precursor for stereocomplex formation in the electrospun polylactide fibers

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ARTICLE INFO

Article history:
Received 15 September 2014
Received in revised form
26 November 2014
Accepted 20 January 2015
Available online 27 January 2015

Keywords:
Precursor
Stereocomplex
Polylactide

ABSTRACT

Cold crystallization of electrospun fibers from poly (L-lactide)/poly (D-lactide) = 5/5 blends results in profuse stereocomplex crystals with little trace of homocrystals. In contrast, homocrystals prevail in the solution cast and melt-quenched films with same composition upon cold crystallization. With aid of FTIR technique it is confirmed that intermolecular ordering between poly (L-lactide) and poly (D-lactide) chains is induced in the electrospun blend fibers because of the interactions from the methyl and carbonyl groups. The intermolecular ordering acts as the precursor to trigger profuse stereocomplex formation in the electrospun blend fibers above glass transition temperature. Moreover, stereocomplex formation in the electrospun blend fibers follows one dimensional growth, as a result of confinement effects in an individual fiber.

1. Introduction

Polylactide, a kind of biodegradable and biocompatible material, is widely used in industrial and medical applications [1–3]. Polylactide has two enantiomers, i.e. poly (L-lactide) (PLLA) and poly (D-lactide) (PDLA). Racemic crystallization between PLLA and PDLA yields stereocomplex crystals where molecular chains of two enantiomers are alternatively packed in the unit cells [4,5]. Thus, stereocomplex formation is favored in the PLLA/PDLA = 5/5 blends. The specific interactions between enantiomeric chains impart peculiar properties to stereocomplex crystals, such as high thermal stability and high hydrolysis resistance [6–8].

Stereocomplex crystals can be obtained via racemic crystallization of PLLA/PDLA blends from solution, melt as well as glass [9–15]. However, homocrystals, composed of individual PLLA or PDLA chains, is always competed with stereocomplex crystals. What is worse, in the PLLA/PDLA = 5/5 blends with high molecular weight (over 10^5 g/mol), stereocomplex formation is significantly suppressed but homocrystallization prevails [6]. It arises from the decrease in the intermolecular diffusion and interactions between PLLA and PDLA chains with the increasing of molecular weight (i.e. kinetic barrier). To overcome this dilemma several approaches have been developed to promote stereocomplex formation in high-molecular-weight polylacide, for example low-temperature mixing, supercritical fluid technology and gelation in ionic liquids [16–19].

In addition, electrospinning from solutions also benefits stereocomplex formation in the PLLA/PDLA = 5/5 blends with high molecular weight [20]. It was argued that chain alignments induced by electrical fields increased the interactions between PLLA and PDLA chains and thus enhanced stereocomplex formation in the electrospun fibers. As claimed by the authors, however, the residual stereocomplex crystal nuclei in the solution could contribute to rapid formation and growth of stereocomplex crystals during electrospinning. In other cases, stereocomplex formation was scarcely induced in the PLLA/PDLA = 5/5 blends by electrospinning because of rapid solvent evaporation [21–24]. However, annealing above glass transition temperature resulted in high amount of stereocomplex crystals with little trace of homocrystals in the electrospun fibers. It arises from reorganization of molecular chains into stereocomplex crystals via cold crystallization, different from phase transformation of homocrystals into stereocomplex crystals through melting re-crystallization at high temperatures [25–28]. To date, detailed mechanism regarding stereocomplex formation in the electrospun fibers via cold crystallization is unclear yet.

In this study, the interactions from the methyl and carbonyl groups in the electrospun PLLA/PDLA = 5/5 blend fibers were disclosed with aid of FTIR technique. It corresponded to

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http://dx.doi.org/10.1016/j.polymer.2015.01.049
0032-3861/

intermolecular ordering between PLLA and PDLA chains. The intermolecular ordering as the precursor readily induced stereocomplex formation above glass transition temperature where enough molecular mobility was gained.

2. Experimental section

2.1. Materials and sample preparation

The PLLA and PDLA were supplied by Changchun Sinobiomaterials Co., Ltd, China. The viscosity-average molecular weight was 193 and 191 kg/mol for PLLA and PDLA, respectively. Weighted PLLA and PDLA were directly dissolved in the mixed solvents of chloroform and dimethylformamidine (10:1, v/v) at room temperature to generate a transparent solution with a concentration of 60 mg/ml; the mass ratio of PLLA and PDLA was 10/0, 9/1, 7/3 and 5/5, respectively. The solution was loaded in a 10 ml syringe with a needle and then pumped continuously at a rate of 25 μL/min. An applied voltage of 10 kV and a distance of 15 cm from the needle to collector (aluminum foils) were adopted. Electrospinning was carried out at room temperature, and the humidity in the atmosphere was about 70%. As a comparison, the solutions were cast onto aluminum foils to generate thin films to allow rapid solvent evaporation. The electrospun fibers and cast films were dried in vacuum at room temperature to remove residual solvents.

