Microwave-Irradiated Ring-Opening Polymerization of D,L-Lactide Under Atmosphere

Shu Jing, Wang Peng, Zheng Tong, Zhao Baoxiu

Research Center for Green Chemistry and Technology, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin, 150090, China

ABSTRACT: Poly(D,L-lactide) (PDLLA) was synthesized by microwave-irradiated ring-opening polymerization catalyzed by stannous octoate (Sn(Oct)$_2$) under atmosphere. The effects of heating medium, monomer purity, catalyst concentration, microwave irradiation time, and vacuum level were discussed. Under the appropriate conditions such as carborundum (SiC) as heating-medium, 0.15% catalyst, lactide with purity above 99.9%, 450 W microwave power, 30 min irradiation time, and atmosphere, PDLLA with a viscosity–average molecular weight (M_η) over 2.0×10^5 and a yield over 85% was obtained. The dismission of vacuum to ring-opening polymerization of D,L-lactide (DLLA) under microwave irradiation simplified the process greatly. The temperature under microwave irradiation and conventional heating was compared. The largely enhanced ring-opening polymerization rate of DLLA under microwave irradiation was the coeffect of thermal effects and microwave effects. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2244–2247, 2006

Key words: microwave irradiation; poly(D,L-lactide); lactide; ring-opening polymerization; atmosphere

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 is easily obtained by a biotechnological process from inexpensive raw materials, such as starch, glucose, and oligosaccharides.[3] Therefore, PLA has raised increasing interest and significant importance. PLA can be prepared in two different ways[4]: ring-opening polymerization (ROP) of lactide (LA) or direct polycondensation of lactic acid. The polycondensation approach is difficult to prepare PLA with high molecular weight, and so the polymer does not have wide practical use because of its poor mechanical properties. The most important and general way to prepare high molecular weight PLA is through ROP. However, both methods need long time and should be run under high vacuum level or in an inert gas environment to complete the polymerization.[1–4]

More recently, there has been growing interest in microwave irradiation for polymerization reactions. For monomers containing polar groups that favor the absorption of microwaves,[5] microwave polymerization has proven to be more rapid and efficient than conventional heating. Wiesbrock et al.[6] introduced microwave-assisted polymerization in details, including step-growth, ring-opening, and radical polymerization. Addition polymerization,[7] condensation polymerization,[8–10] graft polymerization,[11,12] ROP(ring-opening polymerization),[13,14] and radical polymerization[15,16] have been markedly accelerated under microwave irradiation.

Few reports have been found in the literature concerning microwave-irradiation ROP of LA. Liu et al.[17] were the first to report the microwave-irradiated polymerization of D,L-lactide (DLLA). The polymerization rate was much faster than that of conventional heating. However, a high vacuum level or an inert gas environment was essential for the polymerization to occur.

To develop a technique of microwave-irradiated ROP of LA to prepare PLA with high molecular weight efficiently and easily, we investigated the ROP of DLLA in a domestic microwave oven under atmosphere. In our previous work,[18] PDLLA with a viscosity–average molecular weight (M_η) of 2.46×10^4 was prepared in 18 min under atmosphere by microwaves. In this work, PDLLA with an M_η over 2.0×10^5 was obtained. In addition, the influences of reaction conditions were discussed further. To our best knowledge, no data is available in the literature.

EXPERIMENTAL

Materials

D,L-lactic acid as a 85 wt % aqueous solution was purchased in Harbin, China. Stannous octoate

(Sn(Oct)$_2$, 95%, China) was used as a catalyst. The solvents used, i.e., tetrahydrofuran (THF), ethyl acetate, chloroform, and methanol, were analytically pure. All materials were used without further purification.

Procedure

The methods of synthesis and purification of DLLA starting from D,L-lactic acid could be seen in Ref. 18.

The apparatus used for the polymerization was a Gland domestic microwave oven (GuangDong, China, 2450 MHz and 800 W). A mixture of DLLA and Sn(Oct)$_2$ in an open beaker was irradiated at the microwave power of 450 W for some period of time, with a kind of assisted heating medium being used or not. In microwave oven, certain amount of heating medium was placed in a heat-resistant container, and then the beaker containing reactant was placed on the heating medium during the course of microwave irradiation.

To determine the structure and the yield of PDLLA, the cooled crude product was dissolved in chloroform and precipitated in methanol, and the precipitate was dried under vacuum. The yield was determined from the weight ratio of the precipitated polymer to the monomer.

