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Preparation of polylactide by ring-opening polymerisation of lactide

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This study was about to produce high molecular weight polylactide (PLA) with via ring-opening polymerisation. Ring-opening polymerisation PLA in this study as accomplished using tin(II)octoate as the catalyst with addition of small amount of luaryl alcohol as the co-catalyst. The effects of reaction temperature and pressure on synthesised polylactide were investigated. As-synthesised products were characterised by ^{1}H-NMR, FT-IR and MALDI-TOF mass spectrometry. The results showed that as-synthesised products were very similar to PLA characteristics reported previously by other researchers. The melting temperature of polylactide was in the range of 130-145°C. Furthermore, as-synthesised polylactide could not be dissolved completely in many solvents there are just some parts of PLA can be dissolved. Therefore, as-synthesised polylactide could expect to be high molecular weight. In addition, soluble part of polylactide in THF was then characterised by GPC. Moreover, insoluble polylactide was filtered and weighed. With increasing temperature and reducing pressure more residues were collected.

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1. Introduction

Recently, bio-renewable polymers have become more important for innovation regarding the sustainable development of a global society. Polylactide (PLA) is a biodegradable and bio-renewable polymer that can be prepared by both direct condensation of lactic acid and ring-opening polymerisation of lactide [1,2]. Most work has focused on the ring-opening polymerisation because the direct condensation route is an equilibrium reaction, difficulties in removing trace amounts of water during the late stages of polymerisation generally limit the ultimate molecular weight achievable by this approach [2]. The standard catalyst for the ring-opening polymerisation of high molecular weight polylactide is tin(II)octoate. This catalyst has several advantage, such as solubility in organic solvent and molten lactide, stability on storage, a good reaction rate and low levels of racemisation [2,3]. Furthermore, it has been approved by FDA and therefore it is getting attention for synthesis of polymer for food packaging and biomedical application [4]. PLA exhibits a balance of performance properties that are comparable with commercial plastics. In the future, PLA could expect to compensate the utility of commercial plastic from fossil resource [2]. So PLA of high molecular weight is needed to produce devices of high mechanical strength [4]. Soung-Hyu Hyon et al. [5] investigated the synthesis of poly(lactic acid) though polycondensation of the lactic acid monomer obtaining $\overline{M_w}$ lower than 1.6×10^4, whereas ring-opening polymerization of lactides using stannous octoate as the catalyst with $\overline{M_v}$ lower than 6.8×10^5.

This study was about to produce PLA having high molecular weight via ring-opening polymerisation using tin(II)octoate as the catalyst. The effects of reaction temperature and pressure on synthesised polylactide were investigated.

2. Experimental

2.1. Materials

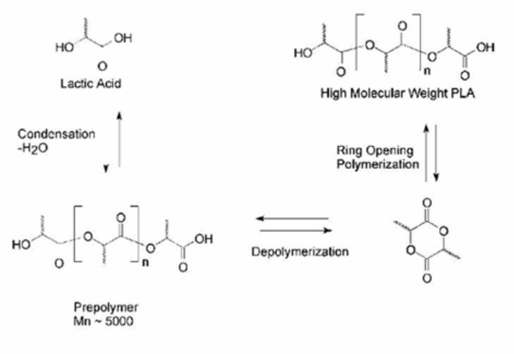
Lactic acid (99.6%), tin(II)octoate (Oct), tin(II)chloride ($SnCl_2$), and lauryl alcohol (95%) were purchased from Fluka. All chemicals were used as received.

2.2. Synthesis of lactide monomer

The polycondensation and depolymerisation of lactide acid to produce lactide monomer were carried out at 180°C for 24 hours at much reduced pressusre. Tin(II)chloride was used as a catalyst at fixed amount of 0.05 wt%. The clear needle-like monomer was collected and then kept in the desiccator under nitrogen atmosphere and room temperature before using for the next step.

2.3. Synthesis of polylactide

Ring-opening polymerisation of lactide was accomplished using tin(II)octoate as the catalyst and addition of luaryl alcohol at the amount of 0.05 and 0.5 wt%, respectively. Reaction pressure was varied at 60 and 150 mmHg and reaction temperature was varied at 160, 180 and 200 °C. PLA were dissolved in chloroform and precipitated in methanol. The white powder PLA was collected and stored in desiccators at room temperature. Schematic 1 showed synthesis of lactide and polylactide [6].



