

Poly(lactic acid) preparation by polycondensation method

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Poly(lactic acid) or PLA was synthesized by direct condensation polymerisation of lactic acid. Polymerisation was carried out with tin(II) chloride as a catalyst and diphenyl ether as solvent. The obtained PLA was characterised by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (¹H-NMR), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). The effects of reaction temperature and reaction time on molecular weight of PLA were investigated. The molecular weight of PLA increased with increasing polymerisation temperature. The highest molecular weight which was about 2×10^5 g/mol was obtained at 180°C for 16 hrs at low reaction pressure. In addition, thermal properties, i.e. T_m and T_g , became decreased as reaction temperature increased. On the other hand, both molecular weight and thermal properties increased as longer polymerisation time proceeded.

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1. Introduction

Poly(lactic acid) (PLA) is one of the most promising biodegradable polymers with a good transparency, high mechanical properties, and good biocompatibilities. PLA is synthesised from raw materials derived from bio-based renewable resources such as corn or sugarcane, which can be good alternatives to fossil resources [1-4]. At the present, PLA is produced industrially by a multi-step process called ring-opening polymerization, including the production and the isolation of intermediate lactide. During this process, water is not produced, so high-molecular-weight PLA can be synthesised. However, as a result of the high process costs of synthesising and purifying lactide, PLA use has been restricted to medical applications such as suture materials [5-6]. Polycondensation of lactic acid is a low cost process because cheap lactic acid in liquid phase is polymerised. However, as the molecular weight of PLA becomes high, it is difficult to remove the water in order to obtain high molecular weight PLA. When the reaction temperature was increased to promote the removal of water, the high molecular weight polymer can not be synthesised because of the decomposition reaction at high temperature [7]. Kim and Woo [5] searched for a good catalyst in the polymerisation, the mixed oxide catalysts were synthesised by sol-gel method and it was characterised by XRD and BET. The results show that the M_v of PLA obtained was about 33,000, when 0.2 wt% of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was used as a catalyst in the polymerisation. Dutkiewicz, Grochowska-Lapienis and Tomaszewski [8] investigated the synthesis of poly(L+) lactic acid which was carried out in a solution of o-dichlorobenzene, p-xylene, o-

chlorotoluene, and diphenylether. Stannous chloride and metallic tin were used as catalysts. The poly(L+) lactic acid with the highest molar mass was obtained in the synthesis carried out in diphenyl ether under vacuum.

The aim of this work was to figure out the suitable condition to obtain high molecular weight PLA by direct polycondensation of lactic acid by using tin(II) chloride as a catalyst and diphenyl ether as solvent.

2. Experimental

Chemicals

Lactic acid (99.6%) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were purchased from Fluka. Diphenyl ether was purchased from VWR International Ltd. All chemicals were used as received.

Reaction procedures

The reaction was conducted in a 250-mL, three-necked flask reactor equipped with a magnetic stirrer and a water-cooling condenser. Lactic acid, 0.05 wt % $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, diphenyl ether were added to the reactor. The temperature gradually increased to 120°C in 3 hrs, and the reaction mixture was stirred continuously. At the same time, the pressure of the system was reduced stepwise and fixed at low pressure, the temperature was varied from 160-200°C, and the reaction time was varied from 8-24 hrs as showed in Table 1. After the reaction finished, it was cooled down to room temperature. White powder was obtained after precipitating in methanol. The product was dissolved in chloroform and purified in methanol. PLA was then filtrated and dried at 60°C under vacuum.

Table 1. PLA characteristics at various polymerization temperature and times.