Measurements

The purity of DLLA was measured by gas phase chromatography (GC). The structure of PDLLA was determined by ^{1}H NMR and FTIR. ^{1}H NMR spectra were recorded on a Bruker AC-P300MHz spectrometer, using tetramethysilane as an internal standard and deuterated dimethyl sulfoxide (DMSO-d$_6$) as a solvent at 25°C. FTIR spectra were recorded on a Nicolet-670FT-IR apparatus with KBr discs. The polydispersity index of crude PDLLA was determined by gel permeation chromatography (GPC) on a Waters410 GPC instrument. THF was used as eluent at a flow rate of 1.0 mL/min, and the molecular weights were calibrated with polystyrene standards.

Intrinsic viscosity ([η]) of crude PDLLA was measured with an Ubbelohde viscometer at 37°C in THF, and M_η was calculated from the following Mark-Houwink (M-H) equation[19]:

$$[\eta] = 1.04 \times 10^{-4} M_\eta^{0.75}$$

RESULTS AND DISCUSSION

Selection of assisted heating medium

In microwave-irradiated synthesis, some assisted heating medium, such as activated carbon, Al$_2$O$_3$, and Fe$_3$O$_4$, are usually used to accelerate and uniformize

TABLE I
Effect of Heating Medium on PDLLA

Medium	Time (min)	M_η (10^{-4})	Color
Activated carbon	10	1.23	Brown
SiC	18	2.46	Pale yellow
Al$_2$O$_3$	60	2.30	Pale yellow
No media	65	2.22	Pale yellow

Condition: Sn(Oct)$_2$/DLLA = 0.15 mol %; DLLA purity = 94.6%.

reactions. Table I lists the results of ROP of DLLA with some typical media at the optimal irradiation time. In each case, the purity of DLLA was 94.6%. The results indicated that carborundum (SiC) was particularly effective for shortening the irradiation time and getting higher molecular weight PDLLA. SiC is a kind of typical semiconductor material with high dielectric loss factor. Therefore, the main advantages of SiC in microwave field are that it can absorb microwaves effectively under low temperature and keep the temperature relatively stable.[20] When the reaction was running with it, the temperature of the reactant system increased rapidly and prevented overheating. The ability of activated carbon to absorb microwave was too strong to control the temperature reasonably. Consequently, the ROP of DLLA assisted by activated carbon was complicated by chain decomposition and carbonization, decreasing the molecular weight of PDLLA and causing discoloration of polymer. Al$_2$O$_3$ weakly absorbed microwaves, and so it barely accelerated polymerization rate. Therefore, based on the data in Table I, SiC was chosen as the best heating medium for further discussion about the ROP of DLLA under microwave irradiation.

Effect of monomer purity

The ROP of LA is extremely sensitive to the presence of hydroxyl groups that act as chain transfer agents. The most likely sources of hydroxyl group are impurities in LA, such as lactoyl lactic acid, lactic acid, and absorbed moisture. The effect of monomer purity on ROP of DLLA is indicated in Figure 1. There are four M_η–time curves with different purity DLLA as monomer. It can be found that the molecular weight of PDLLA obviously increased with increase in the purity of DLLA. PDLLA with the maximum M_η of 2.19 $\times 10^5$ was obtained in 30 min under atmosphere while the purity of DLLA was over 99.9%. It also seemed that the irradiation time corresponding to the top point of each curve prolonged with increase in the DLLA purity. At the same time, during the course of experiments, it was observed that a longer time to make DLLA completely melt was needed while the purity of DLLA was higher. However, this phenome-
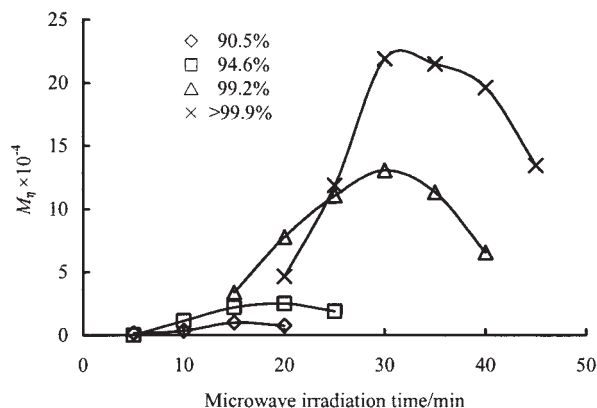
Figure 1 Changes of M_η of PDLLA with time under different lactide purity. Condition: $Sn(Oct)_2/DLLA = 0.15$ mol %.

non was not observed in conventional heating. Liu et al.[21] reported that the temperature of the mixture of LA and catalyst increased more quickly, and the stable temperature was higher than that of the sole LA. It was presumed to be related to the mechanism of microwave heating. The purer monomer decreased the amount of polar molecules in reactant system. As a result, the temperature increased more slowly, and then the irradiation time was prolonged.

