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Improved preparation of *D, L*-lactide from *D, L*-lactic acid using microwave irradiation

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Summary

D, L-Lactide was effectively synthesized by a two-step reaction under microwave irradiation, namely, the polycondensation of *D, L*-lactic acid into oligo(*D, L*-lactic acid) (ODLLA) and the unzipping depolymerization of the ODLLA into *D, L*-lactide. The influences of microwave irradiation power, irradiation time, catalyst type, and catalyst concentration on the polycondensation and the unzipping depolymerization were investigated, respectively. The results revealed that both polycondensation and unzipping reaction were remarkably accelerated and improved by microwave energy, and the reaction time for preparation of *D, L*-lactide catalyzed by zinc powder was shortened by at least 50% compared with conventional heating method. The yield of *D, L*-lactide by microwave method was 40.3% starting from aqueous *D, L*-lactic acid when 1.2% (w/w) of zinc powder was applied as a catalyst and the microwave time was 3.2 hours. An alternative protocol with advantages of fast reaction and a high yield was developed for the preparation of *D, L*-lactide from aqueous *D, L*-lactic acid.

Introduction

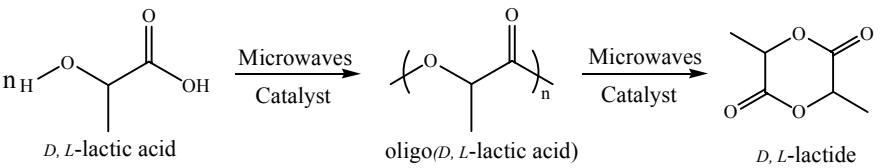
Polylactide (PLA), which is one of the most important biodegradable and biocompatible polyesters that are derived from annually renewable biomass such as corn and sugar beets, has attracted much attention for its favorable material properties [1-5]. The most efficient method for preparation of PLA is the ring-opening polymerization of the dimeric cyclic ester of lactic acid, lactide [1, 4-5].

Lactide is usually prepared by a two-step process: first, the lactic acid is converted into oligo(lactic acid) by a polycondensation reaction; second, the oligo(lactic acid) is thermally depolymerized to form the cyclic lactide via a unzipping mechanism [1]. Over the last two decades, considerable efforts have been made to improve the production process of lactide in order to reduce its production cost. Muller [6] developed a tin compounds catalyzed continuous or semicontinuous process for the preparation of lactide, in particular of optically pure *L*(-)- or *D*(+)-lactide, on an industrial scale. The advantages of this process are a high yield on an industrial scale,

high optical purity, and a better utilization of the actual depolymerisation reactor, thus a high throughput can be achieved even with relatively small units. Gruber and coworkers [7] presented a continuous process for the production of substantially purified lactide and lactide polymers from lactic acid or a lactate ester. Wang et al [8-9] synthesized *D, L*-lactide using a novel La_2O_3-TiO_2 nano-catalyst, they also reported the optimization of the reaction conditions for the preparation of high quality *D, L*-lactide from *D, L*-lactic acid. Ohara et al. [10] recently disclosed a process for consistently producing lactide from ammonium lactate obtained by lactic fermentation, by which the steps in producing lactide could be reduced. However, the conventional method for the preparation of lactide is time and energy consuming.

Microwave technology is a green method for chemical synthesis and process due to its high efficiency, selective and homogeneous heating [11], and its application in chemical synthesis has been extensively explored in the last two decades. Some organic reactions and polymerization reactions are significantly improved by microwave energy, which leads to a remarkable decreased reaction time, increased yields, and enhancement of the regio- and stereoselectivity [12-15]. For the microwave-assisted polycondensation, some homopolymer/copolymers of α-hydroxy acid [16-17], amides [18-19], imides [20-25], ureas [26] have been synthesized rapidly. And increasing attention has been focused on the microwave-assisted depolycondensation [27-28].

