

THE RING-OPENING POLYMERIZATION OF D, L-LACTIDE WITH ONE COMPONENT RARE EARTH CATALYST*

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ABSTRACT

(D, L)-Lactide (LA) was first polymerized with one component of rare earth catalysts $[\text{Nd}(\text{naph})_3, \text{Nd}(\text{oct})_3, \text{Nd}(\text{O-iPr})_3, \text{Nd}(\text{AcAc})_3, \text{Y}(\text{AcAc})_3, \text{Sm}(\text{AcAc})_3, \text{Er}(\text{AcAc})_3]$ respectively in solution and in melt state. The effects of $[\text{Cat}]/[\text{LA}]$ molar ratio, solvents, polymerization time, temperature, various rare earth elements and ligands were investigated in detail. The results showed that both the conversion of polymerization and the molecular weight (MW) of poly (D, L-Lactide) (PLA) in melt polymerization are higher than that in solution polymerization, but the polymerization rate in melt was lower than in solution. The molecular weight distribution (MWD) of PLA is broader with increasing temperature. X-ray study indicated that PLA obtained by $\text{Nd}(\text{AcAc})_3$ in melt polymerization is an amorphous polymer.

INTRODUCTION

It is well known that PLA can be used as a biodegradable polymer in surgery, orthopaedics and drug delivery. In view of these features, the synthesis of PLA, preparation of LA block copolymer and possible application for biomedical materials have been extensively investigated in the past years. In the previous studies, SnCl_4 , $\text{Sn}(\text{Oct})_2$, $\text{Sn}(\text{C}_6\text{H}_5)_4$ and $[(n\text{-C}_4\text{H}_9\text{O})_2\text{AlO}]_2 \text{Zn}^{[1-3]}$ were used as catalysts in synthesizing PLA and LA copolymers. We have reported the polymerization of PLA by new catalysts composed of rare earth compound, trialkyl aluminium and water in toluene with high yield and controllable MW of PLA^[4]. In the present study, it is found that LA can be polymerized with one component rare earth catalyst. By using these catalysts, both the molecular weight and yield of PLA in melt polymerization were remarkably higher than that in solution polymerization, but the polymerization rate in melt state was lower than that in solution. The influences of catalyst concentration, temperature, solvent and time on the polymerization were examined. From the X-ray study, it indicated that the PLA obtained by $\text{Nd}(\text{AcAc})_3$ in melt polymerization is an amorphous polymer.

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EXPERIMENTAL

Materials

All solvents were treated with molecular sieve and then distilled before use. D, L-Lactide was prepared from lactic acid according to the procedure described by Kulkarni et al^[5]. All rare earth compounds were synthesized by the method as previously described^[6].

Polymerization

The polymerization was performed in a 25ml ampoule which was heated, evacuated and filled with nitrogen for several cycles before use. After addition of LA, catalyst, and solvent successively, flushing with nitrogen, ampoules were sealed, and then placed in a silicon oil bath at constant temperature. The melt polymerization was terminated by addition of acetone, PLA was dissolved in acetone and precipitated by petroleum ether containing 5% hydrochloric acid, washed with petroleum ether several times. The polymerization in solution was terminated directly by petroleum ether containing 5% hydrochloric acid. PLA was dried at 50°C under vacuum.

Measurement

The intrinsic viscosity of PLA in tetrahydrofuran (THF) was determined by Ubbelohde viscometer at 37°C. The viscosity-average molecular weight ($\overline{M}_\eta$) was calculated according to the following equation^[7]

$$[\eta] = 1.04 \times 10^{-4} \overline{M}_\eta^{0.75} (\text{dl/g})$$

The molecular weight distribution of the PLA was determined with a Waters Associates Model 208 gel permeation chromatograph with THF as eluent at 37°C. X-ray diffraction study was carried out with a Model Y-4 X-ray diffractometer.

RESULTS AND DISCUSSION

1. *Solution polymerization*

a. The effect of $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$ molar ratio on the polymerization of LA

With neodymium acetylacetonate $[\text{Nd}(\text{AcAc})_3]$ as catalyst for the polymerization of LA, it is found that LA can polymerize easily in toluene solution. Fig. 1 shows the maximum value of MW of PLA at $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$ molar ratio of 1.5×10^{-2} . At lower molar ratio of $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$, the MW of PLA increases with increasing $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$ molar ratio.

