

Production of optically pure poly(lactic acid) from lactic acid

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Abstract Optically pure poly(lactic acid) (PLA) was obtained from lactic acid *via* purification of the corresponding lactide. The optical purity of PLA was determined using polarimetry and NMR. In the depolymerization process, the effect of the reaction conditions and catalysts on optical purity of the lactide was examined with temperature having a significant effect. In addition, the degree of racemization increased with increasing molecular weight of the oligomeric PLA. The effects of temperature, time, solvent, and stirring speed (RPM) on the lactide purification process were examined in order to improve optical purity. Optical purity was maximized when separation was carried out at 25 °C. The optical purity of PLA was significantly affected by that of lactide used.

Keywords Racemization · Optical purity · Poly(lactic acid) · D,L-lactide · Meso-lactide

Introduction

As many petroleum-based plastics are not environmentally friendly, there is a need for biodegradable substitutes. Poly(lactic acid) (PLA) is a well known biodegradable polymer with several applications ranging from plastics and fibers to packaging [1–5]. In order for it to achieve the physical properties suitable as a substitute for petroleum-based polymers, PLA needs to have a sufficiently high molecular weight and optically purity. However, it is difficult to obtain high molecular weight PLA

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that is optically pure using the conventional, direct condensation reaction, due to the occurrence of a depolymerization reaction [6]. Many studies have examined the synthesis of high molecular weight PLA through a variety of routes but have concluded that such processes are not economically viable. The most industrially acceptable process for manufacturing synthetic PLA reported thus far is *via* lactide formation. In this process, a lactic acid monomer is first polymerized into oligomeric PLA, then depolymerized to the lactide, and finally re-polymerized to attain a higher molecular weight through a ring opening mechanism [7–13]. The preparation of optically pure lactide is considered one of the most important processes in this overall mechanism because optical purity of the lactide significantly affects the quality of the final product [14].

Crystallization, extraction, and distillation have been used to obtain the lactide with high optical purity. Crystallization makes use of the difference in the melting points of *D,L*- and meso-lactide (97 and 54 °C) [15, 16]. However, the yield of the *D,L*-lactide obtained using this process is unsatisfactory because the re-crystallization process needs to be carried out several times to achieve high purity. Extraction is based on the difference in solubility between *D,L*-lactide and meso-lactide. In this method, the crude lactide is dissolved in an organic solvent and the resulting solution extracted with water to remove the meso-lactide. The disadvantage of this method is that a long time is required to obtain lactide with high optical purity due to the slow dissolution kinetics of the meso-lactide in water. The cost of this extraction process is proportional to the amount of solvent used with the added difficulty of complete removal of the solvent from the lactide. Distillation is a method that employs the differences in the boiling points of the *D,L*- and meso-lactides. Although the distillation process is theoretically conceivable, its operation is not easy, as it sometimes induces the thermal polymerization of the lactide within the columns. Despite such disadvantages, NatureWorks LLC recently successfully applied the distillation process to produce high molecular weight PLA from lactic acid *via* optically pure lactide.

Recently, many methods have been proposed for separation of optically pure lactide. Among them, water can be used as a medium to separate the optically active lactide from the crude based on the difference in solubility between the *D,L*- and meso-lactides in water. The solubility of *D,L*-lactide in 100.0 g of water is in the range of 0.5–0.6 g/h at 20 °C and 4.0–5.0 g/h at 60 °C, whereas 10.0 g of meso-lactide can dissolve in 100.0 g of water within 1 min under the same conditions [17]. Therefore, the meso-lactide can be removed easily from the crude lactide upon dissolution in water. And the depolymerization process of the oligomeric PLA is as important for obtaining a lactide of high optical purity as separation of the lactide obtained from oligomeric PLA. However, there are no reports of detailed investigations into the optical purity of the lactide obtained from the depolymerization of oligomeric PLA.

In this study, low molecular weight PLA was synthesized initially from lactic acid. The low molecular weight PLA was depolymerized to produce crude lactide, and then optically pure lactide was obtained by removing the meso-lactide. Finally, the PLA was synthesized with optically pure lactide. In previous studies, the effects of the reaction conditions and catalyst on the synthesis of oligomeric PLA were

examined. The aim of this study was to determine how optical purity is affected by the reaction conditions and catalysts used in the depolymerization and separation stages during purification and how the optical purity of PLA was affected according to that of the lactide.

