

Lewis Acid Catalyzed Polymerization of L-Lactide. Kinetics and Mechanism of the Bulk Polymerization

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ABSTRACT: The kinetics of the L-lactide bulk polymerization was studied using tin(II) bis(2-ethylhexanoate) and zinc bis(2,2-dimethyl-3,5-heptanedionato-*O,O'*). Up to 80% conversion, the rate of polymerization using tin(II) bis(2-ethylhexanoate) is higher than that with the zinc-containing catalyst, while at conversions beyond 80%, the latter catalyst has the higher rate of polymerization. Crystallization of the newly formed polymer has an accelerating effect on the polymerization. The difference in the rate of polymerization at high conversions for the two catalysts is caused by a difference in crystallinity of the newly formed polymer. Contaminants in the catalyst and monomer are the true initiators in these L-lactide polymerizations. Initiation as well as polymerization proceeds through a Lewis acid catalyzed transesterification reaction between an activated lactone and a hydroxyl group.

Introduction

Because of the numerous applications in the biomedical field and their potential use in disposable and agricultural applications, homo- and copolymers of polylactones are still gaining interest. One of the reasons for the growing interest in this class of hydrolytically unstable polymers is that their physical and chemical properties can be varied over a very broad range. Like in other polymeric systems, these properties depend strongly on the monomer or comonomers used, the molecular weight, and the microstructure of the resulting polymer. In order to prepare polymers with tailor-made properties a good understanding of the polymerization mechanism is necessary. Despite the growing number of publications concerning the synthesis of polylactones from six-membered and higher ring lactones, there is still a lack of clarity concerning the polymerization mechanism.

One point which is not completely understood is the dependence of the molecular weight on the catalyst concentration when nonionic catalysts are used. The molecular weight is of great importance in order to get good mechanical properties especially when polymers with a low crystallinity and a low T_g (rubbers) are synthesized. Up till now only one catalyst, tin(II) bis(2-ethylhexanoate), has been known to yield high molecular weight polylactones when a low catalyst concentration is used. In this study a new class of catalysts will be presented which allow the synthesis of high molecular weight polylactones. Furthermore, some factors that appear to be pertinent to the polymerization of lactones are presented.

Experimental Section

Materials. L-Lactide and D-lactide (Purac Biochem BV, Gorinchem, The Netherlands) were recrystallized from toluene (Merck, distilled from sodium) under a nitrogen atmosphere. 2,2-Dimethyl-3,5-heptanedione (HDMH) was prepared according to the procedure of Kopecky et al.¹⁴ using ethyl pivalate and 2-butanone as starting materials (yield 70%, bp 90 °C, 30 mmHg).

Zinc bis(2,2-dimethyl-3,5-heptanedionato-*O,O'*), in short Zn(DMH)₂, was synthesized by the method of Finn et al.¹⁵ using toluene, zinc oxide, and HDMH. The product was recrystallized from pentane (yield 70%).

Tin(II) bis(2,4-pentanedionato-*O,O'*), in short Sn(Acac)₂, was prepared according to the method of Wakeshima et al.,¹⁶ using *p*-xylene as a solvent (yield 80%, bp 85–92 °C, 0.05 mbar).

Tin(II) bis(2-ethylhexanoate) (Sigma Chemical Co., St. Louis, MO), in short Sn(Oct)₂, was used as received.

Polymerizations. Bulk polymerizations were carried out in vacuum-sealed silanized glass ampules. After the ampule was charged with monomer, a pentane solution of the catalyst (0.1 wt %) was added, after which the pentane was removed under vacuum. The monomer to catalyst ratio was 1:1 unless stated otherwise. After the ampule was sealed under vacuum, it was immersed in an oil bath. Polymerizations were carried out at 110 °C. After a predetermined time a glass ampule was removed and was quenched in cold pentane whereupon samples were taken for analysis.

