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### New Approaches to Ring Opening Polymerization-Evidences of Step Transfer Polymerization

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## NEW APPROACHES TO RING OPENING POLYMERIZATION—EVIDENCES OF STEP TRANSFER POLYMERIZATION

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**ABSTRACT:** The ring-opening polymerisation of lactones, by different initiator-catalyst systems, has been studied. Tin(II) bis(2-ethylhexanoate) has been used to catalyse the polymerization of lactide with various types of alcohol initiators. <sup>1</sup>H NMR spectroscopy was used to monitor the polymerization process. Mechanistic studies suggest that the polymerisation course, to a large extent, depends on the reactivity of the initiators. In the case of primary or secondary alcohols, e.g. poly(ethylene glycol) and methyl lactate, it is found that when the initiator concentration exceeds that of the catalyst, the number of chains formed also exceed the number of catalyst molecules. The chains are propagated through a shift of the catalyst from one chain to another. GPC chromatography clearly shows oligomer formation in the first stage of the polymerization. In the case of tertiary alcohols, it appears that the number of chains formed is comparable to the number of catalyst molecules. By choosing an appropriate initiator the reaction course and molecular weight can be controlled. A general polymerization mechanism of the ring-opening polymerisation of this type is briefly discussed.

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## Introduction

Biodegradable polymers have attracted much interest in recent years.<sup>1,2</sup> Concerning the polymerisation of lactones, it is established that initiator as well as catalyst are necessary in the lactone polymerization.<sup>3,4</sup> Several reaction mechanisms have been proposed.<sup>4,5</sup> However, due to insufficient experimental data, it is impossible to distinguish among the proposed reaction mechanisms.<sup>5,7</sup> In this study, the lactone polymerisation has been carefully studied using NMR spectroscopy and GPC chromatography. A general polymerisation scheme of ring-opening polymerisation of this type will be briefly discussed.

## Experimental

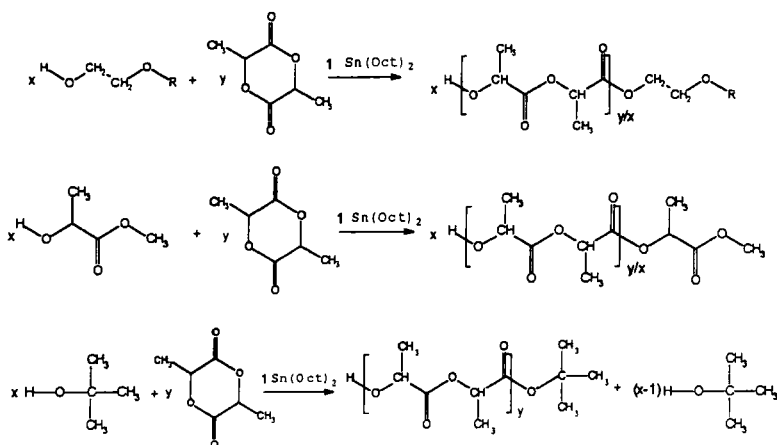
**Materials.** L-Lactide and D,L-lactide were purchased from Purac Biochem BV (Gorinchem, The Netherlands). They were recrystallized from ethyl acetate and dried in vacuum (20 Pa) over  $P_4O_{10}$ . Methyl (S)-(-)-lactate, 2,3-butanediol (Janssen, Geel, Belgium), pinacol (Aldrich), t-butanol (E. Merck, Darmstadt, Germany) were dried before use. Poly(ethylene glycol) with molecular weights of 1000 g/mol (PEG1000) was purchased from Aldrich Co. (Milwaukee, wisc. USA). It was vacuum dried (20 Pa) at 80 °C for 30 min before use. Tin(II) bis(2-ethylhexanoate) (Sigma Chemical Co., St. Louis, MO) was used as received.

