Direct Condensation Polymerization of L-Lactic Acid Catalyzed by Distannoxane

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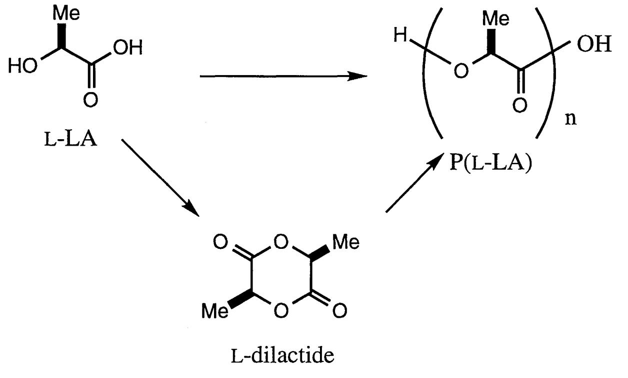
1,3-Disubstituted tetrabutyldistannoxanes effectively catalyze direct condensation polymerization of water-containing L-lactic acid to afford a high-molecular-weight polymer.

Despite its relatively long history, poly(L-lactic acid) (PLA) has recently renewed its recognition as an environmentally benign polymer due to the facile biodegradability.[1] However, direct condensation polymerization of lactic acid (LA) to a high-molecular-weight polymer is rather difficult since the water formed by condensation induces the reverse reaction, resulting in depolymerization. Moreover, the commercially available L-LA produced by fermentation contains ca. 10% water, which requires the catalyst to be water-tolerant. To bypass these difficulties, L-LA is initially converted to the dilactone (dilactide) which is isolable in an anhydrous form and then dilactide is subjected to ring-opening polymerization (Scheme 1). Recently, direct condensation of L-LA has been realized with various Brønsted and Lewis acid catalysts through continuous azeotropic dehydration where the recycling solvent should pass through a tube packed with molecular sieves to maintain the water content in the solvent below 3 ppm.[2]



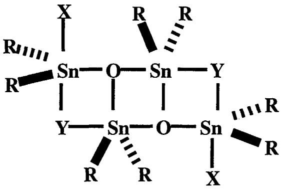
Scheme 1.

Previously, we disclosed that 1,3-disubstituted tetraalkyldistannoxanes **1** catalyzed ester formation between alcohol and carboxylic acid efficiently.[3] Most remarkably, the distannoxane catalysts induce no reverse ester cleavage reaction on account of their hydrophobicity. This characteristic property along with water tolerance of **1** led us to postulate distannoxanes to be effective catalysts for the direct condensation of L-LA to arrive at PLA with high molecular weight. We disclose herein that **1** indeed serves well to this end.

Table 1. Distannoxane-catalyzed condensation polymerization of L-LA

Entry	**1**[a]	Solvent	Temp/°C	Time/h	Mw[b,c]
1	**1a**	none	190	20	14000
2	**1b**	none	190	20	27000
3	**1c**	none	190	20	13000
4	**1d**	none	190	20	11000
5	**1a**	D-limonene	176	24	40000
6	**1a**	decalin	190	24	78000

[a] Concentration: 0.01 mol%/LA. [b] Determined by GPC with reference to polystyrene standards. [c] The yield of polymer is 85-95%.



1a: X = Y = Cl; **1b**: X = Cl, Y = OH;
1c: X = Y = -NCS; **1d**: X = -NCS, Y = OH

First, the condensation without solvent (bulk method) was investigated by using a variety of **1**. A mixture of commercially available L-LA containing ca. 10% water and a distannoxane catalyst (0.01 mol%: 0.0001 equiv/LA) in a flask was stirred and gradually heated up to 190 °C under reduced pressure (2 mmHg). After 30 min, almost of the water contained in L-LA was removed. Then, the mixture was kept on heating at the same temperature for 20 h. PLA was obtained quantitatively and the results are summarized in Table 1 (entries 1-4). The molecular weights of the polymers thus obtained are essentially independent on the substituents, X and Y, but somewhat modest (~27000). It is noteworthy, however, that the catalysts are so active that the employment of only 0.0001 equivalent amount relative to L-LA is enough for completion of the reaction.

We reasoned that the failure to obtain a high-molecular-weight polymer by the bulk method could be attributed to the increased viscosity of the reaction mixture at the latter stage of condensation polymerization where the water formed could not be removed efficiently. Accordingly, the condensation was conducted in solution. D-Limonene and decalin were the solvent of our choice. In other solvents of lower boiling point, the molecular wight of polymer decreased. A typical procedure is as follows. A mixture of L-LA (10.0 g, 100 mmol) and **1a** (6 mg, 0.011 mmol) in decalin (10 ml) was heated under reflux in a Dean-Stark apparatus with vigorous stirring. Most of water was removed after 30 min and a homogeneous solution appeared. After 24 h, the solution was cooled to room temperature and then the polymer separated from the organic phase. The polymer was dissolved in CH_2Cl_2 and reprecipitated by adding hexane (7.2 g, 90%). As expected, a great increase in molecular weight was achieved (entries 5,6, Table 1). It is of great practical significance that simple heating in a Dean-Stark apparatus is only required: no need for other special dehydrating operations that are frequently necessary with other catalysts. It is to be noted that the surface butyl groups surrounding the stannoxane core prevent the water from approaching the catalytically important tin atom to suppress the reverse ester cleavage.

In summary, the distannoxanes have proved to effectively catalyze the condensation polymerization of L-LA. The activity is so high that only a minimum catalyst concentration is sufficient. Since the catalyst is tolerant to water, no special technique for dehydration of the solvent is needed. The bulk method is convenient for producing a relatively low-molecular-weight polymer. On the other hand, the polymer of higher molecular weight is obtained in the solution process. It is recognized that the molecular weight should be more than 25000 for the satisfactory physical properties of the polyesters.[1] In this regard, the both processes are employable and either of them may be sorted out depending on the molecular weight required. Further work for improving the process is under development in our laboratories.

References

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