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# Polylactones: 31. Sn(II)octoate-initiated polymerization of L-lactide: a mechanistic study

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The polymerization of L-lactide was catalysed with Sn(II)2-ethylhexanoate ($SnOct_2$) in the presence or absence of benzyl alcohol. The molecular weights parallel the lactide/benzyl alcohol ratio, but never the lactide/Sn ratio. $^1H$ n.m.r. spectroscopy revealed the existence of benzylester and $-CH(CH_3)OH$ end-groups. Polymerizations conducted at low lactide/catalyst ratios in the absence of an alcohol yield polylactide with a low content of 2-ethylhexanoate end-groups. $^1H$ and $^{119}Sn$ n.m.r. spectroscopy of $CHCl_3$ solutions also demonstrated that $SnOct_2$ forms strong complexes with both benzyl alcohol and ethyl lactate and weaker complexes with lactide. A similar but weaker complexation was also detected for $Bu_2SnOct_2$ in combination with either benzyl alcohol or lactide. A new polymerization mechanism is discussed, assuming the reaction between lactide and OH end-groups bound to a Sn atom via two $sp^3d^2$orbitals.

**(Keywords: polylactones; polymerization; catalysts)**

## INTRODUCTION

Poly(L-lactide) or poly(D,L-lactide), designed to serve as resorbable material for medical or pharmaceutical applications, is usually prepared by Sn(II)2-ethylhexanoate ($SnOct_2$)-initiated bulk polymerizations of L,L- or D,D, L,L-lactide[1–9]. This catalyst is preferred for three main reasons. First, $SnOct_2$ is a highly efficient catalyst and allows almost complete conversions even at monomer/catalyst ratios as high as $10^4$:1 (ref. 7). Second, the risk of racemization is low, and 99% optically pure poly(L-lactide) can be prepared even at 150°C, when the reaction time is limited to a few hours. Third, $SnOct_2$ is a permitted food additive in numerous countries, which means that its toxicity is extremely low compared to other heavy metal salts.

Surprisingly little is known about the polymerization mechanism of $SnOct_2$. It is obvious that $SnOct_2$, like many other metal salts having energetically favourable free d orbitals, can act as transesterification catalyst for alcohols and esters including lactones[10]. Quite recently Nijenhuis *et al.*[7] proposed a polymerization mechanism termed 'cationic', but spectroscopic evidence for the way that $SnOct_2$ interacts with lactide and alcohols is lacking. Also lacking is any information on the end-groups of the resulting polylactides. Kricheldorf and co-workers have studied the polymerization mechanisms of several types of tin compound[11–14], such as, Sn(II)- and Sn(IV)halogenides, dibutyltin and tributyltin alkoxides, halogenides and acetates. The present work is an extension of these studies concentrating on $SnOct_2$-initiated polymerizations of L-lactide.

## EXPERIMENTAL

### Materials

L-Lactide (S-grade) was purchased from Boehringer KG (Ingelheim, Germany) and recrystallized twice from tetrahydrofuran/ligroin. $SnOct_2$ was purchased from Johnson Matthey Alfa Products (Karlsruhe, Germany) and distilled *in vacuo*. Benzyl alcohol, a gift from Bayer AG (Leverkusen, Germany), was distilled over calcium hydride *in vacuo*. Ethyl-D,L-lactate was purchased from Aldrich Co. (Milwaukee, WI, USA) and distilled *in vacuo*.

### Polymerizations

*Without benzyl alcohol.* L-lactide (40 mmol) was weighed into a 25 ml Erlenmeyer flask with silanized glass walls (treated with $Me_2SiCl_2$) and the initiator was added in the form of a 1 M solution in toluene. The reaction vessel was closed with a glass stopper and steel spring, and immersed into a thermostatically controlled oil bath. Finally, the reaction product was dissolved in $CH_2Cl_2$ (40–50 ml) and precipitated into cold methanol (4–5°C).

*With benzyl alcohol as coinitiator.* These polymerizations were conducted as described above, but benzyl alcohol was added to the lactide prior to the injection of catalyst.

All reaction mixtures were prepared in an atmosphere of dry nitrogen.

### Measurements

The inherent viscosities were determined with an automated Ubbelohde viscometer thermostatically controlled at 25°C.

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The 100 MHz $^1H$ n.m.r. spectra were recorded with a Bruker AC-100 FT spectrometer in 5 mm o.d. sample tubes. The 360 MHz $^1H$ n.m.r. spectra were obtained on a Bruker AM-360 FT NMR spectrometer in 3 mm o.d. sample tubes (in $CDCl_3$ containing tetramethylsilane (TMS)).

The g.p.c. measurements were conducted with Kontron HPLC 420 equipped with a Waters differential refractometer. A combination of four Ultrastyragel columns was used with tetrahydrofuran as eluent.

## RESULTS AND DISCUSSION

### *Polymerizations without coinitiator*

Two series of polymerizations were conducted:

A L-lactide + $SnOct_2$ with variation of the monomer/initiator (M/I) ratio.

B L-lactide + $SnOct_2$ and benzyl alcohol with variation of the monomer/benzyl alcohol (M/B) ratio. Benzyl alcohol was selected as coinitiator because its incorporation as benzylester end group is easily detectable by both $^1H$ and $^{13}C$ n.m.r. spectroscopy.

