Polylactones. 20. Polymerization of ε-Caprolactone with Tributyltin Derivatives: A Mechanistic Study

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ABSTRACT: Bulk polymerizations of ε-caprolactone were conducted at 100 °C with the following initiators: tributyltin methoxide, *tert*-butoxide, phenoxide, chloride, bromide, acetate, and thioacetate as well as hexabutyldistannoxane. Time–conversion curves were determined by means of ^{1}H NMR spectroscopy, and rate constants were calculated for the first 10% conversion. The results indicate that tributyltin methoxide is at least a factor of 10^3 more reactive than tributyltin bromide, chloride, acetate, or thioacetate. Whereas initiation with tributyltin methoxide is as rapid or more rapid than propagation, initiation with all other initiators is much slower than propagation. Therefore, the average degrees of polymerization (DP's) exceed the monomer/initiator ratios (M/I). Furthermore, only traces of phenoxide, halogenide, or acetate end groups were found in the isolated polyesters. Therefore, an insertion mechanism is postulated for all initiators involving chain growth via covalent tin–alkoxide bonds and cleavage of the acyl-oxygen bond of the lactone.

Introduction

Tin(II) salts such as tin(II) octoate[1-5] or tin(IV) compounds such as $SnCl_4$[5-8] belong to the most widely used group of initiators for the polymerization of lactide and lactones. Although detailed studies of their reaction mechanisms are lacking, most authors have speculated that these tin compounds initiate anionic or cationic polymerizations.

For the mechanistic studies of the present work, various tributyltin derivatives were chosen as initiators because they have the following advantages. First, they are easily accessible by nucleophilic substitution of commercial tributyltin chloride. Second, they are easy to handle because their sensitivity to moisture is low. Third, they are soluble in lactones and various organic solvents, so that NMR measurements of reaction mixtures are easy to conduct. Fourth, they are monofunctional. The results obtained from tributyltin derivatives should help to explain the polymerization mechanisms of other tin initiators such as tin(II) octoate or tin(IV) compounds, which are more difficult to analyze because of their polyfunctionality.

Experimental Section

Materials. ε-Caprolactone was a gift of Bayer AG (Leverkusen, FRG). It was distilled under nitrogen over calcium hydride and over oligomeric diisocyanatodiphenylmethane. Hexabutyldistannoxane, tributyltin methoxide, and tributyltin chloride were purchased from Aldrich Chemical Co. (Milwaukee, WI) and purified by two distillations in vacuo. Tributyltin bromide was purchased from Alpha Products (D-7500 Karlsruhe 1, FRG) and purified by distillation in vacuo. Tributyltin *tert*-butoxide was prepared from tributyltin chloride and potassium *tert*-butoxide in *tert*-butyl alcohol. Tributyltin phenoxide was prepared from tributyltin chloride and a solution of sodium phenoxide in dry isopropyl alcohol. The acetate and thioacetate were synthesized by adding concentrated solutions of sodium acetate or thioacetate into stirred ice cold solutions of tributyltin chloride in dichloromethane. All initiators were purified by distillation or recrystallization. Their boiling points, melting points, and/or refractive indices are listed in Table I.

Polymerizations. (A) Kinetic Studies. ε-Caprolactone (50 mmol) was weighed into a 25-mL Erlenmeyer flask with silanized glass walls, and 0.5 mL of 1 M solution of an initiator in dry toluene was added. The reaction vessel was closed with a glass stopper and steel spring and immersed into a thermostated oil bath at 100 ± 2 °C. From time to time a small sample was removed and after dissolution in $CDCl_3$ subjected to ^{1}H NMR measurements. Both preparation of reaction mixtures and removal of samples for NMR measurements were conducted in a glovebox under nitrogen dried with P_4O_{10}. The series with Bu_3SnOMe, Bu_3SnBr, or Bu_3SnOAc were repeated with delayed time intervals to check the reproducibility.

(B) Polymerizations Listed in Tables II–IV. ε-Caprolactone (50 mmol) and the initiator were weighed under dry nitrogen into a 25-mL Erlenmeyer flask with silanized glass walls. The reaction vessel was closed with a glass stopper and steel spring and afterward almost completely immersed into a thermostated oil bath. When the reaction time was over, the reaction mixture was dissolved in ca. 80 mL of distilled dichloromethane. A small sample of this solution was subjected to GPC measurements (Figures 5–7), and the main part (>95%) was precipitated into cold methanol. The precipitated polyester was isolated by filtration and dried at 40 °C in vacuo.

