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Ring Opening Polymerization of Poly(L-lactide) by Macroinitiator

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Abstract. 1-dodecanol and other alcohols have been used as initiators for ring opening polymerization of poly(L-lactide) (PLLA) from L-lactide monomers. These initiators are liquid and can evaporate during reaction, which affects yield and polymer molecular weight. We describe synthesis of PLLA from L-lactide initiated by a macroinitiator, poly(butylene succinate) (PBS), with stannous octoate as catalyst. PBS is miscible with the lactide and enhances the efficiency of ring opening polymerization. The optimum mole ratio of PBS, temperature and reaction time were determined. The chemical structure of the synthesised PLLAs were verified by NMR. Differential scanning calorimetry indicated that 0.001 mol% PBS led to the highest melting temperature ~164 °C and melting enthalpy 74 J/g. Gel permeation chromatography showed that polymerization at 160°C for 4 hours led to the highest molecular weight about 24000 g/mol and 84% PLLA yield. In contrast, in similar conditions polymerization, 0.1 mol% of 1-dodecanol, produced a lower molecular weight 6,200 g/mol and 65% yield.

Keywords: Poly(L-lactide), Ring opening polymerization, Macroinitiator of PLA

PACS: 82.35.Pq, 87.15.rp

INTRODUCTION

Poly(lactic acid) (PLA) is a versatile, biodegradable, aliphatic polyester derived from 100% renewable resources [1]. It has extensive applications in biomedical fields, including sutures, bonefixation material, drug delivery microspheres and tissue engineering. PLA has stereoisomers, poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(DL-lactide) (PDLLA). PLLA has gained attention because of its excellent biocompatibility and mechanical properties [2]. In general, there are three methods which can produce PLA with molecular mass in the range 8,000-150,000g/mol: (a) direct condensation polymerization; (b) azeotropic dehydration condensation and (c) polymerization through lactide formation, the ring-opening polymerization[2]. The most important method for synthesis of high molecular weight PLA is ring opening polymerization [2, 3]. Stannous octoate (Sn(Oct)₂) has been widely used as a catalyst because of high reaction rates, solubility in the monomer melt and the ability to produce high molecular weights [4, 5]. A coordination-insertion mechanism has been commonly used, the reaction system should also include hydroxyl or amino-containing compounds acting as initiators. The mechanistic studies have demonstrated that an hydroxyl capped compound can substitute at least one octanoate group of the Sn(Oct)₂ molecule in a rapid equilibration, and the resultant Sn-alkoxide is then the true initiator for the polymerization [2, 5, 6]. Most alcohols can be initiators, e.g. methanol, butanol and 1-dodecanol is commonly used [5]: we label these 'microinitiators'. In this study, we evaluated a macroinitiator, poly(butylene succinate) (PBS), as the initiator in the reaction and compared its efficiency with microinitiators, in particular 1-dodecanol.

EXPERIMENT

Materials

98% L-lactide was donated by Purac (Thailand) Ltd. For ring opening polymerization, the microinitiator, 1-dodecanol, 98% was purchased from Across Co. Ltd and the macroinitiator, poly(butylene succinate) (PBS) grade AZ711TN with $M_n = 42,000$ g/mol, $M_w = 55,000$ g/mol and PDI = 1.30 was sourced from Mitsubishi Chemicals

Corporation, Japan. Stannous octanoate ($\text{Sn}(\text{Oct})_2$) was supplied by Sigma Aldrich. Solvents, including toluene and chloroform, were obtained from RCI Labscan and AR grade and methanol 99% was purchased from Carlo Erba.

Preparation of Poly(L-Lactide) by ring opening polymerization

Poly(L-lactide) (PLLA) was prepared from L-lactide. Before using, it was dried in a vacuum oven at 45 °C for 16h. PLLAs were synthesized by bulk L-lactide ring opening polymerization in a nitrogen atmosphere at 120, 160 and 200°C for 4, 8, 12 and 16 h, initiated with the macroinitiator, PBS (0.1 and 0.001 mol%) and the microinitiator, 1-dodecanol 0.1 mol% (cannot use less than this) at conditions to the optimum one found with the macroinitiator. $\text{Sn}(\text{Oct})_2$ 0.1 mol% was used as a catalyst. After incubation, the polymer was dissolved in chloroform and removed to purify by precipitation in methanol. The precipitate was filtered under vacuum. Finally, PLLA was dried in a vacuum oven at 50 °C for 24 h.