All polymerizations were conducted in bulk at 120°C. The results obtained for series A are summarized in *Table 1*. High yields were obtained in all experiments. The viscosities strongly increase with the M/I ratio, indicating that the $SnOct_2$ is somehow responsible for the formation of dead end-groups. Whether these inactive end-groups are generated as part of the initiation process or later on as a consequence of termination steps is an open question. $^1H$ n.m.r. spectroscopic examination of the polylactides prepared with low M/I ratios ($M/I \leqslant 10$) revealed a weak signal, suggesting that 2-ethylhexanoate (Oct) groups and CH–OH end-groups are present in the polylactides (*Figure 1*). The Oct end-groups are certainly covalently attached to the polylactide chains via ester groups, because repeated reprecipitation from methanol did not cause significant losses (small losses may be attributed to fractionation). Taking into account the initiation mechanism established for butyltin alkoxides[14] and other metal alkoxides[11] (equation (1)), the formation of Oct end-groups may be rationalized by the reaction sequence of equations (2) and (3). The first step, the formation of an anhydride group, is certainly an energetically unfavourable reaction, and the equilibrium of equation (2) is shifted to the left side. However, the subsequent reaction (equation (3)) is energetically more favourable and drives the entire reaction sequence gradually in the direction of octoate end-groups. If the unfavourable reaction sequence of equations (2) and (3) forms part of the initiation process, it is understandable why only a part of the $SnOct_2$ is active at low M/I ratios. The chain growth will most likely proceed via the relatively reactive Sn-alkoxide group as illustrated by equation (4). Upon alcoholysis (or hydrolysis) these Sn-alkoxide groups will be transformed into CH–OH end-groups.

**Table 1** Polymerization of L-lactide with $SnOct_2$ in bulk at 120°C for 24 h

| No. | Lactide/ $SnOct_2$ ratio | Yield (%) | $\eta_{inh}$[a] (dl $g^{-1}$) | DP[b] (theor.) | >CH–OH[c]/ monomer ratio | Octoate[d]/ monomer ratio |
|---|---|---|---|---|---|---|
| 1 | 5 | 86 | 0.15 | 9 | 1:40 | 1:65 |
| 2 | 10 | 94 | 0.17 | 19 | 1:75 | 2:190 |
| 3 | 20 | 94 | 0.19 | 38 | 1:80 | 1:280 |
| 4 | 30 | 93 | 0.22 | 55 | 1:130 | 1:320 |
| 5 | 50 | 96 | 0.26 | 96 | 1:160 | 1:600 |
| 6 | 100 | 92 | 0.43 | 184 | 1:260 | 1:1000 |
| 7 | 200 | 94 | 0.78 | 376 | 1:450 | not measurable |

[a] Measured at 25°C with $c = 2\,g\,l^{-1}$ in $CH_2Cl_2$

[b] Degree of polymerization calculated from the lactide/$SnOct_2$ ratio taking the yield as conversion

[c] From $^1H$ n.m.r. spectroscopic determination of the $-CH(CH_3)OH$ end-groups

[d] From $^1H$ n.m.r. spectroscopic determination of the octoate end-groups

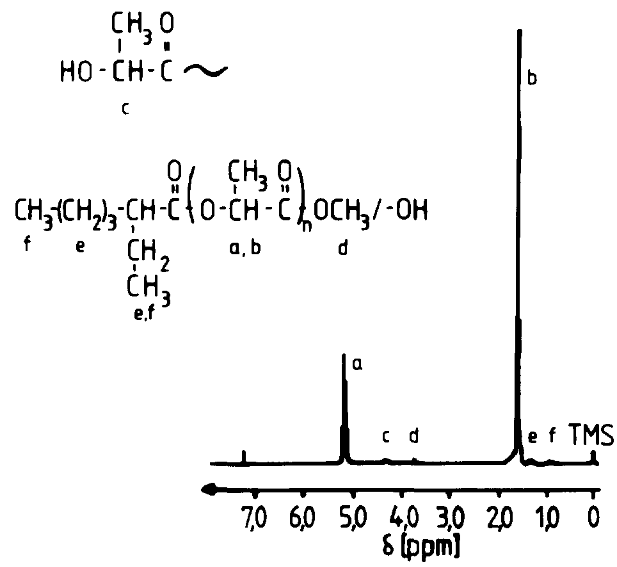
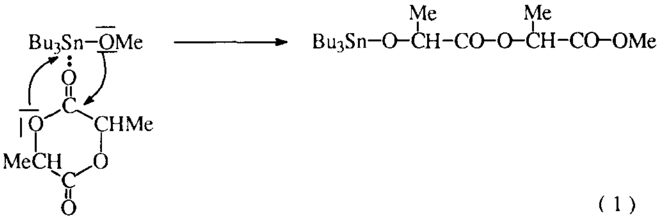
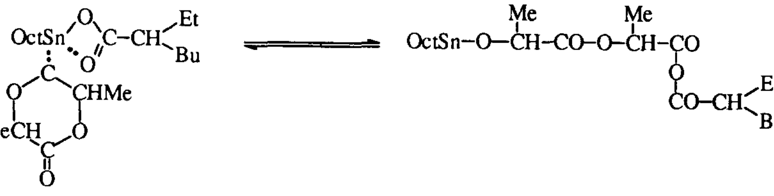


