Polymer 52 (2011) 233–238

Contents lists available at ScienceDirect

Polymer

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

Polymer Communication

A novel phosphorus-containing poly(lactic acid) toward its flame retardation

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ARTICLE INFO

Article history:
Received 30 May 2010
Received in revised form
3 November 2010
Accepted 13 November 2010
Available online 23 November 2010

Keywords:
Flame retardance
Poly(lactic acid)
Chain extension

ABSTRACT

An inherently flame-retardant poly(lactic acid) (PLA) was synthesized via the chain-extending reactions of dihydroxyl terminated pre-poly(lactic acid) (pre-PLA), which was synthesized by direct polycondensation of L-lactic acid using 1,4-butanediol as initiator and stannous chloride ($SnCl_2$) as catalyst, using ethyl phosphorodichloridate as chain extender. The resulting phosphorus-containing poly(lactic acid) (PPLA) was characterized by gel permeation chromatography (GPC), ^1H and ^{31}P nuclear magnetic resonance (^1H, ^{31}P NMR) and homonuclear correlation spectroscopy (COSY) and inductively coupled plasma-mass (ICP). A comprehensive flame retardant property of PPLA was evaluated by microscale combustion calorimetry (MCC), limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimeter test (CCT). PPLA has excellent flame retardancy and also can be used as a flame retardant for commercial PLA. Only 5 wt.% of PPLA added into PLA can obtain good flame retardant properties. As the content of PPLA is further increased to 10 wt.%, PLA can have much better flame retardancy (LOI = 35 and UL-94 V-0 rating), lower peak heat release rate (pHRR) and longer ignition time (TTI) than neat PLA. All those results mean that this novel approach to impart flame retardancy to PLA is very effective.

1. Introduction

Poly(lactic acid) (PLA) is one of the most promising candidates in the field of biobased polymers because it is biodegradable and can be produced from renewable resources (sugar beets, corn starch, etc.). Recently PLA has been considered as alternative in replacing petrochemical polymers due to its excellent mechanical properties, high degree of transparency, and ease of fabrication [1]. Usually, PLA can be synthesized by direct polycondensation of lactic acid, or chain extension after polycondensation and by ring-opening polymerization of lactide [2,3]. Currently, although the main use of PLA is still in biomedical application, its other applications are increasing because of its excellent potential properties. Actually, PLA has been used in electronic industries now, such as the housings of portable word processors [4]. Unfortunately, PLA is still as flammable as common synthetic thermoplastics, such as polyethylene, polyester, and so on owing to its own intrinsic chemical composition and molecular structures. Predictably, the flammability will limit its application and development, especially its potential wide application in the electronic field. Therefore, the improvement of flame retardant performance of PLA has been an important and urgent task.

Unfortunately, so far few research reports have focused on flame retarded PLA in literatures. Several report employed ammonium phosphate, [5,6] melamine phosphate, [7] aluminium hydroxide, [8] silica gel [9] and compounds containing halogen and talc [10] as additive flame retardants for PLA matrix. Lately, Casetta and Bourbigot et al. evaluated the efficiency of intumescent formulations to flame-retardant PLA; those are composed of ammonium polyphosphate (APP), pentaerythritol (PER), lignin and starch [11]. The results show the flame retardancy of PLA has been improved greatly as the flame retardant reached a loading level of 40wt%. In our latest studies, a series of flame retardant toughened PLA composites have been prepared using poly(ethylene glycol) (PEG6000) and ammonium polyphosphate (APP) [12].

In the present study, we developed a novel approach to the preparation of flame-retardant PLA. We used a reactive flame retardant, ethyl phosphorodichloridate, as a chain extender to synthesize poly(lactic acid) containing phosphorus in the backbone (PPLA), shown in Scheme 1. The inherently flame-retardant PPLA has excellent flame retardancy, and can also be used as a flame retardant for PLA. The flame retardancy of PPLA and its blends with PLA has been investigated via microscale combustion calorimetry (MCC), limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimeter test (CCT).

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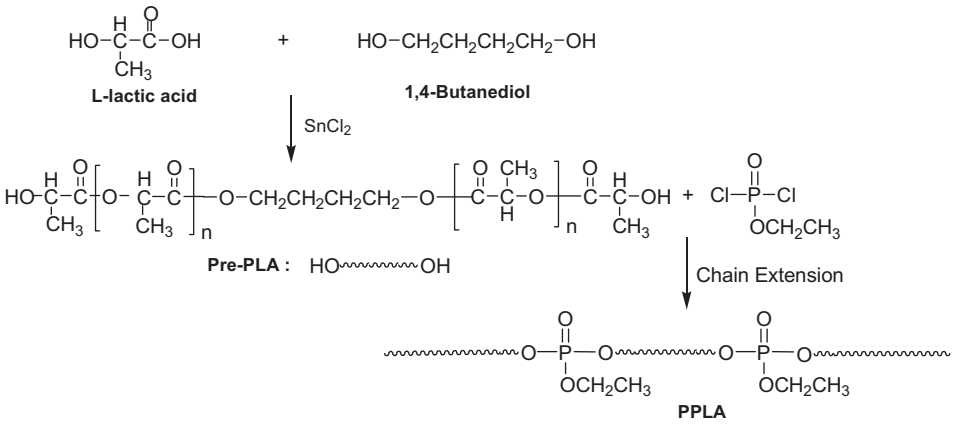
doi:10.1016/j.polymer.2010.11.023



Scheme 1. Pre-polymerization of L-lactic acid using 1,4-butanediol as an initiator and chain extension of PPLA using ethyl phosphorodichloridate as a chain extender.