Characterization of PLLA

Differential Scanning Calorimetry (DSC)

Thermal properties of the samples were analyzed by DSC (Perkin-Elmer, model DSC 4000) primarily to confirm the PLLA character. Approximately 5 mg samples were placed in aluminium pans and subjected to two heating scans from -10 to 200 °C at 10 °C /min. The melting temperature (T_m) and apparent melting enthalpy (ΔH_m) were determined from the first heating scan. The degree of crystallinity χ_c (%) was estimated from the first heating cycle using

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100$$

where ΔH_m is the heat of fusion of PLLA and ΔH_m^0 is theoretical melting enthalpy of perfect PLLA crystal (93 J/g) [7].

Proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$)

To verify the chemical structure of PLLA and demonstrate the action of the macroinitiator, a Bruker Advanced DPX 300 MHz $^1\text{H-NMR}$ spectrometer was used. CDCl_3 was used as a solvent at ambient temperature and tetramethylsilane was used as internal chemical shift standard.

Gel permeation chromatography (GPC)

The M_n , M_w and PDI of PLLAs were measured by GPC. About 7 mg samples were dissolved in 3 ml tetrahydrofuran (THF) via continuous stirring in a water bath at 60 °C for 1 h. 7.8 × 300 mm GPC columns were packed with Styragel HR5E (molecular weight resolution range: 2,000-4,000,000 g/mol). A Waters 2414 refractive index (RI) detector was used. The GPC columns were eluted using tetrahydrofuran at a flow rate of 1.0 mL/min at 40 °C and monodispersed polystyrenes were used for calibration.

RESULTS AND DISCUSSION

Thermal Properties

Figure 1 shows DSC thermograms of neat PBS, L-lactide and PLLAs with varying amounts of PBS macroinitiators and varying temperatures and times. The melting temperatures (T_m) obtained from the first heating scan and enthalpies computed from the curves are shown in Table 1. In Figure 1, we see thermograms of PLLAs initiated by PBS 0.1 mol% at (a) 120 °C and (b) 160 °C for 4, 8, 12, 16 h. We observed a double melting peak in almost all PLLA samples (sample No.1-8 in Table 1). The first melting peak in the range of 70-98 °C is attributed to the melting point of the lactide that its melting peak is also shown in the Figure 1(a-e). The second melting peak appeared between 117 and 124 °C: we attribute this to PBS because it is in the same range as the PBS curves. Normally, the melting temperature of PLA crystal appears between 150 and 170 °C [8, 9]. These results indicated that 0.1 mol% PBS cannot initiate L-lactide to form PLLA in ring opening polymerization under all conditions. This may result from steric hindrance between PBS and the octanoate ligand. Melting curves of PLLAs, in a similar set of

conditions, but with PBS amount decreased to 0.001 mol%, are shown in Figure 1(c) and (d). At 120 °C (Figure 1(c)) and times from 8 to 12 h, a single melting peak appeared at around 150-160 °C, assigned to a PLLA, but by 16 h the PLLA had started to de-polymerize. It was notable that for any reaction time at 160°C initiated by 0.001 mol% PBS led to a single melting peak for PLLA at about 157-165 °C. The DSC results showed that the optimum condition for reaction was 0.001 mol% PBS at 160 °C for 4 h which produced the highest melting point (165 °C) and PLLA crystallinity (80%). Therefore, we used this condition to compare with the microinitiator, 1-dodecanol, and found that the obtained PLLA showed both a lower melting peak and crystallinity (Figure 1(e) and sample No.17 in Table 1) indicating that it not as efficient as an initiator as the macroinitiator, PBS.