The ring-opening polymerization of *D, L*-lactide [29-30] under microwave irradiation and the microwave-assisted preparation of *D, L*-lactide from aqueous *D, L*-lactic acid (85%) was performed in our preliminary reports [31-32]. Recently, Wang et al. [33] reported a microwave-assisted rapid synthesis of *D, L*-lactide from *D, L*-lactic acid (100%) using a new binary catalyst based on tin (II) chloride and Cat-A. To understand the role of microwave irradiation in the reactions and optimize the reaction conditions to enhance the reaction yield, the influences of microwave irradiation power, irradiation time, catalyst type, and catalyst concentration on the polycondensation and the unzipping depolymerization were investigated in detail, respectively (Scheme 1), and the results are presented in this paper.



Scheme 1. Microwave-assisted polycondensation of *D, L*-lactic acid and unzipping depolymerization of oligo(*D, L*-lactic acid)

Experimental

Materials

Aqueous *D, L*-lactic acid (85%) was a commercially available reagent and other chemicals were of analytical grade, and were used without further purification. Double distilled water was used in the purification process.

Instruments

^{1}H NMR spectra were recorded with a Mercury VX-300 spectrometer, using $CDCl_3$ as a solvent and tetramethysilane (TMS) as an internal standard. The number-average molar mass ($\overline{M}_n$) and polydispersity index (PDI) of the ODLLA were determined by gel permeation chromatography (GPC) on a Waters HPLC system equipped with a Model 2690D separation module, a Model 2410 refractive index detector, and Shodex columns (K802.5, and K803, and K805). Chloroform was used as eluent at a flow rate of 1.0 mL·min^{-1}. The temperature of the columns and detector were 35°C and 30°C, respectively. Calibrations were fulfilled with narrow-molecular-weight distributed polystyrene standards. Gas chromatography (GC) analysis was carried out on an Agilent HP 6820 GC instrument equipped with a flame ionization detector (260°C) to determine the content of *D, L*-lactide in the product. Chromatographic separation was performed on a 30 m × 0.25 mm I.D. × 0.25 μm film thickness capillary column coated with cross-linked 5% phenyl methyl polysiloxane and the column temperature was programmed as follows: the initial temperature of 150°C was increased at a rate of 10°C·min^{-1} up to 250°C. Nitrogen carrier gas (250 KPa) at a flow rate of 1.2 mL·min^{-1} was used. The melting point of the *D, L*-lactide was measured with an X-4 digital melting point apparatus.

Microwave-assisted polycondensation of D, L-lactic acid

The polycondensation and the unzipping depolymerization were carried out in a modified domestic microwave oven (Whirlpool T1202, 2450 MHz) with a maximum power output of 850 W, and the output microwave power can be continuously tuned by adjusting the input power of the magnetron. Typically, aqueous *D, L*-lactic acid (200 g, 85%) and varied amount of catalyst were introduced into a three-neck 250 mL round-bottomed flask equipped with a nitrogen bleed, a condenser, and a carefully shielded thermocouple. The polycondensation was carried out with different microwave power with a nitrogen flow under a vacuum of 3.99 KPa and then microwave irradiation was stopped after the temperature of reaction mixture reached 170°C. The polycondensation reaction time was defined as the time for temperature of the reaction mixture to reach 170°C under microwave irradiation. The yield was determined by gravimetric method. After the polyconcensation was stopped, the yield was calculated as the ratio of actual weight of the ODLLA to the theoretical value. The theoretical yield was calculated based on a 100% reaction extent of the lactic acid in feed, which was [(200 × 0.85)/90] × 72=136 grams.

Microwave-assisted unzipping depolymerization of ODLLA

The above-mentioned mixture of ODLLA (130 g) and catalyst was kept in the flask and irradiated in a vacuum of 3.99 kPa under four energy levels of microwave irradiation, 140-340, 140-360, 140-380 and 140-400 W (denoting increasing microwave output from 140 W to the corresponding power within 20 min, respectively). With the temperature of the mixture above 170°C, the unzipping reaction of ODLLA occurred, and *D, L*-lactide was distilled out and collected. The crude product was separated by filtration, washed with cold water, and then dried in vacuum at ambient temperature until a constant weight was achieved. The reaction time for this stage was recorded until no distillate came out.