All reaction mixtures were prepared in a glovebox under dry nitrogen.

Measurements. ^{1}H NMR spectra used for end-group analyses were measured with a Bruker MSL 300 FT-NMR spectrometer at 20–25 °C. Solutions of 50 mg of polycaprolactone in 0.5 mL of $CDCl_3$ (containing 1% TMS for shift referencing) were used in 5-mm-o.d. sample tubes. The kinetic studies (Figures 1–4) were also measured with $CDCl_3$ solution in 5-mm-o.d. sample tubes, but utilizing a Bruker AC-100 FT spectrometer. For the identification of OH end groups, one drop of trifluoroacetic anhydride was added to the contents of the sample tube.

GPC measurements were conducted in dichloromethane at 25 °C. A combination of four Ultrastyragel columns with molecular weight ranges of 50–1.5×10^3, 10^2–10^4, 2×10^2–30×10^3, and 5×10^3–600×10^3 was used for the separation, and a differential refractometer (Waters Md 410) was used for detection.

Intrinsic viscosities used for the calculation of M_w (Table IV) were measured in DMF at 30 °C, while the inherent viscosities were determined in CH_2Cl_2 at 25 °C. A thermostated and automated Ubbelohde viscosimeter was used for all viscosity measurements.

Results and Discussion

Kinetic Measurements. It was demonstrated in a previous part of this series[22] that tributyltin methoxide is an active initiator of the polymerization of numerous lactones. The mechanism was formulated as a coordination insertion mechanism (eqs 1 and 2), starting with the complexing of the monomer to the initiator (via free d orbitals). The chain growth involves cleavage of the acyl-oxygen bond and yields polyester with methyl ester end groups. The nonionic character of this mechanism is mainly based on three arguments. First, the initiator itself is covalent

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Table I
Physical Properties, Elemental Analyses, and Apparent Initiation Rate Constants of Various Tributyltin Initiators

tributyltin deriv	mp °C (lit. mp, °C)	bp °C (lit. bp, °C)	n^{20}_D (lit. n^{20}_D)	elem form (form wt)	elem anal.	% C	% H	$10^{-5}k_{st}$,[a] L mol^{-1} min^{-1}
Bu_3SnOMe		97–98/0 (148/15[9])	1.4710 (1.4789[10])	$C_{13}H_{30}OSn$ (321.07)	calcd			436
					found			
Bu_3SnOPh		124–125/0.1 (124/0.01[11])	1.5171 (1.5169[12])	$C_{18}H_{33}OSn$ (382.64)	calcd	56.44	8.36	130
					found	56.40	8.56	
Bu_3SnOBu		140–141/0.1 (82–83/0.15[13])	1.4697 (1.4657[13])	$C_{16}H_{36}OSn$ (362.69)	calcd	52.94	9.92	105
					found	52.56	10.03	
Bu_3SnOBu_3Sn		178–180/2 (254/56[14])	1.4864	$C_{24}H_{54}OSn_2$ (596.07)	calcd			39
					found			
Bu_3SnOAc	80–81 (84–85[15])	125–129/0.1 (90–100/0/0.001[15])		$C_{14}H_{30}O_2Sn$ (348.69)	calcd	48.18	8.60	46
					found	48.05	8.76	
Bu_3SnSAc		80–84/0.01 (86–88/0.002[16])	1.5023 (1.5015[17])	$C_{14}H_{30}OSSn$ (365.14)	calcd	46.05	8.28	0.19
					found	45.87	8.35	
Bu_3SnBr		120–122 (85/0.1[18])	1.5070 (1.5009[19])	$C_{12}H_{27}BrSn$ (369.94)	calcd			0.94
					found			
Bu_3SnCl		171–173/25 (86/0.1[20])	1.4905 (1.4913[21])	$C_{12}H_{27}ClSn$ (325.49)	calcd			0.20
					found			

[a] Apparent initiation rate constants of the polymerization of ϵ-caprolactone calculated from eq 5 on the basis of the time–conversion curves displayed in Figures 1–3.

