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Microwave-assisted Polymerization of D, L-Lactide with Stannous Octanoate as Catalyst

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Abstract: Poly (lactic acid) (PLA) was synthesized by microwave-assisted ring-opening polymerization of D, L-lactide with stannous octanoate ($SnOct_2$) as catalyst. Its weight-average molar mass (M_w) ranged from 39000 to 67000 and the polydispersity index from 1.3 to 1.7. The polymerization rate was much faster than that of the conventional thermal polymerization. A degradation of newly formed PLA in reaction mixture by microwave irradiation was observed.

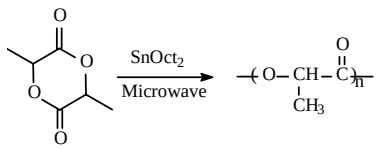
Keywords: Microwave-assisted ring-opening polymerization, Poly (D, L-lactic acid).

Poly (lactic acid) (PLA) is an important member of the polyesters which are used as biomedical materials in bioresorbable suture, implantates and drug controlled release systems[1]. PLA is prepared by two routs[2]: ring-opening polymerization of dimeric cyclic lactide or direct polycondensation of lactic acid. The ring-opening polymerization has attracted much more scientific and industrial interests than the later one, but both methods need long time for the polymerization reactions to be completed[1-3].

We applied microwave irradiation to the stannous octanoate catalyzed ring-opening polymerization of D, L-lactide and found that the polymerization was significantly enhanced.

The equation of this reaction is shown in **Scheme 1**.

Scheme 1



Experimental

A mixture of 0.90g (6.25mmol) D, L-lactide (m.p. 126°C, lit.: 124.5°C[4]) and 96.2 μL (0.065mol/L) $SnOct_2$ solution in toluene (monomer/catalyst molar ratio 1000:1) was subjected to reduced pressure (500Pa, 40°C) for 1 hour to remove the solvent and moisture and the vessel was sealed. Then, the reaction mixture was irradiated with various microwave power levels for different periods of time. The crude polymer was

dissolved in dichloromethane and precipitated by methanol. Reprecipitation was conducted in order to get pure polymer and the obtained PLA was dried in vacuum.

Results and discussions

The results by ring-opening polymerization of D, L-lactide at two microwave power levels, 85W and 170 W, are listed in **Table 1**, which show that PLA was formed in both cases and its weight-average molar mass (M_w) ranged from 39000 to 67000 with polydispersity index from 1.3 to 1.7. The microwave power and irradiation time both had remarkable impact on the polymerization. At 170 W of microwave power for 10, 15, 20, 30 min., the yield of PLA was 43.3%, 56.7%, 55.6% and 36.7% and the corresponding M_w was 59000, 67000, 41000, and 39000, respectively. The optimum irradiation time was 15 min., which gave the highest yield (56.7%) and M_w (67000). When the irradiation time lasted from 15 min. to 20 min., a remarkable decreasing in M_w of PLA occurred (from 67000 to 41000), but the decreasing in its yield was slight (from 56.7% to 55.6% only). However, a longer irradiation (30 min.) led to a lower yield (36.7%). Obviously, newly formed PLA degraded when the irradiation was over 15 min.. It seems that PLA degradation took place in the middle of backbone at first, and then, the broken parts, which could be precipitated by methanol, degraded further to give methanol soluble pieces.

The yield of PLA at 85W for 60 min. (31.1%) was lower than that at 170 W.

Table 1 Results of microwave-assisted ring-opening polymerization of D, L-lactide

Entry	Power (W)	Time (min)	Monomer/catalyst (Molar ratio)	Yield (%)	M_w	M_w/M_n
1	85	60	1000:1	31.1	54000	1.3
2	170	10	1000:1	43.3	59000	1.5
3	170	15	1000:1	56.7	67000	1.7
4	170	20	1000:1	55.6	41000	1.6
5	170	30	1000:1	36.7	39000	1.6

By conventional thermal method (molar ratio of monomer/catalyst 1000:1 under 1063 Pa at 130°C), the ring-opening polymerization of D, L-lactide should take as long as 24 hours to give PLA with M_v of 49000[5]. So, the rate of microwave-assisted method was much faster than that of the conventional method.

Acknowledgments

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