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Synthesis of Poly(D-lactic acid) Using a 2-Steps Direct Polycondensation Process

Sommai Pivsa-Art*, Thikanda Tong-ngok, Supansa Junngam, Rutchaneekorn Wongpajan and Weraporn Pivsa-Art

Department of Chemical and Materials Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Klong 6, Thanyaburi, Pathumthani 12110

Abstract

A two steps direct polycondensation process of poly(D-lactic acid) (PDLA) synthesis was studied. The melt-polymerization was combined with esterification using p-Toluenesulfonic acid without addition of metal catalyst. The pre-polymer product from the first step was subsequently subjected to solid-state polymerization (SSP) under high temperature and reduced pressure. Prior to the SSP process, the pre-polymer was characterized its thermal property to detect the crystallization temperature (T_c). The pre-polymers were annealed at temperature T_c for 2 h until the crystallization peak disappeared. The SSP of pre-polymers was carried out for 30 h to produce the satisfied thermal property and high molecular weight. The synthesized poly(D-lactic acid) showed melting temperature of 177^{o}C, weight average molecular weight of 33,300 Da, and decomposition temperature of 255^{o}C.

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Keywords: Biodegradable Polymer; Direct polycondensation; Poly(D-lactic acid); Thermal property

1. Introduction

Poly(lactic acid), (PLA) is a biodegradable semicrystalline polyester having mechanical property comparable or higher than the commercial polymers. PLA can be synthesized via two processes; direct polycondensation of lactic acid and ring-opening polymerization of lactide, a ring oligomer of lactic acid. The latter process can produce PLA with very high molecular weight within a short polymerization time. However, lactide monomer must be produced by thermal decomposition of the lactic acid oligomer and highly purified before polymerization which arise to high price and handle difficulty of lactide raw material [1]. On the other hand, the direct polycondensation process simply uses inexpensive lactic acid.

* Corresponding author. Tel.: +66-2549-3401; fax: +66-2577-5026.
E-mail address: sommai.p@en.rmutt.ac.th

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However, the chemical equilibria among PLA, H_2O and lactide limits the production of high molecular weight polymer product.

There are 2 stereoisomes of lactic acids; L- and D-lactic acid. Therefore, the polymer products can be synthesized in various forms of poly(L-lactic acid) (PLLA), poly(D-lactic acid) (PDLA), or racemic products. High stereoisomeric excess of each PLLA and PDLA are needed for high thermal property stereocomplex poly(lactic acid) preparation. While PLLA synthesis have been reported but PDLA production is rarely found which may due to high price of D-lactide. The process for PLLA synthesis using direct polycondensation gives higher purity of polymer product. We have studied the synthesis of high purity PLLA from L-lactic acid by a 2 steps direct polycondensation process using *p*-Tolenesulfonic acid as catalyst. Therefore, we have applied this process to synthesize PDLA from D-lactic acid. The process and polymer product property analysis are discussed.

2. Experimental

2.1. Materials and Synthesis Procedure

D-Lactic acid was supplied from 2 sources (1) D-Lactic acid from Musashino Ltd., Japan, and is coded as DLA01 and (2) D-Lactic acid synthesized by the National Project on Bioplastics and Biodegradable Materials, Kasetsart University, Thailand, and is coded as DLA02. 2-Naphthalenesulfonic acid (2-NSA) was purchased from Sigma Aldrich, Germany and used as received.

Poly(D-lactic acid) (PDLA) was synthesized by 2 steps direct polycondensation comprised of mely polymerization and solid state polymerization. In melt polymerization, D-Lactic acid was placed in the 250 ml three-neck flask equipped with agitator and 0.5 wt% 2-NSA was added. The reaction was started at room temperature under atmospheric pressure. Then, the temperature was gradually increased and the pressure was reduced continuously until 160 ^{o}C, 30 torr for 4 h. The pre-polymer of D-lactic acid oligomer having degree of polymerisation of 4-7 was annealed at its crystallization temperature for 2 h. The pre-polymer was ground to fine power and subjected to solid state polymerization (SSP) under 10 torr at temperature under its melting temperature (T_m).