Characterizations. ¹H NMR measurements (300 MHz), performed on a Varian VXR-300, were used to determine the conversion. Spectra were obtained using 1% (w/v) solutions in CDCl₃. Conversion of the crude polymer was determined from the relative intensities of the monomer and polymer methine quartet at δ 4.5.

Molecular weights were determined using a Waters Associates GPC with CHCl₃ as eluent. Calibration was obtained using polystyrene standards that covered a molecular weight range of 1000 to 4×10^6 .

In addition, molecular weights were determined using an Ubbelohde viscometer (Type Oa, ASTM D-445). From the intrinsic viscosity of PLLA solutions in chloroform at 25 °C, the M_v and M_n were determined using the formulas^{6,7}

$$[\eta] = 5.45 \times 10^{-4} \bar{M}_v^{0.73} \quad [\eta] = 3.25 \times 10^{-4} \bar{M}_n^{0.77}$$

Results and Discussion

The structure of the catalysts used in this study are shown in Figure 1. Like in tin(II) bis(2-ethylhexanoate) (Sn(Oct)₂), the oxygen in the two diketonates, tin(II) bis(2,4-pentanedionato-*O,O'*) (Sn(Acac)₂) and zinc bis(2,2-dimethyl-3,5-heptanedionato-*O,O'*) (Zn(DMH)₂), is bonded to the tin and zinc.^{24,25,27} This resemblance in structure of the diketonates with Sn(Oct)₂ was reason to suspect that this class of substances would have catalytic activity in the L-lactide polymerization.

Like Sn(Oct)₂, the two diketonates are molten at 110 °C, which is the polymerization temperature used in this study, and dissolve readily in the monomer melt ensuring homogeneous catalysis for all catalysts.

Good solubility of the catalyst in the monomer melt is important in order to have good reproducibility in the polymerizations. Catalysts which are poorly soluble or insoluble in the monomer melt, like zinc bis(2,4-pentanedionato-*O,O'*),²⁸ aluminum tris(2,4-pentanedionato-*O,O'*),²⁸ magnesium bis(ethanolato),⁸ tetraphenyltin,² or tin(II) bis(methanolato) can also be used for the bulk polymerization of L-lactide, but the reproducibility at low

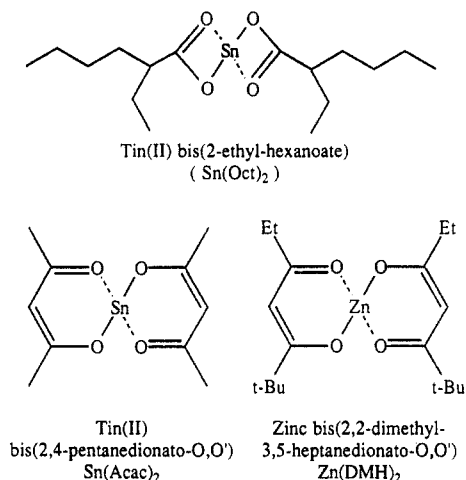


Figure 1. Chemical structure of the three catalysts used in this study.

polymerization temperatures with these heterogeneous catalysts is poor.

As shown in a previous study, the three catalysts of Figure 1 can produce high molecular weight PLLA when used in the ring opening bulk polymerization of L-lactide.¹² The physical and mechanical properties of the resulting PLLA, however, depended strongly on the catalyst.¹² Because the only variable in these polymerizations was the catalysts, which will have different reactivities, there was reason to believe that the kinetics partly determined the physical and mechanical properties of the as-polymerized polymer. Because the polymers obtained with $\text{Sn}(\text{Oct})_2$ and $\text{Zn}(\text{DMH})_2$ showed the largest differences in properties,¹² these two catalysts were used to study the polymerization kinetics.

L-Lactide Polymerization Kinetics. In Table I, the results are shown for the polymerization at 110 °C of L-lactide with $\text{Zn}(\text{DMH})_2$ and $\text{Sn}(\text{Oct})_2$.

As determined by NMR, the conversion for both systems was virtually complete after 72 h. It should be noted that the value of 100.0% conversion is used when no monomer could be detected with the NMR technique used because its concentration was lower than the detection limit.