Polycondensation of D, L-lactic acid under conventional conditions

The conventional polycondensation of *D, L*-lactic acid was performed in a heating mantle under the same reaction conditions as those described in the microwave-assisted polycondensation. The polycondensation was halted when the temperature of reaction reached 180°C.

Results and discussion

Characterizations

Theoretically, three stereo-isomers of lactide can be formed in the process of unzipping depolymerization of poly(*D, L*-lactic acid), namely, *L*-lactide (S, S), *D*-lactide (R, R) and the optically inactive *meso*-lactide (R, S). *D, L*-Lactide is a racemic 1:1 mixture of *D*-lactide and *L*-lactide, and *meso*-lactide is removed from the crude products by filtration, water washing and recrystallization. Theoretical yield of *D, L*-lactide from *D, L*-lactic acid is 50% of moles of the starting materials [34].

The ODLLA obtained by the microwave-assisted polycondensation was characterized by ^{1}H NMR and GPC. The results showed the structure of ODLLA was similar to that of authoritative poly(lactic acid) [35] and the number-average molar mass ($\overline{M}_n$) of ODLLA ranged from 700 to 1300 g/mol with a polydispersity index (PDI) of 2.1~2.6. ^{1}H-NMR (300 MHz, TMS, $CDCl_3$, δ, ppm): 1.47 (3H), 1.56 (3H), 4.38 (1H), 5.18 (3H).

The crude product from microwave-assisted unzipping depolymerization was purified by recrystallization from acetic ether, and then was identified as *D, L*-lactide by ^{1}H NMR and melting point. The content of *D, L*-lactide in the product was determined by GC analysis. The results revealed the majority of *D, L*-lactide yields was around 40%, indicating a higher yield was obtained for *D, L*-lactide preparation by microwaves from aqueous *D, L*-lactic acid. mp124.1-125.1°C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS, δ, ppm): 1.65 (d, 3H), 5.05 (q, 1H).

Influence of the microwave irradiation power on the microwave-assisted polycondensation of D, L-lactic acid

The influence of the microwave irradiation power on the microwave-assisted polycondensation of 200 g *D, L*-lactic acid (85%) was investigated at 60, 80, 100, and 120 W with 0.8% (w/w) zinc powder as the catalyst.

It was observed that small amount of *D, L*-lactide crystal appeared on the wall of the condenser when the reaction temperature reached about 170°C during the microwave-assisted polycondensation process, suggesting an unzipping reaction of the resulting ODLLA, whereas the minimum temperature of the unzipping reaction under conventional heatingis usually above 180°C, reportedly [8-9]. This also showed that the depolymerization temperature of the ODLLA was slightly lowered under microwave irradiation.

Zinc powder has proved to be one of the most effective catalyst for the preparation of *D, L*-lactide under the conventional heating method [6, 9-10]. The effect of microwave irradiation power on the polycondensation was evaluated in terms of the ODLLA yield, the $\overline{M}_n$ of the ODLLA, and the reaction time for the polycondensation to complete (Figure 1). As shown in Figure 1, at 60, 80, 100 and 120 W, it took 190, 140, 115, and 100 minutes for the temperature of polycondensation mixture to reach