**Polymerizations.** An exemplary polymerization is given here. Under nitrogen, PEG1000 (15.00 g, 15 mmol) was introduced to a 50 ml three-necked flask equipped with a magnetic stirrer. The system was vacuum dried at 80 °C for 30 min. Subsequently the flask was purged with nitrogen and heated to 120 °C in an oil bath. Under nitrogen, lactide (10.80 g, 75 mmol) was charged into the flask. After all the solids were molten, tin(II) bis(2-ethylhexanoate) (0.061 g 0.15 mmol) was introduced into the flask. At predetermined times, samples were collected and analyzed immediately by  $^1H$  NMR.

If initiators other than PEGs were used, the polymerization procedure was changed by first adding the lactide to a flask. The lactide was molten after being dried at 80 °C in vacuum for 30 min. After that the initiator and the catalyst were added.

**Characterizations.**  $^1H$  NMR spectra were recorded on a Bruker AM-400 NMR spectrometer. Tetramethyl silane (TMS) signal was taken as the zero chemical shift.

Molecular weights were determined using a Waters Associates GPC with tetrahydrofuran as eluent. Calibration was carried out with polystyrene standards (Polymer Laboratories, Shropshire, UK) at the range of 500 g/mol to 66,000 g/mol. The column used was a PL-gel (Polymer Laboratories) 1000 A + 500 A column combination. The flow rate was 1 ml/min.



Scheme 1. The reaction of lactide with alcohol initiators of different types.

## Results and discussion

**Step transfer polymerisation.** In order to know how the ring is opened, and how the catalyst and the initiator react during the polymerisation,  $^1\text{H}$  NMR spectroscopy was used to follow the reaction process. Various types of initiators, from primary alcohol to tertiary alcohol, were used to initiate the polymerisation of lactide. Scheme 1 illustrates the polymerisation process. To make the discussion more clear, we introduce the term "active-site" to denote the complex of the catalyst, the monomer and the initiator.

Figure 1 shows the  $^1\text{H}$  NMR spectra of the polymers obtained using the primary

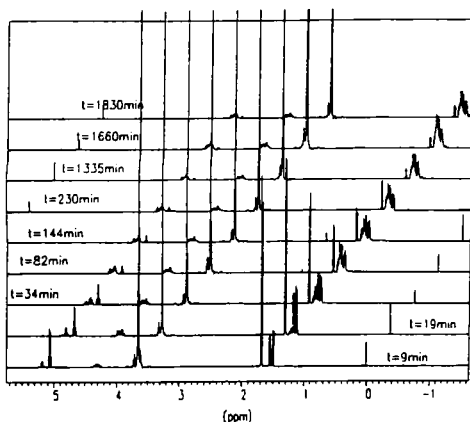


Figure 1.  $^1\text{H}$  NMR spectra during polymerisation of lactide initiated by PEG1000 at 113 °C. The catalyst was  $\text{Sn}(\text{Oct})_2$ . Molar ratio of lactide to PEG1000 to  $\text{Sn}(\text{Oct})_2$  was 5:1:0.01.

alcohol poly (ethylene glycol), with a molecular weight of 1000, as the initiator. The molar ratio of initiator to catalyst is 100:1. The chemical shift of methyl protons of lactide changes from  $\delta$  1.69 ppm to  $\delta$  1.4-1.6 ppm during polymerisation. At the beginning of the reaction, two clearly separated doublets are present in the spectra. The doublets are the signals of methyl protons of first lactide bonded to end groups of PEG.

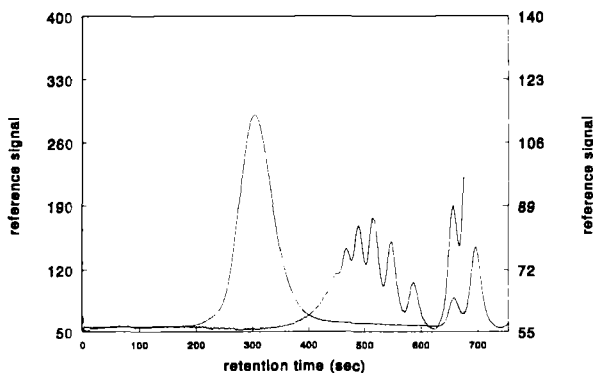


Figure 2. GPC chromatograph of copolymerisation process of lactide with PEG1000. The molar ratio of lactide to PEG1000 to  $\text{Sn}(\text{oct})_2$  was 15:1:0.02. The two graph are the samples of 3 minutes and 20 minutes after the addition of the catalyst.