Sample	Temp (°C)	Time (hrs)	Yield (%)	n	\overline{M}_w ($\times 10^5$ g/mol)	MWD	T _g (°C)	T _m (°C)	Crystallinity (%)
1	160	12	33.97	17	0.49	2.76	47.23	150.49	59.38
2	180	12	25.43	84	1.53	1.80	55.20	151.59	44.88
3	200	12	33.94	92	1.94	1.60	49.33	130.16	41.77
4	180	8	13.25	64	1.25	2.55	55.09	155.51	56.29
5	180	12	25.43	84	1.53	1.80	55.20	151.59	44.88
6	180	16	28.79	105	1.98	1.69	56.60	149.53	45.41
7	180	20	43.54	78	1.72	2.58	55.50	154.15	53.32
8	180	24	48.33	105	1.83	1.84	56.06	150.08	45.81

Characterisation

Molecular weight of PLA was measured by gel permeation chromatography (GPC, Hewlett Packard 1100 Series) using polystyrene as the standard and CHCl₃ as the mobile phase. Nuclear magnetic resonance (NMR) spectra were recorded with a JNM-ECP400 NMR spectrometer at room temperature with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal reference. Fourier transform infrared (FTIR) spectra were taken on a FTS3000 instrument. Thermal analysis was carried out with a differential scanning calorimeter (Perkin Elmer, DSC 7). The measurements were run from 30 to 180 °C at the heating rate of 10 °C/min

3. Results and discussion

In this work the synthesis of PLA was carried out with tin (II) chloride as the catalyst and diphenyl ether as the solvent. The reaction were carried out at various temperatures and times of polymerisation. PLA with the high molecular weight was our goal to reach.

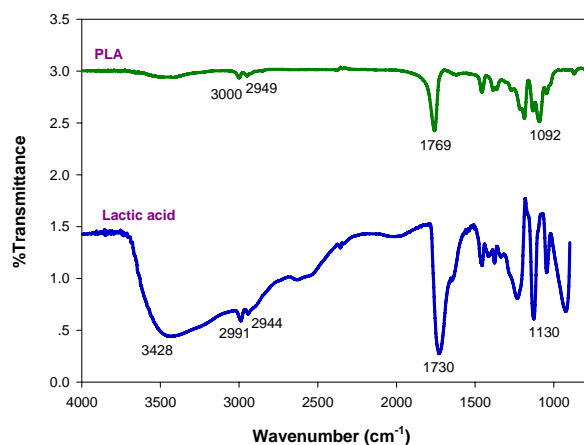


Fig. 1. FTIR spectra of lactic acid and PLA.

Fig. 1 showed FT-IR spectra of lactic acid and poly(lactic acid) synthesised at 180°C for 16 hrs. IR spectra of the other synthesised PLA which were not

shown here were found to be vary similar to those shown in Fig. 1. IR spectra of PLA revealed characteristic absorption peaks of ester (1759 and 1092 cm⁻¹ for -COO- and -O- respectively) and -CH₂- and CH₃ groups (2949–3000 cm⁻¹). As lactic acid was polymerised, the hydroxyl group will react with carboxylic group of another molecule, therefore the broad -OH stretch peak at 3428 cm⁻¹ observed for PLA will be reduced. The hydroxyl absorption peak (in case of PLA) almost disappeared, indicating that the number of hydroxyl groups was reduced and the sharper absorption peak of C=O stretching (1759 cm⁻¹) was observed as the polymer was further synthesised.

Fig. 2 showed ¹H-NMR spectrum of PLA obtained at 180°C for 16 hrs. ¹H-NMR spectra of the other synthesised PLA which were not shown were found similarly. The spectrum revealed the signal of methine proton resonances in the main chain at 5.12 ppm (a) and the signal of methyl proton resonances in the main chain at 1.52 ppm (c). A very weak signal about 4.30 ppm (b) and 1.42 ppm (d) assigned to the methine proton and methyl proton next to the terminal hydroxyl group and carboxyl group, respectively. The above results confirmed that poly(lactic acid) was formed. The polymerisation number (n) of the synthesised PLA could be determined from the ratio of the integrated area of proton (a) to proton (b) [6]. The polymerisation number (n) of the synthesised PLA from Table 1 increased when the reaction temperature and time increased. The results were in accordance with the molecular weight obtained from GPC analysis described below.

