

## Reaction Kinetics for the Synthesis of Oligomeric Poly(lactic acid)

Dong Keun Yoo and Dukjoon Kim\*

*Department of Chemical Engineering, Polymer Technology Institute, Sungkyunkwan University,  
300 Cheoncheon, Jangan, Suwon, Gyeonggi 440-746, Korea*

Doo Sung Lee

*Department of Polymer Engineering, Polymer Technology Institute, Sungkyunkwan University,  
300 Cheoncheon, Jangan, Suwon, Gyeonggi 440-746, Korea*

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**Abstract:** A low-molecular-weight poly(lactic acid) was synthesized through the condensation reaction of L-lactic acid. The effects that the catalyst and temperature have on the reaction rate were studied to determine the optimum reaction conditions. The reaction kinetics increased with temperature up to 210°C, but no further increase was observed above this temperature. Among a few selective catalysts, sulfuric acid was the most effective because it maximized the polymerization reaction rate. Reduction of the pressure was another important factor that enhanced this reactions kinetics.

**Keywords:** poly(lactic acid), reaction kinetics, catalysis, depolymerization.

### Introduction

It has been publicly accepted that the recyclable plastics will replace the petrochemical based ones continuously, and their market-share will reach up to 10 billion dollars in the near future. Poly(lactic acid) (PLA) is one of well known biodegradable polymers that has the most numerous applications in industries as plastics, fibers, and others.<sup>1,2</sup>

Since Dorough reported<sup>3</sup> in the first that the PLA synthetic process via direct condensation reaction has difficulties in attaining high molecular weight due to the occurrence of depolymerization reaction, a few replaceable synthetic routes have been developed. The azeotropic dehydration condensation method was one of them in which the polymerization reaction proceeded in-situ eliminating the majority of condensing water through azeotropic distillation in the presence of catalyst.<sup>4,5</sup> The chain coupling reaction was another one where low molecular weight PLA molecules were coupled to produce high molecular weight ones with the aid of various coupling agents such as isocyanate, acid chloride, anhydride, epoxide, oxazolines, ortho esters, etc.<sup>6-10</sup> As these two processes require quite severe operating conditions and thus are not noted profitable in economics, the most industrially acceptable PLA synthetic process is known via lactide formation reaction.<sup>11-13</sup> In this process, the lactic acid monomer

is first polymerized to oligomeric PLA, depolymerized to lactide, and then re-polymerized to attain high molecular weight by ring opening mechanism.<sup>14-17</sup>

In the commercial PLA synthetic process, however, the rates of reactions involved are of real importance, as they eventually affect the final production rate closely related with industrial profits. In this contribution, the oligomeric PLA synthetic reaction, the first reaction involved in the high molecular weight PLA synthetic process via lactide formation, was studied focusing on the temperature and catalyst effects on its kinetics. This study will help establishing the optimum reaction conditions for maximizing the polymerization reaction rate with minimizing racemization reaction rate.

### Experimental

**Materials.** L-lactic acid was purchased from Aldrich Chemical Company (Milwaukee, WI, USA). Two types of catalysts dibutyltin dilaurate (DBTL, Aldrich) and sulfuric acid (Aldrich) - were used for the synthesis of PLA. These catalysts were selectively chosen, as those were reported to be effective in minimizing the racemization and side reactions.<sup>18</sup>

**Polymerization Procedure and Sampling Method.** A 250 mL three-necked flask was equipped with a mechanical stirrer and a condenser. For each polymerization, 150 g of L-lactic acid with the catalyst, 0.1 wt%, was charged into the

\*e-mail: djkim@skku.edu

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flask. The flask was placed in an oil bath and temperature was raised from room temperature to desired temperature in the presence of nitrogen gas. For L-lactic acid polymerizations in vacuum, each sample was taken per each hour from each different reactor.

**Molecular Weight Measurement.** Three methods were used to measure the molecular weight of PLA synthesized. The viscosity average molecular weight was determined from the intrinsic viscosity measured using a semi-automatic viscometer (AVS350, Schott, Germany). PLA/chloroform solution was placed in a temperature controllable bath, and the viscosity was periodically measured using a Ubbelohde viscometer at 25 °C. Nuclear magnetic resonance spectroscopy (NMR, 500 MHz, Varian, USA) and gel permeation chromatography (GPC, NS-3000i, Futecs, Korea) were used to measure the number average molecular weight. For NMR measurement, the samples were dissolved in solvent of dimethylsulfoxide (DMSO). For GPC measurement, samples were dissolved in chloroform, and the solution was injected into the column at the rate of 1 mL/min.

