Study on Synthesis and Thermal Properties of Polylactic Acid

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Abstract: Poly(lactic acid)(PLA), a kind of aliphatic polyesters, bears wonderful biologic compatibility and biodegradable properties. PLA that can finally biodegrade into CO₂ and H₂O under the influence of microorganism, water, acid or alkali, is harmless and non-toxic to the environment. L-lactide was prepared from lactic acid with stannous caprylate (Sn(Oct)₂) as the catalyst. The high purity L-lactide can be get after 2 to 3 times recrystallization, then Poly lactide acid was obtained by ring-opening polymerization with stannous caprylate (Sn(Oct)₂) as the catalyst. Analysis of the structure of polylactide by IR, test thermodynamic properties of polylactide by DSC and Tg. The glass transition temperature of polylactide is 63.49 ℃, the thermal decomposition temperature of polylactide is 267.29 ℃.

1. Introduction
With the development of science and society, environmental and resource issues have received more and more attention from people, becoming global. Petroleum-based plastic materials are widely applied, but it is difficult to recycle them, resulting in the serious "white pollution" problem. Plastics have long been in great demand. Some plastics are expensive to manufacture, fail to be degraded or fast degraded, causing serious environmental pollution. Although controlled around the world, white pollution still causes multiple disadvantages to the environment and life. Therefore, an environment-friendly plastic has emerged, namely polylactic acid, a corn plastic with corn and other starchy plants produced through biological fermentation.

2. Polylactic acid synthesis

2.1. Lactide synthesis and characterization
Lactic acid has carboxyl and hydroxyl double functional groups, with alcohol and carboxylic acid properties. When lactic acid is heated, it can prepare lactide through dehydration condensation. Generally, a two-step method is adopted, namely lactic acid is first polymerized against the low temperature and catalyst and obtain the oligomeric lactic acid, and split the oligomeric lactide into CO₂ and H₂O. The reaction process is shown in the figure 1:
In lactide preparation, the single metal (zinc powder, magnesium powder) [3], metal oxides (ZnO, MgO, Sb₂O₃, V₂O₅), rare earth metal compounds and salts of these substances can be used as catalysts to make lactic acid dehydrated to form lactic acid oligomer, and split the oligomer into lactide. This experiment applies stannous octoate [4] as used the catalyst.

At present, preparation of lactide generally adopts the 2-step method, but preparation of intermediate lactide witnesses high temperature, vacuum and energy consumption, and lactide ring-opening polymerization requires high lactide purity. Studies have shown that during the polymerization process, the purity of lactide has a significant effect on the relative molecular mass of the product polylactic acid. It is generally required that the lactide intermediate can reach a purity of 99.00% or more, and water content of less than 0.15%, carboxylic acid and moisture content of less than 1.00% for polylactic acid with relatively high molecular mass. Therefore, the preparation of high-purity lactide is one of the key steps in indirect preparation of the lactic acid.

2.1.1. Experimental part

Lactide synthesis is completed in 3 steps: removing free water in the lactic acid, synthesizing oligomeric polylactic acid and splitting the oligomeric polylactic acid to form lactide. After the test obtained the crude crystal of lactide, it was filtered first, and then the lactide was purified with ethyl acetate and absolute ethyl alcohol. The purified lactide was dried and weighed, and placed in the vacuum drying oven for standby application.

This experiment indicated when L-lactide was prepared with the reduced pressure method, the dehydration temperature was about 60°C-80°C, the temperature of synthesized oligomeric lactic acid was about 120°C-150°C, and the temperature of the lactide obtained by pyrolysis distillation was above 180°C. Temperature was controlled within 250°C so as to avoid excessive meso-lactide.

Taking an appropriate amount of lactide and performing infrared detection on lactide, the infrared spectrum obtained is shown in the figure 2:
The infrared spectrum of lactide was analyzed and the results were shown in the table 2:

| Peak position /cm⁻¹ | Analysis results                                         |
|---------------------|----------------------------------------------------------|
| S3001.24            | -CH₃ stretching vibration absorption peak                 |
| 1458.18             | -CH₃ bending vibration absorption peak                    |
| 2949.16             | -CH stretching vibration absorption peak                  |
| 1357.89             | -CH bending vibration absorption peak                     |
| 1759.08             | Ester carbonyl C=O stretching vibration absorption peak   |
| 1271.09             | Ester -C-O-C- antisymmetry stretching vibration absorption peak |
| 1097.50             | Ester -C-O-C- symmetry stretching vibration absorption peak |
| 933.5,651.94        | Ring skeleton vibration absorption peak                   |
| 3502.73             | Weak free hydroxyl absorption peak                        |

From the infrared spectrum, it is not difficult to see that the substance is lactide, a cyclic structure. And no strong and broad -OH absorption bands were observed above 3000 cm⁻¹, indicating that the -OH-containing impurities (mainly lactic acid and water) in the crude product were substantially removed through washing and recrystallization.