When the monomer conversion is plotted against the polymerization time, no linear part in the conversion curve is observed, ruling out the possibility that the polymerization reaction is zero order in monomer, as was for instance found for the bulk polymerization of ϵ -caprolactone with triphenyltin acetate.⁴

Under the assumption that the polymerization is first order in monomer, the logarithm of the ratio of the initial monomer concentration to the monomer concentration at time t ($\ln [M_0]/[M]$) is plotted against the polymerization time as is shown in Figure 2. The slope of the initial straight line equals the apparent polymerization rate constant. For the $\text{Sn}(\text{Oct})_2$ - and $\text{Zn}(\text{DMH})_2$ -catalyzed polymerizations these are 15.3×10^{-5} and $6.3 \times 10^{-5} \text{ s}^{-1}$, respectively.

Initiation in this system for both catalysts is fast as can be seen by the lack of an induction period in Figure 2. Although the initial rate of polymerization using $\text{Sn}(\text{Oct})_2$ exceeds the one using $\text{Zn}(\text{DMH})_2$ the L-lactide conversion in both systems is equal after about 13 h. At reaction times beyond 13 h, the conversion of monomer by $\text{Zn}(\text{DMH})_2$ exceeds that by $\text{Sn}(\text{Oct})_2$. The initial linear part in Figure 2 extends up to about 80% conversion for both the $\text{Zn}(\text{DMH})_2$ and the $\text{Sn}(\text{Oct})_2$ catalyst. The decrease in slope at about 80% conversion is very strong for $\text{Sn}(\text{Oct})_2$ and very small if not negligible for $\text{Zn}(\text{DMH})_2$. The

reason for this decrease in slope is that at this point the polymerization reaction becomes diffusion controlled. Apparently, the rate of diffusion in the $\text{Zn}(\text{DMH})_2$ system is much higher in comparison to the $\text{Sn}(\text{Oct})_2$ system. This is a result of the difference in crystallinity of the newly formed polymer between the two systems. In Table II the heat of fusion of the polymer melting endotherm and the peak melting temperature of the two polymerizing systems are compared. Here we see that crystallization of the polymer starts somewhere between 40 and 60% conversion. Once crystallization of the polymer has started, the crystallinity of the $\text{Zn}(\text{DMH})_2$ system is at all times higher than the $\text{Sn}(\text{Oct})_2$ system. (A more detailed analysis concerning the solid-state formation of PLLA during the bulk polymerization will be published in a second article.¹³)

Crystallization of the newly formed polymer will influence the rate of polymerization in two different ways. In the first place, because polymer is withdrawn from the polymer/monomer solution as a result of the crystallization, the viscosity of this solution will decrease. This will have a favorable effect on the rate of diffusion of the monomer. Secondly, the monomer and catalyst will be concentrated in the remaining amorphous regions. This means that as a result of the higher crystallinity of the polymer in the $\text{Zn}(\text{DMH})_2$ -catalyzed system the monomer concentration in the amorphous phase will be higher and the diffusion of the monomer to the active catalyst sites will be faster when compared to the $\text{Sn}(\text{Oct})_2$ -catalyzed system. This is clearly shown in the fact that the rate of polymerization of the $\text{Zn}(\text{DMH})_2$ system hardly decreases above 80% conversion whereas the $\text{Sn}(\text{Oct})_2$ system is highly decelerated. This situation is schematically depicted in Figure 3a,b.

