

Polylactones 49: Bu_4Sn -initiated polymerizations of ϵ -caprolactone

H.R. Kricheldorf*, I. Kreiser-Saunders

Institut für Technische und Makromolekulare Chemie, Bundesstr. 45, D-20146 Hamburg, Germany

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Abstract

^1H NMR spectra of mixtures of Bu_4Sn and benzyl alcohol indicate the formation of a weak complex. Furthermore, Bu_4Sn catalyzed polymerizations of ϵ -caprolactone at 100°C are accelerated by addition of benzyl alcohol, but a coordination–insertion mechanism based on a reaction between two ligands of the Sn-catalyst was not definitely proven. In contrast it was found that Bu_4Sn is sensitive to oxidation by oxygen (air), a process which yields mainly Bu_2SnO and only a trace of Bu_3SnOBU . Hence, the Bu_2SnO dissolved in Bu_4Sn is the main initiator, but added benzyl alcohol acts as coinitiator yielding benzyl ester chain ends. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ring-opening polymerization; ϵ -Caprolactone; Tetraethyltin

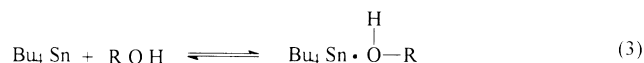
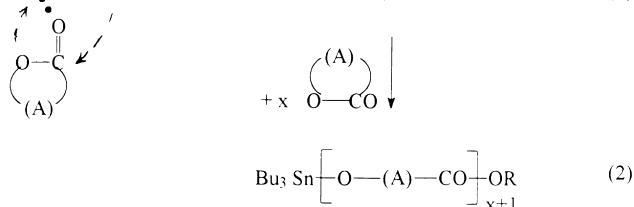
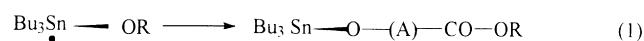
1. Introduction

Tin compounds are well known as highly effective esterification or transesterification catalysts [1,2] and they are also known as efficient initiators of ring-opening polymerizations of lactones and related heterocycles. In previous parts of this series [3,4] we have demonstrated that Sn(IV) alkoxides or phenoxides initiate a coordination–insertion mechanism which is schematically outlined in Eqs. (1) and (2). An open question is which mechanism is operating, when the tin catalysts/initiators do not contain an alkoxide (or phenoxide) group. Catalysts of this type are tin carboxylates, such as Sn(II) 2-ethylhexanoate (SnOct_2) or $\text{Bu}_2\text{SnOct}_2$ and tetraaryl or tetraalkyltin derivatives. These tin compounds either form a tin–alkoxide bond in the first stage of the polymerization process or they catalyze (in combination with a coinitiator) an alternative polymerization mechanism such as that speculatively outlined in a previous study [5].

In this connection it was the purpose of the present work to investigate the reactivity of Bu_4Sn as potential polymerization catalyst/initiator. To the best of our knowledge, tetraalkyltin compounds have never been used as catalysts/initiators of lactones. Interestingly tetraphenyltin has been reported [6] to polymerize L-lactide at temperatures $>120^\circ\text{C}$. Unfortunately mechanistic details have not been

disclosed and Ph_4Sn proved to be poorly soluble in inert solvents so that mechanistic studies by means of NMR methods are difficult to perform. In contrast Bu_4Sn is a liquid which is soluble in ϵ -caprolactone (ϵ -CL) and numerous inert solvents. It is easy to purify by fractionated distillation, and thus, well suited for mechanistic studies. The present work should allow us to answer three questions:

1. Is neat Bu_4Sn a catalyst/initiator of the ring-opening polymerization of ϵ -CL?
2. Does Bu_4Sn form a Sn–alkoxide bond under the given reaction condition so that a polymerization mechanism analogous to that of Eqs. (1) and (2) can proceed?
3. Does Bu_4Sn in combination with an alcohol initiate a polymerization mechanism according to Eqs. (3)–(5)?