Table II
Bulk Polymerizations of ϵ-Caprolactone Initiated with Tributyltin Methoxide at 100 °C

no.	M/I[a]	time, h	yield, %	η_{inh},[b] dL/g	DP calcd[c]	DP ^{1}H NMR[d]
1	10	1	25	0.18		17
2	20	8	77	0.19	16	25
3	50	2	84	0.25	42	43
4	50	24	88	0.26	45	49
5	100	4	91	0.37	91	95
6	100	48	77	0.37	77	78
7	150	6	95	0.48	142	132
8	200	8	96	0.59	192	185

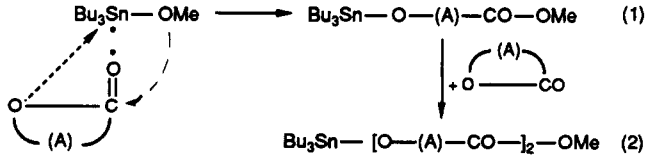
[a] Initial monomer/initiator ratio. [d] Measured at 25 °C with c = 2 g/L in CH_2Cl_2. [c] Degree of polymerization calculated according to eq 8. [d] Degree of polymerization from ^{1}H NMR end-group analyses of the methyl ester end groups.

Table III
Bulk Polymerizations of ϵ-Caprolactone Initiated with Tributyltin Phenoxide or Tributyltin *tert*-Butoxide at 100 °C

no.	initiator	M/I[a]	time, h	yield, %	η_{inh},[b] dL/g
1	Bu_3SnOPh	10	1	93	0.40
2	Bu_3SNOPh	20	8	96	0.55
3	Bu_3SnOPh	50	24	91	0.60
4	Bu_3SnOPh	100	48	93	0.74
5	Bu_3SnO-*t*-Bu	10	1	86	0.29
6	Bu_3SnO-*t*-Bu	20	8	91	0.31
7	Bu_3SnO-*t*-Bu	50	24	88	0.35
8	Bu_3SnO-*t*-Bu	100	48	91	0.46

[a] Initial monomer/initiator ratio. [b] Measured at 25 °C with c = 2 g/L in CH_2Cl_2.

and no theoretical or experimental argument supports the assumption of an ionic chain end. Second, β-lactones react



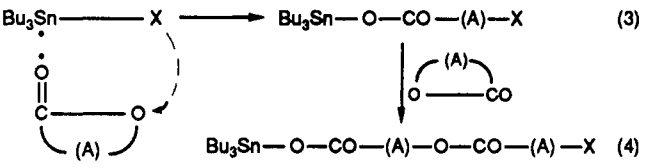
with tributyltin methoxide in the same way as higher membered lactones, yet they react in different way if anionic initiators are used.[23,24] Third, tributyltin methoxide enables a racemization free polymerization of L,L-lactide even at high temperatures (100–180 °C) in contrast to anionic and cationic initiators.[25]

Table IV
Bulk Polymerizations of ϵ-Caprolactone Initiated by Various Tributyltin Derivatives at an M/I Ratio of 5:1 at 100 °C

no.	initiator	time, h	yield, %	ret time,[a] min	$[\eta]$,[b] cm^3/g	M_w[c]
1	Bu_3SnOMe	24	22.6	30.62		
2	Bu_3SnOMe	4	25.3	29.82		
3	Bu_3SnBr	100	41.1	24.28	0.2955	23400
4	Bu_3SnCl	100	94.9	24.18	0.3212	26230
5	Bu_3SnOAC	24	78.9	24.73	0.2374	17340
6	Bu_3SnOAc	100	85.5	24.40	0.3214	26250
7	Bu_3SnSAc	24				
8	Bu_3SnSAc	100				

[a] GPC retention time of elution peak maximum in CH_2Cl_2 at 25 °C. [b] Intrinsic viscosity measured in CH_2Cl_2 at 25 °C. [c] Calculated from intrinsic viscosities measured in DMF at 30 °C and the Mark–Houwink constants of ref 18.

Two questions should be answered in this work. First, how does the reactivity of tributyltin compounds vary with the nature of the substituent attached to tin (X in eqs 3 and 4)? Second, does the propagation mechanism in all cases proceed via acyl-oxygen bond cleavage (eq 2) or does it in some cases involve cleavage of the alkyl-oxygen bond (eqs 3 and 4)?



In order to obtain a crude estimate of relative reactivities, bulk polymerizations of ϵ-caprolactone with various tributyltin compounds were conducted under identical conditions, and time–conversion curves were determined by means of ^{1}H NMR spectroscopy.