Crystallization of the polymer influences not only the rate of polymerization but also the equilibrium monomer concentration. As a result of the polymer crystallization the monomer/polymer equilibrium will be drawn to the polymer side, decreasing the apparent equilibrium monomer concentration. In Table I it is shown that the equilibrium monomer concentration is smaller than 0.1%, which is the detection limit of the NMR technique. However, when the polymerization is performed in a solution where no crystallization can occur, the final monomer concentration is on the order of 1–20% depending on solvent quality and polymerization temperature.^{9,17} From the experiences in our laboratory, it is a known fact that when amorphous polylactides are synthesized with $\text{Sn}(\text{Oct})_2$ as a catalyst, the final monomer concentration will be in the range 0.5–1% under optimum polymerization conditions. Also when polymerizations are carried out at 180 and 200 °C the equilibrium monomer concentration is 5 and 7% respectively, independent of the catalyst used.³ At these temperatures no crystallization of the polymer during the polymerization does occur. In this case, it is of course difficult to distinguish whether the increased monomer concentration is a result from a shift in the monomer/polymer equilibrium due to the high polymerization temperature or a direct result from the low crystallinity.

Molecular Weight. During the polymerization of L-lactide, the viscosity average molecular weight, determined by gel permeation chromatography, continues to increase up to $\approx 60\%$ conversion. After this point the molecular weight does not increase significantly. Both catalysts are able to form ultrahigh molecular weight PLLA. As can be seen from Figure 4, no clear distinction between the results, concerning the molecular weight in

Table I
Conversion of L-Lactide as a Function of Time at a Polymerization Temperature of 110 °C with the Catalysts Zn(DMH)₂ and Sn(Oct)₂^a

polymerization time (h)	conversion (%) (Zn(DMH) ₂ catalyst)	conversion (%) (Sn(Oct) ₂ catalyst)	polymerization time (h)	conversion (%) (Zn(DMH) ₂ catalyst)	conversion (%) (Sn(Oct) ₂ catalyst)
0.5	7.1	39.5	18	98.2	95.5
1.0	21.4	56.3	24		97.9
2.0	39.2	61.1	24.5	98.9	
3.0	47.9	78.4	36.0	98.8	98.7
4.0	62.9	83.4	48.0	100.0	99.8
6.0	76.7	87.3	60.0	100.0	99.4
8.0	83.2	89.8	72.0	100.0	99.9
12.0	92.6	93.6	84.0	100.0	100.0

^a The monomer to catalyst ratio was 11250.

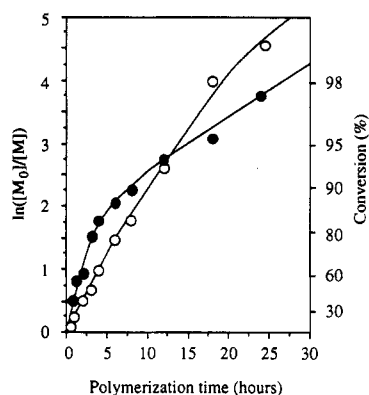


Figure 2. $\ln([M]_0/[M])$ versus the polymerization time for Sn(Oct)₂ (●) and Zn(DMH)₂ (○). The reaction conditions are the same as in Table I.

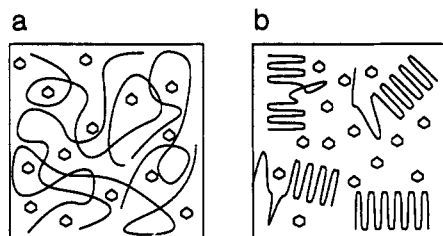


Figure 3. Crystallization of the polymer (black lines) in (a) leading to concentration of the monomer (hexagons) in the remaining amorphous regions. The viscosity of the amorphous regions of the system also decreases.

Table II
Heat of Fusion and the Peak Melting Temperature of the PLLA Melting Endotherm of Systems Catalyzed with Sn(Oct) and Zn(DMH)₂

conversion of L-lactide (%)	Sn(Oct) ₂		Zn(DMH) ₂	
	ΔH_m (J·g ⁻¹)	T_m (°C)	ΔH_m (J·g ⁻¹)	T_m (°C)
40	0		0	
61	15	128	16	127
77	24	154	28	156
83	31	162	51	176
99	70	190	89	200
100	77	192	95	200

relation to the conversion, of the Sn(Oct)₂ and Zn(DMH)₂ catalysts can be made.