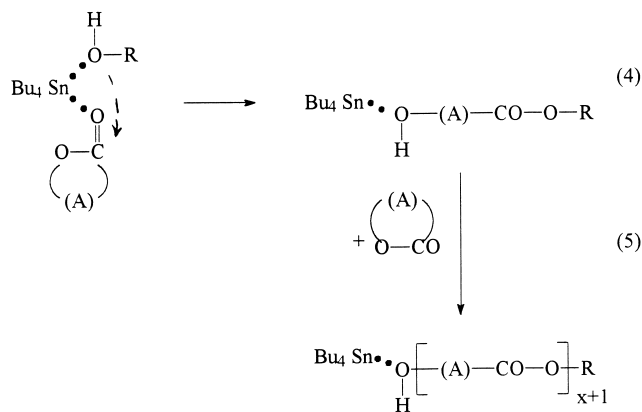


* Corresponding author.

Table 1
 ^{119}Sn NMR chemical shifts of various Bu_3Sn compounds recorded in $\text{CDCl}_3/\text{SnMe}_4$

$\text{Bu}_3\text{Sn-X}$	^{119}Sn NMR chemical shifts δ (ppm)
$\text{Bu}_3\text{Sn-Bu}$	-9.9 (+158.3) ^a
$\text{Bu}_3\text{Sn-SnBu}_3$	-81.0
$\text{Bu}_3\text{Sn-O-SnBu}_3$	+95.1
$\text{Bu}_3\text{Sn-O-Bzl}$	+114.1
$\text{Bu}_3\text{Sn-O}_n\text{-Bu}$	+104.5
$\text{Bu}_2\text{Sn O}$	-247.3

^a Relative intensity approximately 1%.



2. Experimental

2.1. Materials

Tetrabutyltin, tributyltin chloride, hexabutyldistannane, hexabutyldistannoxane, ϵ -CL and benzylalcohol were purchased from Aldrich Co. (Milwaukee, WI). The benzylalcohol was distilled in vacuo and the ϵ -CL was distilled

over freshly powdered calcium hydride in vacuo. The tetrabutyltin was fractionated by distillation in vacuo and a middle fraction making up $\approx 50\%$ of the crude product was used for the experiments.

2.2. Tributyltin alkoxides

Potassium *tert*-butoxide (0.2 mol) was dissolved in the minimum amount of refluxing *tert*-butanol and *n*-butanol (0.2 mol) or benzylalcohol (0.2 mol) were added. Tributyltin chloride (0.2 mol) dissolved in hot tetrahydrofuran was rapidly added and the reaction mixture was refluxed for 2 h. After cooling the precipitated KCl was filtered off, the solvents were evaporated and the product was distilled in a vacuum of 10^{-3} mbar. For the NMR data see Tables 1 and 2.

2.3. Time-conversion curves

ϵ -CL (50 mmol) was weighed into a glass vessel equipped with a gas-inlet tube and a ground glass joint. A 1 M solution of Bu_4Sn in dry toluene was added and the reaction vessel was closed with a glass stopper and a steel spring. The reaction vessel was then immersed into an oil bath preheated to 100°C , and a sample for H NMR measurements was removed from time to time. The preparation of the reaction mixture and the removal of "NMR samples" was either conducted in the presence of air, by bubbling dry nitrogen through the reaction vessel or under argon.

2.4. Oxidation of Bu_4Sn

Air was bubbled through Bu_4Sn (50 mmol) at a temperature of 100°C , whereby a turbidity appeared within 24 h. After 48 h the reaction mixture was cooled to 20°C and filtered. The precipitated product was washed with diethyl-ether, dried and characterized. By the comparison of the IR-spectra with a commercial sample and by elemental analyses the precipitate was identified as Bu_2SnO . The

Table 2
 Polymerization of ϵ -caprolactone (CL) with Bu_4Sn as initiator and BzOH as coinitiator (48 h, 100°C)

Sample number	Monomer/initiator ^a	Monomer/coinitiator ^b	Yield (%)	η_{inh}^c (dl/g)	M_n^d	M_w/M_n^d	DP^e (^1H NMR)	M_n^f calculated
10	200	50	87	0.18	5500	1.4	58	5700
11	200	100	79	0.24	7000	1.5	115	11 400
12	200	150	82	0.27	7800	1.6	165	17 100
13	200	200	86	0.31	9000	1.5	215	22 800
14	200	300	86	0.30	9000	1.5	310	34 200
15	200	500	88	0.31	9500	1.6	520	57 000
16	200	800	79	0.34	11 500	1.6	–	91 500

^a Molar feed ratio of ϵ -CL/ Bu_4Sn .

