Polymer Degradation and Stability 114 (2015) 8–15

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Effect of atactic poly(3-hydroxybutyrate) block on the crystallization and degradation behavior of 6-arm poly(L-lactide)-*b*-atactic poly(3-hydroxybutyrate)

Ni Jiang, Hideki Abe*

Bioplastic Research Team, Biomass Engineering Program Cooperation Division, RIKEN Center for Sustainable Resource Science, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan

ARTICLE INFO

Article history:
Received 11 December 2014
Received in revised form
15 January 2015
Accepted 25 January 2015
Available online 3 February 2015

Keywords:
Diblock copolymer
Structure effect
Crystallization
Degradation
Molecular mobility

ABSTRACT

6-arm poly(L-lactide) (6a-PLLA) homopolymer and a series of 6-arm poly(L-lactide)-*b*-atactic poly(3-hydroxybutyrate) (6a-PLLA-*b*-PHB) diblock copolymers were synthesized by ring-opening polymerization in the presence of Zn compound as catalyst and D-mannitol as initiator. The two block segments were found to be miscible according to the single T_g detected by the DSC. The structure effect of atactic PHB (ataPHB) block on the thermal stability, crystallization kinetic, melting behavior, and enzymatic degradation of diblock copolymer were investigated. The TGA results indicated that the thermal degradation of block copolymers started from the ataPHB block and thereby enhanced the thermal stability of PLLA block. No obvious changes were observed in the nucleation mechanism and crystal structure of the PLLA block, but the amorphous ataPHB block interrupted its crystallization, and induced lower crystallization rate and imperfect crystals. The enzymatic degradation rate of PLLA domains was determined in the presence of proteinase K. It was found that the erosion rate is strongly dependent on the length of ataPHB blocks. The degradation behavior was discussed from two aspects, i.e., the molecular mobility and retardation effect from ataPHB block.

1. Introduction

Poly(L-lactide) (PLLA) has attracted more and more attention from both fundamental research and practical application because of its good biodegradability and mechanical properties [1–3]. It has great potentials for substitution of petroleum-based polymers. However, the practical applications of PLLA have been significantly limited by its low thermal stability and inherent brittleness [4]. Therefore, both chemical and physical approaches have been developed for improving these properties [5–9]. Chemical method is frequently realized by copolymerization to produce graft or block copolymers, such as poly(vinyl alcohol)-g-poly(L-lactide), poly(L-lactide)-*b*-poly(oxypropylene)-*b*-poly(L-lactide), and poly(L-lactide)-*b*-poly(ε-caprolactone) [10–12]. For the physical approachs, the most easy and efficient way is to blend the PLLA with different kinds of fillers or other polymers with complementary property features, such as carbon nanotubes, poly(ε-caprolactone), and poly(butylene succinate) [13,14].

Microbial polyhydroxyalkanoates (PHAs) are produced by a wide variety of bacteria as an intracellular carbon and energy storage material [15]. Among them, poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are commercially available and produced on an industrial scale. However, the widespread application is also limited because of its brittleness, low impact resistance, and high production cost. Microbial PHBs that composed of (*R*)-3HB units are crystallizable and brittle. In contrast, chemically synthesized atactic PHB (ataPHB) is fully amorphous. Therefore, ataPHB with lower T_g is suitable for the chemical modification of PLLA. In addition, the copolymers of PLLA and PHB could act as compatibilizers for the blends of PLLA and PHB homopolymer or their copolymers and thereby regulate their nanosize structure, which are expected to enhance the properties of the blends. It will be more interesting to use star-shaped compatibilizer, where the chemical crosslinking point from the chemical structure may lead to more prominently effects. However, due to the difficulties with the ring-opening polymerization of

---

* Corresponding author. Tel.: +81 48 467 9394; fax: +81 48 462 4662.
E-mail address: habe@riken.jp (H. Abe).

http://dx.doi.org/10.1016/j.polymdegradstab.2015.01.026
0141-3910/© 2015 Elsevier Ltd. All rights reserved.

β-butyrolactone (BBL), studies on copolymers of PLLA and PHB are rare [9,16].

At the same time when we do chemical modification for more demanding applications, the change of chemical structure of polymers may greatly affect their crystallization and biodegradability which are the most essential properties of biodegradable polymers for application. So it is of great significance to demonstrate the influence of chemical structure on crystallization and degradation behavior of polymers. Extensive studies on the crystallization and degradation behavior of PLLA homopolymer have been carried out by many researchers. Three crystalline forms (α, β, and γ) have been reported for PLLA and the crystallization from melt or from solution leads to the most common α form crystal [17,18]. The crystallization kinetic of PLLA from the melt has also been analyzed by a number of research groups. It was found that PLLA shows a peculiar behavior with a maximum crystallization rate at around 100 °C and a discontinuity at around 110–120 °C. The appearance of the discontinuity has been correlated to the transition between regimes II and III [19], and it depends on the molecular weight, tacticity, and species for copolymerization [20]. The enzymatic degradation of PLLA and its copolymers by proteinase K from *T. album* was reported in several articles [21–24]. Although proteinase K has no specific adsorptive functional domain, it can irreversibly adsorb onto the PLLA surface for the hydrolysis reaction. Cai et al. studied the effect of the crystallinity on the enzymatic degradation of PLLA by proteinase K, and concluded that the degradation rate increases with decreasing crystallinity [21].