Experimental

Materials

L-lactic acid was purchased from Purac Co. (Barcelona, Spain). Stannous oxide (SnO, Aldrich, Milwaukee, WI, USA), stannous octoate (Sn(II)oct, Aldrich), and stannous chloride (SnCl₂, Aldrich) were used as catalysts for lactide preparation. *Tert*-butyl and *tert*-amyl alcohol were purchased from E. Merck Co. (Darmstadt, Germany). Ethyl alcohol and chloroform (CDCl₃) were purchased from Aldrich. All these materials were used without further purification.

Synthesis of oligomeric PLA

An aqueous solution of L-lactic acid (90 wt%) was dehydrated at 200 °C to produce oligomeric PLA, without a catalyst, under a nitrogen atmosphere for 6 h using a 1,000 ml reaction vessel equipped with a Dean-Stark trap. Oligomeric PLA with different molecular weights was obtained by carrying out the prepolymer synthesis reaction at different pressures ranging from 10 to 20 torr. The molecular weight of the oligomeric PLA was determined using a method described elsewhere [18]. For each molecular weight, three specimens were taken.

Synthesis of lactide

A 1,000 ml 4-necked flask was equipped with a mechanical stirrer and a thermometer. The reactor was connected to a distillation column (2 cm ID × 30 cm length) filled with stainless steel packing materials. The prepolymer produced was charged into the flask and mixed with the catalysts. The flask was heated and reduced at the prescribed temperature and pressure in order for the crude lactide to be expelled by distillation and collected in the receiver. The receiver was placed in an oil bath and kept at approximately 90 °C to prevent the crude lactide from solidifying. The distillation reaction was completed in 2 h. The composition of the crude lactide in the molten state was determined as described elsewhere [19].

Optical purification of lactide

60.0 g of molten crude lactide was mixed with 60.0 g of water at 25 °C and stirred continuously. The resulting solution was immersed immediately in a circulator (LCB-R12, Lab Tech., Korea) and filled with acetone at −15 °C in order for it to be cooled immediately. The mixture was then stirred continuously for a predetermined time. The solution obtained after the stirring was separated by a centrifuge (Sigma,

2–5, Germany). The resulting crystals were dried at 40 °C under reduced pressure for 48 h.

Polymerization of lactide

Ring-opening polymerization of the lactide was conducted in the bulk phase using stannous octoate (SnOct₂) as a catalyst. The lactide was charged into the reactor with a mechanical stirrer and thermometer. The reactor was placed in a silicon oil bath kept at 140 °C and vigorously shaken until the lactide melted and the catalyst was completely mixed with the molten lactide. The polymerization reaction was carried out at 140 °C under reduced pressure for 4 h. The synthesized polymer was dissolved in dichloromethane and precipitated with cold methanol. This process was repeated twice to purify the polymer. The resulting polymers were dried at 40 °C under reduced pressure for 24 h.

Characterization

The specific optical rotation, $[\alpha]$, of the crude and purified lactide at 10.0 g/l in chloroform was measured at 25 °C using a JISICO polarimeter (PI-1020) at a wavelength of 578 nm. Two methods were used to measure the molecular weight of the synthesized PLA. The viscosity average molecular weight was determined from the intrinsic viscosity measured using a semi-automatic viscometer (AVS350, Schott, Germany). PLA/chloroform solution was placed in a temperature-controlled bath, and the viscosity was periodically measured at 25 °C using an Ubbelohde viscometer. Nuclear magnetic resonance spectroscopy (NMR, 500 MHz, Varian, USA) was used to analyze the composition of the purified lactide (¹H-NMR) and the optical purity of the PLA (¹³C-NMR). For NMR measurements, the samples were dissolved in chloroform-*d*₁ (CDCl₃) with tetramethylsilane (TMS) as the standard. Five samples were prepared for each measurement and the average value was taken for its determination. The optical purity was analyzed using analysis of variance (ANOVA) [20] method to ascertain the differences among the data sets.

Results and discussion

Synthesis of lactide

Six samples of oligomeric PLA, with average molecular weights of 350, 600, 980, 1,380, 2,180, and 3,100 g/mol were prepared. The lactide was produced from the oligomeric PLA using a back-biting reaction of the OH end groups [21]. In this reaction, the carbon atom of the PLA carbonyl group is attacked by its OH end group, the most electrophilic point in a repeating PLA unit.