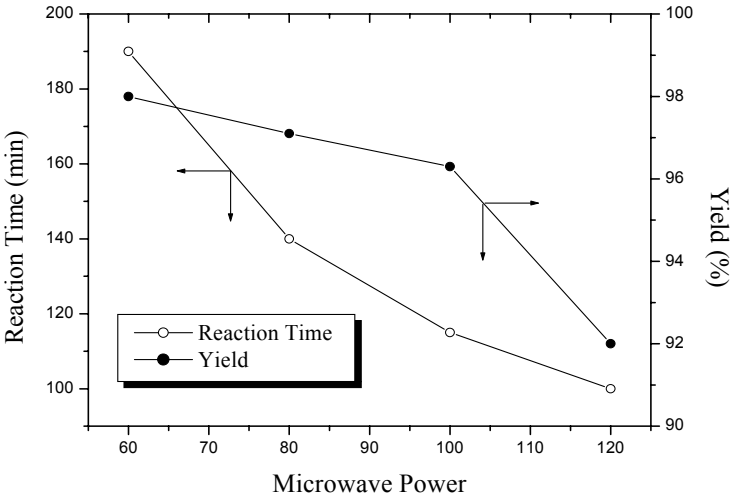


Figure 1. Effect of microwave irradiation power on polycondensation time and yield of ODLLA. [weight: 200 g of 85% *D, L*-lactic acid; zinc powder conc.: 0.8% (w/w)]

170°C, with corresponding ODLLA yield of 98.0, 97.1, 96.3, and 92.0%. Obviously, a higher microwave irradiation power reduced the reaction time and led to a decrease in the yield of ODLLA. This can be attributed to the higher temperature of the reaction mixture under higher microwave irradiation. At higher temperature, the unreacted *D, L*-lactic acid and other low molecular weight fractions in the reaction mixture are more likely to be distilled out and thus caused the decrease in the ODLLA yield. It can also be observed that the decrease in the yield of ODLLA became more significant when the microwave irradiation power was above 100 W, hence an appropriate microwave irradiation power level for the polycondensation was 80 W when 200 g of aqueous *D, L*-lactic acid (85%) was used.

Comparisons also were made between the microwave-assisted and the conventionally heated polycondensations in terms of the reaction time and the $\overline{M}_n$ of the ODLLA (Figure 2). Under microwave irradiation, the reaction time was 190, 140, 115, and 100 minutes at 60, 80, 100, and 120 W, respectively; and the corresponding $\overline{M}_n$ of the resulting ODLLA was 1,480, 1,250, 960, and 790 g/mol, respectively. It is concluded that the lower the microwave power was, the higher the $\overline{M}_n$ of the resulting ODLLA was. Under conventional heating, ODLLA with an $\overline{M}_n$ of 710 g/mol was obtained after 305 minutes reaction at 180°C. The results indicate that the polycondensation of *D, L*-lactic acid was significantly improved under microwave irradiation. Compared with the polycondensation under conventional heating condition, the polycondensation reaction time under microwave irradiation in the presence of zinc powder is shortened by above 50% (from 305 minutes to 140 minutes) at 80 W, which is similar to that reported by Sándor et al. [17].

The improvement of the polycondensation under microwave irradiation can be contributed to the unique advantage of the "microwave dielectric heating", which mainly originates from the dipolar polarization and ionic conduction of polar molecules in the alternating electric field. Lactic acid molecule has polar groups and can be heated up by microwaves effectively; water can also strongly absorb the microwave irradiation, thus the water generated in the polycondensation process can

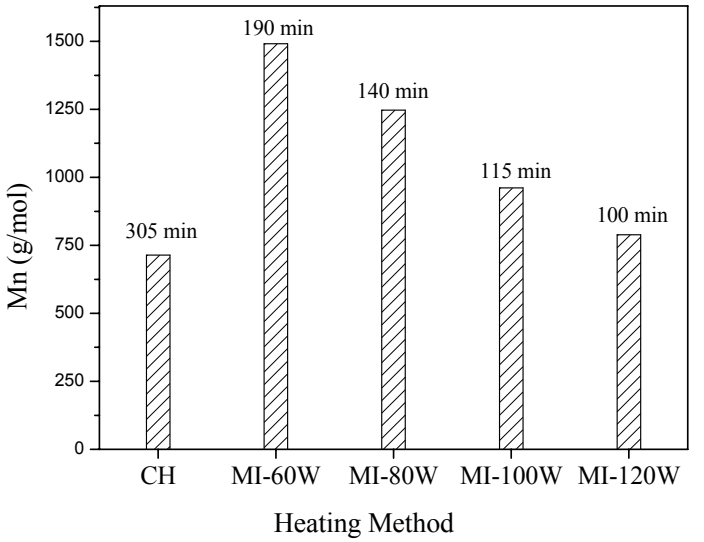


Figure 2. Comparisons of reaction time and $\overline{M}_n$ of ODLLA obtianed by conventional heating (CH), and microwave irradiation (MI) at different power levels. [weight: 200 g of 85% *D, L*-lactic acid; zinc powder conc.: 0.8% (w/w)]