## Results and Discussion

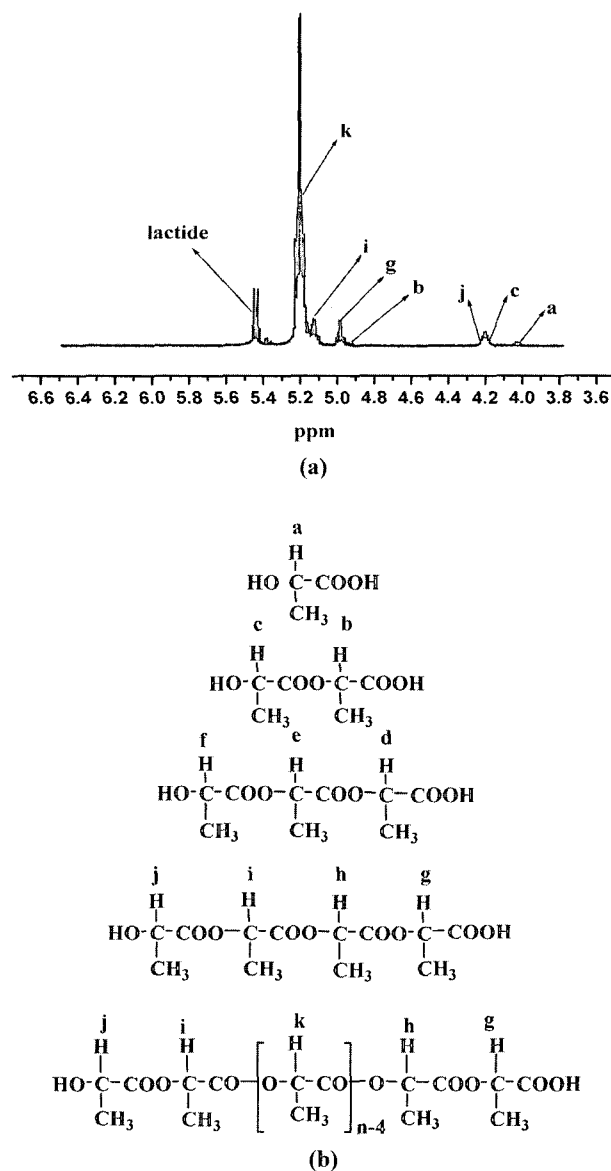
The following Mark-Houwink equation was used to determine the viscosity average molecular weight. The parameters involved in eq. (1) were obtained for the PLA/chloroform system at room temperature.<sup>19</sup>

$$[\eta] = 5.45 \times 10^{-4} M_v^{0.73} \quad (1)$$

Figure 1 shows the typical NMR spectrum of PLA sample taken during polymerization reaction. Each proton in the PLA molecule was well characterized by separate peak assignment as shown in Figure 1(b). Number average molecular weights of samples were determined from NMR spectra and eq. (2) derived from the theory that the length of a polymer molecule can be calculated from the number of protons in a molecule per proton positioned in its end group.<sup>20</sup>

