การศึกษาสมบัติเฉพาะของพอลิแอลแลกติกแอซิดที่เตรียมโดยกระบวนการ พอลิเมอไรเซชันแบบบัลค์ โดยใช้ทิทาเนียมบิวทอกไซด์และองค์ประกอบของแสตนนัท Characterization of poly(L-lactic acid) prepared by bulk polymerization process using titanium(IV) butoxide and stannous(II) compounds

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บทคัดย่อ

ศึกษาสมบัติเฉพาะของพอลิแอลแลกติกแอซิด (PLLA) จากแลกติกแอซิดมอนอเมอร์ โดยใช้ทิทาเนียมบิวทอก ไซด์ (TNBT) และองค์ประกอบของแสตนนัท (SnCl₂.2H₂O และSn(Oct)₂) เป็นตัวริเริ่มปฏิกิริยา ซึ่งตรวจสอบ โครงสร้างทางเคมีของ PLLA โดยFT-IR, ¹H-NMR และ ¹³C NMR จาก TG/DTA พบว่า PLLA เริ่มเกิดการสลาย ตัวที่อุณหภูมิประมาณ 210-230 °C และสลายตัวหมดที่อุณหภูมิประมาณ 270-400°C ค่า T และ T อยู่ที่ 55°C และ 135-145°C ตามลำดับ จากการตรวจสอบน้ำหนักโมเลกุลด้วยเทคนิค GPC พบว่า PLLA ที่สังเคราะห์ได้ คือ 8200 และ 18500 กรัมต่อโมล ซึ่งสังเคราะห์โดยใช้ TNBT และ องค์ประกอบของ Sn ตามลำดับ

Abstract

Characterization of Poly(L-lactic acid)(PLLA) was carried out by L-lactic acid monomer using Titanium(IV) butoxide (TNBT) and Stannous(II) compound(SnCl₂.2H₂O) and Sn(Oct)₂) as catalyst. PLLA chemical structure was confirmed by FT-IR, ¹H NMR, ¹³C NMR. The results from TG/DTA showed the PLLA started to degrade around 210-230°C and completely decompose at 270-400°C. T_g and T_m obtained from DSC were 55°C and 135-145°C, respectively. Molecular weight of PLLA determined by gel permeantion chromatography (GPC), were 8200 and 18500 g/mol when using TNBT and Sn(II) compounds as a catalyst, respectively

คำสำคัญ: พอลิเมอไรเซชันแบบควบแน่น, พอลิแอลแลกติกแอซิด, แอลแลกติกแอซิด, พอลิเมอร์ชีวภาพ **Keywords:** Polycondensation, Poly(L-lactic acid), L-lactic acid, Biopolymer

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1. Introduction

The production of plastics is expanding systematically and can also cause large amount of waste. This due to the fact that the majority of conventional plastics are not readily degraded under biological conditions. Both recycling and combustion are the process which permit only a partial solution of the above-mentioned problem. Thus, in recent years there is an intensive development in investigations of biodegradable polymer, exclusively the poly(lactic acid) (PLA) (Hideto et.al., 1991)

Homopolymer of poly(L-lactic acid)(PLLA) or poly(D-lactic acid)(PDLA) are semicrystalline (60-70% crystalline) with glass transition temperature(T_{i}) and melting transition temperature(T_{i}) at around 55 and 140-190°C, respectively. PLA is biocompatible and degraded by hydrolytic chain scission into lactic acid, natural intermediate in carbohydrate metabolism (Catia Bastioli, 2004).

The degradation of PLLA depends on amorphous phase and crystalline phase. The molecular weight decreases rapidly during the first 50 days while crystalline phase less degradable the amorphous phase (Ann-Christine, 2002)

PLLA are biodegradable aliphatic polyester which usually has been prepared by ring-opening polymerization(ROP) of L-lactide. Recently, it has become accepted that the polycondensation of L-lactic acid(LA) can be used in preparing a high polymer of PLLA of LA by using Sn(II) compounds as a catalyst, actively by proton acid as the co-catalyst.

The objective of this study is to prepare and characterize PLLA which synthesize from LA monomer through polycondensation in bulk state using TNBT and Sn(II) compounds as a catalyst.