Higher molecular weight material was only found after some reaction time, meaning that sudden chain growth can be excluded.

As the molar ratio of initiator to catalyst is 100:1, the catalyst must shift from one initiator to another to give every initiator molecule an equal opportunity to react. We use the term "step transfer" for this phenomenon.

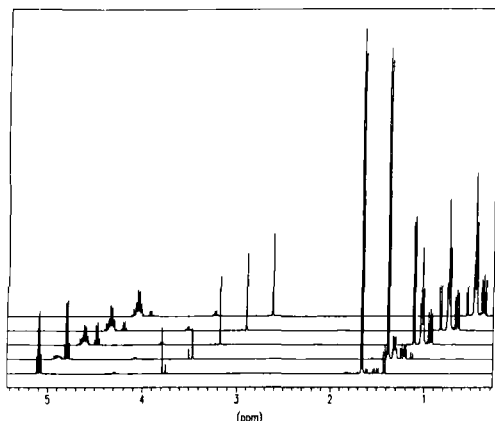


Figure 3.  $^1\text{H}$  NMR spectra during polymerization of lactide initiated by methyl lactate at  $115^\circ\text{C}$ . The catalyst was  $\text{Sn}(\text{oct})_2$ . Molar ratio of lactide to methyl lactate to  $\text{Sn}(\text{oct})_2$  was 15:1:0.01.

As the reaction proceeds, the spectra become increasingly complex due to the increase of lactide unit at the chain.

Quantitatively, it was found that little polymerisation has taken place up to 80-90% conversion of the initiator in this system.<sup>8</sup> Also, no high molecular weight polymer was found at an earlier stage of the reaction. Figure 2 is the GPC chromatography of the polymerisation system. At the first stage of the reaction, only oligomer peaks were found.

Figure 3 shows the  $^1\text{H}$  NMR spectra of the reaction mixture that is formed during the polymerisation of lactide initiated by the secondary alcohol, methyl lactate. The consumption of methyl lactate can be shown by investigating the change in peak area of the peaks at 3.74 ppm and 3.78 ppm. The singlet at 3.78 ppm denotes the methyl proton of methyl lactate before reaction and the peak at 3.74 ppm

denotes the one after reaction. From this figure it can also be seen that the two doublets found in the first curve of figure 1 among 1.4 - 1.6 ppm does not appear here. Since the presence of the two doublets indicates that the initiation reaction is prior to the propagation reaction, lack of them means that the propagation occurs also at the initial stage. In fact, even the earliest sample showed a peak at 1.61 ppm implying propagation. Because methyl lactate should have a similar reactivity as the propagating lactate end group, these facts lead to the conclusion that intramolecular propagating process, i.e. the sudden chain growth, is not significant in these polymerisations.

Figure 4 displays the  $^1\text{H}$  NMR spectra of the *tert*-butanol initiated polymerisation. The singlet at 1.45 ppm and 1.27 ppm denotes the reacted and unreacted initiator. It can be seen that large amount of initiator, indicated by the peak at 1.27 ppm, remains unreacted even after nearly all of the monomer has been consumed. This indicates that intermolecular propagating processes does not take place.