be easily heated up and subsequently removed by distillation from the reaction mixture under vacuum. In the microwave-assisted polycondensation of *D, L*-lactic acid, the effective absorption of microwave irradiation by the reaction mixture enabled the rapid temperature increase hence led to the rapid reaction rate and shortened reaction time; the microwave irradiation also facilitated the successful removal of the water and helped the polycondensation reaction, which is a reversible reaction, to move forward and give ODLLA with higher $\overline{M}_n$.

Influence of the catalysts on the microwave-assisted polycondensation of D, L-lactic acid

The influence of the catalysts on the microwave-assisted polycondensation of *D, L*-lactic acid were investigated under 80 W microwave irradiation with varied concentration of zinc powder, zinc *D, L*-lactate ($Zn(LA)_2$), zinc oxide (ZnO), titanium oxide (TiO_2) and tin(II) chloride ($SnCl_2$) (Table 1), which have already proved to be efficient catalysts in the conventional heating method.

ODLLA was synthesized effectively with an $\overline{M}_n$ ranging from 730 to 1,310 g/mol and yield ranging from 96.5 to 97.8% by using these four catalysts. The shortest reaction time is 140 minutes with zinc power and the longest reaction time is 190 minutes using TiO_2 as catalyst.

It can also be observed that the yields of the ODLLA did not differ much with the four catalysts. The results reflected the fact that high yield of ODLLA can be obtained when an appropriate microwave irradiation power level was employed, the catalyst type and concentration can only affect the rate of the polycondensation and the $\overline{M}_n$ of the resulting ODLLA. However, these influences, as a whole, were less important than the effect of microwave irradiation power level on the polycondensation. It seems that the enhancement of microwaves on the reaction rate and $\overline{M}_n$ of ODLLA plays a dominant role during the polycondensation although the effect of catalyst exists.

Table 1. Influence of catalyst on the microwave-assisted polycondensation of *D, L*-lactic acid [a]

Entry	Catalyst	Catalyst Conc. [% (w/w)]	Reaction time (min)	M_n (g/mol)	PDI	Yield (%)
1	Zinc powder	1.2	140	1,310	2.4	97.3
2	Zinc powder	0.8	140	1,250	2.6	97.1
3	$Zn(LA)_2$	1.2	160	1,080	2.2	97.6
4	$Zn(LA)_2$	0.8	160	1,000	2.3	97.8
5	ZnO	1.2	170	980	2.3	97.2
6	ZnO	0.8	170	730	2.1	96.7
7	TiO_2	1.2	190	930	2.4	97.5
8	$SnCl_2$	1.2	180	1,160	2.1	96.5

[a] irradiation power: 80 W.

Influence of the microwave power on the microwave-assisted unzipping depolymerization reaction of ODLLA

The unzipping depolymerization of the ODLLA, which is a competitive reaction against the polycondensation of *D, L*-lactic acid, tends to take place when increasing the reaction temperature during the polycondensation process. The unzipping depolymerization of the ODLLA was carried out under vacuum (3.99 KPa) and four microwave irradiation power levels, using 130 grams of ODLLA varied amount of catalysts. The microwave irradiation was set at 140 W at the beginning and then gradually increased to corresponding power levels of 340, 360, 380, and 400 W in 20 minutes, this procedure was to allow further polycondensation of the low molar mass ODLLA in the mixture and avoid the loss of the low molar mass ODLLA. These four processes were designated as 140-340, 140-360, 140-380 and 140-400 W, respectively.