From the slopes of the linear curves obtained up to 10% conversion, apparent rate constants for the start reaction (k_{st}) were calculated according to eq 5, where V_{st} is the

$$V_{st} = k_{st}[I][M] \quad (5)$$

initial reaction rate, k_{st} is the apparent overall initial rate constant, [I] is the initial initiator concentration, and [M] is the initial monomer concentration. The results are summarized in Figures 1–3 and Table I. This evaluation is, of course, a simplification, because propagation steps

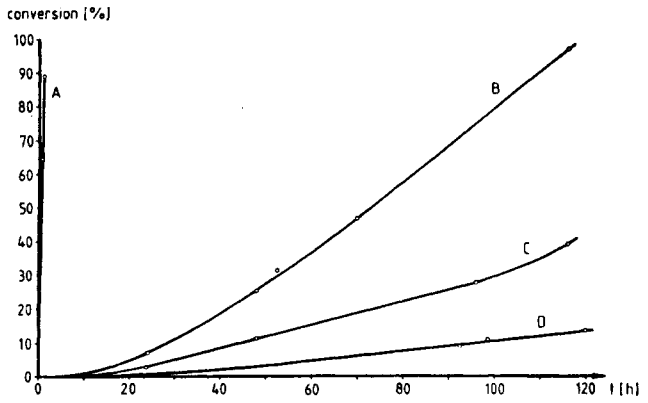


Figure 1. Time–conversion curves of bulk polymerizations of ϵ-caprolactone conducted at 100 °C with the following initiators (M/I = 100:1): (A) Bu_3SnOMe; (B) Bu_3SnCl; (C) Bu_3SnOAc; (D) Bu_3SnSAc.

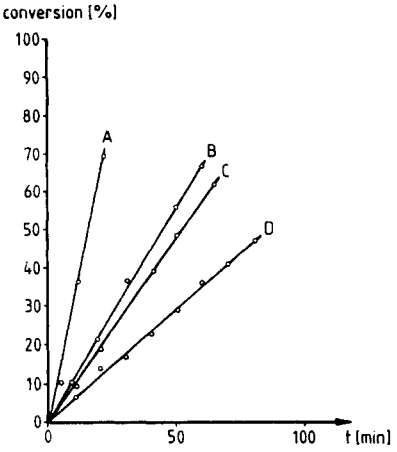


Figure 2. Time–conversion curves of bulk polymerizations of ϵ-caprolactone conducted at 100 °C with the following initiators (M/I = 100:1): (A) Bu_3SnOMe; (B) Bu_3SnOPh; (C) Bu_3SnO-*t*-Bu; (D) $Bu_3SnOSnBu_3$.

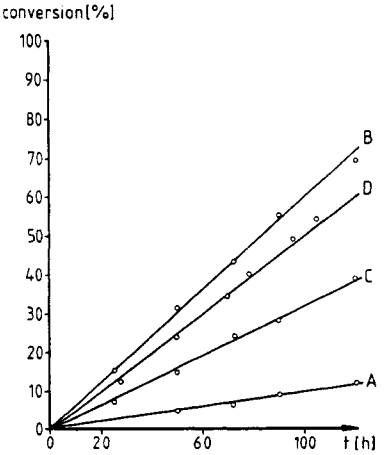


Figure 3. Time–conversion curves of bulk polymerizations of ϵ-caprolactone conducted at 100 °C with the following initiators (M/I = 100:1): (A) Bu_3SnCl; (B) Bu_3SnBr; (C) Bu_3SnCl + 5% $Bu_3SnOSnBu_3$; (D) Bu_3SnCl + 10% $Bu_3SnOSnBu_3$.

(eq 6, where V_p is the propagation rate, k_p is the apparent

$$V_p = k_p[\text{I-(M)}_n][\text{M}] \quad (6)$$

propagation rate constant, and [I-$(M)_n$] is the concentration of growing chains) occur during the first 10% conversion, whereas the reaction of initiators is not necessarily complete in all cases. Nonetheless, the rate

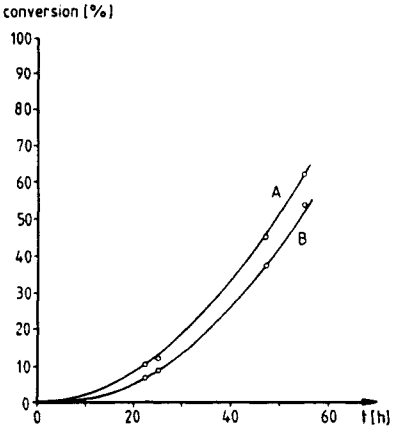
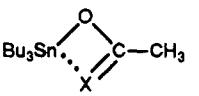


Figure 4. Time–conversion curves of bulk polymerizations of ϵ-caprolactone conducted at 100 °C with the following initiators (M/I = 100:1): (A) Bu_2SnBr_2; (B) Bu_2SnCl_2.

constants obtained in this way allow semiquantitative classification of all initiators according to their reactivity.