2. Experimental

LA (85-90 wt% in water) was purified by distillation under vacuum. Polymerization of PLLA was carried out by condensation in bulk state using TNBT, SnCl₂.2H₂O or Sn(Oct)₂ as a catalyst. 10 g of LA was added into a two-neck reactor equipped with Dean-stark trap (see figure 1) and then 0.5 g of catalyst (TNBT, SnCl_.2H_O or Sn(Oct) was added. The mixture was heated at 140°C under atmosphere condition. The resulting polymer were dissolved in dichlomethane and filtered to remove catalyst. The polymer was precipitated by pouring the polymer solution into an excess of methanol, filtered and dried in an oven at 60°C for 24 hour. The chemical structure of poly(L-lactic acid) was characterized by FT- IR, ¹³C NMR and ¹H NMR. The thermal behaviors of Poly(L-lactic acid) were characterized using by TG-DTA and DSC technique. The molecular weights of the polymer were measured by gel permeation chromatography (GPC).



Figure 1. Apparatus for polycondensation reation

3. Results and discussion

3.1. Fourier transform infrared spectrophotometer (FT-IR)

Figure 2 shows FT-IR spectrum of LA, PLLA-TNBT ,PLLA-SnCl₂ and PLLA-Sn(Oct)₂. The characteristic peaks of PLLA-TNBT, PLLA-SnCl₂ and PLLA-Sn(Oct)₂ were 1293 cm⁻¹ indicated C-O stretching, 1457 cm⁻¹ indicated C-C stretching, 1760 cm⁻¹ indicated C=O stretching and 2949 cm⁻¹ indicate C-H stretching. As L-lactic acid was polymerized, the hydroxyl group (-OH) will react with carboxylic group (COOH) therefore the -OH stretch peak at 3440 cm⁻¹ was reduced in the PLLA spectrum.

3.2. Nuclear magnetic resonance (NMR)

Figure 3 shows ¹H NMR spectra of PLLA-TNBT which was similar to the ¹³C NMR spectrum of PLLA-SnCl₂ and PLLA-Sn(Oct)₂. They composed of three peaks located to methyl, methane and carbonyl carbon atom, respectively. ¹H NMR spectrum of PLLA-TNBT is shown in Figure 4. The methine bond and methyl group was observed at 5.1 and 1.5 ppm, respectively.

3.3. Thermo-Gravimetric/Differential Thermal Analyzer (TG/DTA)

Figure 5 shows the TG/DTG curves of PLLA at a heating rate of 10°C. Both, PLLA-SnCl₂ and PLLA-TNBT started to degrade at around 230°C and completely decomposed at 270°C but PLLA-Sn(Oct)₂ completely decomposed at 378°C.

3.4. Differential scanning colorimeter (DSC)

Figure 6 shows the DSC curve of PLLA– TNBT, PLLA–SnCl₂ and PLLA–Sn(Oct)₂. The phase transition temperatures were observed at 55 and 135–145°C, corresponding to the glass transition temperature (T_g) and melting temperature (T_m) of PLLA, respectively. T_m of PLLA increases with increasing molecular weight of PLLA.

3.5. Gel permeation chromatography (GPC)

Molecular weight of poly(L-lactic acid) were obtained form GPC. The molecular weight of poly (L-lactic acid) as a function of a reaction time are



Figure 2. FT-IR spectra of L-lactic acid, PLLA-Sn(Oct), PLLA-TNBT and PLLA-SnCl





Figure 3. ¹³C NMR spectra of PLLA-TNBT



Figure 4. ¹H NMR of PLLA-TNBT



Figure 5. TG/DTA of PLLA-TNBT, PLLA-SnCl₂ and PLLA-Sn(Oct)₂



Figure 6. DSC curve of a) PLLA-SnCl₂, b) PLLA-TNBT and c) PLLA-Sn(Oct)₂





Figure 7. Molecular weight of differential of PLLA-TNBT, PLLA-SnCl and PLLA-Sn(Oct)

displayed in Figure 6. It can be observed that the reaction time increased with an increasing MW of PLLA. PLLA- $Sn(Oct)_2$ had the molecular weight higher than PLLA- $SnCl_2$ and PLLA-TNBT. This due to the fact that TNBT catalyst decomposed in water and $SnCl_2$ had water in structure. The maximum molecular weight of PLLA-TNBT, PLLA- $SnCl_2$ and PLLA- $Sn(Oct)_2$ obtained at 40 hour reaction time were 8400, 18600 and 18950 g/mol, respectively.

4. Conclusion

Poly (L-lactic acid) was successfully synthesized via polycondensation in bulk state using TNBT, $SnCl_2.2H_2O$ and $Sn(Oct)_2$ as catalysts at different polymerization time. T_g and T_m at 55 and 135-145°C respectively. PLLA-Sn(Oct)_2 system gave a lower rate of decomposition than PLLA-SnCl_2 and PLLA-TNBT system. The maximum molecular weight of Poly(L-lactic acid) obtained at 40 hour reaction time of PLLA were observed using Sn(Oct)_2 as a catalyst was 18950 g/mol.

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