After a sharp initial increase of \bar{M}_v , it increases less than proportional going to higher conversion. \bar{M}_n and \bar{M}_w show the same increase with conversion. The molecular weight distribution (\bar{M}_w/\bar{M}_n) starts at 1.2 at low conversion and ends at 2 at full conversion.

Figure 4 clearly shows that the increase of the molecular weight is not proportional to the conversion. This would have been expected when every catalyst molecule would initiate one or two living polymer chains. In that case the

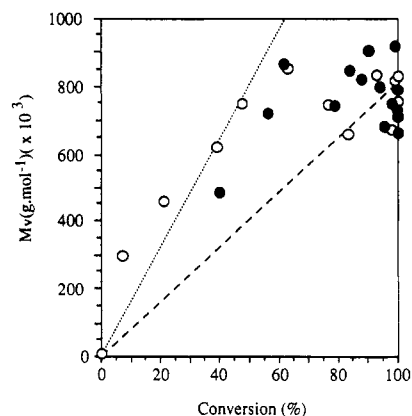


Figure 4. PLLA viscosity average molecular weight determined by GPC versus the conversion for Sn(Oct)₂ (●) and Zn(DMH)₂ (○).

conversion curve in Figure 4 would have been represented by the dotted and the dashed line. Although these lines depict the change of \bar{M}_n as a function of the conversion and not the change in \bar{M}_v (which is shown in Figure 4), neither lines agree with the change of the molecular weight with conversion. The polymerization mechanism apparently does not involve a simple initiation by the catalyst itself, as was suggested in earlier publications.

Because the \bar{M}_v (like the \bar{M}_n and \bar{M}_w) increases less than proportional to the conversion and also because the molecular weight distribution increases with conversion, it can be concluded that the number of polymer chains increases during the polymerization. This would mean that after the initial stage of the polymerization new initiation and propagation takes place at the same time. The increase of the number of polymer chains and the propagation of all these chains apparently causes the average molecular weight to stay more or less constant after 60% conversion.

The living character of the L-lactide polymerization in solution polymerizations has been well established with complexation catalysts like aluminum tris(isopropoxide),⁹ aluminum zinc μ -oxo alkoxide,¹¹ and (tetraphenylporphyrinato)aluminum alkoxide.¹⁰ Although in the explanation of Figure 4 we do not expect chain termination or true chain transfer to take place, the polymerization would have to be studied in more detail in order to determine whether it can be considered a (pseudo) living polymerization.

In the bulk polymerization, the crystallization of the polymer starts somewhere between 40 and 60% conversion (Table II).¹³ This means, looking at Figure 4, that the increase of the molecular weight stops just after polymer crystallization has started. Yet because amorphous poly-[D-lactide-co-L-lactide] polymers can be synthesized with the same molecular weight under identical conditions, it

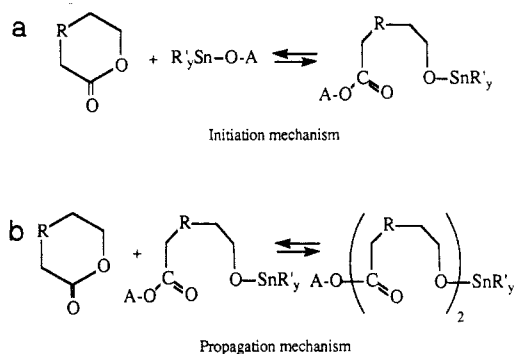


Figure 5. Schematic representation of the initiation and propagation mechanism of a lactone with a tin alkoxide catalyst. The character A represents an alkyl group and R' represents the other groups bound to Sn. The value of y is 3 for Sn(VI) compounds and 1 for Sn(II) compounds.

is not likely that the molecular weight is influenced by the polymer crystallization.