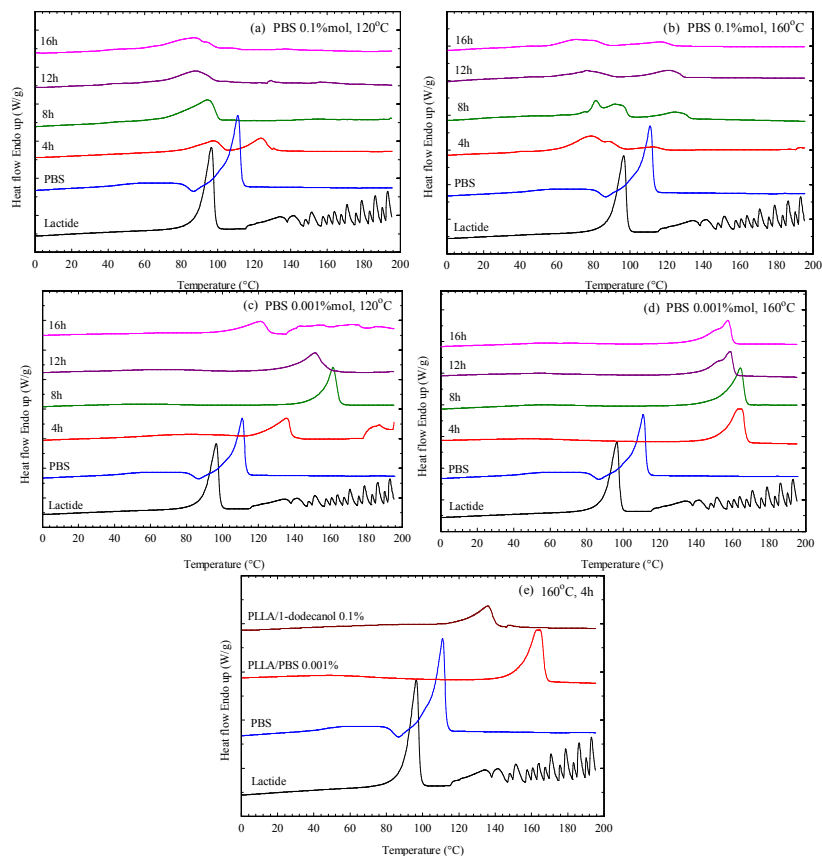


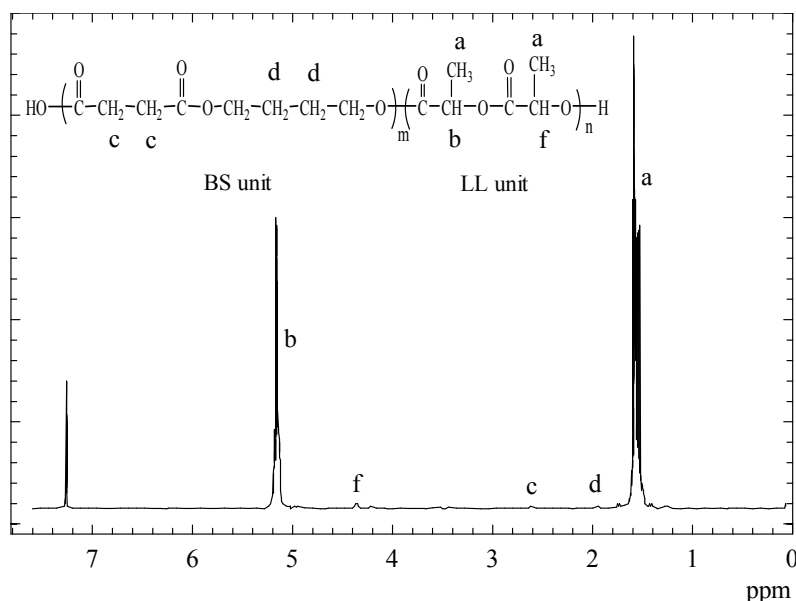
FIGURE 1. DSC thermograms of PLLAs initiated by (a) PBS 0.1 mol%, 120°C, (b) PBS 0.1 mol%, 160°C, (c) PBS 0.001 mol%, 120°C, (d) PBS 0.001 mol%, 160°C with different time and (e) PBS 0.001 mol% and 1-dodecanol 0.1 mol% at 160°C for 4h

Chemical structure

Figure 2 shows the ¹H-NMR spectrum of PLLA initiated by PBS 0.001 mol% at 160 °C for 4 h. The signals at 1.56 (peak a), 5.16 (peak b) and 4.36 ppm (peak f) correspond to the methyl proton (-OCH₃), methane proton (-OCH) and terminal methane proton (HOCH) in the L-lactide (LL) unit [3, 6, 10]. The signal at 2.6 ppm (peak c) was assigned to methylene proton (-C=OCH₂CH₂) in the butylene succinate (BS) monomer [6, 10]. The terminal methylene proton (HOCH₂CH₂) signal belonging to BS unit should appear at 4.35 ppm, but it entirely disappeared in this spectrum: this clearly demonstrated that the hydroxyl group of PBS had initiated the L-lactide in ring opening polymerization and the polymer chains were terminated by L-lactide hydroxyl group (4.36 ppm) [6], indicating that the PLLA structure had formed. Moreover, the ¹H-NMR spectra of all PLLAs initiated by PBS 0.001 mol% at 160 °C for every duration were similar.