In this work, in order to study the influence of ataPHB with different length on the crystallization and degradation behavior of PLLA, 6-arm PLLA (6a-PLLA) homopolymer and a series of 6-arm poly (L-lactide)-*b*-atactic poly(3-hydroxybutyrate) (6a-PLLA-*b*-PHB) diblock copolymers were prepared by ring-opening polymerization in the presence of Zn compound. The thermal stability, crystallization behavior and degradation behavior of 6a-PLLA and 6a-PLLA-*b*-PHB were investigated by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized optical microscopy (POM), and scanning electron microscope (SEM) in detail.

2. Experimental

2.1. Materials

L-Lactide (L-LA) (Purac Co.) was recrystallized from toluene solution under isothermal condition at 65 °C. Racemic BBL was dried by CaH_2 and distilled under reduced pressure before use. The lipase of proteinase K was purchased from Sigma Company and used as received without further purification.

2.2. Synthesis

6a-PLLA and 6a-PLLA-*b*-PHB were synthesized in the presence of diethylzinc as catalyst. The L-LA monomer, diethylzinc catalyst, D-mannitol initiator and dichloromethane solvent were placed into a reactor in glove box. The polymerization was carried out at 40 °C under sealed condition for three days. For diblock copolymer, after the polymerization of L-LA, BBL was transferred into the reactor in glove box and then reacted at 40 °C again. The produced polyester was dissolved in chloroform and precipitated in methanol. The precipitate was dried in vacuo at room temperature. To remove the residual Zn compounds in the products, chloroform solutions of polymers (0.5% w/v) were washed with acetic acid for 3 times and then precipitated in methanol.

2.3. Enzymatic degradation

In order to eliminate the effect of crystallinity on the degradation of PLLA, the samples and a 0.1 mm Teflon spacer were first sandwiched between two Teflon sheets and pressed at 190 °C for 3 min. Then, they were immersed immediately into liquid nitrogen to preserve the amorphous state. Square specimens for degradation with dimension of 10 mm × 10 mm × 0.1 mm (about 12 mg) were cut from the melt-quenched amorphous films. The enzymatic degradation was performed in 1.0 ml Tris-buffer (0.05 M, pH = 8.6) containing 0.2 mg/ml proteinase K. The enzymatic degradation (8, 16, 24, and 32 h) was carried out in a mechanical shaker with a speed of 100 rpm at 37 °C. After degradation, the films were washed with distilled water and dried for 1 day under vacuum, and then the weight loss of the films was determined. The surface alteration of films was examined with the scanning electron microscope.

2.4. Characterization

The molecular structures of 6a-PLLA homopolymer and a series of 6a-PLLA-*b*-PHB diblock copolymers were determined by ^{1}H NMR analysis with JEOL R-400 spectrometers. The ^{1}H NMR spectra were recorded at 23 °C in a $CDCl_3$ solution of polymer (about 9 mg/mL). The molecular weight of the polymers was determined by gel permeation chromatography (GPC) measurements at 40 °C using a Shimadzu10A system and 10A refractive index detector with Shodex K-806 M and K-802 columns. Chloroform was used as the mobile phase at a flow rate of 0.8 mL/min. The system was calibrated by using polystyrene standards with a low polydispersity. Thermal gravimetric analysis (TGA) was carried out at a heating rate of 10 °C/min under nitrogen atmosphere. Thermal analysis of samples was conducted by DSC using a Perkin–Elmer Pyris 1 equipped with a cooling accessory under a nitrogen flow of 20 mL/min. The samples were heated from −30 to 200 °C at a rate of 20 °C/min. The melting temperature (T_m) was determined as the peak temperature of the DSC endotherms. For the measurement of the glass transition temperature (T_g), the samples maintained at 200 °C were rapidly quenched to −30 °C and then heated to 200 °C at a heating rate of 20 °C/min. The T_g was taken as the midpoint of the change in heat capacity. The wide-angle X-ray diffraction patterns of samples were recorded at 23 °C on a Rigaku RINT2500 system using nickel-filtered Cu KR radiation operated at 40 kV and 200 mA. The scan was carried out in the 2θ range of 5–40° at a scan speed of 1.0°/min. The spherulitic morphologies were observed with optical microscope equipped with crossed polarizers and a Linkam hot stage. For the SEM observation of films after degradation, the samples were coated with Au and performed with a JSM-6330F scanning electron microscope (JEOL) operated at an acceleration voltage of 5 kV at room temperature.

3. Results and discussion

3.1. Synthesis and characterization

6a-PLLAm homopolymer and a series of 6a-PLLAm-*b*-PHBn diblock copolymers (m and n denote the designed molar ratio between monomers and initiator) were synthesized by ring-opening polymerization in the presence of diethylzinc as catalyst and D-mannitol as initiator. Table 1 lists the polymer yields, number-average molecular weights (M_n), polydispersity (M_w/M_n), and the molar ratio of repeat units between PLLA and ataPHB (M) of the samples. With the introduction of ataPHB, the yields of polymerization decreased gradually from 91.8% to 58.7%, which maybe result from the lower conversion of BBL. Single peaks were found for all the synthetic samples from the GPC results, and the M_n and M_w/M_n