The crude lactide produced from the oligomeric PLA was analyzed by polarimetry to clarify the relationship between the depolymerization conditions and racemization. The depolymerization product of the oligomeric PLA was crude lactide, composed of L-lactide, D-lactide, and meso-lactide, as well as other

impurities such as lactic acid, lactic acid dimer (lactoyllactic acid), and water. The optical purity of the lactide synthesized was determined by Eq. 1:

$$R \times [\alpha]_{\text{L}}^{25} + (1 - R) \times [\alpha]_{\text{D}}^{25} = [\alpha]_{\text{obs}}^{25} \quad (1)$$

where R is the optical purity of L-lactide. The optical specific rotations of 100% optically pure L-lactide, D-lactide, and meso-lactide at 25 °C are referred to as: $[\alpha]_{\text{L}}^{25} = -270^\circ$, $[\alpha]_{\text{D}}^{25} = +270^\circ$ and $[\alpha]_{\text{M}}^{25} = 0^\circ$ [22]. $[\alpha]_{\text{obs}}^{25}$ is the value observed by the polarimeter. (Other impurities were excluded in Eq. 1 because their degree of optical rotation was very small compared to D- and L-lactide).

Figure 1 shows the effect of the catalyst on the optical purity of the crude lactide at different temperatures when the depolymerization reaction was carried out using PLA with a molecular weight of 600.0 g/mol, a reaction pressure of 20 torr, and a catalyst concentration of 0.1 wt%. The optical purity of the crude lactide decreased from 92 to 80% with increasing temperature from 200 to 240 °C. This result can be explained in terms of racemization. D-lactide and meso-lactide were produced as the L-lactate unit changed to the D-lactate unit through racemization. The main reaction pathway for racemization is considered to be a deprotonation process. As the α -proton in the lactide is highly acidic, deprotonation is facile in the presence of weak bases [23]. A basic impurity (octoate, oxide, and chloride) derived from each catalyst is sufficiently alkaline to deprotonate the lactide. Racemization occurs as the proton abstracted from one face of the lactide is added to the opposite face of the same molecule. Deprotonation during depolymerization can be facilitated by increasing the temperature. The optical purity of crude lactide was slightly higher when SnO was used Sn-based catalysts. Without adding catalyst, the slightly lower value was obtained. This is probably because other impurities (lactic acid, lactoyllactic acid, etc.) except lactide were produced in higher quantities in the case of no added catalyst. Therefore, the observed optical rotation was lower because

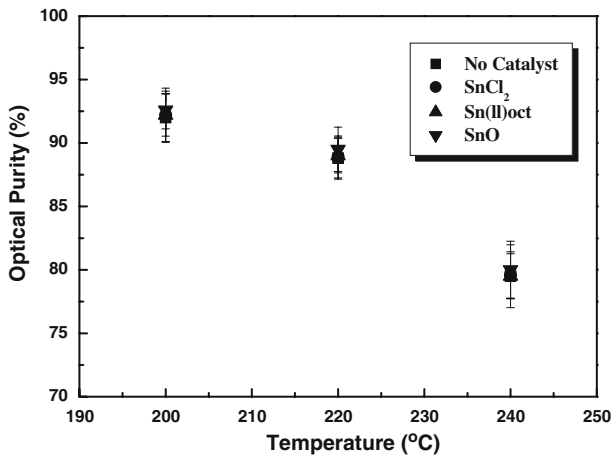


Fig. 1 Optical purity (%) of the crude lactide produced from the depolymerization reaction of PLA at different temperatures using: no catalyst (*filled square*); SnCl₂ (*filled circle*); Sn(II)oct (*filled triangle*); and SnO (*filled inverted triangle*), respectively

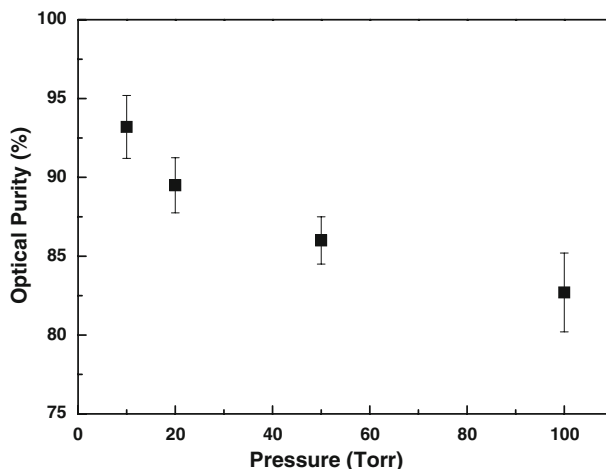


Fig. 2 Optical purity (%) of the crude lactide produced from the depolymerization reaction of PLA at different pressures

the ratio of L-lactide decreased with increasing levels of impurities in the crude lactide.