TABLE 1. DSC data for PLLA initiated by PBS with various conditions

Samples	Initiator (mol%)	Reaction Condition		Melting Temperatures (°C)			ΔH_{PLLA} (J/g)	Crystallinity of PLLA (%)
		Temp (°C)	Hours	Lactide	PBS	PLLA		
PBS				-	110	-	-	-
L-lactide				96	-	-	-	-
1			4	98	124	-	21.6	23
2			8	95	-	-	-	-
3		120	12	87	-	156	2.3	2
4	PBS		16	87	137	-	1.9	2
5	(0.1%)		4	79	113	-	5.3	6
6		160	8	81	125	-	15.1	16
7			12	76	121	-	18.6	20
8			16	70	117	-	12.0	13
9			4	-	136	-	-	-
10		120	8	-	-	161	66.5	71
11			12	-	-	151	62.4	67
12	PBS		16	-	121	-	-	-
13	(0.001%)		4	-	-	165	74.6	80
14		160	8	-	-	164	71.5	77
15			12	-	-	159	54.7	59
16			16	-	-	157	56.0	60
17	1-dodecanol (0.1%)	160	4	-	-	148	39	42

**FIGURE 2.** $^1\text{H-NMR}$ spectrum of PLLA initiated by PBS 0.001 mol% at 160°C for 4h

Molecular weight

Number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity indices (PDI) of synthesized PLLAs initiated by PBS for all conditions and PLLA initiated by 1-dodecanol at 160 °C for 4 h were measured by gel permeation chromatography. The yield of PLLAs promoted with different reaction conditions and initiators were calculated and also shown in Table 2. It is notable that PLLA initiated by PBS at 160 °C for 4 h

showed the highest molecular weight (24,000 g/mol) and yield (84%) than other conditions. The higher molecular weight and yield indicated a more complete reaction. Therefore, we concluded that the optimum conditions for ring opening polymerization of L-lactide initiated by macroinitiator (PBS) were 160 °C and 4 h incubation. In addition to compare efficiency between macro- and micro-initiator, the commonly used microinitiator, 1-dodecanol, was used at this condition. We found that the molecular weight and yield of PLLA initiated by 1-dodecanol was lower than one initiated by PBS in the same conditions. This showed that the macroinitiator was more efficient under our conditions. A higher temperature was required for reaction, so the microinitiator evaporated easily and led to lower efficiency.

TABLE 2. Molecular weight and yield of PLLA initiated by PBS and 1-dodecanol with various conditions

Samples	Initiator (mol%)	Reaction condition		M _n (g/mol)	M _w (g/mol)	PDI	yield %
		Temp (°C)	Hours				
9	PBS (0.001%)	120	4	6800	7700	1.1	35
10			8	12000	15000	1.3	70
11			12	12000	15000	1.2	73
12		16	5000	5600	1.1	23	
13		160	4	16000	24000	1.5	84
14			8	14000	22000	1.6	76
15			12	8800	19000	2.2	72
16	16		13000	21000	1.8	71	
17	1-dodecanol (0.1%)	160	4	5460	6200	1.1	65

CONCLUSIONS

We synthesized PLLA via ring opening polymerization of L-lactide initiated by PBS as a macroinitiator and determined the optimum reaction conditions. Our results showed that the most suitable PBS concentration was 0.001mol%, the optimal temperature was 160 °C and incubation time was 4 h leading to a high yield (84%) and molecular weight (24,000 g/mol) of synthesized PLLA. This compared with the PLLA initiated by 1-dodecanol with lower yield (65%) and molecular weight (6,200 g/mol). We concluded that the macroinitiator, PBS, was a better initiator under our conditions.

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REFERENCES

1. R.E. Drumright, P.R. Gruber, and D.E. Henton, *Adv. Mater.* **12**, 1841-1846 (2000).
2. M.S. Lopes and A.L. Jardini, *Chem. Eng. Trans.*, (2014).
3. X. Kaitian, A. Kozluca, et al., *Turk. J. Chem.* **20**, 43-53 (1996).
4. G. Swift, *Acc. Chem. Res.* **26**, 105-110 (1993).
5. M. Ryner, K. Stridsberg, et al., *Macromolecules.* **34**, 3877-3881 (2001).
6. C. Ba, J. Yang, et al., *Biomacromolecules.* **4**, 1827-1834 (2003).
7. H. Xiao, W. Lu, and J.T. Yeh, *J. Appl. Polym. Sci.* **113**, 112-121 (2009).
8. Z. Jing, X. Shi, et al., *Polymer.* **92**, 210-221 (2016).
9. F. Qi, M. Tang, et al., *Eur. Polym. J.* **71**, 314-324 (2015).
10. R. Supthanyakul, N. Kaabbuathong, and S. Chirachanchai, *Polym. Degrad. Stab.* **142**, 160-168 (2017).