Effect of catalyst concentration

Figure 2 shows the changes in molecular weight of PDLLA with different catalyst concentration. The molecular weight of polymer was strongly dependent on the amount of catalyst. With the increasing of catalyst concentration from 0.075 to 0.3%, the molecular weight of PDLLA increased until it reached a maximum at 0.15%. However, beyond that value, the mo-
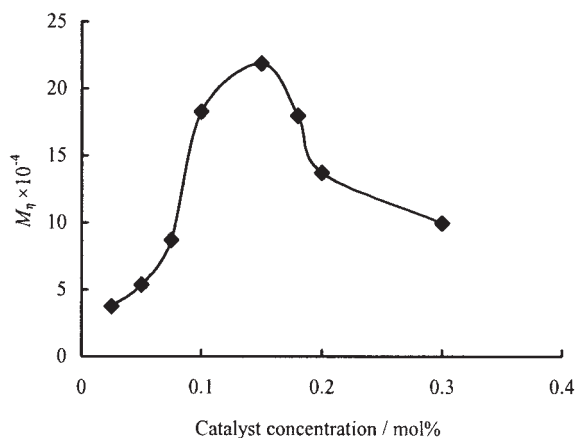

Figure 2 Changes of M_η of PDLLA with different catalyst concentration. Condition: irradiation time = 30 min; DLLA purity > 99.9%.

TABLE II
Effect of Vacuum Level on Polymerization of D,L-LA

Irradiation time (min)	Vacuum level of 0.098 MPa		Atmosphere	
	M_η (10^{-5})	Yield (%)	M_η (10^{-5})	Yield (%)
25	1.10	80.2	1.18	82.0
30	2.21	83.0	2.11	86.3
35	2.05	82.2	2.15	87.1
40	1.94	81.5	1.96	85.4
45	1.26	79.9	1.34	82.5

Conditions: $Sn(Oct)_2/DLLA = 0.15$ mol %; DLLA purity > 99.9%.

lecular weight of PDLLA began to decrease. This is because $Sn(Oct)_2$ catalyzes not only the polymerization of LA but also the decomposition of polymer. The catalysis rate to decomposition increases with the increase in catalyst concentration. While the catalyst concentration increases up to a certain value, the catalysis rate to decomposition will be faster than that of the polymerization. On the other hand, the higher concentration of catalyst increases the number of active species than decreasing the average amount of monomer for chain propagation on every active species.

Effect of vacuum level

A high vacuum level or inert gases are necessary for ROP of LA under conventional heating. To study the effect of vacuum level on microwave irradiation, experiments were carried out under atmosphere and high vacuum (2000 Pa), respectively. The results about the M_η and corresponding yield of PDLLA were summarized in Table II.

It was found that the M_η and appearance of PDLLA were not influenced by vacuum level. Satisfactorily, the yield of PDLLA under atmosphere was a little higher than that under vacuum. It was observed that small amount of DLLA crystallized on the beaker wall while the polymerization was terminated under these two conditions. However, the crystallization of DLLA was more obvious under vacuum than under atmosphere. The weight ratio of the precipitate polymer to the crude polymer ranged from 90–97% and was almost same under these two different conditions in the same time. The yield loss consists of the crystallized monomer and other product that could not be precipitated. The lower yield under vacuum was mainly due to the more crystallized monomer.

It is a breakthrough to carry out ROP of DLLA under atmosphere successfully. It simplifies the process greatly. The unnecessary of vacuum is due to the improved selectivity and accelerated reaction rate under microwave irradiation.

Thermal effects and nonthermal effects

In literature,[22] the ROP of DLLA should take as long as 24 h to get PDLLA with M_w of 1.8×10^5 under conventional heating method (at 140°C under 0.05 mmHg). In our previous work,[23] PDLLA with M_η about 2.0×10^5 needed 6 h at 160°C under 2000 Pa. It should be mentioned that microwave irradiation shortened the polymerization time to 30 min and dismissed vacuum. There is a controversial discussion as to whether the increase in reaction speed not only emerges from thermal effects, but also from (nonthermal) "microwave effects."[6] To confirm which effects are the main factors to accelerate polymerization speed in our experiments, the temperature of reactant had been tested. It was found that the temperature of the reactant under microwave irradiation assisted by SiC increased rapidly and was kept in a relatively fixed value subsequently. The fixed temperature was about 180°C, which is higher than the optimal temperature (160°C) under conventional heating. The decomposition rate of polymer increased obviously while the temperature exceeded 170°C under conventional heating. Microwave irradiation can make the ROP of DLLA run smoothly under higher temperature. On the other hand, the higher temperature under microwave irradiation was not enough to accelerate the polymerization rate so largely. Therefore, it was considered that the enhanced polymerization rate originated not only from thermal effect but also from nonthermal microwave effect in microwave-irradiated ROP of DLLA.