**Figure 1** 360 MHz $^1H$ n.m.r. spectrum of a polylactide initiated with $SnOct_2$ (M/I = 5) at 120°C (no. 1, *Table 1*)

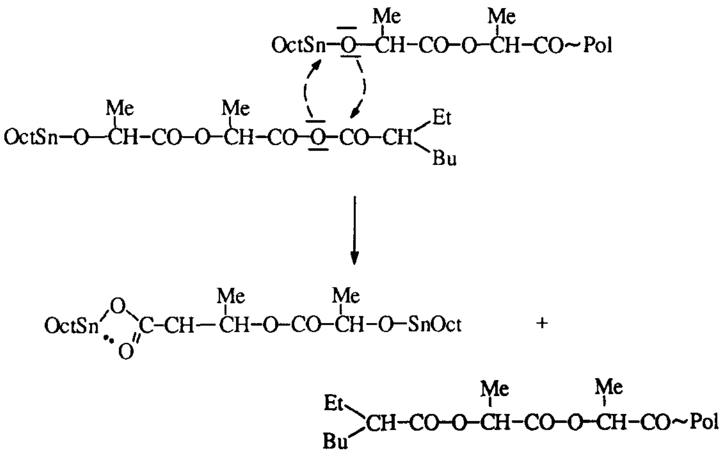
However, it should be emphasized that OH groups containing impurities may play the role of efficient coinitiators, initiating most of the isolated polylactide chains. As indicated by $^1H$ n.m.r. spectroscopy, $SnOct_2$ contains small amounts of water, even after distillation or after drying over $P_4O_{10}$. The $^1H$ n.m.r. spectra measured in $CDCl_3$ display a singlet signal at $11.3 \pm 0.2$ ppm, the intensity of which depends on the extent of drying. This observation and the chemical shifts of benzyl alcohol or ethyl lactate (discussed below, *Table 3*) suggest that $SnOct_2$ forms strong complexes with water. Furthermore, L-lactide may contain small amounts of lactyllactic acid resulting from hydrolysis of lactide even after recrystallization. Therefore, the reaction sequence of equations (2)–(4) presumably plays a minor role and (co)initiation by water or other OH groups (e.g. equation (5), R = H) plays the major role. Coinitiation with water results in polylactides bearing carboxyl end-groups, which are difficult to detect by n.m.r. spectroscopy.



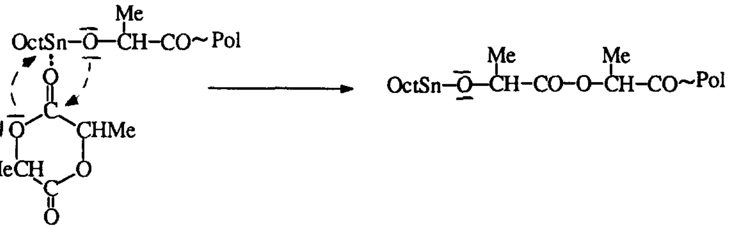
(1)



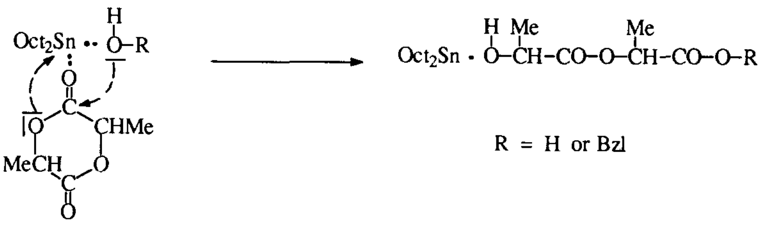
(2)



(3)



(4)



(5)

*Polymerizations with coinitiator*

When benzyl alcohol is used as coinitiator (*Table 2*) the inherent viscosities increase with the M/B ratio. The $^1$H n.m.r. spectroscopic examination of all polylactides revealed the presence of benzylester end-groups but the absence of octoate end-groups (*Figure 2*). This result clearly demonstrates that the energy of activation of initiation involving alcohols is much lower than that of initiation by neat $SnOct_2$ (e.g. equation (2)). This result is in perfect agreement with the previously reported synthesis of A–B–A triblock copolymers based on polyethylene glycols (as B block) and L-lactide[15]. When $SnOct_2$ was used as catalyst, a complete esterification of the poly(ethylene glycol) was found, with no incorporation of octoate end-groups.

In addition to benzylester end-groups, CH–OH end-groups were again found in almost identical quantities (*Table 2*). This observation suggests the formulation of the schematic polymerization mechanism outlined in equation (5), details of which will be discussed below.

