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Notes

Rapid Melt Polycondensation of L-Lactic Acid under Microwave Irradiation

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Introduction

Poly(lactic acid) (PLA) is expected to have wide application not only as biodegradable plastics, but also as biomedical material because of its advantages of biodegradability, biocompatibility, drug permeability and good mechanical properties.[1,2] Furthermore, lactic acid (LA) is easily obtained by a biotechnological process from inexpensive raw materials, such as starch, glucose and oligosaccharides.[2] Therefore, PLA has raised increasing interest and significant importance.

PLA can be prepared in two different ways[3]: ring-opening polymerization (ROP) of lactide or direct polycondensation of LA. The process of ROP can synthesize polymer with higher molecular weight, but it is lengthy which makes PLA rather expensive. The process of polycondensation is relatively simple, but it is not easy to prepare polymer with high molecular weight. Recently, with the rapid improvement of catalyst and synthesis methods, polycondensation shows more promising and more interesting. However, under conventional heating, both processes need long reaction time, usually tens of hours.[4-8] The shortening of reaction time is of great importance in reducing the energy consumption of PLA production.

Microwave technology is a green method for chemical synthesis because of its high efficiency and homogeneous heating.[9] Some polymerization reactions are also significantly improved by microwave energy and the microwave-assisted preparations of biodegradable polymers have been studied.[10-14]

Since the polycondensation of LA is accompanied by the release of water, and both LA and its oligomers are polar in nature, it is reasonable to expect microwave irradiations to influence the reaction. In literature, only Keki and coworkers[13] investigated the microwave-irradiated polycondensation of LA. However, the molecular weight of PLA that they prepared was no more than 2,000 g/mol, which had no practical application because of the low molecular mass and poor mechanical properties. Based on the experience of our previous works[10,14] about microwave-irradiated polymerization, we extended our investigation to the microwave-irradiated melt polycondensation of LA. In this paper, poly (L-lactic acid) (PLLA) with viscosity average molecular weight (M_v) of 5.08×10^4 was prepared. The effects of catalyst, microwave power level and irradiation time were discussed.

Experimental

Materials. L-Lactic acid was supplied as a 85 wt% aqueous solution by YanCheng HuaDe Biological Engineering Co., Ltd.(China). Stannous octoate ($Sn(Oct)_2$), Tin(II) chloride ($SnCl_2$), *p*-toluenesulfonic acid (TSA), zinc oxide (ZnO), tetrahydrofuran (THF), chloroform ($CHCl_3$) and methanol were all analytically pure degree. All materials were used without further purification.

Oligomerization. The oligomerization and polycondensation were carried out in a self-modified Gland-type domestic microwave oven (GuangDong, China, 2450 MHz and 800 W). Thirty grams of a 85 wt% aqueous solution of LA was irradiated at the microwave power of 320 W, first at a reduced pressure of 40 KPa for 15 min, then at 5 KPa for another 20 min. Then, a certain quantity of oligo(L-lactic acid) (OLLA) was formed. The M_v of OLLA was measured to be about 4,000 g/mol.

Polycondensation. A 150 mL one-necked flask was equipped with a mechanical stirrer and connected with a vacuum system. Fifteen grams of OLLA (see the previous paragraph) was charged into the flask and mixed with a predetermined amounts of catalyst. Then, the mixture was irradiated at a certain microwave power under mechanical stirring. The pressure was reduced to reach 5 KPa quickly, at which pressure the reaction was continued for a predetermined time to get the product of PLLA.

Measurement. Fourier transform infrared (FTIR) spectra of the polymer were recorded on a Nicolet-670 FTIR apparatus with KBr discs. ^{1}H NMR spectra were recorded on a Bruker AC-P300 MHz apparatus with tetramethylsilane (TMS) as an internal standard and with dimethyl sulphoxide (DMSO-d_6) as a solvent. Gel permeation chromatography (GPC) measurements were carried out on a Waters 410

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GPC instrument, using THF as eluent. Calibrations were fulfilled with narrow-molar-mass distributed polystyrene standards.

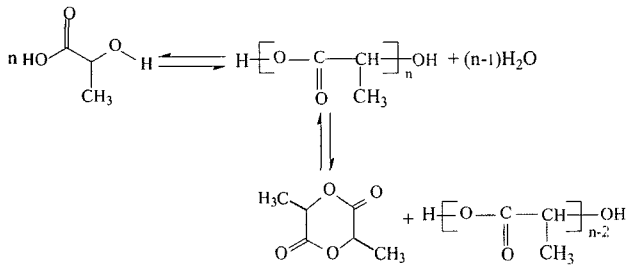
Intrinsic viscosity ([η]) of PLLA was measured with an Ubbelohde viscometer at 37 °C in THF, and viscosity average molecular weight (M_v) was calculated from the following equation[15]: $[\eta]=1.04\times10^{-4}M_v^{0.75}$

Results and Discussion

Characterization. The polymer obtained was confirmed as PLLA by means of FTIR spectroscopy and ^{1}H NMR spectroscopy. FTIR (KBr): 1758cm^{-1}(>C=O), 2946 (-CH_3), 2996 (-CH). ^{1}H NMR (DMSO-d_6): δ=1.45 ppm (3H, -CH_3), 5.19 (1H, -OCH-). The FTIR and ^{1}H NMR spectra of polymer were in agreement with those of an authorized PLA specimen. The GPC results showed that the polydispersity index (M_w/M_n) of PLLA with the M_v of 5.08×10^4g/mol was 1.59.