L-Lactide Polymerization Mechanism. Several publications have been devoted to the elucidation of the lactone polymerization mechanisms using catalysts like Sn(II) and Sn(IV) compounds.^{1-7,29,30} However the nature of the initiation mechanism of most tin compounds still remains unclear. With respect to the L-lactide polymerization, only in the case of tin alkoxides has it been shown that the initiation follows the scheme depicted in the mechanism of Figure 5.^{1,8} Important confirmation for this mechanism is the formation of an ester end group of the growing polymer chain. This type of initiation and the propagation according to the mechanism in Figure 5 has been confirmed for numerous other metal alkoxides.^{8-11,26}

In the case of the lactide polymerization with tin carboxylates, the initiation mechanism of Figure 5a would necessitate the formation of an energetically unfavorable anhydride.⁴ Moreover, because the anhydride could not be shown in end group analysis¹ the initiation most likely does not follow the mechanism shown in Figure 5a. Also, when other tin compounds like tin halogenides⁵ and tetraphenyltin are used, the true nature of the initiating species remains unclear. It has been suggested several times that impurities in the catalyst or the monomer function as initiator or cocatalyst.^{1,2,4,6,7}

Well-known initiators of the lactide, or in general lactone, polymerizations are hydroxyl-containing compounds like alcohols and water.²⁰ One source of hydroxyl groups in our polymerizations is impurities in the lactide like water, lactic acid, and lactic acid-lactate. Another source of hydroxyl groups is the catalyst itself which will contain water as a result of the production method¹⁸ and its extreme hygroscopicity. The water present in the Sn(Oct)₂ participates in a hydrolysis equilibrium which causes the presence of free 2-ethylhexanoic acid and stannous hydroxide. The downfield absorption of the acidic proton of the 2-ethylhexanoic acid clearly shows in the NMR of Sn(Oct)₂ and stannous hydroxide precipitates after a few hours in pentane or toluene solution of Sn(Oct)₂.

To determine the influence of the catalyst concentration on the molecular weight, polymerizations were carried out with monomer to catalyst molar ratios varying from 500 to 30 000. The molecular weights (\bar{M}_n) were calculated from intrinsic viscosity measurements. The experimentally found points in Figure 6 show an excellent correlation with a theoretical curve, also shown in Figure 6, which was calculated assuming a total hydroxyl content in the lactide of 0.133 mequiv/mol (which is within the specifications of the supplier) and a hydroxyl concentration in the catalyst equivalent to a water content of 2 wt %. In this situation,

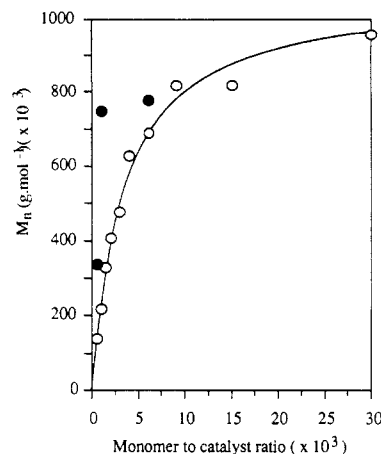


Figure 6. Drawn line representing the theoretical curve assuming a moisture content in the catalyst of 2% and a hydroxyl content of the monomer of 0.133 mequiv/mol. Sn(Oct)₂ (○) and Sn(Acac)₂ (●) were used as catalysts. The conversion for all samples was more than 99.5%.

the maximum molecular weight would be 10.8×10^5 at infinite low catalyst concentration.

When Sn(Acac)₂ is used, high molecular weight PLLA can be obtained at a high catalyst concentration ($\bar{M}_n = 7.4 \times 10^5$ and $M/C = 1000$) in contrast to the Sn(Oct)₂-catalyzed polymerizations. This is most likely caused by the fact that Sn(Acac)₂ cannot be contaminated with water because it is a very reactive substance which reacts instantly with water and oxygen to form tin oxides. These oxides are almost inactive in the lactide polymerization at 110 °C.¹⁹ However, it cannot be excluded that other tin-oxo or tin-hydroxyl contaminants initiate the polymerization. An illustrative example is distannoxane. It has been shown that hexabutyldistannoxane, which is a contaminant of tributyltin bromide and tributyltin chloride, considerably increases the rate of polymerization when these compounds are used as lactone polymerization catalysts.¹ Another distannoxane, hexaethyldistannoxane, has been shown to react with ϵ -caprolactone forming in high yield the compound $\text{Et}_3\text{SnO}(\text{CH}_2)_5\text{COOSnEt}_3$.³² The trialkyltin carboxylate side of this molecule will catalyze the polymerization,^{1,4} and the trialkyltin alkoxide will both initiate and catalyze the polymerization at the same time.^{1,3,8} This example shows that contaminations other than water could account for the \bar{M}_n dependency of the catalyst concentration and the relatively low molecular weight of 3.3×10^5 found at an M/C of 500 for the Sn(Acac)₂.