**Table 2** Polymerization of L-lactide (in bulk at 120°C) with $SnOct_2$ and benzyl alcohol as coinitiator

| No. | Lactide/ $SnOct_2$ ratio | Lactide/ benzyl ratio | Yield (%) | $\eta_{inh}$[a] ($dl\,g^{-1}$) | DP[b] (calc.) | DP[c] (n.m.r.) | DP[d] (n.m.r.) |
|---|---|---|---|---|---|---|---|
| 1 | 100 | 10 | 60 | 0.13 | 12 | 50 | 50 |
| 2 | 100 | 20 | 82 | 0.22 | 33 | – | – |
| 3 | 100 | 40 | 92 | 0.28 | 73 | 120 | 130 |
| 4 | 100 | 60 | 90 | 0.35 | 110 | 210 | 220 |
| 5 | 100 | 100 | 90 | 0.41 | 180 | 330 | 350 |
| 6 | 100 | 150 | 91 | 0.44 | 270 | – | 500 |
| 7 | 200 | 40 | 78 | 0.23 | 74 | 130 | 140 |
| 8 | 200 | 100 | 85 | 0.50 | 170 | 320 | 330 |
| 9 | 200 | 200 | 94 | 0.68 | 370 | 480 | 550 |
| 10 | 200 | 400 | 95 | 0.72 | 760 | – | – |

[a] Measured at 25°C with $c = 2\,g\,l^{-1}$ in $CH_2Cl_2$

[b] Degree of polymerization calculated from the lactide/benzyl alcohol ratio taking the yields as conversion

[c] From $^1$H n.m.r. spectroscopic determination of the $CH(CH_3)OH$ end-groups

[d] From $^1$H n.m.r. spectroscopic determination of the benzylester end-groups

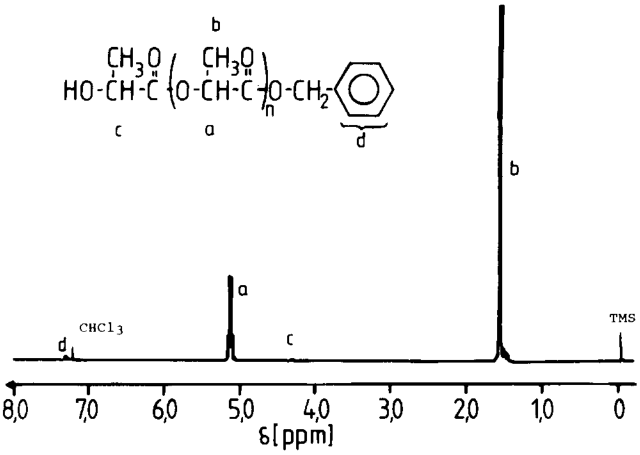


**Figure 2** 360 MHz $^1H$ n.m.r. spectrum of a polylactide initiated with $SnOct_2$ (M/I = 100) and benzyl alcohol (M/B = 20) at 120°C (no. 2, *Table 2*)

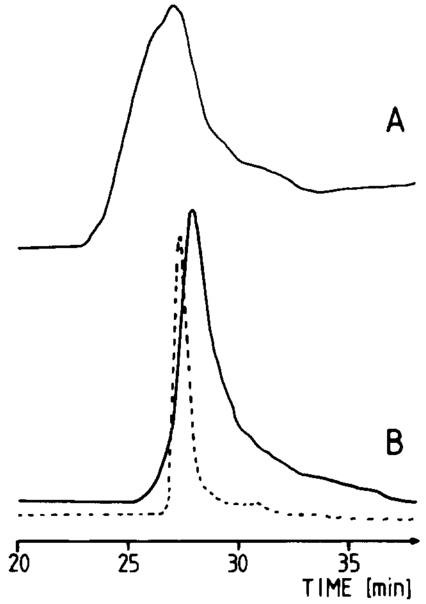


**Figure 3** G.p.c. measurements of (A) sample N, *Table 2* ($M_w/M_n = 2.5$); (B) sample no. 12, *Table 5* ($M_w/M_n = 2.1$) + polystyrene standard ($M_w = 33\,500$, $M_w/M_n = 1.05$)

The quantification of both kinds of end-group demonstrates that the degrees of polymerization (DP in *Table 2*) are higher than calculated for a quantitative initiation with benzyl alcohol. However, this discrepancy may be attributed to fractionation resulting from the precipitation into methanol. Oligolactides with benzylester end-groups were indeed detected in the filtrate. Furthermore, g.p.c. measurements of the crude reaction mixtures display a relatively broad molecular weight distribution, with $M_w/M_n$ ratios > 2 (*Figure 3*). Thus these results clearly show that even the alcohol-initiated polymerizations do not follow the living pattern with regard to the molecular weight distribution.

### *Complexation of monomer and coinitiators*

The mechanism formulated in equation (5) postulates the association of both benzyl alcohol and L-lactide with $SnOct_2$ via free d orbitals. To the best of our knowledge, spectroscopic evidence for the formation of such complexes has not been reported to date. Therefore two series of $^1H$ n.m.r. spectroscopic measurements were conducted in $CDCl_3$ solution. In one series, $SnOct_2$ and benzyl alcohol were combined in various molar ratios in the hope that the signals of the OH and $CH_2$ groups would indicate the formation of a complex. The results, summarized in *Table 3*, clearly indicate that the postulated complexation indeed takes place. As illustrated by *Figure 4*, the signal of the OH group experiences a strong downfield shift which in a semilogarithmic plot shows an almost linear dependence on the $SnOct_2$/benzyl alcohol ratio (*Figure 5*). Even the $CH_2$ signal exhibits a downfield shift of 0.25 ppm (*Table 3*).