^b Molar feed ratio of ϵ -CL/benzylalcohol.

^c Measured at 25°C with $c = 2$ g/l in CH_2Cl_2 .

^d GPC measurements calibrated with the Mark-Houwink equation $[\eta] = 1.395 \times 10^{-4} \times M_w^{0.786}$ (Ref. [15]).

^e Apparent degree of polymerization determined from the concentration of benzyl ester endgroups.

^f Theoretical M_n calculated from the ϵ -CL/benzylalcohol ratio and 100% conversion.

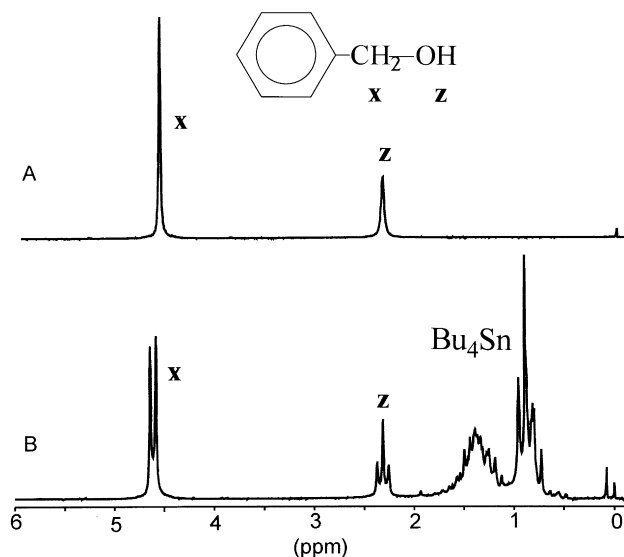


Fig. 1. 100 MHz ^1H NMR spectra: (A) neat benzyl alcohol; and (B) equimolar mixture of benzyl alcohol and Bu_4Sn .

filtered Bu_4Sn was stored at 20°C for 24 h, whereby a small amount of Bu_2SnO precipitated again.

2.5. Measurements

The IR-spectra were recorded from KBr pellets using a Nicolet "Impact 410" FT-IR spectrometer. The 100 MHz ^1H NMR spectra were recorded with a Bruker AC-100 FT-NMR spectrometer in 5 mm o.d. sample tubes using CDCl_3/TMS as solvent and shift reference. The 25.2 MHz

^{13}C NMR spectra were recorded with the same FT-NMR spectrometer. The 134.2 MHz ^{119}Sn NMR spectra were recorded with a Bruker AM 360 FT-NMR spectrometer in 10 mm o.d. sample tubes using CDCl_3 as solvent and SnMe_4 as internal shift reference.

The GPC measurements were performed with a Kontron HPCL apparatus equipped with a Waters differential refractometer Md 410. Four columns having pore sizes of 10^{-2} , 10^{-3} , 10^{-4} and 10^{-5} Å were used in combination with dry tetrahydrofuran as eluent.

3. Results and discussion

3.1. Model reactions

The first step of the present work was to find out whether a complexation (donor-acceptor interaction) took place between Bzl-OH and Bu_4Sn . For this purpose, ^1H NMR spectra of Bzl-OH , Bu_4Sn or mixtures of Bzl-OH and Bu_4Sn were recorded and compared. The spectra displayed in Fig. 1 were representative for these measurements. The addition of Bu_4Sn clearly changes the spectrum of Bzl-OH . The coupling between OH and CH_2 protons becomes detectable due to an interruption of the proton exchange between the OH groups. Obviously the Bu_4Sn forms a weak complex with Bzl-OH which reduces for steric and electronic reasons the acceptor properties of the O-atom. Furthermore, ^{119}Sn NMR spectra of Bu_4Sn and $\text{Bu}_4\text{Sn}/\text{Bzl-OH}$ mixture were recorded but no significant shift difference was observed. The ^{119}Sn NMR chemical