It is analogous to other catalytic polymerizations^[8,9], the polymerization active centers may be destroyed by trace amount of impurities which diffused slowly into static polymerization system. When $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$ molar ratio is over

1.5×10^{-2} , although the catalyst active centers is increased, but the monomer concentration remains constant, causing the molar ratio of the monomer vs. the catalyst becomes smaller and the MW of PLA drops gradually.

b. Effect of time on the polymerization of LA

The relationship among the conversion of LA (in %), the MW of PLA and polymerization time are indicated in Fig. 2 (which shows that the time is an important factor in the polymerization of LA). Both conversion and MW of PLA were increased remarkably with prolongation of time, owing to the rate of polymerization is not large enough at 125°C, and the life of active species of catalyst might be relatively long. The result is in accord with the polymerization of LA catalysed by rare earth coordination catalysts^[4].

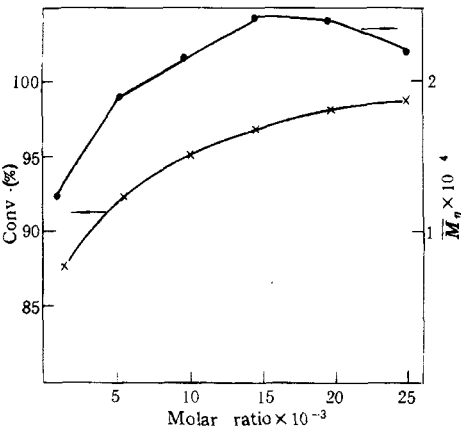


Fig.1 The effect of $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$ on the polymerization of LA. toluene, 398K, 36h, $[\text{LA}]=2.0 \text{ mol/L}$

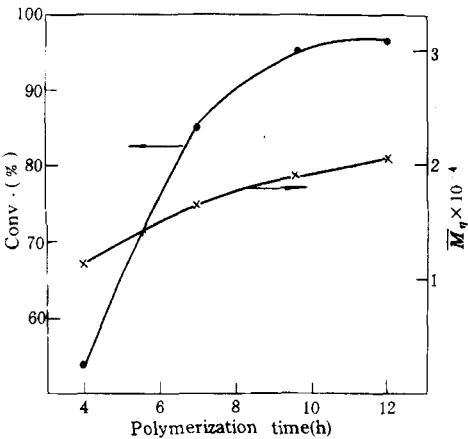


Fig.2 The effect of time on the polymerization of LA, toluene, $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]=1.67 \times 10^{-3}$, $[\text{LA}]=2.0 \text{ mol/L}$, 398K

c. Effect of monomer concentration on the polymerization of LA

The effect of LA concentration on the polymerization was examined. Fig. 3 shows that both the MW of PLA and the polymerization conversion are the function of monomer concentration at 125°C in toluene, the larger the monomer concentration, the higher the MW and yield of PLA, it is analogous to most other solution polymerization.

Table 1 Effect of various solvents on the polymerization of LA

Solvent	Tetrahydrofuran	Acetylacetate	Chloroform	Toluene
Conv. (%)	94.0	91.0	92.0	88.0
$\overline{M}_n \times 10^{-4}$	1.78	2.16	0.95	2.59

$[\text{Nd}(\text{AcAc})_3]/[\text{LA}]=1.67 \times 10^{-3}$; $[\text{LA}]=2.0 \text{ mol/L}$; 373K; 20h

d. Effect of solvents on the polymerization of LA

The polymerization was carried out in tetrahydrofuran, acetyl acetate, chloro-

c. Effect of $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$ molar ratio on the melt polymerization of LA

Fig. 4 shows that the $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$ molar ratio within a suitable range of 5×10^{-3} to 0.67×10^{-3} does not significantly influence the conversion. However, the MW of PLA reaches a maximum value at $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$ molar ratio of 1.07×10^{-3} , but it drops in linearly with increasing of catalyst.