$$DP_n = \frac{(k+i+g+b+j+c)}{(j+c)} \quad (2)$$

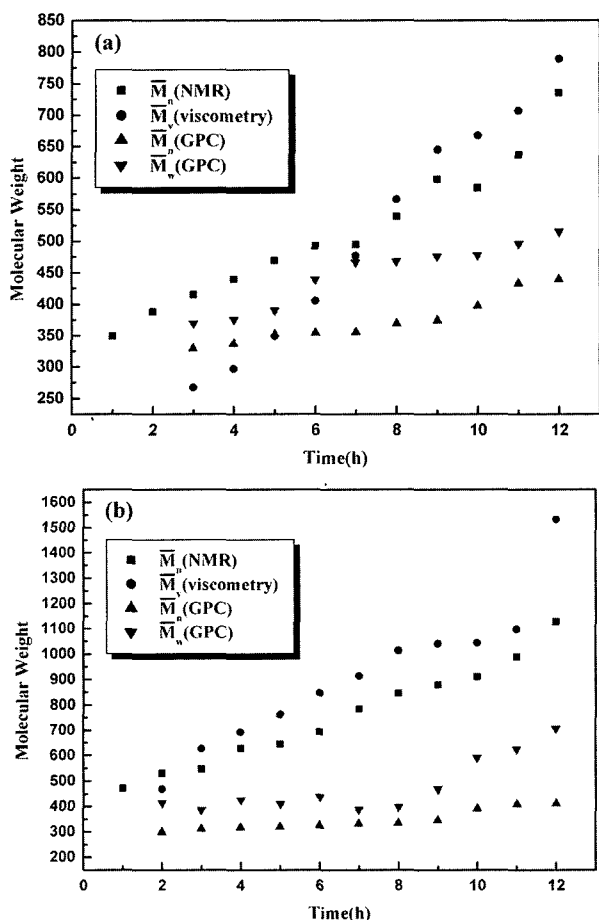
Figure 2(a) and (b) show the polymerization reaction kinetics of oligomeric PLA at 180 °C where molecular weights were measured by different methods. The molecular weights measured by viscosity and NMR methods increased monotonically with the progress of reaction and their values were very similar each other, but those by GPC quite different. GPC resulted in much lower molecular weights than the other two methods and it did not show monotonically increasing molecular weight behavior any more. It was presumably due to the calibration difficulty in GPC at low molecular weight range. Considering the measurement accuracy and convenience, the NMR method was chosen



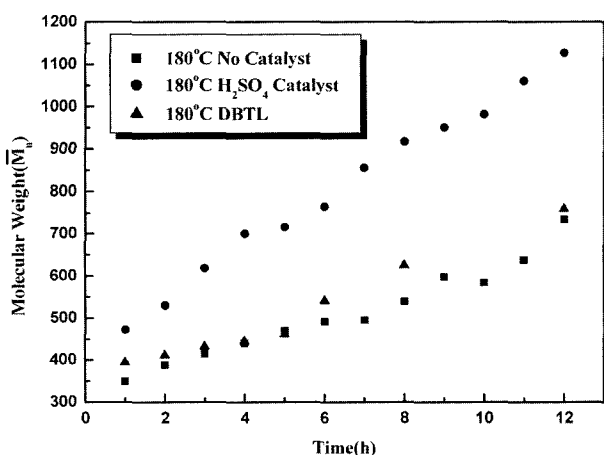
**Figure 1.** (a) <sup>1</sup>H NMR spectrum of low molecular weight PLA in DMSO-*d*<sub>6</sub> and (b) labeling of the different constitutive units of lactic acid oligomers.

for further analysis.

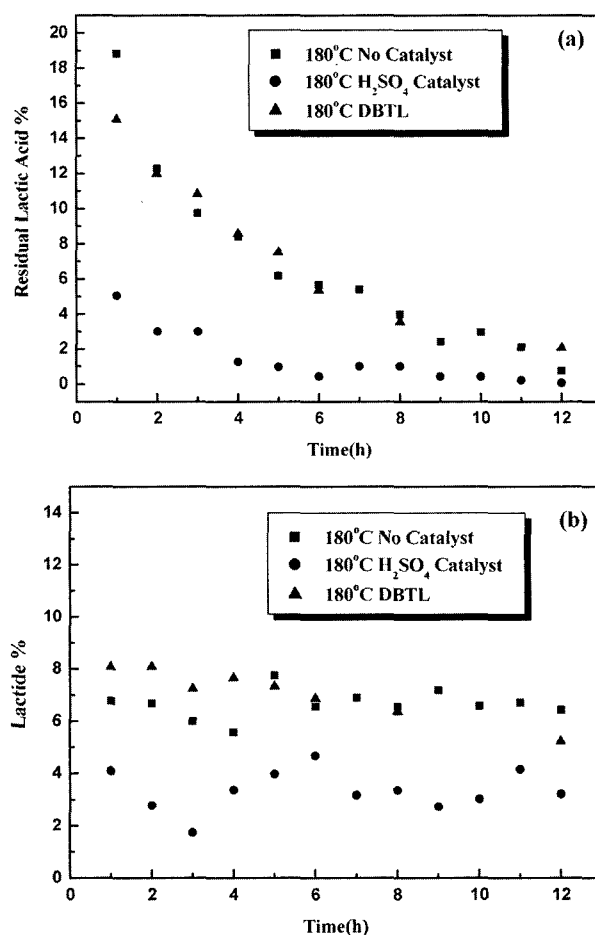
Figure 3 shows the catalyst effect on the rate of polymerization at 180 °C. Sulfuric acid led to much higher reaction rate than other catalyst systems. Figure 4 shows the catalyst effect on the variation of residual monomer (lactic acid) and lactide concentrations during the polymerization reaction. Monomer concentration decreased steadily with the progress of reaction, but its decreasing rate was highly affected by the type of catalyst it decreased much faster when sulfuric acid was used than others. The lactide concentration was maintained below 4% when sulfuric acid was used, while it was higher than 6% when DBTL or no catalyst was used.