Tributyltin methoxide was found to be the most reactive initiator. Its reactivity is at least a factor of 10^3 higher than that of tributyltin halogenides, tributyltin acetate, or tributyltin thioacetate (Figure 1). Its reactivity is also slightly higher than that of tributyltin *tert*-butoxide or hexabutyldistannoxane (Figure 2). The reactivity of the latter catalysts is obviously affected by the bulkiness of their substituents. In agreement with this interpretation the phenoxide shows intermediate reactivity (Figure 2). The low reactivity of both acetate and thioacetate groups is conceivable because they form stronger bonds with the tin atom involving a vacant d orbital of the tin atom (see scheme of formula 7). This internal stabilization has, for



(7)

example, the consequence that tributyltin acetate and tributyltin thioacetate are more stable to hydrolysis as demonstrated by the fact that these compounds may be synthesized from aqueous acetate or thioacetate solutions.

When bulky polymerizations of ϵ-caprolactone were conducted with crude and redistilled tributyltin bromide and chloride, considerably lower rates of polymerization were found for the purified initiators. Their purity was determined by GC to be on the order of 99.5%. The crude initiators contained a catalytically active impurity, which, on the basis of the gas chromatograms, was identified as hexabutyldistannoxane. The result of a deliberate contamination of tributyltin chloride with the distannoxane is illustrated by the measurements displayed in Figure 3. The accelerating effect of hexabutyldistannoxane also suggests that the presence of moisture or OH-group-containing impurities (e.g., lactic acid in lactide) may have an accelerating effect, since their reaction with tin halogenides yields active Sn–O bonds.

Finally, dibutyltin dibromide and dibutyltin dichloride were used as initiators to study the effect of the second halogen atom. However, both time–conversion curves exhibited a strong acceleration effect (Figure 4), and thus a straightforward discussion of the reaction rates was not feasible.

Mechanism of Tributyltin Alkoxide or Tributyltin Phenoxide Initiated Polymerization. Even when it is agreed that the mechanism for initiation with tributyltin alkoxides and phenoxides is as shown in eqs 1 and

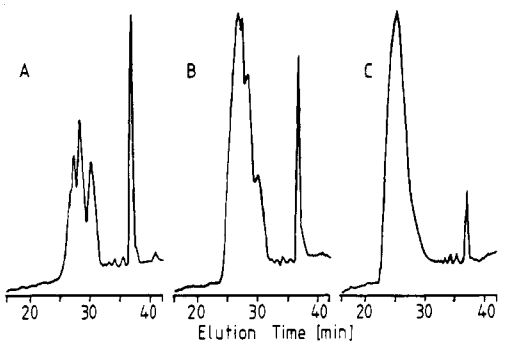


Figure 5. GPC measurements (25 °C in CH_2Cl_2) of the reaction mixtures obtained from ε-caprolactone and tributyltin methoxide at 100 °C: (A) M/I = 10; (B) M/I = 20; (C) M/I = 100 (nos. 1, 2, and 6, Table II).

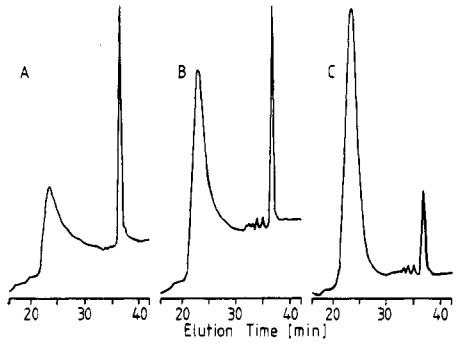


Figure 6. GPC measurements (25 °C in CH_2Cl_2) of the reaction mixture obtained from ε-caprolactone and tributyltin phenoxide at 100 °C: (A) M/I = 10; (B) M/I = 20; (C) M/I = 50 (nos. 1, 2, and 3, Table III).

2, the question remains to be answered whether initiation or propagation is more rapid. The answer to this question is important for the relationship between the M/I ratio and the molecular weight (eq 8) and for the molecular

$$DP = \frac{[M] \times \% \text{ conversion}}{[I] \times 100} \quad (8)$$

weight distribution. To shed more light on this problem, we conducted several polymerizations with varying M/I ratios. The isolated polyesters were characterized by inherent viscosities, ^1H or ^{13}C NMR end-group analyses, and GPC measurements (Tables II and III and Figures 5 and 6).