3. Results and Discussions

3.1. Thermal Analysis of PDLA

The pre-polymers and PDLA synthesized from D-lactic of different two sources, DLA01 and DLA02 were analyzed their thermal properties using differential scanning calorimetry method. The results are shown in Fig. 1

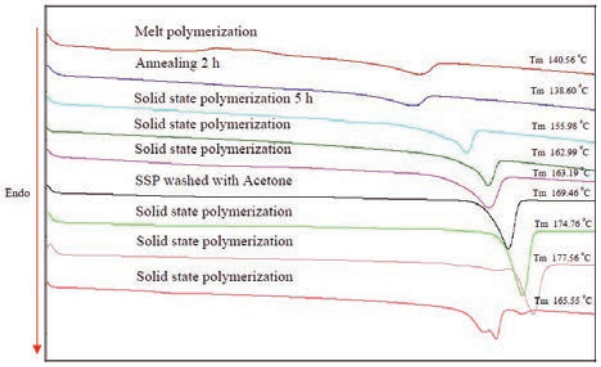

Fig. 1. DSC analysis of PDLA synthesized from DLA01

The oligomer from melt polymerization was subjected to solid state polymerization to extend the chain length and increase the polymer molecular weight starting from 130 ^{o}C, pressure 10 torr for 5 h. The melting temperature (T_m) of polymer sample was 155.98 ^{o}C. Then, the polymer was further polymerized 145 ^{o}C, 10 torr for 5 h. The Tg of PDLA increased to 163 ^{o}C. Further polymerized 150 ^{o}C, 10 torr, 5h increased T_m 164 ^{o}C, and next 5 h polymerization at 155 ^{o}C (total 20 h) increased Tm to 169.46 ^{o}C. The highest T_m of PDLA was found at the reaction time of 30 h of 177.56 ^{o}C. But after 30 h further polymerization decreased the T_m of PDLA which indicated the decreased in the thermal chain scission. Some parts of PDLA samples was dissolved in acetone to remove oligomers and impurities and analyzed the thermal property. The T_m of PDLA from DSC results showed sharp peak.

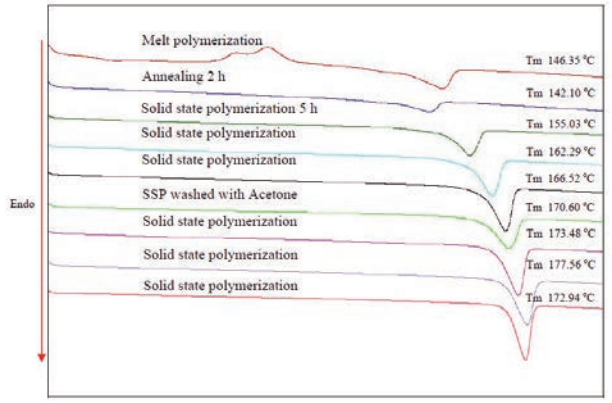

Fig. 2. DSC analysis of PDLA synthesized from DLA02

The pre-polymer of DLA02 from melt polymerization process was subjected to solid-state polymerization similar to the polymerization of DLA01 using starting condition of 130 ^{o}C, pressure 10 torr for 5 h. The melting temperature of each 5 h of solid-state polymerization increased with same tendency. After 30 h the T_m of PDLA was 177.56 ^{o}C. It was also found that the melting temperature of polymer of polymerization beyond 30 h decreased which confirmed chain scission under high temperature.

3.2. Thermogravimetric analysis (TGA) of PDLA

Poly(D-lactic acid)s synthesized from DLA01 and DLA02 were subjected to thermogravimetric analysis (TGA). The results are shown in Fig. 3 and 4. It was found that PDLA of DLA01 showed onset degradation temperature at 255 ^{o}C while the PDLA of DLA02 started to degraded at 327^{o}C.