2. Experimental part

2.1. Materials

L-Lactic acid was supplied from Guangshui Chemical Reagent Corp (Hubei, China). 1,4-Butanediol was provided by Bodi Chemical Reagent Corp. (Tianjin, China). Stannous chloride ($SnCl_2 \cdot 2H_2O$) was provided by Jinshan Chemical Reagent Corp. (Chengdu, China), ethanol and phosphoryl trichloride ($POCl_3$) were provided by Kelong Chemical Reagent Corp. (Chengdu, China). Trichloromethane ($CHCl_3$) was provided by Changlian Chemical Corp. (Chengdu, China). PLA resin (Mw = 10^5 g/mol) was provided by Nature Works (Grade: 4032D).

2.2. Preparation of ethyl phosphorodichloridate [13]

A typical procedure was as follows: 0.001 mol of $POCl_3$ and 100 mL of ether were first added into a 500 mL 3-necked round-bottom flask equipped with condenser and magnetic stirrer, and kept below 5 °C by the immersion of the flask in an ice-water bath. At this temperature, 0.001 mol of ethanol was added into the flask slowly and the reaction maintained for 2 h. Then, the flask was heated to 10 °C and maintained for 20 min. After that, the contents were distilled to remove ether at ambient pressure, followed by collecting the distillate (ethyl phosphoryldichloride) at 68–74 °C as the reactor pressure was reduced to 0.1 MPa. The FTIR spectra (KBr disc) of the ethyl phosphoryldichloride: 2940–2955, 1456 cm^{-1} ($-CH_2-$, $-CH_3$); 1246 cm^{-1} (P=O); 1089, 1027, 981 cm^{-1} (P–O–C); 500–600 cm^{-1} (P–Cl). ^1H NMR ($CDCl_3$, 400 MHz) δ: 4.20 (q, 2H); 1.45 (t, 3H).

2.3. Chain extension of PLA prepolymer using ethyl phosphoryldichloride

A representative procedure was divided to two steps: (a) preparation of the precursor, dihydroxyl terminated pre-poly(lactic acid) (pre-PLA), and (b) chain extension of pre-PLA. For the first step, a typical procedure was as follows: after L-lactic acid (L-LA), 1, 4-butanediol (BD) and stannous chloride ($SnCl_2 \cdot 2H_2O$) were added into a flask ($SnCl_2$:BD:L-LA = 0.5:1:100, weight ratio), the flask was heated in an oil bath to 80 °C with stirring as the reactor pressure was reduced to 0.1 MPa. After 3 h, it was heated to 160 °C and kept for 4.5 h so that the esterification reaction took place. After the esterification reaction, the reactor pressure was reduced to 70 Pa, and in another 5 h the pre-poly(lactic acid) was obtained. For chain extension of pre-poly(lactic acid) to prepare PPLA, a typical procedure was as follows: 30.0 g of pre-PLA and 1.78 mL of ethyl phosphoryldichloride were charged in a 3-necked round-bottom flask equipped with an overhead stirring. The polymerization was carried out in an oil bath at a temperature of 160 °C for 10 min, then the reactor pressure was reduced to 50 Pa, and 1 h later the chain-extended PLA containing phosphorus was obtained. In order to purify the PPLA and remove the unreacted pre-PLA and ethyl phosphoryldichloride, the resulting product was dissolved in chloroform, and then was precipitated in excess methanol. The same purification process was carried out twice in order to obtain purified PPLA. Finally, the product was dried in a vacuum oven at 60 °C until constant weight was attained.

2.4. Instrumentation

The chemical structure of the resulting polymers was characterized by ^1H and ^{31}P nuclear magnetic resonance (^1H, ^{31}P NMR, Bruker FT-80A NMR, d_6-DMSO as a solvent) and FTIR (Nicolet FTIR 170SX infrared spectrophotometer, KBr powder), respectively. Molecular weight was measured by using gel permeation chromatography (GPC, Waters; 2414 detector, $CHCl_3$ as a solvent). The phosphorus contents of the phosphorus-containing PLA were analyzed using an IRIS ADV inductively coupled plasma-mass (ICP) spectrometer. The flame retardancy and flammability were determined by LOI test (JF-3 oxygen index meter, Jiangning, China; using sheet dimensions of 130 mm × 6.5 mm × 3 mm according to ASTM D2863-97), UL-94 measurement (CZF-2-type, Jiangning, China; using sheet dimensions of 130 mm × 13 mm × 3 mm according to ASTM D3801) and cone calorimeter test (FTT cone calorimeter; square specimens, 100 mm × 100 mm × 6 mm were irradiated at a heat flux of 35 kW/m^2 according to ISO 5660 standard procedures without the use of the "frame and grid"). The microscale combustion calorimeter test (MCC, FTT) was also carried out according to ASTM D7309-07. All the specimens sheets for various tests were made by hot pressing at 10 MPa for 5 min at 170 °C into a suitable thickness and size, according to the corresponding test standards.

3. Results and discussion

3.1. Synthesis and structural characterization of phosphorus-containing PLA (PPLA)

1,4-Butanediol was used as an initiator for polymerization of lactic acid in the presence of stannous chloride, as shown in Scheme 1, so as to obtain dihydroxyl terminated pre-poly(lactic acid) (pre-PLA) with Mn of 0.8 × 10^4 g/mol (Mw = 1.1 × 10^4 g/mol, PDI = 1.4),