Figure 2 shows the pressure dependence of the optical purity of crude lactide when the reaction was carried out using PLA with a molecular weight of 600.0 g/mol. The reaction temperature was 220 °C with 0.1 wt% SnO used as the catalyst. The optical purity increased from 82 to ca. 93% with decreasing pressure from 100 to 10 torr, due to the basic compounds (water and impurities derived from the catalyst) being eliminated with greater ease at lower pressures. Therefore, the degree of racemization decreased significantly with decreasing pressure.

Figure 3 shows the effect of the PLA molecular weight on the optical purity of the lactide. The reaction was carried out at 220 °C and 20 torr with 0.1 wt% SnO catalyst. The optical purity decreased when the molecular weight of PLA was >600.0 g/mol. This can be explained in terms of the enolization of oligomeric PLA. Enolization is another pathway for racemization and is related to the acidity of the α -proton on the methyl group next to the carbonyl group [24], as shown in Fig. 4. In the case of oligomeric PLA, enolization occurred because the α -proton is highly acidic, the degree of which increased with increasing molecular weight of the oligomeric PLA. This is probably because a longer oligomeric PLA contains more reaction sites that can enolize than a shorter oligomeric PLA.

Figure 5 shows the effect of the catalyst concentration on the optical purity of PLA when the depolymerization reaction was carried out using PLA with a molecular weight of 600.0 g/mol at 220 °C and 20 torr. The optical purity of the lactide decreased when the concentration of the catalyst was >0.1 wt%. Racemization is proportional to the amount of the basic impurities derived from the catalysts. The optical purity of the lactide decreased because the degree of racemization increased with the basic impurities derived from the catalysts.

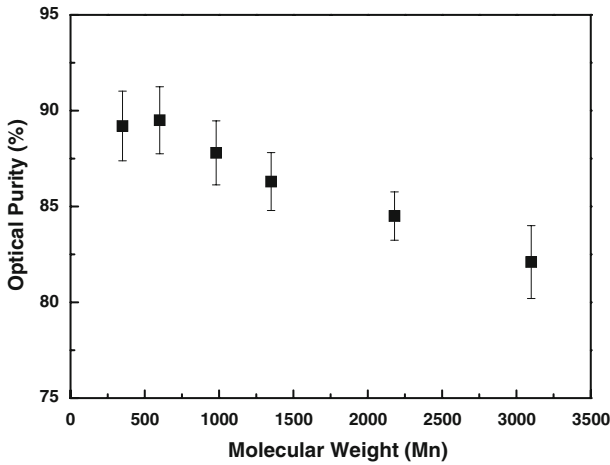


Fig. 3 Optical purity (%) of the crude lactide produced from the depolymerization of PLA with different molecular weights

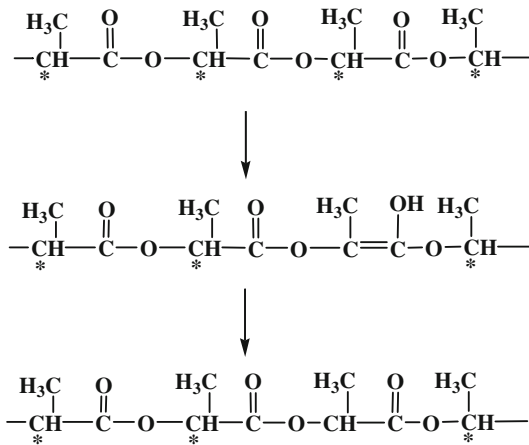


Fig. 4 Schematic diagram of the racemization of PLA through enolization

The optical purity data of the lactide synthesized were analyzed by two-way and one-way ANOVA methods. The two-way ANOVA results in Table 1 which were obtained from Fig. 1 show that the temperature has significant effect on the optical purity as the *p*-value analyzed was 0.000, but the catalyst type does not as its value of 0.974. For the two-way ANOVA analysis, the interaction term between temperature and catalyst type was not statistically significant as the *P*-value was 1.000. The one-way ANOVA results in Table 2 indicate that the pressure (*p* = 0.010) and molecular weight (*p* = 0.032) were found to be statistically significant but the catalyst concentration (*p* = 0.739) was not.