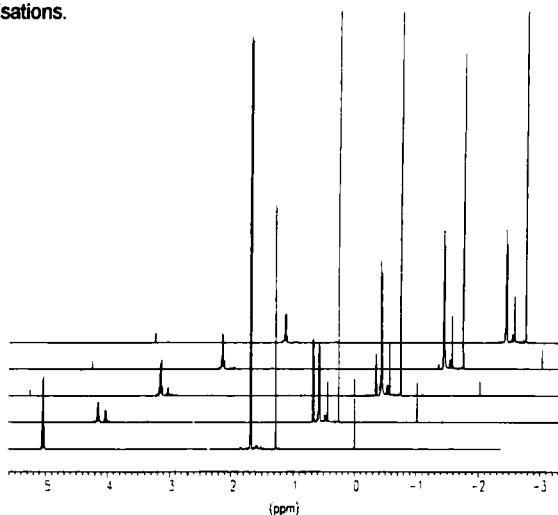


Figure 4.  $^1\text{H}$  NMR spectra during polymerization of lactide initiated by methyl *tert*-butanol at 115 °C. Molar ratio of lactide *tert*-butanol to  $\text{Sn}(\text{oct})_2$  was 15:1:0.01.

Pinacol, another tertiary alcohol, did not initiate the polymerisation directly but instead rearranged to yield water and pinacolone. The water produced in the rearrangement initiated the reaction.

Based on the experimental facts mentioned above and results of other laboratories, the polymerisation process may be described as follows:

**Initiation** There are some results which are already known:

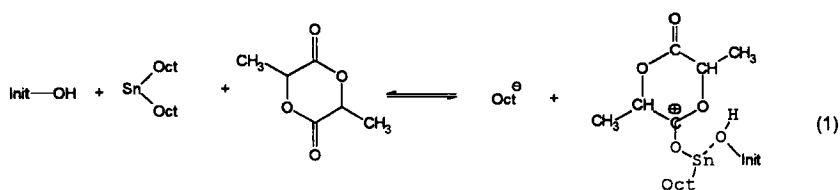
The carboxyl-oxygen bond of the lactone is opened during reaction.<sup>9</sup>

When tin halogen, tributyltin acetate or thioacetate compounds are used as catalysts, hydroxyl containing impurities are necessary to make the reaction proceed.<sup>4,10</sup> Also, when  $\text{tin}(\text{II})(\text{oct})_2$  is used as a catalyst, hydroxyl group bearing compound must be present as

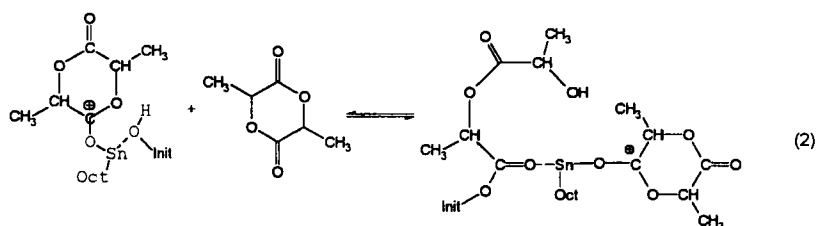
initiator. It is not the Sn-oxycarbonyl insertion that leads to the polymerisation because in that case an energetically unfavourable anhydride end groups has to be formed.<sup>9</sup> This is confirmed by the fact that the addition of acid does not affect the molecular weight while the addition of alcohols reduced molecular weight greatly.<sup>11</sup>

When tin-alkoxy compounds are used as catalysts, however, the polymerisation takes place through the insertion of a lactone to Sn-alkoxy bond. The tin-alkoxy compounds function both as catalyst and initiator.

It seems that the polymerisation starts with the formation of an Sn-O linkage. In tin-alkoxy compounds, the Sn-O linkage is already available. In other words, these compounds are both catalyst and initiator at the same time. In tin halogen, tributyltin acetate and tin(II) bis(2-ethylhexanoate) catalysed polymerisation, this Sn-O linkage can be formed through combination of lactone to the related tin compounds<sup>5</sup> or through combination of alcohol with the tin compound. When the lactide/catalyst complex combines with a hydroxyl group, reaction would take place (equation 1). Then, another lactide monomer will