When ethyl lactate is used as a coinitiator and a model of an active chain end the shift effects are even greater (*Table 3*). The most interesting result in this case is the downfield shift of the CH signal, which amounts to 0.76 ppm when studied over the full range of SnOct/lactate ratios. As illustrated in *Figure 6*, even a molar ratio of

**Table 3** $^1H$ n.m.r. chemical shifts[a] of benzyl alcohol, ethyl-D,L-lactate or L-lactide in the presence of $SnOct_2$

| Substrate/ $SnOct_2$ ratio | δ of benzyl alcohol[b] | | δ of ethyl-D,L-lactate[c] | | L-lactide | |
|---|---|---|---|---|---|---|
| | $CH_2$ | OH | CH | OH | CH[d] | $CH_3$ |
| ∞ | 4.46 | 3.55 | 4.19/4.26 | 3.68 | 5.14 | 1.64 |
| 4:1 | 4.52 | 5.00 | – | – | – | – |
| 2:1 | 4.58 | 5.33 | 4.40/4.47 | 5.55 | 5.15 | 1.64 |
| 1:1 | 4.63 | 6.38 | 4.50/4.57 | 6.89 | – | – |
| 1:2 | 4.66 | 7.37 | 4.66/4.73 | 8.78 | 5.18 | 1.64 |
| 1:4 | 4.69 | 8.15 | 4.83/4.90 | 10.28 | – | – |
| 1:8 | 4.71 | 9.60 | 4.93/5.00 | 10.93 | 5.20 | 1.64 |
| 1:16 | 4.71 | 10.30 | 4.96/5.03 | 11.10 | – | – |

[a] Measured at 25°C in $CDCl_3$ relative to internal TMS
[b] The maximum Δδ is 0.25 for the $CH_2$ and 6.75 for the OH signal
[c] The maximum Δδ is 0.76 for the CH, 7.7 for the OH and 0.1 for the $CH_2$ signal
[d] $J = 6.5$ Hz; maximum Δδ = 0.06

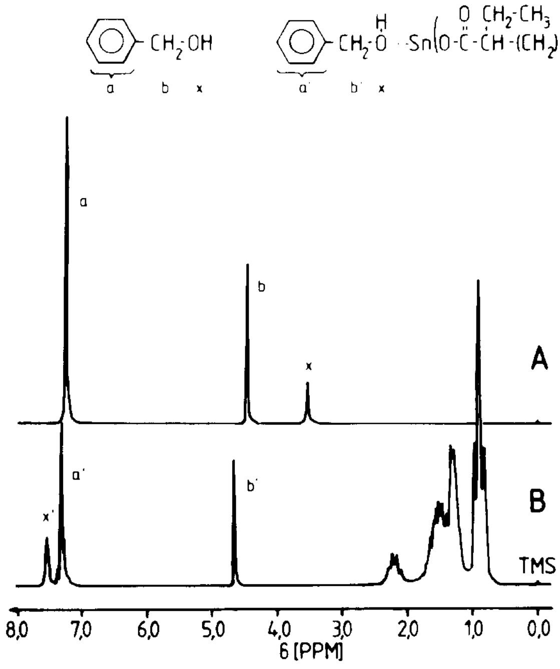


**Figure 4** 100 MHz $^1H$ n.m.r. spectra of (A) neat benzyl alcohol; (B) benzyl alcohol + $SnOct_2$ (molar ratio 1:2)

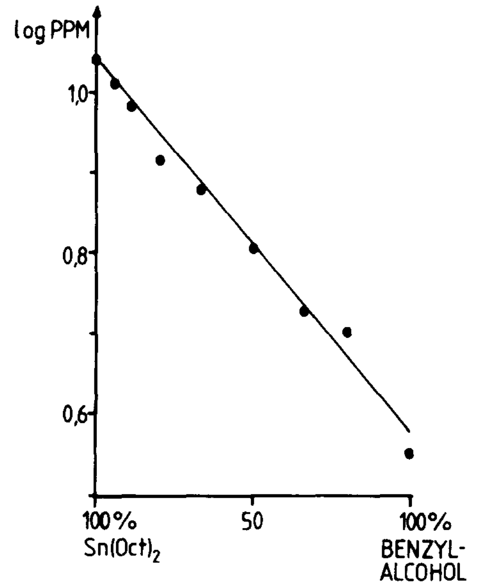


**Figure 5** Semilogarithmic plot of the chemical shifts of the OH signal of benzyl alcohol *versus* mole percentage of $SnOct_2$ in $CDCl_3$ solution