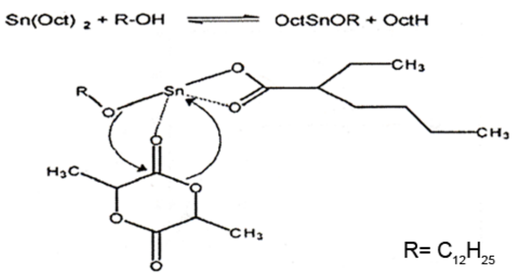
Schematic 1 PLA production via prepolymer and lactide.

2.4 Characterizations

Molecular weight of PLA was measured by gel permeation chromatography (GPC, Hewlett Packard 1100 Series) using polystyrene as the standard and THF as the mobile phase. Nuclear magnetic resonance (NMR) spectra were recorded with a JNM-ECP400 NMR spectrometer at room temperature with CDCl$_3$ as solvent and tetramethylsilicone (TMS) as internal reference. Fourier transform infrared (FTIR) spectra were taken on a FTS3000 instrument. MALDI-TOF mass spectrum were recorded with a microTOF, BRUKER using methanol and dichloromethane as solvents and scan range was about 50 m/z to 3000 m/z.

3. Results and discussion

PLA synthesised by ring-opening polymerisation of lactide using tin(II)octoate as a catalyst is generally thought to occur via a coordination-insertion mechanism with ring opening of the lactide to add two lactic acid molecules to the growing end of the polymer chain as shown in schematic 2 [7].



Schematic 2 Ring-opening polymerisation of lactide was accomplished using tin(II)octoate as the catalyst with addition of luaryl alcohol.

Lactide monomers are generally obtained by depolymerisation of lactic acid oligomers produced by polycondensation. Characterisation of the products was performed by various techniques and the results showed that as obtained lactide and PLA exhibited the same characteristic as recorded by many previous researches [8]. The results can be described as followed. FT-IR spectra of lactide monomer and PLA were showed in Fig. 1.

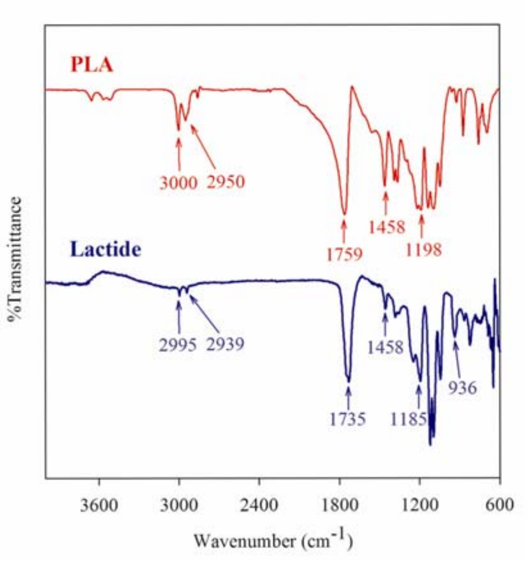


Fig. 1. FT-IR spectra of polylactide and lactide monomer.

IR spectra exhibited characteristic absorption peaks of both PLA and lactide at 3000-2939 cm^{-1} for –CH stretching, 1759-1735 cm^{-1} for –C=O stretching, 1458 cm^{-1} for –CH$_3$ bending, and 1198-1185 cm^{-1} for –C–O–C– vibration. However, as expect, absorption peak at 936 cm^{-1} for –CO–O– ring of lactide could not appear in IR spectrum of PLA. This peak is characteristic for lactide monomer and has been used to differentiate between PLA and lactide. Moreover, PLA was also characterised by ^{1}H-NMR and MALDI-TOF mass spectrometry. Fig. 2 showed H^1-NMR spectrum of as-synthesised PLA which was similar to as that showed in reference [9]. The backbone signals of as-synthesised PLA appearing at 1.6(b) and 5.2(a) ppm were, respectively, assigned to methyl and methenyl protons. The quartet signal at 4.4(c) ppm of the methenyl proton neighbour of the hydroxyl end group was observed and weak signal at 1.5(d) ppm was assigned to methyl end group. Fig. 3 showed MALDI-TOF mass spectrum of as-synthesized PLA. Periodic decrement of about 72 m/z can be observed in the spectrum. It corresponds to the lost of molecular weight of PLA repeating unit. This confirmed that PLA can be obtained by ring-opening polymerisation.