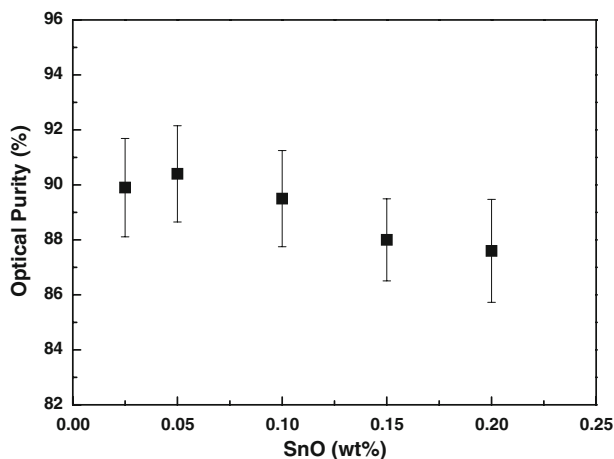


Fig. 5 Optical purity (%) of the crude lactide produced from the depolymerization reaction of PLA using different concentrations of the SnO catalyst

Table 1 Two-way ANOVA results for the optical purity data of the lactide synthesized from oligomeric PLA

Sources of variables	Sum of squares (SS)	Calculated <i>F</i> -value	<i>p</i> -value
Temperature (<i>A</i>)	1,758.4	51.16	0.000
Type of catalyst (<i>B</i>)	3.7830	0.07300	0.974
<i>A</i> × <i>B</i>	1.0670	0.01000	1.000

The level of significance was set at $\alpha = 0.05$

Table 2 One-way ANOVA results for the optical purity data of the lactide synthesized from oligomeric PLA

Sources of variables	Sum of squares (SS)	Calculated <i>F</i> -value	<i>p</i> -value
Pressure	6.1865×10^{-2}	5.235	0.010
Molecular weight	5.3768×10^{-2}	2.957	0.032
Catalyst concentration	3.3125×10^{-2}	0.4962	0.739

The level of significance was set at $\alpha = 0.05$

Optical purification of lactide

Figure 6 shows a typical NMR spectrum of the lactide sample obtained by purification of the crude. The signals were assigned to the chemical structure of the lactide, as shown in Fig. 6 [6, 25]. The $-\text{CH}_3$ signal of the *D,L*-lactide was observed at 1.70 ppm, while that of the meso-lactide was observed at 1.72 ppm. The fractional amounts of *D,L*- and meso-lactide in the product were calculated by comparing the integral areas of these signals [6, 26].