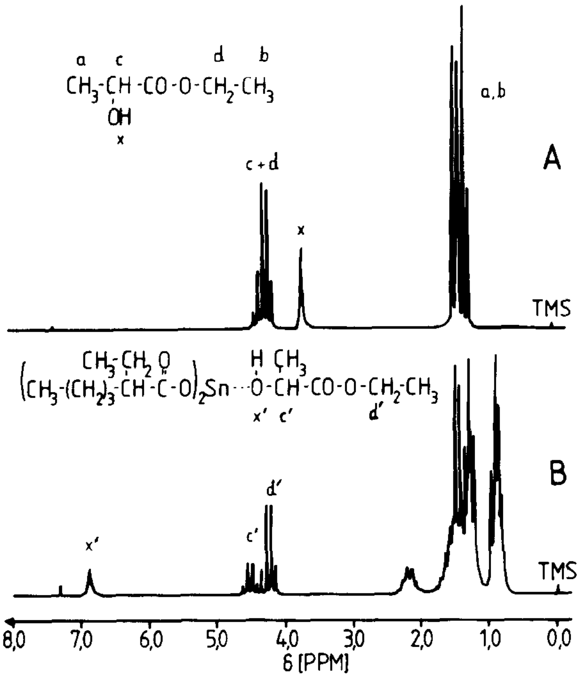
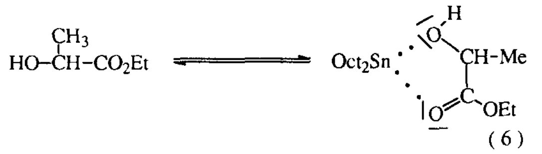


**Figure 6** 100 MHz $^1H$ n.m.r. spectra ($CDCl_3$) of (A) ethyl-D,L-lactate; (B) ethyl-D,L-lactate + $SnOct_2$ (molar ratio 1:1)

1:1 suffices to bring about a clear separation of the CH and $CH_2$ quadruplets, which overlap when the neat ethyl lactate is measured in $CDCl_3$. These conspicuous downfield shifts suggest that the interaction of ethyl lactate with $SnOct_2$ is stronger than in the case of benzyl alcohol. Since the OH group of lactic acid is neither more basic nor more nucleophilic than that of benzyl alcohol, a stronger binding of ethyl lactate is best rationalized by the assumption that the lactate acts as a bidentate ligand (equation (6)):



$$\mathrm{Oct_2Sn} + \mathrm{HO{-}\overset{CH_3}{C}H{-}CO_2Et} \rightleftharpoons \mathrm{Oct_2Sn}\begin{matrix}\cdot\cdot\,O(H){-}CH{-}Me\\ \cdot\cdot\,O{=}C{-}OEt\end{matrix} \qquad (6)$$

This assumption is supported by the finding that even the $CH_2$ signal of the ethyl group shows a downfield shift of 0.1 ppm. This shift effect is small, but it amounts to 40% of the shift effect observed for the $CH_2$ signal of benzyl alcohol, though the $CH_2$ group in ethyl lactate is quite distant from the OH group.

When L-lactide is combined with $SnOct_2$ in $CDCl_3$, the $CH_3$ signal does not exhibit any shift effect and the downfield shift of the CH signal is weak (*Table 3*). Furthermore, when L-lactide is added to a 1:1 mixture of benzyl alcohol and $SnOct_2$, the signals of benzyl alcohol shift very little. Only the OH signal displays a 0.2 ppm upfield shift, which is poor compared to the 2.7 ppm downfield shift relative to neat benzyl alcohol. These results suggest that L-lactide is a relatively poor ligand, which does not displace a significant fraction of benzyl alcohol from its $SnOct_2$ complex. Remarkable is the splitting of the $^1H$ n.m.r. signal of the aromatic protons when lactide is present in mixtures of benzyl alcohol and $SnOct_2$ (*Figure 7*). However, a straightforward interpretation of this effect cannot be offered at this time.

The conclusion that alcohols are better ligands for $SnOct_2$ than L-lactide is supported by $^{119}Sn$ n.m.r. measurements in $CDCl_3$ solution. The data in *Table 4* show that the downfield shift of the $SnOct_2$ signal increases in the order:

lactide < benzyl alcohol ≪ ethyl lactate

Finally, it should be mentioned that $^{13}C$ n.m.r. spectroscopy was also used to study the complexation of $SnOct_2$. Solutions of neat benzyl alcohol or L-lactide in $CDCl_3$ were compared with equimolar mixtures of

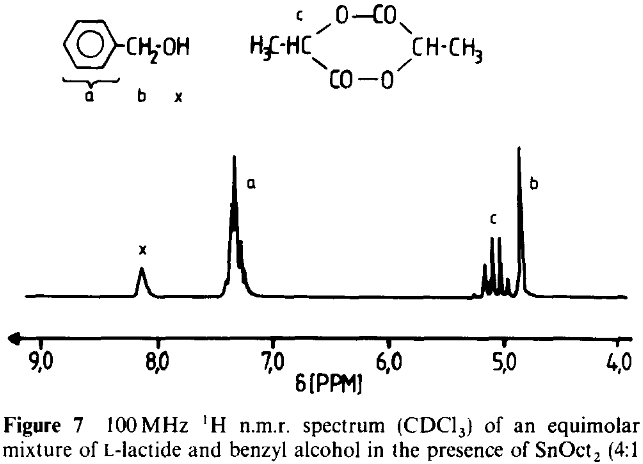


**Figure 7** 100 MHz $^1H$ n.m.r. spectrum ($CDCl_3$) of an equimolar mixture of L-lactide and benzyl alcohol in the presence of $SnOct_2$ (4:1 molar relation to lactide)