The inherent viscosities increase with decreasing M/I ratio regardless of initiator. However, ^1H NMR end-group analyses indicate that the polymerizations obey eq 8 only in the case of tributyltin methoxide. ^1H NMR measurements of reaction mixtures after 0.5 h demonstrate that the initiator is consumed before the conversion is complete. These observations along with the data of Table II suggest that initiation is slightly faster than propagation when tributyltin methoxide is used. This suggestion is reasonable, taking into account that the steric demands of a methoxide group are lower than those of a chain end.

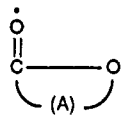
However, in the case of *tert*-butoxide the bulkiness is greater than that of the active chain end, and in the case of phenoxide both electron density and polarizibility of the oxygen is lower due to interaction with the aromatic ring. Therefore, both initiators should be less reactive than the active chain end and thus less reactive than tributyltin methoxide. This conclusion is confirmed by the experimental data. First, the lower reactivity is documented by the kinetic data (Figures 1 and 2). Second, *tert*-butyl ester or phenyl ester end groups of isolated polyesters are difficult to detect, particularly by ^{13}C NMR spectroscopy even at low M/I ratios. Third, the inherent viscosities are higher than those of methoxide-initiated samples at identical M/I ratios. Fourth, the GPC curves of unfractionated reaction mixtures show characteristic differences (Figures 5 and 6).

In the case of polymerizations with methoxide the maximum of the elution curves shifts to higher molecular weights with increasing M/I ratio (Figure 5). In the case of phenoxide the maximum does not change, and only the low molecular weight fraction gradually vanishes at higher M/I (Figure 6). These results taken together prove that k_p is significantly higher than k_{st} for both initiators.

In connection with the GPC measurements, the role of backbiting degradation needs a short comment. The GPC curves of Figures 5 and 6 display the presence of cyclic oligomers. This result perfectly agrees with previous studies on the transesterification activity of tributyltin methoxide.[22] It fits in with the existence of backbiting degradation that long reaction times result in lower yields of methanol-insoluble polycaprolactone, because the cyclic oligomers are soluble (nos. 3/4 and 5/6, Table II).

Propagation Mechanism of Tributyltin Acetate or Tributyltin Halogenide Initiated Polymerizations. When tributyltin halogenides, tributyltin acetate, and tributyltin thioacetate are used as initiators, it is not a priori clear that the chain growth proceeds according to eqs 1 and 2. The alternative mechanism of eqs 3 and 4 must be taken into consideration because it has been demonstrated that several metal bromides and chlorides, including $SnBr_4$,[26] react in such a way that ring opening of the alkyl-oxygen bond is cleaved and an ε-Br–C bond is formed (eq 3, X = Br). A similar ring cleavage by tributyltin acetate or thioacetate followed by an analogous propagation mechanism should result in polyesters with DP's obeying eq 8 and a concentration of (thio)acetate end groups inversely proportional to the M/I ratio (eq 9).

$$Bu_3Sn-X-COCH_3 \rightarrow Bu_3Sn-OCO-(A)-X-COCH_3 \quad (9)$$



X = O, S

However, when tributyltin halide, acetate, or thioacetate was used as initiator at M/I ratios of 100:1, no end groups were detectable in the 300-MHz ^1H NMR spectra of the samples precipitated from methanol. Therefore, a series of polymerizations at low M/I ratio (5:1) was conducted including tributyltin methoxide for comparison (Table IV). In agreement with the kinetic data and the mechanism of eqs 1 and 2, only oligoesters were obtained with tributyltin methoxide (nos. 1 and 2 in Table IV). The formation of oligoesters was confirmed by GPC measurements of the crude reaction mixture (Figure 7A) and by their solubility in methanol. However, good yields of high molecular weight polycaprolactone were obtained with all other initiators (nos. 3–8, Table IV). The high molecular weights are evident from GPC measurements (Figure 7B) and from viscosity measurements (Table IV). Furthermore, only trace amounts of acetate end groups were detectable when tributyltin acetate or thioacetate was used as initiator (nos. 5–8, Table IV; Figure 8). These results clearly contradict the mechanism of eqs 3 and 4 or eq 9.