2.2. Polylactic acid synthesis and characterization

Two methods for preparing polylactic acid: The first is direct polycondensation of lactic acid. The advantage of this method is the reaction is relatively simple and inexpensive. The disadvantage is the molecular weight of the product, its distribution, and the terminating group, and the order of copolymerization are difficult to master. The second is ring-opening polymerization of the lactic acid cyclic dimer-lactide. With this method, it is proper to compose polymer with the molecular weight and microstructure adjustable. Lactide ring-opening polymerization is currently the most studied method
for synthesizing polylactic acid, and is also an effective method for obtaining high molecular weight polylactic acid. The reaction formula[5] is shown in the figure 3:

\[
\begin{align*}
\text{O} & \quad \text{CH}_3 \\
\text{C} & \quad \text{CH} \quad \text{C} \\
\text{O} & \quad \text{CH} \\
\text{H} & \quad \text{CH}_3
\end{align*}
\]

\text{Ring Opening}

Polymerization

\text{High Polymer}

\text{H} \\
\text{O} \\
\text{CH} \quad \text{CO} \\
\text{OH}

\text{Figure 3}

2.2.1. Experiment part

Taking an appropriate amount of lactide into an ampoule, adding an appropriate amount of stannous octoate as the catalyst, vacuuming the ampoule with a vacuum pump, and sintering the ampoule bottleneck against the flame of an alcohol burner, placing the ampoule in an oil bath at 140°C and heating for 24 hours to obtain polylactic acid;

The moisture content in lactide has great influences on polymerization of the polylactic acid. If it is too high, the stannous octoate will be hydrolyzed, resulting in transfer of the reaction chain, making it difficult to obtain effective control and repetition of the reaction, eventually making the polymer molecular weight greatly reduced. Vacuum in the ampoule has certain influences on the experiment. At high temperatures, the oxygen in the air hinders polymerization reaction, making polymerization of the polylactic acid lower.

The reaction temperature has great influences on experiments. During the reaction, the lactide must be in a molten state, and the temperature must be above 100°C. Since the reaction is reversible, within a certain temperature range, the temperature is raised appropriately, beneficial to polylactic acid compound. But when the temperature is above 150°C, side reaction will occur, thus the temperature should be controlled below 150°C.

Short reaction time and incomplete synthesis of polylactic acid will lower polymerization. The reaction time should not be too long. Since the reaction is reversible, the polylactic acid will decompose and polymerization will decrease. The reaction time should be 24 hours to 48 hours.

Taking an appropriate amount of polylactic acid, dissolving it with chloroform to achieve a solution, performing infrared detection, as shown in the figure 4:
Polylactic acid infrared spectrum is analyzed as the table 3:

| Peak position /cm$^{-1}$ | Analysis results                                      |
|------------------------|-------------------------------------------------------|
| 3018.60                | Methyl stretching vibration absorption peak           |
| 2941.44                | Methyne stretching vibration absorption peak          |
| 1757.15                | Carbonyl C=O stretching vibration absorption peak     |
| 1521.84, 1419.61       | -CH(CH$_3$)$_3$) bending vibration absorption peak    |
| 1215.15, 756.10        | -C-O-C- stretching vibration absorption peak         |
| 3672.32                | -OH stretching vibration peak                        |

Contrast between the infrared spectrum and the infrared spectrum of lactide indicated the peak of 933.5 cm$^{-1}$, namely the external deformation vibration peak of C-H on the ring disappeared, indicating L-lactide had been opened. However, there was a peak at around 3672.32 cm$^{-1}$, indicating there was -OH at the end of the polymer, and polylactic acid contained some impurities with -OH, and polymerization of polylactic acid was not high.

Take appropriate amount of lactide and test the results of DCS and Tg as the figure 5:
Since the polylactic acid obtained in the experiment was not purified, containing impurities such as lactide oligomeric polylactic acid, and several glass transition temperatures appeared on the image, indicating the polylactic acid contained unequal polylactic acids, and literature 63.49°C was the glass transition temperature of the polylactic acid.

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**Figure 5** Polylactic acid DSC analysis diagram

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**Figure 6** Polylactic acid Tg analysis diagram
Analysis of Tg diagram of the polylactic acid indicated a large transition from endothermic to exothermic at a temperature of 267.29°C in the diagram (Figure 6), and it can be concluded that the thermal decomposition temperature of the polylactic acid was 267.29°C.

3. Conclusion

1. This study prepares lactide with vacuum distillation, and having the temperature of free water removal controlled at about 60°C, which could be raised appropriately. The temperature of the synthetic polylactic acid was 120°C to 150°C. The temperature must be properly controlled. The third step that distillation obtained lactide temperature must be above 180°C, but not exceeding 250°C so as to avoid the formation of excessive meso-lactide.

2. This study adopts some impurities in lactide easily soluble in water. When the crude crystal of lactide was filtered, the lactide was washed with an appropriate amount of distilled water, effectively removing water-soluble impurities in the lactide. The subsequent purification of the crude crystal of lactide was carried out through ethyl acetate in combination with absolute ethyl alcohol so as to remove some impurities remaining in the lactide and rapidly cooling the crystal, effective for purifying the lactide.

3. This study applies stannous octoate as a catalyst to prepare lactide and polylactic acid, with fine effects, indicating that stannous octoate was an effective catalyst for this experiment. When polylactic acid was further synthesized, the temperature used was about 140°C, and the reaction time was 24 hours, and polylactic acid could be synthesized, indicating this condition was suitable for synthesis of the polylactic acid. In this experiment, the glass transition temperature of the polylactic acid was 63.49°C, and the thermal decomposition temperature was 267.29°C.

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