2.2. Characterizations

Fourier transform infrared spectroscopy (FTIR) measurements were conducted by a Thermo Nicolet FTIR spectrometer with a resolution of 2 cm^{-1}. To monitor in situ structural evolution, samples sandwiched between two ZnSe plates were mounted onto a KER3100-08S hot stage and then placed in the sample compartment of the FTIR equipment. Prior to measurements background spectra were collected for automatic subtraction from sample spectra. The samples were heated to the preset temperature at a rate of 40 °C/min for isothermal crystallization and at a rate of 5 °C/min for nonisothermal crystallization, respectively; and sample spectra were collected with a total of 16 scans. Thermal behaviors were recorded by a TA Q2000 differential scanning calorimetry (DSC) instrument at a heating rate of 10 °C/min in a flowing nitrogen atmosphere. The crystalline phase was determined by a Bruker D8 ADVANCE X-ray diffractometer (XRD) at room temperature; and the wavelength of the X-ray was 0.154 nm. The morphology of the electrospun fibers was probed by a Nova NanoSEM 450 scanning electron microscope (SEM). A thin gold layer was sputtered prior to SEM measurements.

3. Results and discussion

As demonstrated by the XRD profiles in Fig. 1a, diffuse diffraction is observed for the electrospun fibers and there is no difference between PLLA and its blends with PDLA. It means that little crystallization is induced during electrospinning, arising from that rapid evaporation of solvents makes amorphous chains have little chance to rearrange into crystals. After being heated above glass transition temperature (~60 °C), however, amorphous chains in the electrospun fibers undergo cold crystallization through molecular rearrangements. It is manifested by an exothermic peak in the temperature range between 60 and 90 °C, as shown by the DSC heating traces in Fig. 1b. Upon further heating crystals generated during cold crystallization melt at high temperatures, responsible for the appearance of endothermic peaks. The electrospun PLLA fibers exhibit an endothermic peak around 176 °C due to the melting of homocrystals. As a comparison, the electrospun PLLA/PDLA blend fibers show a melting peak around 225 °C. It corresponds to the melting of stereocomplex crystals with dense molecular packing in the unit cells [6]. Moreover, formation of stereocomplex crystals is increased with the PDLA content in the blend fibers, accompanied by the decrease in the amount of homocrystals. What is more, in the PLLA/PDLA = 5/5 blend fibers stereocomplex crystals prevail with little trace of homocrystals. It is correlated with alternative arrangement of PLLA and PDLA chains in the unit cells of stereocomplex crystals. The DSC heating traces indicate that stereocomplex crystals can be overwhelmingly obtained via cold crystallization in the electrospun PLLA/PDLA = 5/5 blend fibers, consistent with other observations [21–23].

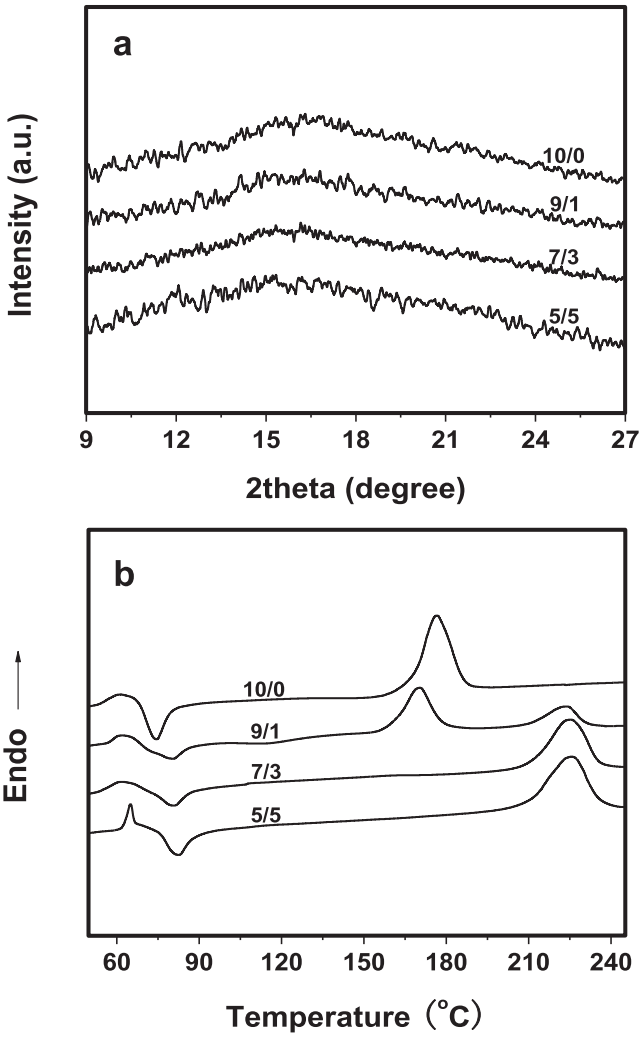

Fig. 1. XRD profiles (a) and DSC heating traces (b) of electrospun PLLA/PDLA blend fibers with the indicated composition.

To further understand stereocomplex formation in the electrospun PLLA/PDLA blend fibers via cold crystallization, isothermal annealing at 80 °C for 2 h and 110 °C for 1 h was carried out, respectively. Fig. 2 gives the corresponding results. Only homocrystals are presented in the electrospun PLLA fibers after annealing, irrespective of annealing temperatures. Homocrystals are indicated by the reflections at 2θ of about 16.5 and 18.8° in the XRD profiles and by a melting peak around 176 °C in the DSC heating traces, respectively. In contrast, annealing of electrospun blend fibers results in the XRD diffractions at 2θ around 12, 20.8 and 24°, corresponding to the formation of stereocomplex crystals. Moreover, stereocomplex formation is at expense of homocrystals,