Characterization

The structure of PDLLA was confirmed by FTIR and ^{1}H NMR spectra. FTIR: $\lambda = 1456$ cm^{-1}(—CH$_3$), 1758 (O—$\overset{|}{\underset{}{C}}$=O), 2947 and 2998(—CH). ^{1}H NMR (DMSO-d$_6$): $\delta = 1.45$ ppm(3H, —CH$_3$), 5.17(1H, —OCH—). The above results were in agreement with those of an authorized PLA specimen.

The GPC results showed that the M_w is 2.43×10^5 g mol^{-1} and the polydispersity index (M_w/M_n) was 2.1 while the M_η was 2.04×10^5 g mol^{-1} as determined by the M-H equation.

CONCLUSIONS

This article has shown that the microwave-irradiated ROP of DLLA could be carried out efficiently under atmosphere. The reaction conditions, such as heating medium, LA purity, irradiation time, and catalyst concentration, had great influences on the molecular weight of PDLLA. PDLLA with an M_η over 2.0×10^5 and a yield over 85% was obtained in a very short irradiation time (30 min). Different from conventional heating, the microwave-irradiated ROP of DLLA dismissed vacuum because of the improved selectivity and accelerated reaction rate. Comparing the temperature under microwave irradiation with conventional heating, it was considered that the enhanced polymerization rate originated not only from thermal effects but also from microwave effects.

Microwave-irradiated polymerization of LA has the advantages of rapid speed and benign conditions over conventional heating, which is a potential new route to synthesize the high molecular weight PDLLA. With the rapid development of manufacturing level of microwave apparatus and researches on microwave-irradiated synthesis, it is sure that the industrialization of ROP of DLLA under microwave irradiation will become true in the near future.

References

1. Andreopoulos, A. G.; Hatzi, E.; Doxastakis, M. J Mater Sci: Mat Med 1999, 10, 29.
2. Moon, S. I.; Lee, C. W.; Miyamoto, M.; Kimura, Y. Polymer 2001, 42, 5059.
3. Kricheldorf, H. R. Chemosphere 2001, 43, 49.
4. Bendix, D. Polym Degrad Stab 1998, 59, 129.
5. Mingis, D. M. P. Chem Soc Rev 1991, 20, 1.
6. Wiesbrock, F.; Hoogenboom, R.; Schubert, U. S. Macromol Rapid Commun 2004, 25, 1739.
7. Bogdal, D.; Gorczyk, J. J Appl Polym Sci 2004, 94, 1969.
8. Vogel, B. M.; Mallapragada, S. K.; Narasimhan, B. Macromol Rapid Commun 2004, 25, 330.
9. Mallakpour, S.; Kowsari, E. J Appl Polym Sci 2004, 93, 2218.
10. Gao, C. L.; Zhang, S. B.; Gao, L. X.; Ding, M. X. J Appl Polym Sci 2004, 92, 2415.
11. Singh, V.; Tripathi, D. N.; Tiwari, A.;Sanghi, R. J Appl Polym Sci 2004, 95, 820.
12. Zheng, T.; Wang, P.; Zhang, Z. Q.; Zhao, B. X. J Appl Polym Sci 2004, 95, 264.
13. Wiesbrock, F.; Hoogenboom, R.; Abeln, C. H.; Schubert, U. S. Macromol Rapid Commun 2004, 25, 1895.
14. Zhang, C.; Liao, L. Q.; Liu, L. J. Macromol Rapid Commun 2004, 25, 1402.
15. Zhang, H. Q.; Schubert, U. S. Macromol Rapid Commun 2004, 25, 1225.
16. Goretzki, C.; Krlej, A.; Steffens, C.; Ritter, H. Macromol Rapid Commun 2004, 25, 513.
17. Liu, L. J.; Zhang, C.; Liao, L. Q.; Wang, X. L.; Zhuo, R. X. Chin Chem Lett 2001, 12, 663.
18. Zhang, K.; Wang, P.; Li, W. K.; Shu, J. Polym Mater Sci Eng 2004, 20, 46.
19. Deng, X. M.; Yuan, M. L.; Xiong, C. D.; Li, X. H. J Appl Polym Sci 1999, 71, 1941.
20. Janney, M. A.; Calhoun, C. L.; Kimrey, H. J Ceram Soc 1992, 75, 41.
21. Liu, L. J.; Liao, L. Q.; Song, Y.; Yu, Z. J.; Zhang, C. Polym Bull 2003, 5, 1.
22. Chen, L. X.; Jiang, Y. H.; Li, S. P. J Wuhan Univ Tech: Mater Sci Ed 2001, 16, 10.
23. Shu, J.; Wang, P.; Tian, L. Y.; Zheng, T.; Zhao, B. X. Chem Eng, to appear.