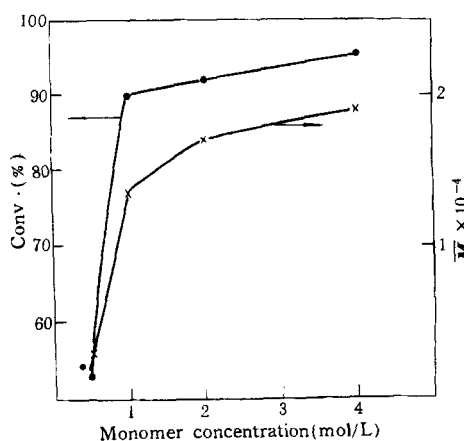


Fig. 3 The effect of monomer concentration on the polymerization of LA Toluene, $[\text{Nd}(\text{AcAc})_3]/[\text{LA}] = 1.67 \times 10^{-3}$, 398K, 20h

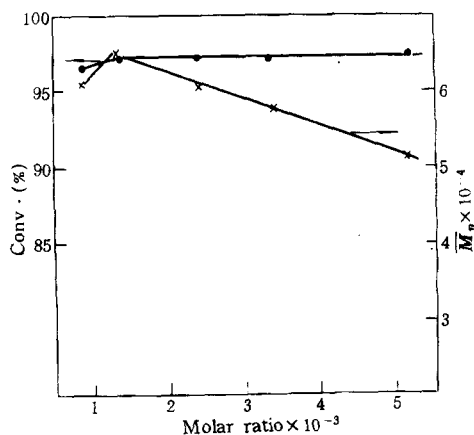


Fig. 4 The effect of $[\text{Nd}(\text{AcAc})_3]/[\text{LA}]$ molar ratio on the melt polymerization of LA. 413K, 48h

d. Effect of temperature on the melt polymerization of LA

In general, from the characteristics of kinetics and thermodynamics of melt polymerization, high temperature are frequently used to obtain reasonable polymerization rates^[10].

Further study demonstrates that the melt polymerization of LA may be carried out better at near 140°C, as shown in Fig. 5. This result is almost identical with bulk polymerization of LA catalyzed by tin-ethylhexanoate^[11]. Although the polymerization rate can be increased with further raising of temperature, but the MW of PLA decreases obviously and the distribution of MW of PLA becomes broader as indicated in Fig. 6. This might be caused by side-reactions, such as degradation, ester exchange and chain transfer reaction.

By comparing the results in Table 2 and 3 with that in Table 1, it can be found that both polymerization conversion and the MW of PLA in melt polymerization are higher than that in solution polymerization, due to higher monomer concentration in melt polymerization. In order to obtain high polymerization conversion, the polymerization time must be prolonged in melt polymerization. It means that the polymerization rate may be lower than that in solution polymerization, because at very high conversion, the reaction system becomes extremely viscous, all diffusions of active chain and monomer are very difficult.

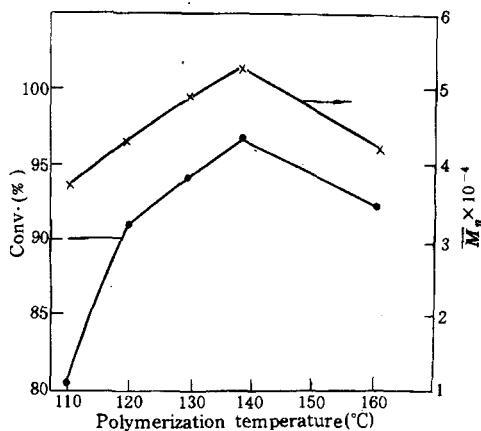


Fig.5 The effect of temperature on the melt polymerization of LA. [cat]/[LA]= 5.0×10^{-3} , 48h

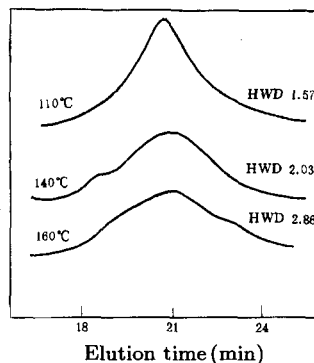


Fig.6 Dependence of the distribution of MW of PLA on polymerization temperature

In the study of X-ray diffraction of the PLA prepared by neodymium acetylacetonate, no sharp peak were observed. Therefore it is an amorphous polymer. This result is in consistent with our previous report^[4].

Keywords:

Ring-opening polymerization; (D, L)-Lactide; Poly (D, L-Lactide); Rare earth catalyst

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