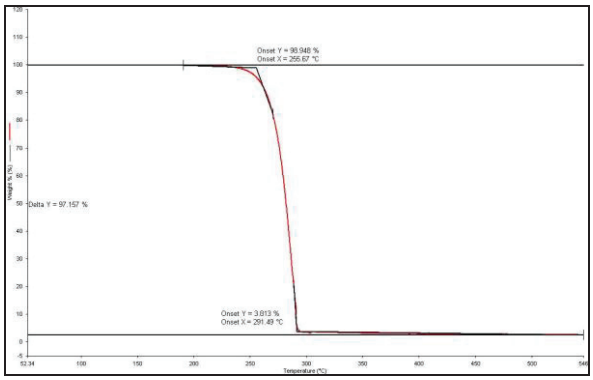

Fig. 3. Thermogravimetric Analysis of PDLA synthesized from DLA01

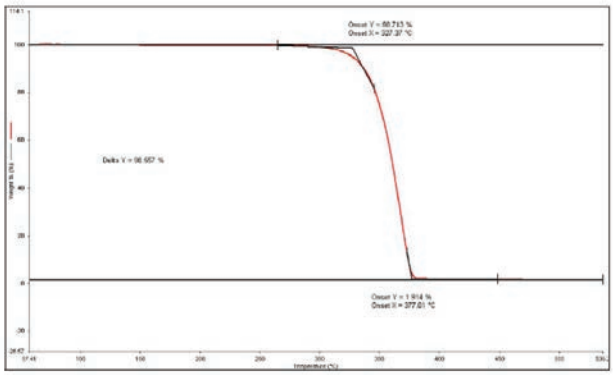

Fig. 4. Thermogravimetric Analysis of PDLA synthesized from DLA02

3.3. Polymer Molecular Weight Analysis

PDLA synthesized from DLA01 and DLA02 were analyzed their molecular weight in the solid state polymerization by Gel Permeation Chromatography (GPC). The results are shown in Fig. 5 and 6.

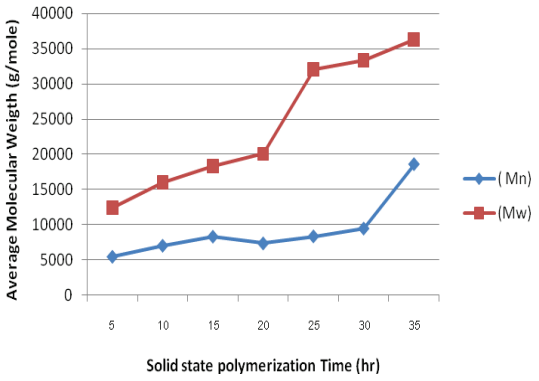

Fig. 5. Relationship of polymer molecular weight and solid state polymerization time of DLA01

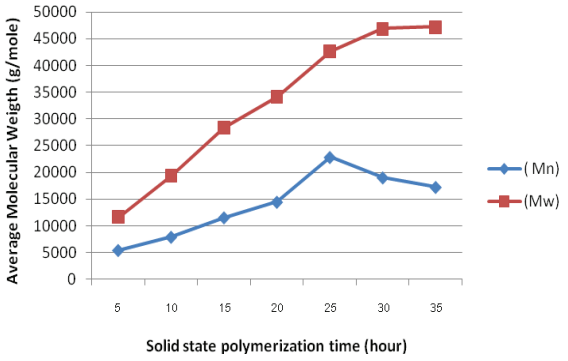

Fig. 6. Relationship of polymer moleclar weight and solid state polymerization time of DLA02

It was found that PDLA synthesized from DLA01 and DLA02 showed increasing of molecular weight with increasing reaction time while DLA02 showed higher molecular weight at same reaction time. The molecular weight distribution (Mw/Mn) also showed the same tendency of increasing with reaction time. The color of both PDLA is white. The PDLA synthesized via direct polycondensation of D-lactic acid showed high melting temperature which can be applied to stereocomplex poly(lactic acid) synthesis from high enantiomeric PLLA and PDLA.

4. Conclusion

Poly(D-lactic acid) (PDLA) was successfully synthesized by a 2 step direct polycondensation process from D-lactic acid using 2-Naphthalenesulfonic acid (2-NSA) as catalyst. D-lactic acids from 2 sources; DLA01 and DLA02, were studied to compare the property of synthesized polymers. Melt polymerization of D-lactic acid was carried out at 160^{o}C, 30 torr with gradually increasing of temperature and reduced pressure. The pre-polymer synthesized was further polymerized by solid-state polymerization under reduced pressure to 10 torr. The produced PDLA showed satisfied high molecular weight. The PDLA synthesized from DLA02 showed higher thermal stability than the polymer synthesized from DLA01.

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