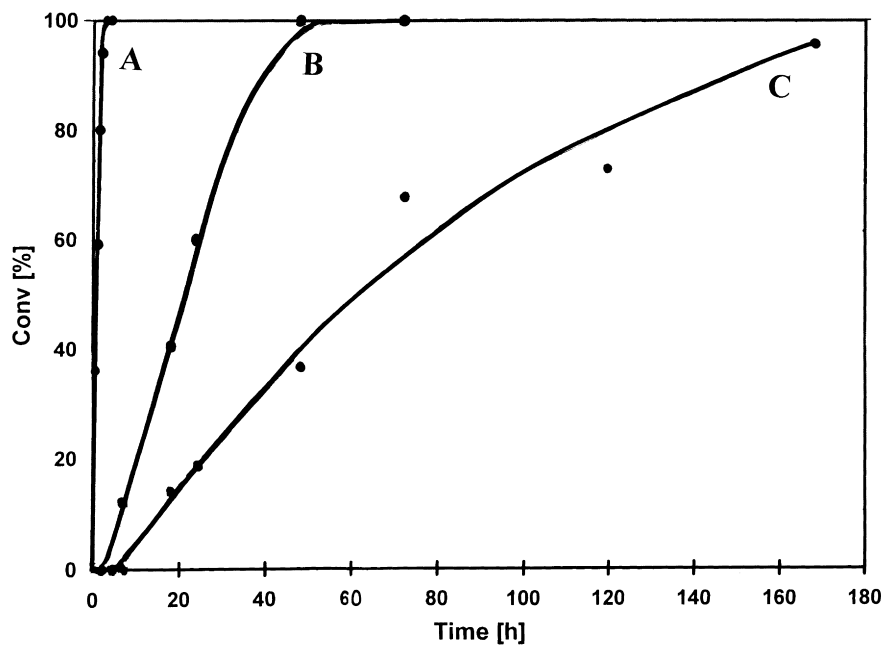


Fig. 2. Time-conversion curves of $\epsilon\text{-CL}$ initiated in bulk at 100°C with: (A) $\text{Bu}_3\text{Sn-OBzl}$; (B) $\text{Bu}_4\text{Sn} + \text{Bzl-OH}$ (1:1); and (C) Bu_4Sn handled in air.

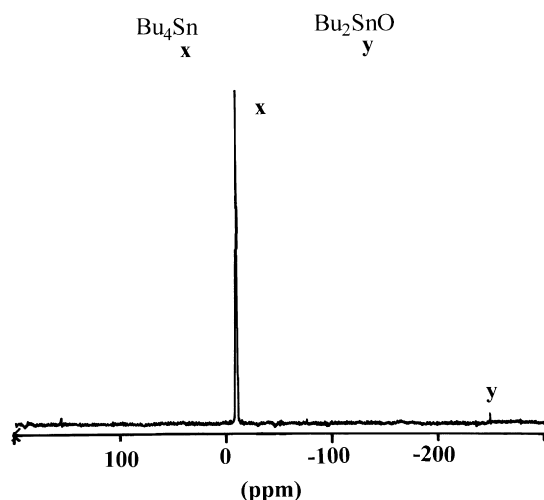


Fig. 3. ^{119}Sn NMR spectrum of Bu_4Sn after oxidation with air and removal of the precipitated Bu_2SnO .

shifts of Sn compounds relevant to this work were compiled in Table 1.

In order to find out whether Bu_4Sn alone or in combination with Bzl-OH could initiate the polymerization of $\epsilon\text{-CL}$, 1 M solutions of both components in dry toluene were added to neat $\epsilon\text{-CL}$ at various temperatures, and time-conversion curves were recorded by means of ^1H NMR spectroscopy. It was found that at least a temperature of 100°C is needed to obtain significant conversions in a time interval of 2 days. When a Bu_4Sn sample purified by distillation, but handled in the presence of air, was used as initiator the time-conversion curve "C" in Fig. 2 was obtained. With addition of Bzl-OH curve "B" was recorded. These results prove:

1. Bu_4Sn may act as initiator of the ring-opening polymerization of lactones,
2. the addition of benzyl alcohol (and presumably other primary alcohols) has an accelerating effect.