**Figure 2.** Variation of average molecular weight during the polymerization of lactic acid at 180°C using (a) no catalyst and (b) H<sub>2</sub>SO<sub>4</sub> catalyst measured by different methods:  $\bar{M}_n$  (NMR) (■),  $\bar{M}_w$  (viscometry) (●),  $\bar{M}_w/\bar{M}_n$  (GPC) (▲), and  $\bar{M}_w$  (GPC) (▼), respectively.



**Figure 3.** Variation of the number average molecular weight ( $\bar{M}_n$ ) of PLA as a function of reaction time for different catalyst systems using no catalyst (■), H<sub>2</sub>SO<sub>4</sub> (●), and DBTL (▲), respectively.



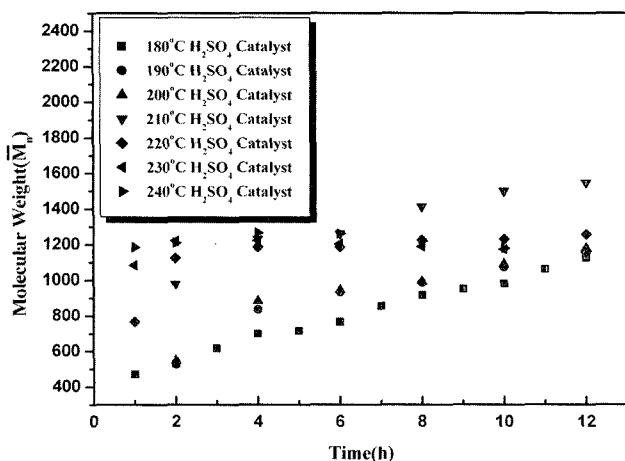
**Figure 4.** Variation of the concentrations of (a) residual lactic acid and (b) lactide as a function of reaction time for different catalyst systems using no catalyst (■), H<sub>2</sub>SO<sub>4</sub> (●), and DBTL (▲), respectively.

This was because the scission position of ester linkage is affected by the type of catalyst. In general, the strong acid catalysts like sulfuric acid are reported to minimize the racemization reaction as those decompose the carbonyl - oxygen bond, while the weak proton acid catalysts alkyl - oxygen bond.<sup>18</sup> Concentrations of residual monomer and lactide were calculated from eqs. (3) and (4), respectively with Figure 1.

$$\begin{aligned} &\text{Residual monomer concentration(\%)} \\ &= \frac{(a)}{(lactide + k + i + g + b + j + c + a)} \times 100(\%) \quad (3) \end{aligned}$$

$$\begin{aligned} &\text{Lactide concentration(\%)} \\ &= \frac{(lactide)}{(lactide + k + i + g + b + j + c + a)} \times 100(\%) \quad (4) \end{aligned}$$

Figure 5 shows the temperature dependence of PLA polymerization reaction kinetics when the sulfuric acid was used as a catalyst. The reaction rate increased with increasing



**Figure 5.** Variation of the number average molecular weight ( $\bar{M}_n$ ) of PLA as a function of reaction time at different temperatures in the presence of  $\text{H}_2\text{SO}_4$  catalyst: 180 (■), 190 (●), 200 (▲), 210 (▼), 220 (◆), 230 (◄), and 240°C (►), respectively.

