Polymerization of L–Lactic Acid through Direct Polycondensation

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Introduction

Polylactic 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.

Polylactic 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 production cost of PLA.

The aims of our research are produced high molecular weight polymer by direct polycondensation, and products are environmentally friendly because this procedure without use catalysts and solvents. The product are obtained while give the preferred polymer properties such as high purity and low cost.

Experimental

Material. 90%-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 is 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 30 h. The polymerization was done without catalysts and organic solvent. Samples are taken in interval of 3 h from reactor.

Analysis and Characterization. The weight-average molecular weight (Mw) was obtained by GPC (gel permeation chromatography). The analyzer was composed of a GL Sciences pump, a GL Sciences RI 704 RI detector, and a Shimadzu C-R8A. A combination of two columns of Shodex K803 and K804 were placed in series and used $CHCL_3$ as the eluent at 40°C. The molecular weight was calibrated according to polystyrene standards (which molecular weight of polystyrene are 4000 Da, 20,000 Da and 28000 Da).

Different Scanning Calorimetry (DSC) was used to measure of glass transition temperature (Tg), the melting temperature (Tm), and the enthalpy of crystal fusion (ΔHm) of polymer on a Shimadzu DSC TA-60WS thermal analyzer at a heating rate of 10°C/min. α-Alumina was used as reference sample. The analysis was done for 5 mg of sample from -50 to 200°C. To obtained temperature -50°C liquid nitrogen was used as coolant.

The crystallinities (Xc) of PLA were calculated using equation 1,

$$Xc\ (\%) = \frac{\Delta Hm}{\Delta Hm^\circ} x 100\% \qquad (1)$$

where ΔHm and ΔHm° are the experiment and theoretical heat of melting of polymers, respectively, while ΔHm° is 93 J/g.

Results and discussion

Figure 1 shows the effect of polymerization temperature on the molecular weight of PLA. It can be seen that the molecular weight increases linearly with an increases polymerization time. The molecular weight of polymers were raised when the length of the ester chain increased. The molecular weight of PLA at 150°C slowly increased. Later at 180°C the molecular weight sharply increased from 150°C. At 200°C, the molecular weight of PLA significantly increased Table 1 summarizes the molecular weight (measured from the GPC) and thermal properties of polymers (measured from DSC).

Thermal properties. Thermal properties of polymer were investigated used DSC. Table 1 shows that the glass transition points of polymers increase with increase on the polymerization temperature. In general, the thermal properties of PLA, such as Tg, Tc and Tm, were increased the molecular weight.
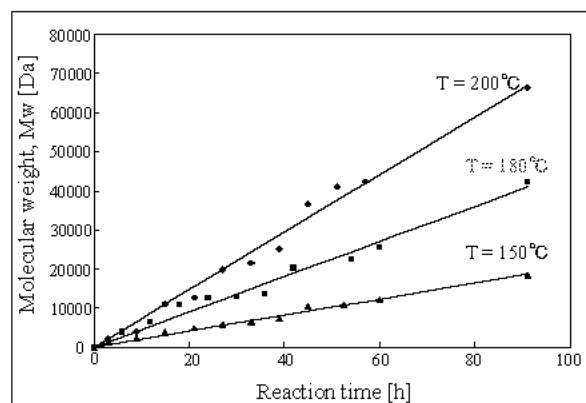

Figure 1. The effect of polymerization temperature on the molecular weight of PLA

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 racemication during the reaction, as the temperature increased.

Table 1. Properties of PLA

Polymerization Temp [°C]	Mw [Da]	Tg [°C]	Tc [°C]	Tm [°C]	Xc [%]
150	18386	35.65	95.18	143.85	24.67
180	42448	42.18	102.6	146.64	25.28
200	66305	47.07	nd	nd	-

nd = not detected

The crystallinity degree and microscopic morphology of PLA vary with its thermal history (e.g., annealing) and stereosequence distribution (e.g., S-length distribution). According theories of polymer chain folding, the lamellar thickness is dependent on the crystallization temperature. Some kinds of structural defects due to the stereoconfiguration are rejected from crystalline domains, and this result in a reduction of the lamellar thickness. The distribution of S-lengths in the polymer causes some fraction of the defects, which may be incorporated into the crystalline domains. The presence of defect structures is reflected in the value of enthalpy of fusion of crystallization (ΔHm) (S. Shyamroy, et al).

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 solvents, catalyst and monomers.The polymerization of L-LA at higher temperature cause occur racemication. The racemication was decreased to thermal properties of polymers.

References

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