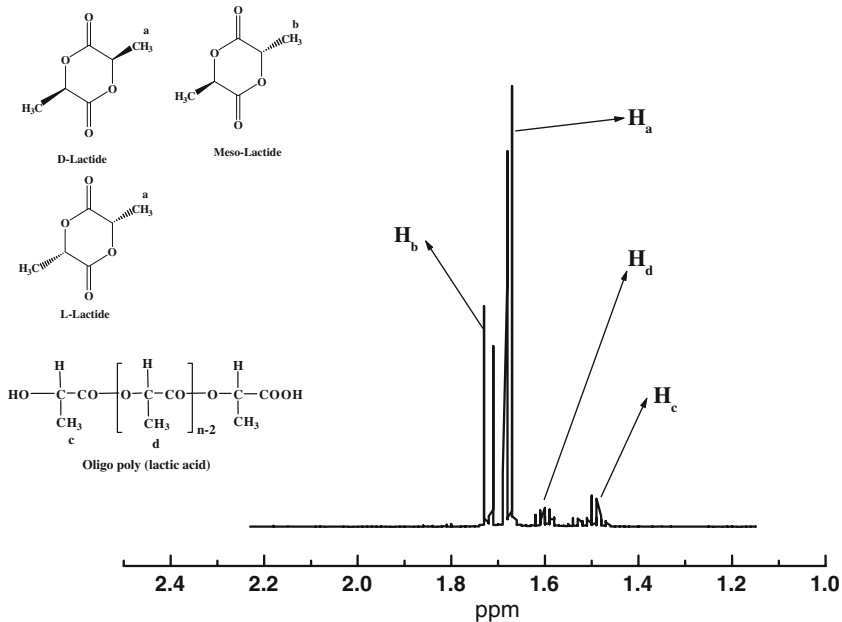


Fig. 6 ¹H-NMR spectra of the lactide and oligomeric PLA in the crude lactide

Figure 7 shows the effect of temperature on the meso-lactide fraction with stirring time when crude lactide was mixed with an equal weight of water. The mixture was stirred at a predetermined temperature for a predetermined time. As shown in Fig. 7, the fraction of the meso-lactide was similar at temperatures ranging from 5 to 45 °C, with minimum values of 3.8, 2.0, 1.3, 1.5, and 1.5% at 5, 15, 25, 35, and 45 °C, respectively. The fraction of the meso-lactide decreased significantly with increasing temperature, up to 25 °C, due to solubility in water decreasing with decreasing temperature. When the temperature was >35 °C, the remaining weight of the D,L-lactide decreased significantly with increasing temperature. Although the solubility of the meso-lactide in water increased with increasing temperature, the solubility of the D,L-lactide also increased significantly. The fraction of the meso-lactide did decrease greatly, however, within the first 10 min as the molten crude lactide came in contact with water in the initial step, as described in the “[Experimental](#)” section. The fraction of meso-lactide decreased gradually after 10 min. D,L-lactide crystals containing minor portions of meso-lactide were formed when the crude lactide was immersed in water. These meso-lactide portions were more soluble and crystallized to a lesser extent and thus could be removed as soon as the water could penetrate and make contact.

Figure 8a shows the change in the meso-lactide fraction when the crude lactide was mixed with an equal weight of water and other solvents (ethyl alcohol, *tert*-amyl alcohol, and *tert*-butyl alcohol) and stirred at 25 °C for 1 h. A lower fraction of the meso-lactide was observed when water was used as the solvent. This was attributed to the higher solubility of the meso-lactide in water.

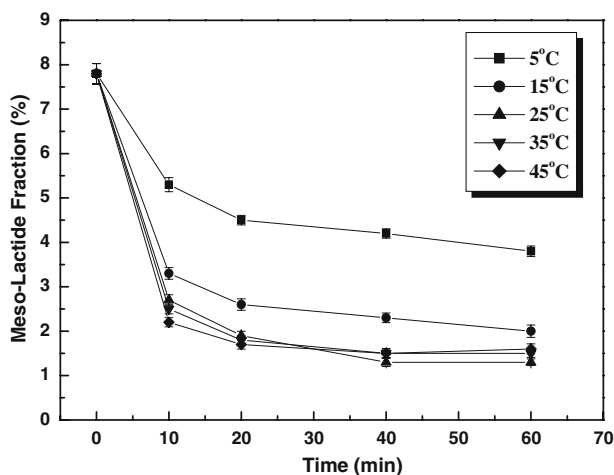


Fig. 7 Meso-lactide fraction as a function of the separation time at different temperatures

Figure 8b shows the effect of the stirring speed on the meso-lactide fraction when the crude lactide was mixed with an equal weight of water and stirred from 10 to 500 RPM at 25 °C for 1 h. When the stirring speed was increased from 10 to 200 RPM, the fraction of the meso-lactide decreased from 2.5 to 1.3%. In contrast, there was a small change in the fraction of the meso-lactide when the stirring speed was >200 RPM. These results can be explained in terms of the size of the crystallized D,L-lactide that was influenced mainly by the stirring speed in the above experiments. In the case of the larger crystals, the meso-lactide is retained in the crystals at higher concentrations compared with smaller crystals, which is the reason why a large amount of meso-lactide was observed at the lower stirring speed. It can be concluded that the stirring speed plays a key role in minimizing the remaining meso-lactate through improvement of the optical purity of the lactide by controlling the crystal size.

Figure 9 shows the optical purity of the lactide obtained after a purification step as shown in Fig. 7. The optical purity of lactide reached a maximum value of ca. 97% when the crude lactide was purified with water at 25 °C. This is probably because D-lactide is barely removed while the meso-lactide and other impurities are eliminated.

The meso-lactide fraction data of the lactide purified were analyzed by two-way and one-way ANOVA methods. The two-way ANOVA results in Table 3 from Fig. 7 show that the temperature ($p = 0.000$) and stirring time ($p = 0.000$) have significant effect on their responses. The interaction term between temperature and stirring time was also found to be statistically significant ($p = 0.000$). The one-way ANOVA results in Table 4 show that the solvent type ($p = 0.000$) and RPM ($p = 0.000$) were statistically significant. The ANOVA analysis for Fig. 9 ($p = 0.016$) was also found to be statistically significant.