From these results it may be concluded that the initiation step obeys eq 1, followed by a much faster propagation via tin alkoxide chain ends according to eq 2. The considerably

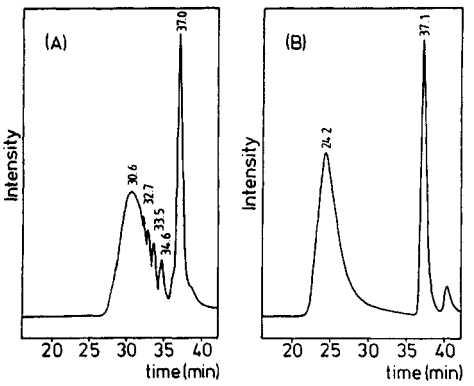


Figure 7. GPC measurements conducted at 25 °C in dichloromethane: (A) reaction mixture no. 1, Table II; (B) reaction mixture no. 5, Table IV.

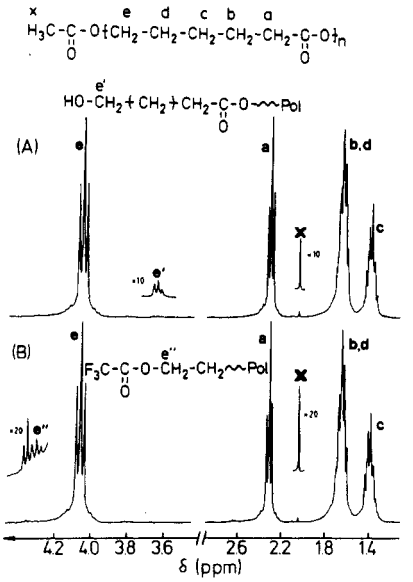


Figure 8. 300-MHz ^{1}H NMR spectra of the polycaprolactone isolated from polymerization no. 5, Table IV, after washing with methanol: (A) pure polycaprolactone; (B) same solution after addition of trifluoroacetic anhydride.

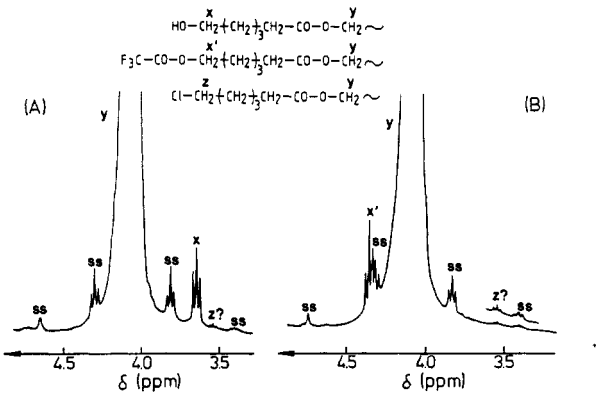


Figure 9. 300-MHz ^{1}H NMR spectra of the polycaprolactone isolated from polymerization no. 3, Table IV, after washing with methanol: (A) pure polycaprolactone; (B) same solution after addition of trifluoroacetic anhydride.

faster propagation ($V_p \gg V_{st}$ by a factor of 10^3–10^4) has the consequence that only a small fraction of tin acetate or thioacetate is active as initiator. This conclusion is confirmed by the detection of significant amounts of CH_2OH end groups, resulting from the methanolysis of tributyltin alkoxide chain ends. The identification of these CH_2OH end groups is based on their chemical shifts and on their reactions with phenyl isocyanate[25] or trifluoroacetic anhydride,[27] which entails a characteristic downfield shift of the signal (Figure 8).

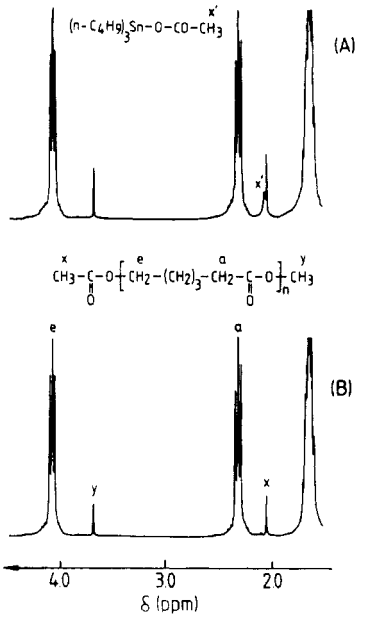


Figure 10. 300-MHz ^{1}H NMR spectra of a tributyltin methoxide initiated poly(ϵ-caprolactone) terminated after 1 h by addition of acetic anhydride: (A) crude reaction mixture; (B) polymer isolated after precipitation with methanol.