In Figure 4 it can be seen that Sn(Oct)₂ and Zn(DMH)₂ produce PLLA with the same molecular weight. This is the result of the high monomer to catalyst ratio (11 250) that is used in this polymerization. As a result of the low catalyst concentration contaminants in the catalyst play a minor role in determining the final molecular weight of the polymer. Moreover, because the Zn(DMH)₂ was more than 98% pure as checked by NMR and elemental analysis, no difference in the molecular weight of the final polymer was expected.

With respect to the Sn(Oct)₂-catalyzed polymerization of the polar aprotic lactide, first of all coordination of the lactide carbonyl to free p or d orbitals of the dissolved Sn(Oct)₂ will take place. Due to solvation of the Lewis acid catalyst^{22,29} the complex will have a cationic character depicted in the resonance structures in Figure 7. As a result of the resonance, the electron density at the carbon is decreased, making it more susceptible to nucleophilic attack by hydroxyl-containing compounds which, as

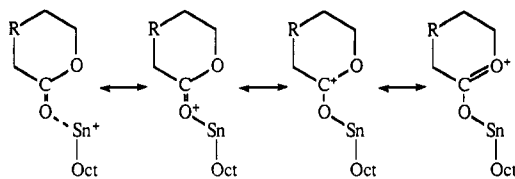


Figure 7. Resonance structures of the lactone/ $\text{Sn}^+(\text{Oct})$ complex.

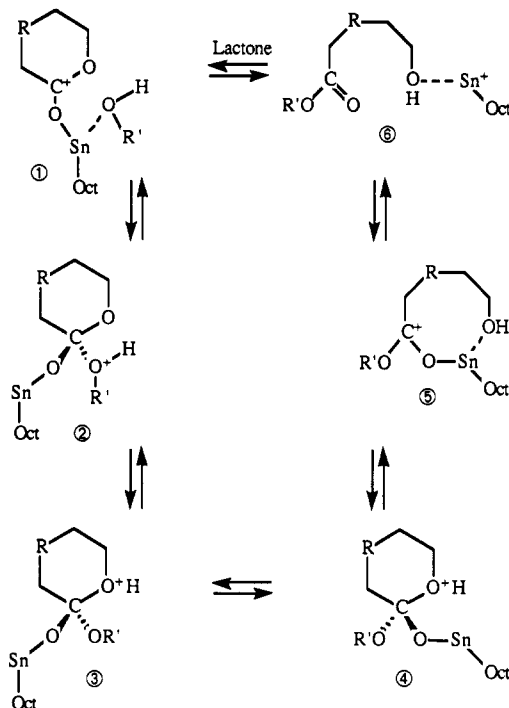


Figure 8. Reaction mechanism of the $\text{Sn}(\text{Oct})_2$ -catalyzed lactone polymerization.

discussed before, are likely to be the true initiators of the polymerization.