**Table 4** $^{119}Sn$ n.m.r. chemical shifts $\delta$ (relative to internal $SnMe_4$) of $SnOct_2$ or $Bu_2SnOct_2$ and its complexes measured in $CDCl_3$ at 25°C

| | $\delta$ (ppm) |
|---|---|
| $SnOct_2$ | −529.6 |
| $SnOct_2$ + L-lactide[a] | −527.7 |
| $SnOct_2$ + benzyl alcohol[a] | −524.8 |
| $SnOct_2$ + ethyl-D,L-lactate[a] | −509.8 |
| $Bu_2SnOct_2$ | −154.2 |
| $Bu_2SnOct_2$ + L-lactide | −153.5 |
| $Bu_2SnOct_2$ + benzyl alcohol | −151.5 |
| $Bu_2SnOct_2$ + ethyl-D,L-lactate[a] | −152.4 |

[a] Molar ratio 1:1

**Table 5** $Bu_2SnOct_2$-initiated polymerizations of L-lactide in bulk at 120°C for 24 h

| No. | Lactide/ $Bu_2SnOct_2$ | Lactide/ benzyl alcohol | Yield (%) | $\eta_{inh}$[a] ($dl\,g^{-1}$) | Octoate/ monomer[b] | Benzylester/ monomer[c] |
|---|---|---|---|---|---|---|
| 1 | 5 | – | 89 | 0.48 | 1:250 | – |
| 2 | 10 | – | 90 | 0.47 | 0 | – |
| 3 | 20 | – | 94 | 0.52 | 0 | – |
| 4 | 50 | – | 67 | 0.45 | 0 | |
| 5 | 100 | | 63 | 0.40 | 0 | |
| 6 | 200 | – | 35 | 0.29 | 0 | – |
| 7 | 100 | 20 | 86 | 0.10 | 0 | 1:40 |
| 8 | 100 | 40 | 92 | 0.15 | 0 | 1:80 |
| 9 | 100 | 60 | 90 | 0.19 | 0 | 1:120 |
| 10 | 100 | 100 | 90 | 0.23 | 0 | 1:160 |
| 11 | 100 | 150 | 88 | 0.30 | 0 | 1:200 |
| 12 | 100 | 200 | 86 | 0.32 | 0 | 1:270 |

[a] Measured at 25°C with $c = 2\,g\,l^{-1}$ in $CH_2Cl_2$
[b] Molar ratio of octoate end-groups/monomer units
[c] Molar ratio benzylester end-groups/monomer units

$SnOct_2$. Regardless of which carbon was compared, the maximum shift effect was only on the order of 0.2 ppm. In other words, $^{13}C$ n.m.r. spectroscopy proved to be rather useless for studying interactions of $SnOct_2$ with substrates of interest.

### *The reactivity of $Bu_2SnOct_2$*

Whereas $SnOct_2$ is mentioned as catalyst in numerous patents and papers, no information is available on the catalytic activity of $Bu_2SnOct_2$ in polymerizations of lactide or lactones. In the case of $Bu_2SnOct_2$, one more orbital is occupied by electrons. Assuming that the reactivity of Sn(II) and Sn(IV) compounds is based on a $sp^3d^2$ hybridization, $Bu_2SnOct_2$ has two orbitals free for the binding of monomers and coinitiators, provided that the octoate groups are monodentate ligands. However, if the octoate groups behave as bidentate ligands, no orbital is available and $Bu_2SnOct_2$ should not show any catalytic activity.

In order to obtain a first idea about the catalytic activity of $Bu_2SnOct_2$, two series of polymerizations were studied under reaction conditions comparable with those of *Tables 1* and *2*. The first series (nos 1–5, *Table 5*) was conducted without a coinitiator. The results indicate that neat $Bu_2SnOct_2$ is indeed a polymerization catalyst and high yields are obtainable at low monomer/initiator ratios. However, the results obtained with $Bu_2SnOct_2$ differ in several aspects from those found for $SnOct_2$ (*Table 1*):

1. The viscosities (molecular weights) do not increase with the monomer/catalyst ratio.
2. Octoate end-groups are barely detectable in the $^1H$ n.m.r. spectra of reprecipitated polylactides. The termination steps typical for neat $SnOct_2$ seem to be less efficient or absent in the case of $Bu_2SnOct_2$.
3. Both yields and viscosities decrease at monomer/catalyst ratios above 20 (compared at constant temperature and reaction time). Clearly, $Bu_2SnOct_2$ is a less active catalyst.

In the second series of polymerizations with $Bu_2SnOct_2$ (nos 6–12, *Table 5*) benzyl alcohol was added in various molar ratios. The results obtained in this series agree largely with those compiled in *Table 2*. The molecular weights parallel the lactide/benzyl alcohol ratio. $^1H$ n.m.r. spectroscopy revealed benzylester end-groups in all samples and their quantity parallels the monomer/coinitiator ratio. There are two reasons why the concentration of benzylester end-groups is somewhat lower than expected from the feed ratio: first, fractionation, because oligomers remain dissolved in methanol; and second, side reactions which were not elucidated, with one exception. Precipitation of polylactide into methanol results in methanolytic cleavage of ester bonds with formation of methylester end-groups. This side reaction is negligible only when the methanol is cold and filtration of the polylactide rapid.