The polyesters isolated from tributyltin bromide or chloride initiated polymerizations show again CH_2OH end groups (Figure 9). In addition to these chain ends, however, traces of CH_2Br and CH_2Cl end groups seem to be present (Figure 9). Their identification is based on their chemical shifts (which is slightly different from that of CH_2OH) and on their insensitivity to trifluoroacetic anhydride (Figure 9). The formation of ϵ-bromo and ϵ-chlorocaproyl end groups can be explained by the following reaction sequence. The first step is the halogen transfer involving cleavage of the alkyl-oxygen bond according to eq 3 (X = Br, Cl). The resulting tributyltin ϵ-halocaproate reacts with another lactone by analogy with eq 1, and the further rapid chain growth obeys eq 2. ϵ-Halocaproate (or acetate) ester end groups are finally formed by the reaction between anhydride end groups and tin alkoxide end groups (eq 10). This reaction is slow and thus not necessarily

$$\begin{aligned} &Bu_3Sn\text{–}[O\text{–}(A)\text{–}CO\text{–}]_n + \\ &\quad Bu_3Sn\text{–}[O\text{–}(A)\text{–}CO\text{–}]_m\text{–}X\text{–}COCH_3 \rightarrow \\ &\quad\quad CH_3CO\text{–}[O\text{–}(A)\text{–}CO\text{–}]_n + \\ &\quad\quad\quad Bu_3Sn[\text{–}O\text{–}(A)\text{–}CO\text{–}]_m\text{–}X\text{–}SnBu_3 \quad (10) \end{aligned}$$

quantitative, because the concentration of both kinds of end groups is very low. The acylation mechanism of eq 10 is confirmed by the ^{1}H NMR spectroscopic observation that tributyltin thioacetate yields small amounts of acetate end groups. The alternative mechanism of eq 3 necessarily results in the formation of thioacetate groups and thus is clearly not operating. An unambiguous distinction between both end groups is easily feasible by ^{1}H NMR spectroscopy, because the thioacetate group absorbs 0.2–0.3 ppm downfield of the acetate group.

Additional evidence in favor of the acylation step of eq 10 was obtained in the following way. A tributyltin methoxide initiated bulk polymerization of ϵ-caprolactone was conducted at 100 °C (M/I = 50:1), and after nearly complete conversion (determined by GPC in dichloromethane) acetic anhydride was added. ^{1}H NMR spectra

of the reaction mixture (measured in $CDCl_3$) recorded at 300 MHz indicated that after 1 h the active Bu_3SnOCH_2 end group was completely transformed into an acetate end group and tributyltin acetate (Figure 10A). Also the polymer isolated after precipitation with methanol contains equimolar amounts of methyl ester and acetate end groups (Figure 10B).

The successful acetylation of the active end group not only is of interest as a model of the reaction mechanism of eq 10 but is also the basis for future preparative studies. Tributyltin alkoxide initiated polymerizations of lactones terminated with acid anhydrides (or acid chlorides) enable the synthesis of oligo- or polylactones with two variable, well-defined end groups. As will be demonstrated in a future part of this series, termination with methacrylic anhydride allows the synthesis of biodegradable macromers (eq 11).

$$\begin{aligned} &Bu_3Sn\text{-}[O\text{-}(A)\text{-}CO\text{-}]_nOCH_3 + \\ &\qquad (CH_2{=}C(CH_3)\text{-}CO\text{-})_2O \rightarrow \\ &CH_2{=}C(CH_3)\text{-}CO\text{-}[O\text{-}(A)\text{-}CO\text{-}]_n\text{-}OCH_3 + \\ &\qquad Bu_3Sn\text{-}O\text{-}CO\text{-}C(CH_3){=}CH_2 \quad (11) \end{aligned}$$

Conclusions

The results discussed above suggest that the propagation steps of lactone polymerizations initiated by tributyltin derivatives proceed via tin alkoxide end groups and cleavage of the acyl-oxygen bond. The initiation steps depend on structure and reactivity of the individual tributyltin derivatives. An initiation step slightly faster than propagation is characteristic for the tributyltin methoxide initiator. Nevertheless, despite the quasiliving character of these polymerizations, "backbiting" and transesterification entail broad molecular weight distributions as demonstrated previously.[22]

References and Notes

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Registry No. Bu_3SnOMe, 1067-52-3; Bu_3SnOPh, 3587-18-6; Bu_3SnOBu, 2724-79-0; Bu_3SnOBu_3Sn, 56-35-9; Bu_3SnOAc, 56-36-0; Bu_3SnSAc, 23059-95-2; Bu_3SnBr, 1461-23-0; Bu_3SnCl, 1461-22-9; ϵ-caprolactone, 502-44-3; ϵ-caprolactone (homopolymer), 24980-41-4; ϵ-caprolactone (SRU), 25248-42-4.