The polymerization starts when the hydroxyl-containing compound $\text{R}'\text{OH}$ reacts with the lactone/ $\text{Sn}^+(\text{Oct})$ complex through a nucleophilic attack at the carbon (structures 1 and 2 in Figure 8). The proposed mechanism more or less follows a transesterification mechanism that is comparable with that of ester hydrolysis²¹ and can be considered a Lewis acid catalyzed alcoholysis. A comparable mechanism has been proposed for the metal-catalyzed alcoholysis reaction of 2-butoxyethyl benzoate and *n*-heptyl alcohol with cobalt, zinc, or manganese catalysts.²³

After reaction complex 6 (in Figure 8) has been formed, the coordination with a new lactone will generate species 1 again, where in this case R' is the growing polymer chain. In the proposed mechanism the catalyst is not chemically bound to the growing chain end (structure 6 in Figure 8). This implies that one catalyst molecule can switch from one chain end to another and that the number of polymer chains able to polymerize can be larger than the number of catalyst molecules.

The proposed mechanism agrees with the increase of the molecular weight with the conversion, as shown in Figure 4. During the polymerization, initiation of new polymer chains will continuously take place. For this reason, the number average molecular weight will not continuously increase with the conversion and it will also result in an increase of the molecular weight distribution during the polymerization. Ester-ester interchange reactions are not expected to play a role in the development of the molecular weight. The lack of ester-ester interchange reactions in this specific polymerization has been suggested by Schindler et al.^{33,34}

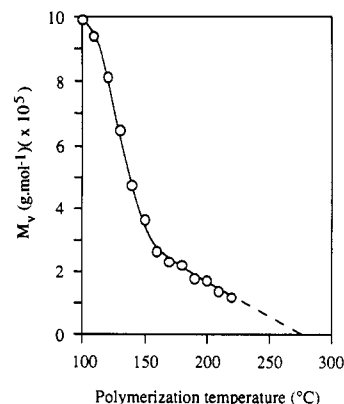


Figure 9. Effect of the polymerization temperature on the \bar{M}_n of PLLA. The monomer to catalyst ratio was 18 750 (from ref 6).

With the data shown in Figure 6 it can be calculated that with an M/C higher than 4050 the number of polymer chains exceeds the number of catalyst molecules. At higher M/C values the experimentally determined molecular weight still agrees well with the theoretical curve, indicating that after this point each catalyst molecule actually is polymerizing several polymer chains.

Polymerization Temperature and the Molecular Weight. The decrease of the molecular weight of PLLA with increasing polymerization temperature was already shown by Leenslag et al.⁶

The polymerization mechanism of Figure 8 does not directly account for the decrease in molecular weight when the polymerization temperature is increased. However, due to the electrophilic nature of the coordination complex, degradation of the previously formed polymer can occur. This effect will be enhanced by the diminished coordination of the hydroxyl compound at the lactone/ $\text{Sn}^+(\text{Oct})$ complex, an equilibrium which is also influenced by the increasing temperature. Secondly, cationic polymerization through the lactone/ $\text{Sn}^+(\text{Oct})$ complex would also explain the racemization of the optically active polymer which occurs at elevated polymerization temperatures.^{19,31}

Conclusions

Besides $\text{Sn}(\text{Oct})_2$, other coordination catalysts like the metal β -diketonates zinc bis(2,2-dimethyl-3,5-heptanedionato-*O,O'*) ($\text{Zn}(\text{DMH})_2$) and tin(II) bis(2,4-pentanedionato-*O,O'*) ($\text{Sn}(\text{Acac})_2$) can be used for the polymerization of L-lactide to give high molecular weight PLLA.

Compared with $\text{Sn}(\text{Oct})_2$, $\text{Zn}(\text{DMH})_2$ is initially less active in the L-lactide polymerization. Total conversion of the monomer, however, is reached at the same time. This is a result of the difference in the degree of crystallinity that occurs during the polymerization. Crystallization has an accelerating effect on the polymerization. Due to a higher crystallinity of the $\text{Zn}(\text{DMH})_2$ -catalyzed system, it has a higher rate of polymerization at high conversion compared with the $\text{Sn}(\text{Oct})_2$.

At low polymerization temperatures, the final molecular weight is determined by hydroxyl-containing contaminants in both catalyst and monomer. Initiation as well as polymerization takes place through Lewis acid catalyzed transesterification reaction between the activated lactone and hydroxyl groups.

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