Figure 3 illustrates the temperature-time profiles of the unzipping depolymerization reaction mixture under the four microwave power levels. In the presence of 0.8%

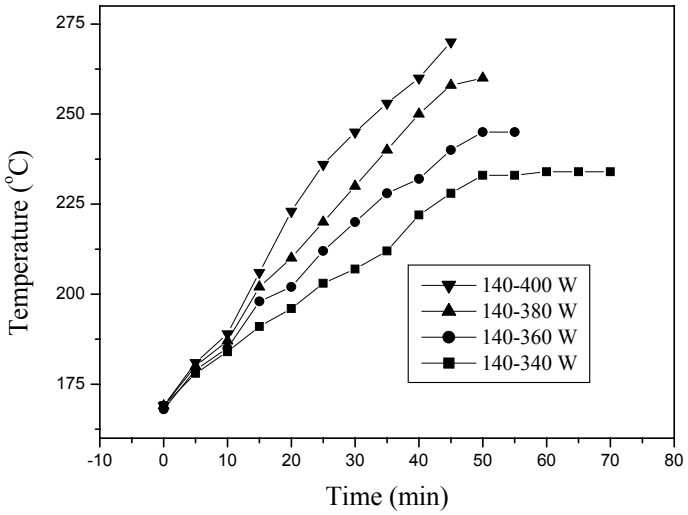


Figure 3. Temperature profiles of unzipping depolymerization of ODLLA under microwave irradiation. [weight: 130 g of ODLLA, $\overline{M}_n$: ~1000 g/mol, zinc powder conc.: 0.8% (w/w)]

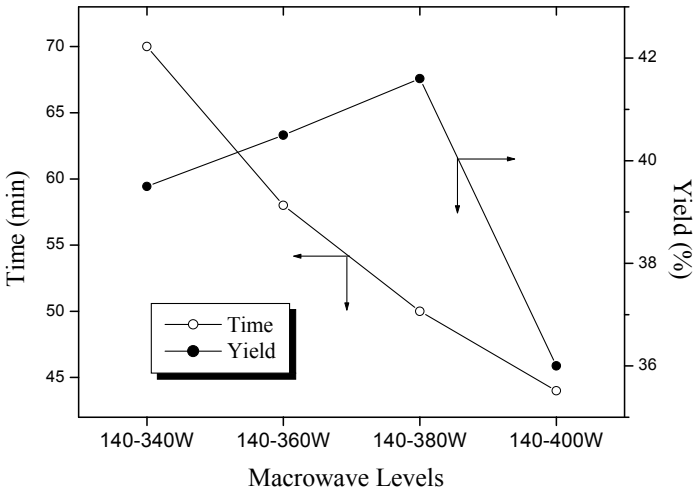


Figure 4. Effect of microwave energy on the reaction time and yield of *D, L*-lactide. [weight: 130 g of ODLLA, $\overline{M}_n$: ~1000 g/mol, zinc powder conc.: 0.8% (w/w)]

(w/w) zinc powder, the temperature of 130 grams of ODLLA increased rapidly under microwave irradiation. After 20 minutes' irradiation, the temperature increased from 170°C to 196, 202, 210, and 223°C under microwave power levels of 140-340, 140-360, 140-380 and 140-400 W, respectively. At 45 miutes, the corresponding temperature was 228, 240, 258, and 270°C. Apparently, the temperature of the reaction mixture increased with the microwave irradiation power at the same irradiation time.

In the presence of 0.8% (w/w) zinc powder, as shown in Figure 4, the reaction time tended to decrease with the increasing microwave irradiation power level for the four energy levels, whereas the yield of *D, L*-lactide increased first and decreased subsequently. The shortest microwave irradiation time was 44 min with a yield of 36.0 % under 140-400 W. The highest yield of *D, L*-lactide was 40.5 % at 140-380 W for 50 min. The results indicated that 140-380 W of microwave irradiation matched the rate of unzipping depolymerization, that is, 170~258°C was the optimum range for the microwave-assisted unziping depolymerization (Figure 3) and a high yield of *D, L*-lactide can be obtained by microwave method. The unzipping depolymerization time under microwave irradiation was reduced by 2/3 compared with that in the thermal unzipping depolymerization [8-9] indicating that the unzipping depolymerization was significantly accelerated under microwave irradiation.

