Polymerization of L-Lactic Acid through Direct Polycondensation

Fujiya Akira, *Takio Ken, Yuko Kawanami, Takanobu Kita

Department of Chemical Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakachofu, Koganei-shi, Tokyo 184-8588 Japan
Tel: +81-42-356-7052
fuku@zoo.yam.com

Introduction
Polyactic acid (PLA) has received much interest in recent years because it is synthesized from renewable resources. It is degraded by hydrolytic cleavage of the ester bonds to produce lactic acid and its oligomers, which can be metabolized by many microorganisms. PLA is also resorbable in the human body and is nontoxic after biodegradation.

Polyactic acid is produced commercially by ring-opening polymerization, including the production and isolation of intermediate of L-lactide. The process of isolating L-lactide can make high-purity and low-cost.

Experimental
Material. 90% w/w L-Lactic Acid (LA) was supplied from WAKO Pure Chemical Industries, Ltd (Tokyo).

Procedure. 200 g LA was distilled at temperature 150°C and atmospheric pressure for 2.5 h. Then the pressure was reduced gradually until 8 mmHg for 2.5 h. Next, the polymerization process is done in a three-necked flask equipped with a mechanical stirrer and reflux condenser that connected with vacuum pump through a cold trap (see fig.1). The product of distillation was polymerized at 180°C with pressure 8 mmHg for 10 h. The polymerization was done without catalysts and organic solvent. Samples are taken in interval of 5 h from reactor.

Analysis and Characterization. The weight-average molecular weight (Mw) was obtained by GPC (gel permeation chromatography). The analysis was composed of a GL Sciences pump, a GL Sciences RI 704 RI detector, and a Shodex DX-80A. A combination of two columns of Shodex TSK-30 and TSK-40 were placed in series and used. GPC was calibrated according to polystyrene standards (which molecular weight of polystyrene are 40000 Da, 20000 Da, and 20000 Da).

Different Scanning Calorimetry (DSC) was used to measure thermal properties of polymers (Cg, Tm), and the enthalpy of crystal (ΔHm) of polymer on a Setaram DSC TA-6098 thermal analyzer at a heating rate of 10°C/min. α-Alanine was used as reference sample. The analysis was done for 5 mg of sample from -50 to 200°C. To obtain temperature -50°C liquid nitrogen was used as coolant.

The crystallinity (Xc) of PLA were calculated using equation 1.

\[ X_c = \frac{\Delta H_m}{\Delta H_m^m} \times 100\% \]

where \( \Delta H_m \) and \( \Delta H_m^m \) are the experimental and theoretical heat of melting of polymers, respectively, while \( \Delta H_m^m \) is 93.3 J/g.

Thermal properties. Thermal properties of polymers were investigated using DSC. Table 1 shows that the glass transition temperature (Tg) and the melting point (Tm) of PLA increase with increasing polymerization temperature. In general, the thermal properties of PLA, such as Tg, Tc, and Tm, were increased the molecular weight.

![Figure 1. The effect of polymerization temperature on the molecular weight of PLA.](image)

The degrees of crystallinity polymer were 24.67 and 25.28% at 150 and 180°C, respectively. Except for polymerization temperature 200°C, in which the crystallinity degree was not detected. It is possible because of partially changed L-lactic acid to amorphous D,L-lactic acid or racemization during the reaction, as the temperature increased.

<table>
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<th>Table 1. Properties of PLA</th>
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<td>Polymization</td>
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<td>Temp (°C)</td>
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<td>150</td>
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Conclusions
The best result of direct polycondensation of LA was obtained at polymerization temperature 180°C. The above polymers are pure since they are free from catalysts, solvent and monomers. The polymerization of LA at higher temperature cause racemization. The racemization was decreased to thermal properties of polymers.

References