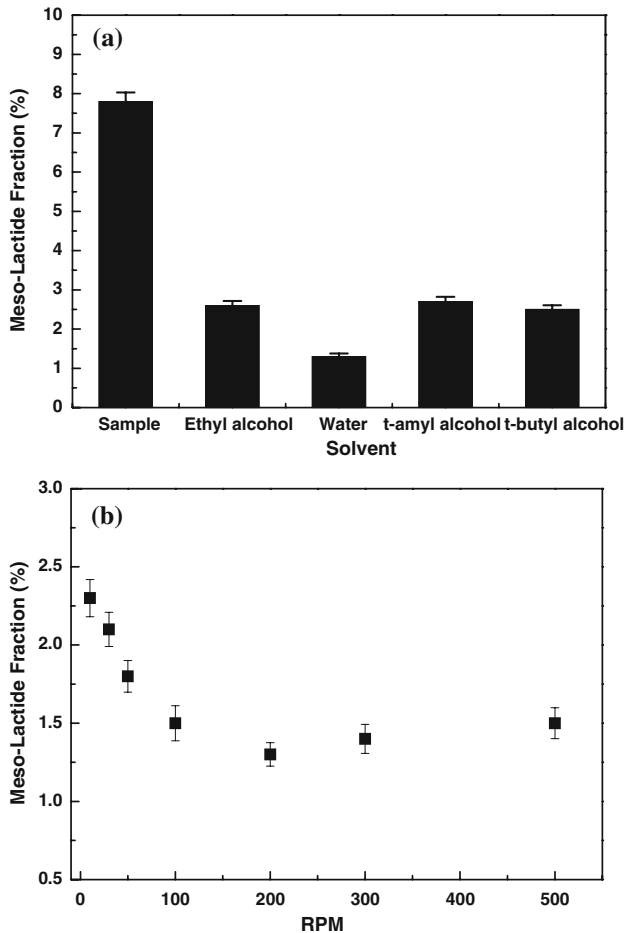


Fig. 8 Meso-lactide fraction as a function of (a) solvent used and (b) stirring speed (RPM)

Synthesis of PLA

The following Mark–Howink equation was used to determine the viscosity average molecular weight. The parameters involved in Eq. 2 were obtained for the PLA/chloroform system at room temperature [27].

$$[\eta] = 5.45 \times 10^{-4} M_v^{0.73} \quad (2)$$

The crude and purified lactides were used for investigating the effect of impurities and optical purity on the synthesis of PLA. (The crude lactide composition were D,L-lactide: 85.2 wt%, meso-lactide: 7 wt%, and hydroxyl impurities: 7.8 wt%. In case of the purified lactide, the composition were 98.2, 1.3, and 1.5 wt%) from Table 5, it can be readily seen that higher molecular weight PLA was produced when purified lactide was used. The crude lactide contains more

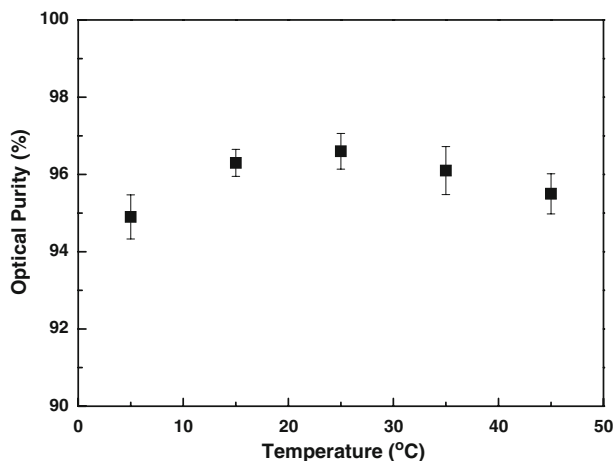


Fig. 9 Optical purity (%) of the purified lactide at different separation temperatures

Table 3 Two-way ANOVA results for the meso-lactide fraction data of the lactide purified

Sources of variables	Sum of squares (SS)	Calculated <i>F</i> -value	<i>p</i> -value
Temperature (<i>A</i>)	104.35	448.2	0.000
Time (<i>B</i>)	20.780	119.0	0.000
<i>A</i> × <i>B</i>	1.6220	2.323	0.013

The level of significance was set at $\alpha = 0.05$

Table 4 One-way ANOVA results for the meso-lactide fraction data of the lactide purified

Sources of variables	Sum of squares (SS)	Calculated <i>F</i> -value	<i>p</i> -value
Type of solvent	7.3457×10^{-4}	37.80	0.000
RPM	5.7578×10^{-4}	13.77	0.000

The level of significance was set at $\alpha = 0.05$

Table 5 Molecular weights, optical purity, and yields of PLAs synthesized with crude and purified lactide

	M_v	OP (%) ^a	OP (%) ^b	Yield (%)
Crude lactide	4,530	91.1 (± 0.73)	91.7 (± 0.71)	37.3 (± 0.63)
Purified lactide	80,400	97.3 (± 0.92)	98.1 (± 1.06)	78.5 (± 1.49)

^a Determined by polarimeter

^b Determined by ^{13}C -NMR spectra

hydroxyl group impurities (lactic acid, lactoyl lactic acid, and water) than the purified lactide and lactide polymerization is very sensitive to the presence of hydroxyl groups as they can affect polymerization through interaction with initiator formation, chain transfer, and transesterification.