Influence of the $\overline{M}_n$ value of ODLLA on the microwave-assisted unzipping depolymerization reaction of ODLLA

It was reported that ODLLA with high molar mass was unsuitable for the thermal unzipping reaction duo to the manner of heat transfer [36-37], in which heat is transferred to the reactants from the heat source through heat radiation, convection and conduction. As reported by Muller [6], the $\overline{M}_n$ value of ODLLA formed in the process of conventional polycondensation was controlled around 650 g/mol for the thermal unzipping depolymerization, which can run to approximately 73% conversion

of ODLLA to lactides. For the ODLLA obtained by microwave-assisted polycondensation, as mentioned above, the $\overline{M}_n$ was relatively higher than that by conventional heating. Therefore, with five ODLLA with an $\overline{M}_n$ of 790, 960, 1,280, 1,430 and 2,800 g/mol, respectively, the influence of the $\overline{M}_n$ of the ODLLA on the microwave-assited unzipping depolymerization was investigated at140-380 W for 50 minutes.

Suprisingly, no decreasing but increasing of the *D, L*-lactide yield can be observed with the increasing $\overline{M}_n$ of the ODLLA under microwave irradiation (Figure 5). For the five ODLLA samples with an $\overline{M}_n$ of 790, 960, 1,280, 1,430 and 2,800 g/mol, *D, L*-lactide was obtained with a yield of 41.0, 41.2, 41.8, and 42.3 % after the ODLLA was irradiated at140-380 W for 50 minutes. These results suggested that the optimum $\overline{M}_n$ of ODLLA for the unzipping depolymerization reaction was not constrained around 650 g/mol under microwave irradiation, and furthermore, an appropriate increase in $\overline{M}_n$ of ODLLA from 790 to 2,800 g/mol can improve the yield of *D, L*-lactide. It can also be attributed to the enhanced homogeneity of the temperature distribution in the reaction mixture under microwave irradiation.

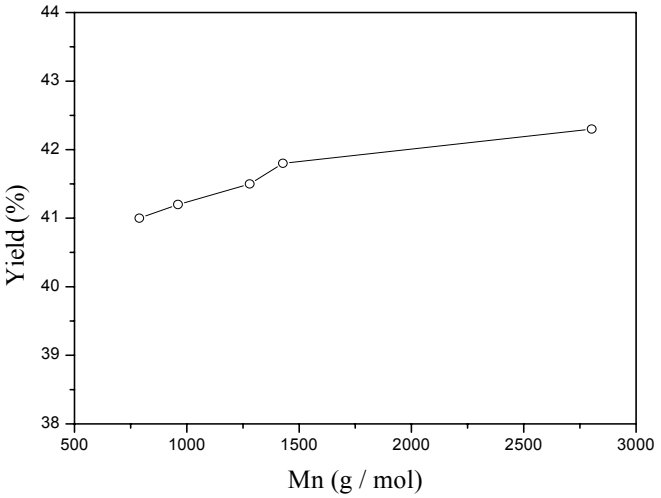


Figure 5. Effect of $\overline{M}_n$ of ODLLA on yield of *D, L*-lactide. [weight: 130 g of ODLLA; zinc powder conc: 0.8% (w/w); irradiation power: 140-380 W]

Influence of the catalysts on the microwave-assisted unzipping depolymerization reaction of ODLLA

Table 2 summarizes the effect of different catalysts on the microwave-assisted unzipping depolymerization reaction of ODLLA. The unzipping depolymerization reaction time ranged from 50 to 150 minutes and the yields of *D, L*-lactide ranged from 12.4 to 41.4 %. Among these catalysts, zinc powder, ($Zn(LA)_2$) ZnO and $SnCl_2$ were found to be more effective with corresponding *D, L*-lactide yield of 41.4, 38.0, 37.2, and 36.7%, respectively.