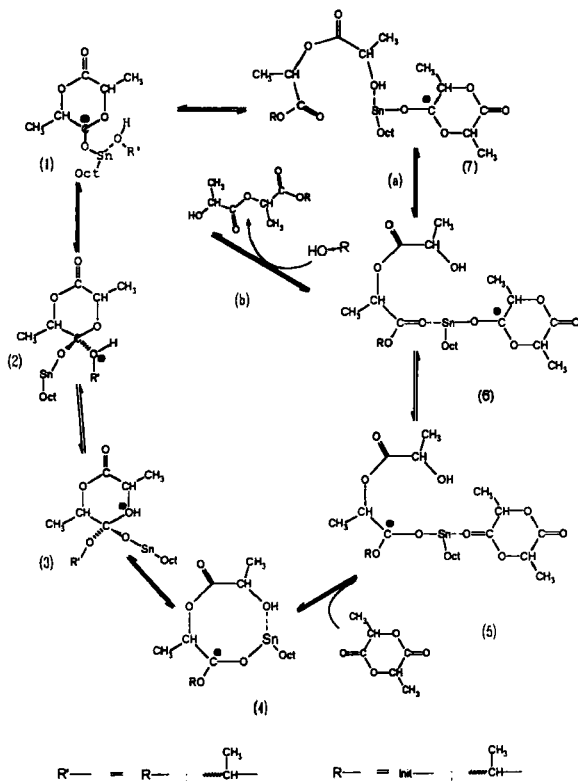


coordinate to the Sn atom to form a new complex (equation 2).



**Propagation Reaction** Although the propagation rate may differ from the initiation rate, both reaction mechanisms are the same. The only complexity comes from the fact that in the reaction mixture, the hydroxyl chain end and the initiator hydroxyl group are present at the same time. The active-site may react with hydroxyl group via either intramolecular attack (a of scheme 2) or intermolecular attack (b of scheme 2) to undergo a chain growth or chain transfer growth. This process may last until all the monomer is consumed.

Thus, the dependence of the reaction mechanism on the initiator can be explained as follows. As the active chain may go to either intramolecular (a of scheme 2) or



**Scheme 2.** The reaction mechanism of the  $\text{Sn}(\text{oct})_2$  catalyzed lactide polymerization.

intermolecular reaction (b of scheme 2), the reactivity of initiator will influence the tendency. When the initiator is highly reactive, for example, in the case of a primary alcohol, the reaction through intermolecular process (b of scheme 2), i.e. step chain transfer, will have high priority. In other words, the initiator reacts fast. When the initiation rate is comparable with the propagation rate, as in the case of methyl lactate, the choice between (a of scheme 2) and (b of scheme 2) has no preference. Step transfer growth also happens when the initiator is far less

**Equilibrium Character and Termination Reaction** It is found that there is about 3 percent of unreacted monomer left in the polymerisation system after the reaction<sup>5</sup>. This was considered to be the result of a polymer-monomer equilibrium and not the result of toxication of the catalyst. In order to check this, fresh monomer was added to the reaction system that



had reached its maximum conversion as verified by  $^1\text{H}$  NMR spectroscopy. After a few hours of polymerisation, again, ca. 3 percent of unreacted lactide was found. This result supports the idea of the polymer-monomer equilibrium and hinted that no actual termination reaction occurred.

When tin-alkoxyl compounds or other metal-alkoxyl compound are used as initiator, the ratio of catalyst to initiator is precisely 1:1. The polymerisation takes place as if there is no transfer happened. This is true only when there is no water or hydroxyl group bearing compounds present. Otherwise, according to the discussion above, the hydroxyl group will participate in the polymerisation and lower the molecular weight of the product.

### Conclusions

The formation of Sn-O linkage is important for the initiation reaction. The active centre is not bound to a single chain end when the reactivity of initiator is high. Inter- and intramolecular propagating processes are determined by the reactivity of initiator. By choosing an appropriate combination of catalyst and initiator, the polymer process, molecular weight can be adjusted.

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