Both results support at first glance a polymerization mechanism such as that outlined in Eqs. (4) and (5).

However, the problem of mechanistic studies of a sluggish initiator (or catalyst) such as Bu_4Sn consists of the potential presence of highly active impurities. From previous studies it was known [4] that the activity of $\text{Bu}_3\text{Sn-X}$ compounds as initiators of lactones may vary at least by a factor of 10^3 with alkoxides of primary alcohols being the most active species.

Therefore, we have studied, on the one hand, the purity of the commercial Bu_4Sn and side reactions yielding reactive Sn-O bonds, on the other. According to GC analyses of the Bu_4Sn the crude product contained a less volatile impurity at a concentration of 0.4–0.5%. After fractionated distillation the concentration of this impurity was lowered to a level of 0.1–0.2%. Furthermore, the ^{119}Sn NMR spectra of the crude and of the distilled Bu_4Sn exhibited a weak signal at +158.3 ppm indicating an impurity at a concentration of

$1 \pm 0.5\%$. A comparison with various Bu_3Sn derivatives (Table 1) did not yield an identification and it was not clarified whether the impurity observed in the ^{119}Sn NMR spectra was identical with the impurity detected in the GC measurements. However, the results described below suggest that this impurity had no significant influence on the catalytic activity of Bu_4Sn .

Furthermore, several model reactions were conducted to elucidate if $\text{Bu}_3\text{Sn-OR}$ groups were formed by side reactions in the first stage of the polymerization process. For instance an equimolar mixture of Bu_4Sn and Bzl-OH was heated to 100, 120 or 150°C for 20 h to see, if a cleavage of the Sn-C bond according to Eq. (6) takes place. Yet no reaction was detectable. In contrast, a cleavage of the Sn-Sn bond was observed when Bu_6Sn_2 was heated with Bzl-OH to temperatures $\geq 100^\circ\text{C}$. Therefore, any initiator activity of Bu_6Sn_2 in the presence of an alcohol can be attributed to the intermediate formation of a tributyltin alkoxide (Eq. (7)). When Bu_4Sn was heated with an equimolar amount of benzyl acetate to see if the Sn-C bonds react with an ester group, no reaction was found at 100 or 120°C (after 20 h).

Finally it was observed that time-conversion measurements of Bu_4Sn initiated polymerization of $\epsilon\text{-CL}$ at 100°C were poorly reproducible when different charges of the reactants were used or when their handling was conducted in air or under nitrogen. These observations suggested that oxygen might play the role of an activator. Therefore, model reactions were conducted in such a way that air was bubbled through neat Bu_4Sn at 100 or 120°C . Within 24 h a turbidity was formed and after 48 h a larger quantity of a white precipitate, which was identified as Bu_2SnO , was obtained. Though a detailed investigation of the oxidation was not intended in this work, it was of interest with regard to the initiation of lactones, to find out whether water plays a key role in this process. For instance, when dibutyltindibutoxide is formed as primary oxidation product, water is needed for the formation of Bu_2SnO (Eqs. (8) and (9)), but the dibutoxide is itself an excellent initiator of the polymerization of lactones. However, the oxidation experiments conducted with moist air and with dry air indicated that the presence of water slowed down the formation of Bu_2SnO . Furthermore, dibutylether was identified as volatile by-product and not *n*-butanol. Therefore, it is clear that the oxidation of Bu_4Sn does not proceed according to Eqs. (8) and (9) but according to Eq. (10). Further details of this oxidation were not studied and a similar reaction was not detected in the literature [2].

Bu_2SnO is known to have the structure of a highly associated oligo or polystannoxane which is insoluble in inert organic solvents. When the precipitated Bu_2SnO was filtered off immediately after cooling and the filtered Bu_4Sn allowed to stand at 20°C another small quantity of Bu_2SnO had precipitated after 24 h. After removal of this second crop the oxidized Bu_4Sn remained clear.