Figure 6 shows the effect of the concentration of zinc powder, $Zn(LA)_2$, ZnO and $SnCl_2$ on the yield of *D, L*-lactide. The highest yield of *D, L*-lactide for each catalyst is

Table 2. Effect of catalysts on the microwave-assisted unzipping depolymerization of oligo(*D, L*-lactic acid)[a]

Entry	Catalyst	Reaction time (min)	Lactide Yield (%)
1	Zinc powder	50	41.4
2	$Zn(LA)_2$	85	38.0
3	ZnO	80	37.2
4	$SnCl_2$	80	36.7
5	TiO_2	150	12.4

[a] weight: 130 g of ODLLA; $\overline{M}_n$: ~1,000 g/mol; catalyst conc.: 1.2% (w/w); irradiation power: 140-380 W.

41.4 (zinc powder), 39.3 ($Zn(LA)_2$), 38.3 (ZnO) and 37.9% ($SnCl_2$), corresponding to a catalyst concentration of 1.2, 2.0, 1.6 and 2.0% (w/w), respectively. It can be concluded that zinc powder was a suitable catalyst for microwave-assisted unzipping depolymerization reaction of ODLLA and the optimum concentration of zinc powder is about 1.2% (w/w). The results revealed that the the catalysts had an important impact on the microwave-assisted unzipping depolymerization reaction of ODLLA.

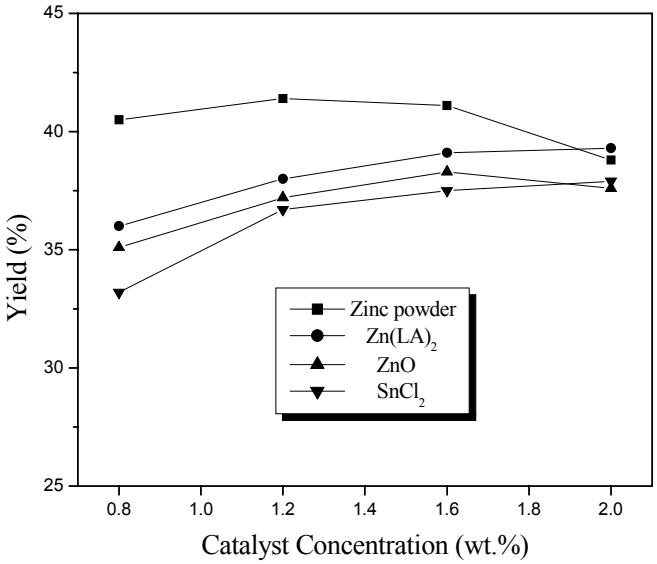


Figure 6. Effect of catalyst concentration on the yield of *D, L*-lactide. (weight: 130 g of ODLLA; $\overline{M}_n$: ~1000 g/mol; irradiation power:140-380 W)

Conclusions

The polycondensation of *D, L*-lactic acid and the unzipping depolymerization of ODLLA into *D, L*-lactide were performed with significantly improved reaction rate and yield under microwave irradiation. Compared with conventional method, reaction

time taken for the preparation of *D, L*-lactide catalyzed by zinc powder was shortened by at least 50%. The effect of microwave irradiation played a predominant role during the polycondensation, which not only significantly accelerated the rate of the polycondensation but also improved the $\overline{M}_n$ of the resulting ODLLA. ODLLA with an $\overline{M}_n$ of 10^3 g/mol and yield of 97% was obtained using zinc powder as a catalyst when 200g of aqueous *D, L*-lactic acid (85%) was irradiated for 140 min with 80 W microwave irradiation power. For the microwave-assisted unzipping depolymerization of ODLLA, the effect of catalyst species became obvious. Zinc powder is a suitable catalyst for microwave-assisted unzipping reaction. Under 140-380 W of microwave energy level for 50 min, the yield of unzipping ODLLA (130 g) was 41.4% using 1.2% (w/w) of zinc powder as the catalyst.

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