The optical purity of the synthesized PLA was first determined by Eq. 3:

$$L \times [\alpha]_{\text{L}}^{25} + (1 - L) \times [\alpha]_{\text{D}}^{25} = [\alpha]_{\text{obs}}^{25} \quad (3)$$

where L is the ratio of the L-lactate in the PLA and the optical specific rotation of 100% optical pure poly(L-lactic acid) and poly(D-lactic acid) at 25 °C are referred to as: $[\alpha]_{\text{L}}^{25} = -151^\circ$ and $[\alpha]_{\text{D}}^{25} = +151^\circ$ [21].

When the purified and crude lactides were used, the optical purities of synthesized PLA were 97.3 and 91.3%. (The optical purity of the crude lactide and purified lactide were 89.5 and 96.6%).

In addition, the optical purity of the synthesized PLA was determined by ^{13}C -NMR. According to literature, the signals at 16.9, 69.3, and 169.3 ppm are assigned to the methyl (CH_3), methine (CH), and carbonyl (COO) functionalities, respectively [28]. Peak A denotes the isotactic lactyl units and the multiplets B and C indicate different optical isomers in the polymer chain as shown in Fig. 10.

$$\text{Optical Purity} = A / (A + B + C) \quad (4)$$

In the case of the purified lactide, optical purity of the PLA was 98.1%, similar to the value (97.3%) determined by Eq. 3.

When the PLA was synthesized using the purified lactide, a higher optical purity of PLA was obtained as the purified lactide contains less D-lactate due to the removal of meso-lactide by purification. In case of crude lactide, little racemization might occur during polymerization because of impurities, such as lactic acid and lactoyllactic acid. But the effect of impurities in the presence of crude lactide on the racemization might not be significant at reaction temperature. (It may not be high temperature for occurring racemization greatly) The optical purity of PLA might be significantly affected by that of the lactide used. Therefore, preparation of a lactide with high optical purity is the most important process in PLA production. PLA with ca. 98% in the purity was produced using lactide obtained according to the purification method.

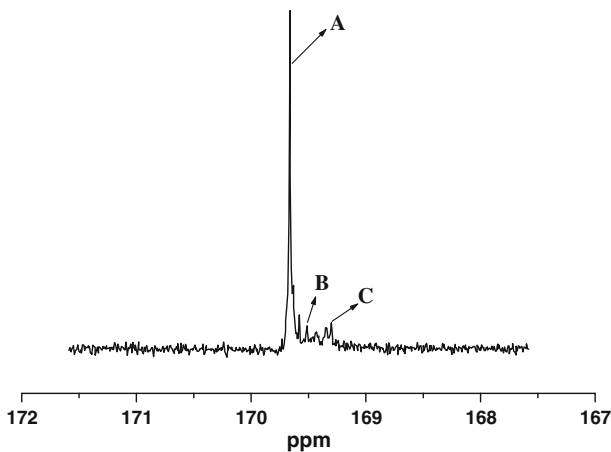


Fig. 10 ^{13}C -NMR spectra of carbonyl carbon atoms in the PLA

Conclusion

PLA with high optical purity was produced from L-lactic acid through the depolymerization of oligomeric PLA and the separation of crude lactide. In the depolymerization step, temperature had a more significant effect on optical purity of the lactide than the catalysts. A higher optical purity of the lactide was obtained at a lower pressure. The degree of racemization increased with increasing molecular weight of oligomeric PLA and optical purity of the lactide decreased when the concentration of the catalyst was >0.1 wt%. In the separation of optically pure lactide, temperature had a significant effect on the meso-lactide fraction. It was observed that this fraction was minimized when separation was carried out at 25 °C, greatly decreasing during the first 10 min and then gradually between 20 and 60 min. A lower fraction of meso-lactide was obtained when water was used as the medium. The meso-lactide fraction also decreased as the stirring speed was increased to 200 RPM. It was concluded that stirring speed plays a key role in minimizing the remaining meso-lactate by producing smaller crystals at higher stirring speeds. The optical purity of the lactide obtained after the final purification step showed a maximum value of approximately 97%. The optical purity of PLA was significantly affected by that of the lactide used, whereby an optical purity of 98.1% was achieved using a lactide obtained through purification.

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