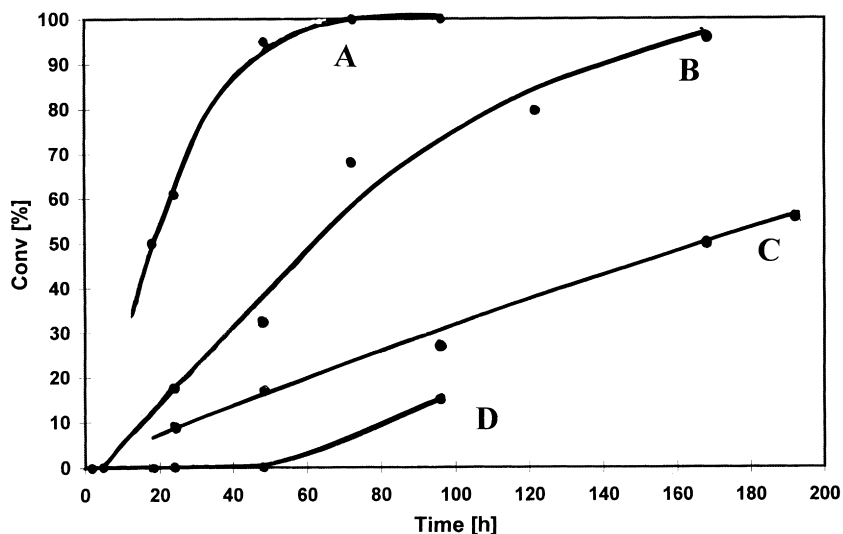
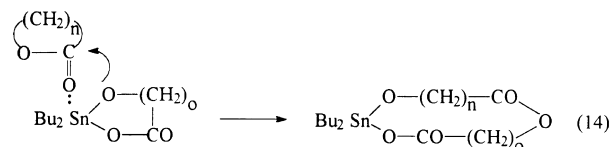
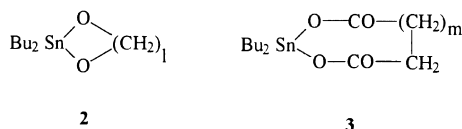
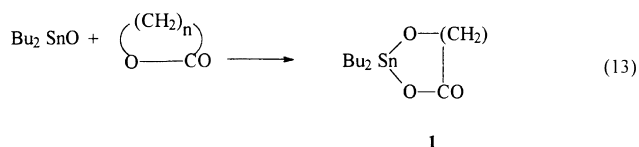
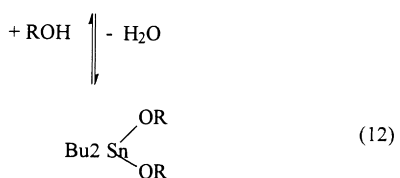
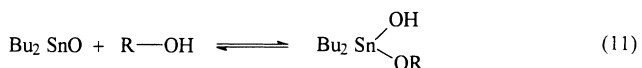
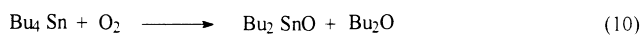
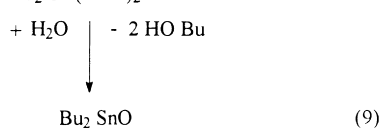
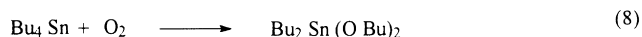
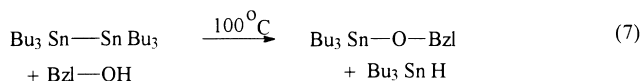
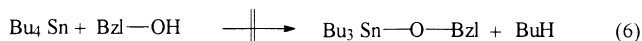


Fig. 4. Time-conversion curves of ϵ -CL initiated in bulk with: (A) Bu_4Sn oxidized with air at 100°C ; (B) Bu_4Sn distilled and handled in air; (C) Bu_4Sn distilled and handled in nitrogen; (D) Bu_4Sn distilled and handled in argon.