Thermal properties of PLA were characterized by DSC. Fig. 4.1 and 4.2 showed the DSC thermograms of PLA prepared at different reaction pressures and temperatures. The melting temperature of as-synthesized polylactide was indicated in the thermograms and varied in the range of 130-145°C. Therefore reaction temperature and reaction pressure of ring-opening polymerization were lower influence to melting temperature of as-synthesized PLA.

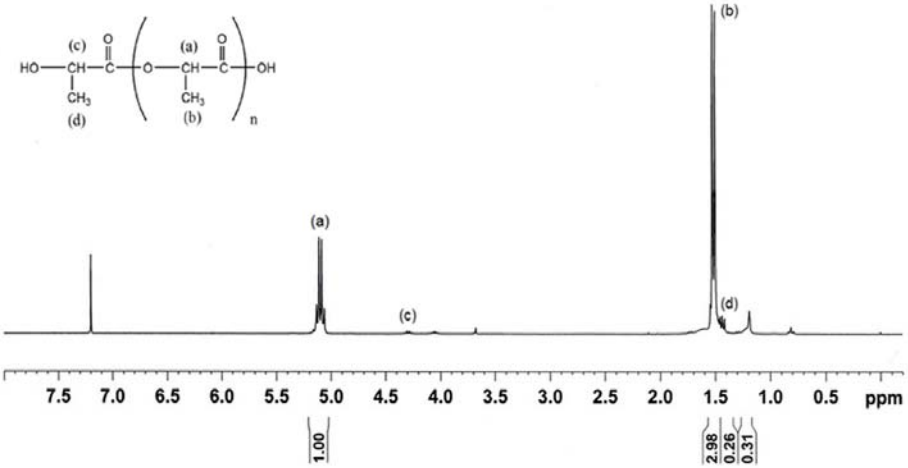


Fig. 2. ^{1}H-NMR spectrum of polylactide.

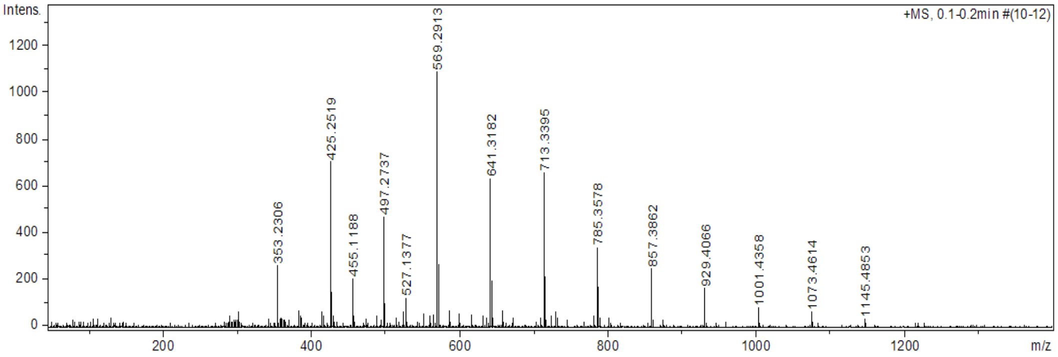


Fig. 3. MALDI-TOF mass spectrum of polactide.