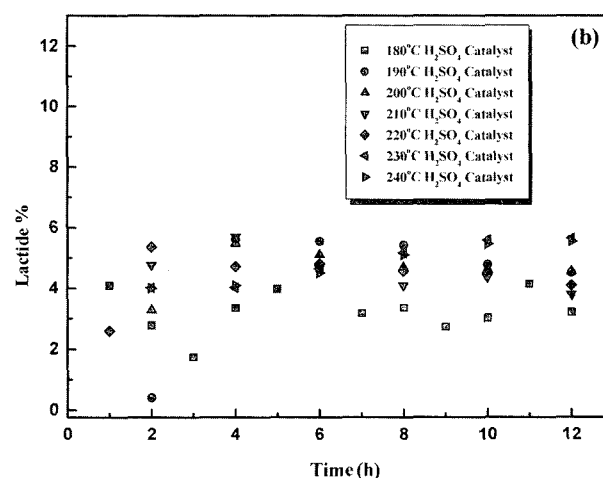
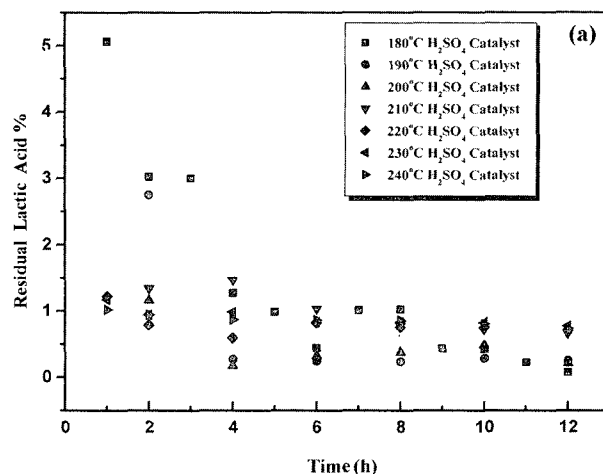
temperature up to 210°C, above which its effect was negligible as it even decreased with temperature. It was because the depolymerization reaction took place at higher rates at higher temperatures. At higher temperatures the lactic acid monomers reacted very fast to increase its chain length at initial stage, but soon it was invariant as the depolymerization reaction took place at almost the same rate as the polymerization reaction.

Figure 6 shows the variation of lactic acid and lactide concentrations during the oligomeric PLA synthetic reaction. Relatively high lactic acid concentration was observed at the initial reaction stage, when the reaction temperature was relatively low. Lactic acid concentration decreased with increasing temperature up to 200°C. At temperatures above 200°C, however, even slight increase of monomer concentration was observed, as the reaction rate was not further affected by reaction temperature. The similar behavior was observed for the lactide concentration during the reaction.

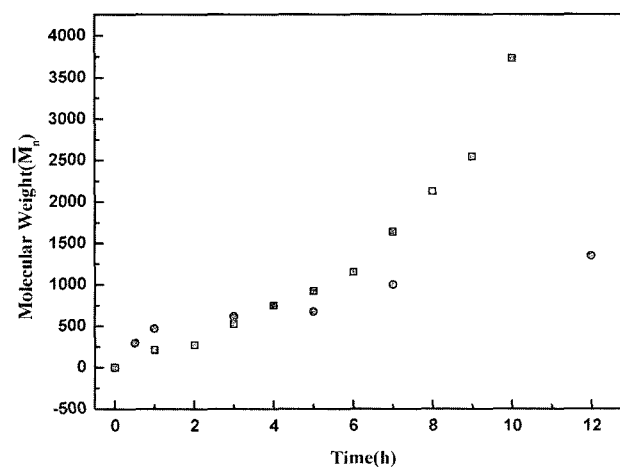
Figure 7 shows the pressure effect on the polymerization reaction rate. As predicted, the condensation reaction proceeded much faster to forward direction when the water, a by-product, was continuously eliminated by reduction of pressure. For this reason, the molecular weight increased at much higher rate when the reduced pressure was applied to the reactant system.

## Conclusions

In the oligomeric PLA synthesis, the type of catalyst had more significant effect than the temperature on the reaction kinetics in the temperatures ranging from 180 to 220°C. The highest polymerization rate with the least production of lactide was observed when the sulfuric acid was used as cat-



**Figure 6.** Variation of concentrations of (a) residual lactic acid and (b) lactide as a function of reaction time at different temperatures with  $\text{H}_2\text{SO}_4$  catalyst: 180 (■), 190 (●), 200 (▲), 210 (▼), 220 (◆), 230 (◄), and 240°C (►), respectively.



**Figure 7.** Variation of the number average molecular weight ( $\bar{M}_n$ ) of PLA as a function of reaction time at reduced (■) and atmospheric pressure (●), respectively.

alyst. The maximum reaction rate was observed around the temperature from 200 to 210°C, as the reaction rate decreased with temperature above 210°C due to the enhancement of depolymerization rate. Higher polymerization rate was obtained at the reduced pressure.

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