However, a ^{119}Sn NMR spectrum revealed that this oxidized Bu_4Sn still contained $1 \pm 0.5\%$ of dissolved Bu_2SnO (Fig. 3). Bu_2SnO is not only known to be a good esterification and transesterification catalyst [1,2], it is also known as a good initiator of ring-opening polymerizations of β -lactones [7–9]. Therefore, it is obvious that Bu_2SnO , once it has been formed plays the role of an efficient initiator in Bu_4Sn .



3.2. Polymerizations

In order to elucidate the role of oxidation products in the catalytic activity of Bu_4Sn in greater detail, four samples with different pretreatments were used as initiators for polymerizations of ϵ -CL at 100°C in bulk. Time-conversion curves were recorded by means of ^1H NMR spectroscopy and compared (Fig. 4). Curve A was obtained from Bu_4Sn oxidized with air at 100°C and filtered from the precipitated Bu_2SnO . Curve B resulted from Bu_4Sn handled in air at room temperature (identical with curve C in Fig. 2). Curve C of Fig. 4 was recorded with Bu_4Sn that was distilled and handled under nitrogen.

The linear part (the first 48 h) of curve D was obtained from Bu_4Sn that was distilled and handled under argon. Since no polymerization occurred in the latter case, the reaction vessel was finally (after 48 h) opened in the

Table 3
 Polymerization of ϵ -caprolactone (CL) with Bu_4Sn as initiator and BzOH as coinitiator (48 h, 100°C)

Sample number	Monomer/initiator ^a	Monomer/coinitiator ^b	Yield (%)	η_{inh}^c (dl/g)	$M_n^{\text{calculated}^d}$	M_n^e	M_w/M_n^e	DP^f ($^1\text{H NMR}$)
32	50	200	28	0.14	5700	4000	14.	60
33	100	200	54	0.22	11 400	7800	1.3	140
34	150	200	70	0.23	17 100	7000	1.4	120
35	200	200	65	0.25	22 800	8000	1.4	160
36	300	200	72	0.28	34 200	9600	1.3	150
37	500	200	81	0.34	57 000	11 600	1.4	130
38	800	200	68	0.35	91 500	12 400	1.4	120

^a Molar feed ratio of ϵ -CL/ Bu_4Sn .

^b Molar feed ratio of ϵ -CL/benzylalcohol.

^c Measured at 25°C with $c = 2$ g/l in CH_2Cl_2 .

^d Theoretical M_n calculated from the ϵ -CL/benzylalcohol ratio and 100% conversion.

^e GPC measurements calibrated with the Mark–Houwink equation $[\eta] = 1.395 \times 10^{-4} \times M_w^{0.786}$. (Ref. [15]).

^f Apparent degree of polymerization determined from the concentration of benzyl ester endgroups.

presence of air and from this time on a slow polymerization took off.

In summary, the time–conversion curves displayed in Fig. 4 clearly demonstrate that the catalytic activity of Bu_4Sn parallels the extent of its exposure to oxygens. Hence, it may be concluded that Bu_4Sn -initiated polymerizations of lactones are mainly the result of an initial formation of reactive covalent Sn–O bonds, with Bu_2SnO playing the key role.

These results lead to the question how Bu_2SnO initiates the ring-opening polymerization of lactones. Two routes can be envisaged. First, in the presence of alcohols dibutyltin alkoxides will be formed according to Eqs. (11) and (12). These alkoxides will initiate a normal coordination–insertion mechanism (Eqs. (1) and (2)) as it has

been demonstrated for dibutyltin dimethoxide [3]. Second, in the absence (or perhaps even in the presence) of alcohols lactones may undergo a direct insertion into the stannoxane bonds of Bu_2SnO so that a cyclic initiator of structure 1 is formed (Eq. (13)). Such heterocycles prepared by a reaction of Bu_2SnO with free hydroxy acids have been described by other authors [9,10]. Furthermore, the direct insertion of lactones into distannoxanes has been reported by Sakai and coworkers [11]. Cyclic tin alkoxides of structure 2 are known as reactive initiators of lactones [12–14] allowing ring-expansion polymerizations even at 20°C . In contrast, the cyclic dicarboxylate 3 was found to be almost inert at temperatures $<80^\circ\text{C}$. Therefore, it is most likely that the heterocycles of structure 1 initiate the polymerization of lactones by insertion into the tin–alkoxide bond (Eq. (14)). A definite proof for this mechanism is still lacking, but pertinent studies of the polymerization mechanism are currently in progress.