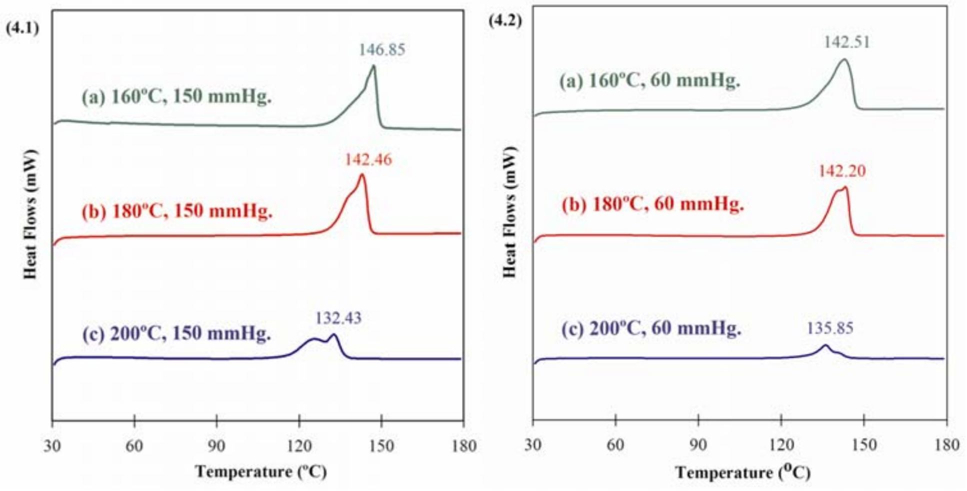


Fig. 4. DSC thermograms of polylactide polymerized at different reaction pressures and temperatures.

Table 1. Conditions of PLA synthesis and PLA characteristics.

Condition of preparation of PLA		$\overline{M}_w$ (× 10^4 g/mol)	$\overline{M}_n$ (× 10^4 g/mol)	Polydispersity Index
Temperature (°C)	Pressure (mmHg)			
160	150	3.10	1.74	1.71
180	150	3.14	1.95	1.61
200	150	5.05	3.08	1.64
160	60	3.45	2.30	1.50
180	60	2.30	1.60	1.43
200	60	-	-	-

In this study, when as-synthesised PLA was dissolved in THF there were two fractions were formed. A soluble part of PLA dissolved in the THF phase and an insoluble part settled down at the bottom. The soluble PLA was then characterised by GPC and insoluble part was filtered and weighted. Table 1 showed the number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$) and polydispersity index (PDI) of the soluble PLA from GPC. It was found that when the reaction pressure was more reduced the higher molecular weight of soluble PLA could be obtained. However, as-synthesised PLA prepared at 60 mmHg and 200 °C was not characterized by GPC because it almost did not dissolve in THF. From GPC results it could be implied that the molecular weight of the soluble PLA was not just true molecular weight of as-received product and this could be supposed that the synthesised product expected to have high molecular weight.

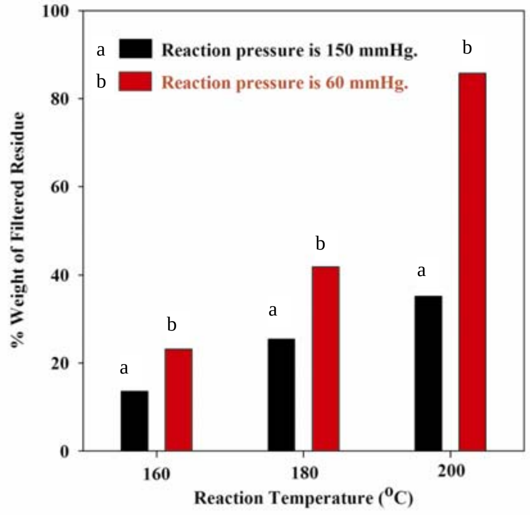


Fig. 5. Percentage of filtered residue of polylactide.

The insoluble PLA in THF solution was filtered by PTFE filter with pore size diameter about 0.45 μm. Then the PLA filtrate was weighed and compared to other reaction conditions. Fig. 5 showed the percentage of filtered PLA after filtration. It was found that the percentage of PLA residue increased with reducing reaction pressureand increasing reaction temperature. From this data it could be supposed that the higher percentage of the filtrate, the longer molecular chain was obtained. On the other hand, it may be said that lower molecular weight or smaller chain of PLA had the lower percentage of filtered residue PLA. Therefore, the molecular weight of PLA was increased with reducing reaction pressure.

4. Conclusion

PLA having various molecular weights can be obtained by ring-opening polymerisation with using tin(II)octoate as the catalyst and addition of luaryl alcohol. Melting temperature of as-synthesized polylactide was in the range of 130-145 ^{o}C. Molecular weight of soluble PLA became higher as reaction pressure was more reduced. Moreover, insoluble polylactide was more collected by increasing temperature and reducing pressure at the reaction.

Acknowledgement

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