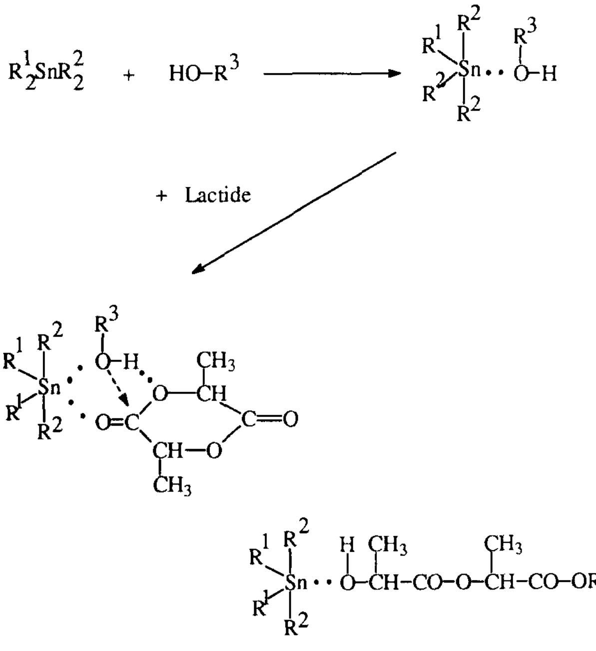
Finally, the capability of $Bu_2SnOct_2$ to form complexes with either monomer, coinitiator or chain end was investigated. $Bu_2SnOct_2$ was mixed in $CDCl_3$ with L-lactide, benzyl alcohol or ethyl lactate in molar ratios of 1:1 and 4:1. Regardless of which mixture was studied, almost no shift effect was detectable. A downfield shift of 0.2 ppm of the OH proton of ethyl-D,L-lactate was the maximum effect. Again, no shift effects were detectable in the $^{119}Sn$ n.m.r. measurements (*Table 4*). These findings clearly demonstrate that $Bu_2SnOct_2$ is an extremely weak Lewis acid compared to $SnOct_2$. This negative result obviously corresponds to the lower catalytic activity of $Bu_2SnOct_2$.

### *Mechanistic discussion*

This mechanistic discussion is based on the assumption that the tin catalysts under investigation are active via free $sp^3d^2$ orbitals. The easy formation of octahedral complexes involving $sp^3d^2$ orbitals is well documented for tin compounds and has been known for centuries in the case of $H_2SnCl_6$ (*Spiritus fumans* Libavii). The strong complexation of nucleophiles, particularly ethyl-D,L-lactate, and the catalytic activity of $Bu_2SnOct_2$ suggest that the octoate groups act mainly as monodentate ligands. In consequence, three $sp^3d^2$ orbitals are free in the case of $SnOct_2$ and two in the case of $Bu_2SnOct_2$. The high Lewis acidity (and thus hygroscopicity) of $SnOct_2$ is obviously due to its need for at least one more ligand to occupy the fourth orbital. With one additional ligand, $SnOct_2$ can form a tetrahedral or quadratic configuration of four occupied orbitals in analogy to

$Bu_2SnOct_2$. The reactivity of the latter catalyst is further reduced by the steric effect of the two butyl groups.

Taking into account that both catalysts favour the incorporation of an alcohol as coinitiator, and considering the strong complexation of alcohols (e.g. OH end-groups), the following polymerization mechanism may be proposed. The first step consists of a coordination between catalyst and alcohol or OH end-group (equation (7)). Coordination of a second alcohol is possible, but does not entail any reaction. However, binding of a lactone (equation (8)) will catalyse the reaction with the complexed alcohol (equation (9)), inasmuch as the complexation of the lactone polarizes its carbonyl group. The reaction sequence formulated for $Bu_2SnOct_2$ in equations (7)–(9) is analogous to the mechanism of equation (5) formulated for $SnOct_2$. It is characteristic for this mechanism that the propagation steps exclusively involve free orbitals of the catalyst, and neither covalent nor ionic bonds. The experimental data presented in this work and by other authors[16] do not definitely prove this mechanism, but the mechanism is consistent with all experimental data and also explains the catalytic activity of $Ph_4Sn$ (ref. 17).



(7)

(8)

(9)

In contrast, the cationic mechanism proposed by Nijenhuis *et al.*[7] lacks experimental evidence. It is not clear why the $SnOct_2$ dissociates completely before attacking lactide. Furthermore, a strong interaction with lactide prior to a reaction with an OH group is in total contradiction to the results presented in this work. The slight racemization observed by Nijenhuis *et al.*[7] was attributed to the cationic character of the polymerization. However, lactide is particularly sensitive to the presence of bases, because the α-proton is highly acidic ($pK_s < 18$; acetone has $pK_s$ 19). It has been demonstrated[13] that a weak base such as potassium benzoate is capable of partially racemizing L-lactide at 80°C in dilute solution. Therefore, it is highly probable that a slight racemization of L-lactide above 100°C is the result of reversible deprotonation by octoate groups.

Taken together, the polymerization mechanism proposed in this work is neither a cationic, anionic nor pseudoanionic mechanism, and is probably best called a 'complexation mechanism' or second-order insertion mechanism.

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