Finally, two series of polymerizations of ϵ -CL were conducted with a twofold aim. Firstly, it should be determined whether the number average molecular weights (M_n 's) parallel the ϵ -CL/ Bu_4Sn ratio or the ϵ -CL/alcohol ratio. Secondly, it was of interest to see, if the Bu_4Sn /alcohol system allows synthesis of high molecular weight (M_n 's $\geq 50\,000$ Da) poly(ϵ -CL). The results of both series of polymerizations (performed with a Bu_4Sn handled in air) were summarized in Tables 2 and 3. The molecular weights were characterized by three kinds of measurements:

- measurements of inherent viscosities,
- GPC measurements calibrated with the Mark–Houwink equation published for poly(ϵ -CL) [15],
- calculations of degrees of polymerizations (DPs) from $^1\text{H NMR}$ spectroscopic analyses of the benzylester endgroups (NMR spectrum of a benzylester terminated poly(ϵ -CL) is shown in Fig. 5.)

All three series of measurements agree in that the M_n 's slightly increases with the ϵ -CL/ Bu_4Sn ratio and also with

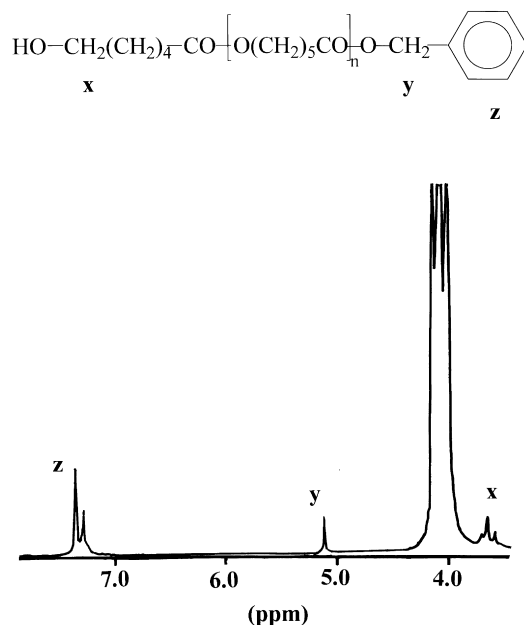


Fig. 5. 100 MHz $^1\text{H NMR}$ spectrum of a benzyl ester terminated poly(ϵ -CL) prepared with oxidized Bu_4Sn at 100°C ($M/I = 50$).

the ϵ -CL/alcohol ratio. However, this increase was far inferior to proportionality. These results suggest the existence of a complex initiation mechanism involving the direct reaction of ϵ -CL with Bu_4SnO (Eqs. (13) and (14)). From the preparative point of view, it is evident that the Bu_4Sn /alcohol system is not an attractive initiator since it neither allows a proper control of the M_n 's nor yields high molecular weight poly(ϵ -CL).

4. Conclusion

The results of this work demonstrate that Bu_4Sn is highly sensitive to oxidation by O_2 . The main reaction product of this (most likely radical) oxidation process is Bu_2SnO that is known to be an efficient initiator of ring-opening polymerizations of lactones. Addition of alcohols has an accelerating effect and the alcohols are incorporated in the form of alkyl ester endgroups. However, the M_n 's do not exactly parallel the monomer–alcohol feed ratio. Therefore, it may be concluded that when Bu_4Sn is exposed to air it will initiate a normal coordination–insertion mechanism involving covalent Sn–O bonds (analogous to the mechanism formulated in Eqs. (1) and (2)). At the current stage of our research it is not possible to definitely exclude the existence of the alternative insertion mechanism outlined in Eqs. (4) and (5). However, this mechanism has certainly no chance to compete, when covalent Sn–O bonds are present in a consent ratio ≥ 0.1 mol% relative to

Bu_4Sn . Finally, it may be concluded, that regardless of the mechanism, Bu_4Sn is not an attractive initiator for preparative purposes.

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