Table 1 (Sample 1-3) showed effect of the polymerisation temperature on the obtained PLA. It was found that with increasing temperature from 160 - 180°C the molecular weight of poly(lactic acid) increased from 0.49×10⁵ - 1.94×10⁵ g/mol, but they did not parallel the thermal properties of PLA, i.e. T_m, T_g and %crystallinity. At the reaction temperature 200 °C, the melting temperature (T_m) showed reduction. At the low temperature, MWD of synthesised PLA was high and decreased with increasing temperature. The effects of the polymerization time on the synthesized PLA also showed in Table 1 (Sample 4-8). Yield of synthesized PLA increased as longer polymerization time proceeded. The

molecular weight was a function of reaction time by increasing when time of polymerization increased. In addition, the molecular weight of PLA reached the highest value of 1.98×10^5 g/mol when the reaction was carried out

for 16 hrs. However, after 16 hrs, the molecular weight became slightly reduced, because of the poor thermal stability of PLA. PLA belongs to the group of polymers that are relatively sensitive to thermal degradation.

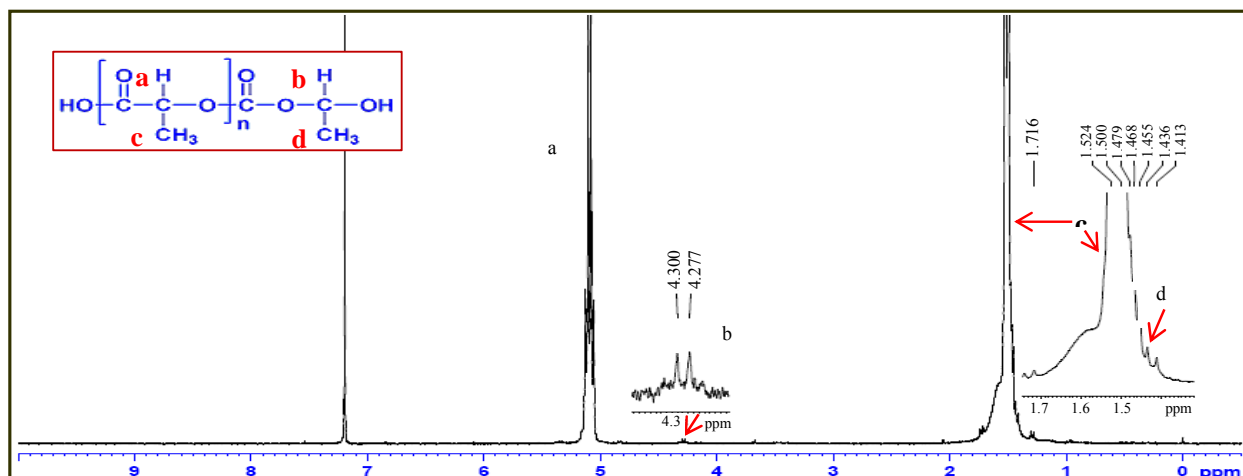


Fig. 2. $^1\text{H-NMR}$ spectrum of PLA.

Several reasons which can be given for its poor stability are [9-10]:

(1) Hydrolysis by trace amounts of water, catalysed by hydrolysed monomer.

(2) Zipper-like depolymerisation, catalysed by the remaining polymerisation catalysts.

(3) Oxidative, random main-chain scission.

(4) Intermolecular transesterification to monomer and oligomeric esters.

(5) Intramolecular transesterification resulting formation of the monomer and oligomeric lactides of low molecular weight [5].

On the contrary, MWD, T_m and %crystallinity in table 1 decreasing when molecular weight increased. By the way, T_g of all PLA in Table 1 are around 55-56 °C.

From the experiments, we can conclude that the optimal reaction conditions are at the reaction temperature of 180°C at time of 16 hrs, and at the pressure of 40 mmHg with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as the catalyst and diphenyl ether as the solvent.

4. Conclusions

PLA can be synthesised by the direct bulk condensation polymerization of lactic acid using tin (II) chloride as the catalyst and diphenyl ether as the solvent at different polymerisation temperatures and times. The longer the polymerisation temperature and time, the trend of higher the molecular weight PLA obtained. The highest molecular weight about 1.98×10^5 g/mol with good thermal properties was obtained at 180 °C for 16 hrs at low reaction pressure.

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