Catalyst Screening and Optimization. The polycondensation system of LA involves two reaction equilibria: dehydration equilibrium for esterification and ring-chain equilibrium involving the depolymerization of PLLA into lactide (Scheme I).

For obtaining a high polymer of PLLA, the two equilibrium reactions should be controlled in parallel. In the melt polycondensation, one possible way to promote polycondensation is to activate the dehydrative reaction and deactivate the formation of L-lactide by the possible selection of a catalyst. On the other hand, the starting LA and its primary condensates contains both carboxyl and hydroxyl groups in a high ratio, causing a high polarity for the reaction system,

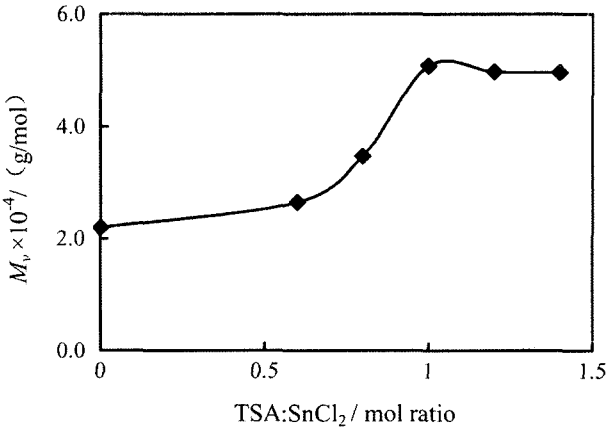


Scheme I. Two equilibrium reaction in the polycondensation of L-lactic acid.

whereas the resultant PLLA consists of less polar ester groups, leading to a great decrease in polarity. This polarity change is the main cause of the deterioration of catalyst activity. Therefore, we first prepared OLLA with sufficient degree of polymerization by the noncatalytic dehydration of LA, and then the catalyst was added to it for the continuation of its polycondensation.

We selected some typical catalysts to test in order to find an effective catalyst. The effects of various catalysts are shown in Table I. The results indicated that $SnCl_2$ was of good dispersibility and solubility in reaction system and could make the M_v of PLA higher. However, $SnCl_2$ as catalyst couldn't get the polymer with satisfactory color. Fortunately, TSA as catalyst could make the color of polymer pale. Therefore, in order to get PLLA with greater M_v and paler color, it was suitable to use a kind of compound catalyst system with $SnCl_2$ as main-catalyst and TSA as co-catalyst.

Figure 1 shows the effects of molar ratio of TSA to $SnCl_2$ on the M_v of PLLA in the melt polycondensation catalyzed by $SnCl_2$/TAS system. When the ratio was 1.0, the M_v increased up to 5×10^4 g/mol after 40 min. While the ratio reached 1.2 and 1.4, the M_v did not increased continuously. Moreover, the addition of TSA to $SnCl_2$ made the color of PLA paler. Therefore, the optimal amount of TSA to $SnCl_2$ should be a molar ratio of 1.0. The probable mechanism[7] of



*Reaction Conditions: MP =528 W, $SnCl_2$:OLLA=0.45 wt%

Figure 1. Effects of mol ratio of TSA to $SnCl_2$ on the M_v of PLLA.

Table I. Effects of Various Catalysts on Melt Polycondensation of OLLA

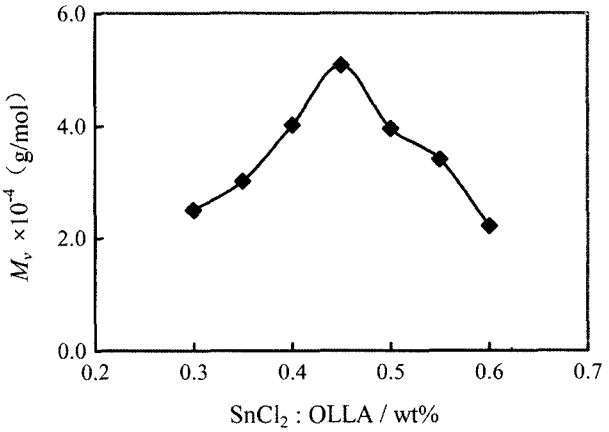
Run	Catalyst	$M_v\times10^{-4}$/ (g/mol)	Appearance	Dispersibility	Solubility
1	ZnO	1.166	Pale brown	Common	Not
2	$Sn(Oct)_2$	1.074	Brown	Good	In the end dissolve
3	$SnCl_2$	2.198	Pale brown	Good	Good
4	TSA	0.916	White	Good	Good

[a]Reaction Conditions: Microwave power (MP)=528 W, Cat.: OLLA=0.45 wt%.

TSA to discolor and increase the M_v of PLLA is that the addition of TSA increases the acidity of system which can promote the dehydration and reaction rate. On the other hand, because TSA is not involved in the esterification, it can fill the open coordination sites of the catalyst to prevent side reactions. If the molar ratio of TSA is too high, the catalyst activity is hindered which will prevent the continuous propagation of molecular chain. Moreover, while the ratio of TSA is between 0 and 0.5, the M_v of PLLA increased slowly. It was considered that the low amount of TSA was not adequate to change the acidity of whole reaction system obviously and fill the open coordination sites of the catalyst effectively. As the result, the reaction rate of chain propagation hasn't large increase.

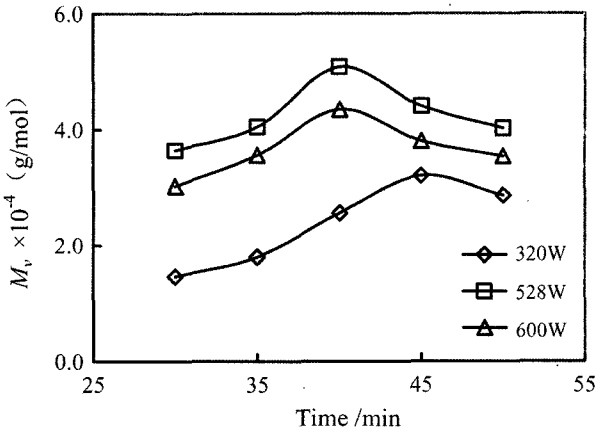
Figure 2 shows the typical results of the melt polycondensation of LA with various amounts of $SnCl_2$ at constant TSA to $SnCl_2$ ratio of 1.0. The results indicated that the optimal amount of $SnCl_2$ was 0.45 wt% relative to the amount of OLLA and the highest molecular weight of polymer was 5.08×10^4 g/mol. The molecular weight of polymer was strongly dependent on the amount of catalyst. With the increase in catalyst concentration from 0.3 to 0.45%, the molecular weight of PLLA increased until it reached maximum at 0.45%. However, beyond that value, the M_v of PLLA began to decrease. It was considered that $SnCl_2$ catalyzed not only the polycondensation of OLLA but also the decomposition of polymer. The catalysis rate increased with the catalyst concentration increasing. While the concentration increased to a certain value, the catalysis rate to decomposition became faster than that to polycondensation.[16]

Effects of Microwave Power and Irradiation Time. The microwave power and irradiation time also had great influence on the polycondensation of LA. Three levels of microwave power (320, 528, and 600 W) were examined. The changes of M_v with irradiation time under different power level are indicated in Figure 3.



*Reaction Conditions: MP=528 W, TSA:$SnCl_2$=1.0 (mol ratio), t=40 min.

Figure 2. Effects of $SnCl_2$ amount on the M_v of PLLA.



*Reaction Conditions: $SnCl_2$: OLLA=0.45 wt%, TSA:$SnCl_2$=1.0 (mol ratio).

Figure 3. Effects of microwave power level and irradiation time on the M_v of PLLA.

For the three microwave power levels, M_v-time curves were parabola-like, that is, increasing first and then decreasing. The greatest M_v value were 3.20×10^4 g/mol at 45 min for 320 W and 5.08×10^4 and 4.35×10^4g/mol at 40 min for 528 and 600 W, respectively. During the period of experiments (≤50 min), the order of M_v was 320 W<600 W <528 W. It seemed that with a reasonably stronger microwave power, the polycondensation took place faster. However, when the power extended a certain degree (>528 W), the increase in it was harmful to the increase in molecular weight of polymer. It was considered that the higher power made the temperature of system too high, and then, made the degradation and by-reactions easily occur.[17,18] The decreasing of the M_v of PLLA after reaching the maximum value indicated that PLLA was degraded by microwaves at the experimental power level (320, 528, and 600 W). It was deduced that degradation and polymerization occurred almost simultaneously at the three power level. With the irradiation time prolonging, the amounts of both terminal hydroxyl and carboxyl groups decreased, and the high viscosity of system inhibited the activity of reactive groups. The polymerization became difficult gradually, while the degradation was not influenced seriously.

In our pervious work,[18] under conventional heating (at 165 °C under 5 KPa), the polycondensation of OLLA should take as long as 480 min to get PLLA with the M_v of 4.86×10^4 g/mol. Obviously, the reaction rate under microwave irradiation has an immense increase compared with conventional heating.

Conclusions

This paper has shown that the melt polycondensation of

LA can be achieved efficiently under microwave irradiation and the reaction time can be shortened considerably compared with conventional heating. The polycondensation was successfully conducted with $SnCl_2$ activated by TSA. At the optimal amount of catalysts, namely 0.45 wt% $SnCl_2$ and equal mol ratio of TSA, PLLA with the M_v of 5.08×10^4 g/mol was obtained at 528 W for 40 min.

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