Polylactones. 40. Nanopretzels by Macrocyclic Polymerization of Lactones via a Spirocyclic Tin Initiator Derived from Pentaerythritol

Hans R. Kricheldorf* and Soo-Ran Lee

Institut für Technische und Makromolekulare Chemie der Universität Hamburg, Bundesstr. 45, D-20146 Hamburg, FRG

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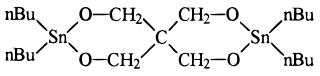
ABSTRACT: A spirocyclic initiator was synthesized from dibutyltin oxide and pentaerythritol. This spirocyclic distannoxane was characterized by elemental analyses, NMR spectroscopy, and a stoichiometric reaction with γ-thiobutyrolactone. ϵ-Caprolactone (ϵ-CL) was polymerized in bulk at 70 °C with variation of the monomer/initiator ratio. The molecular weights paralleled roughly the M/I ratio and high molecular weight poly(ϵ-CL) was obtained (M_w's up to 160 000). In contrast, homopolymerizations of β-D,L-butyrolactone (β-D,L-BL) in bulk at 75 °C did not give high molecular weights (M_w up to 25 000) but high yields. The spiro-macrocyclic poly(ϵ-CL) was selectively ring-opened with dimercapto ethane, whereby a four-around star polyester was obtained. The end groups were identified by ^{1}H NMR spectroscopy. Furthermore, spirocyclic block copolymers were prepared by batchwise copolymerization of β-D,L-BL and ϵ-CL. Furthermore, spirocyclic random copolyesters were obtained from mixtures of β-D,L-butyrolactone and ϵ-CL. The block or random character of all copolylactones was characterized by ^{13}C NMR spectroscopy and DSC measurements. Only in the case of block copolymers, crystallized blocks of ϵ-CL were found. The structure of the end groups and the polymerization mechanism are discussed.

Introduction

Tin compounds such as tin(II) 2-ethylhexanoate,[1−11] Bu_3SnOMe or $Bu_2Sn(OMe)_2$,[12−15] $BuSnCl_3$,[16,17] Bu_2SnO,[18] and stannoxanes[14,18] are among the most efficient and useful initiators for the polymerizations of lactides, lactones, and aliphatic cyclocarbonates. A new and highly interesting group of initiators based on tin are cyclic compounds containing at least one tin alkoxide bond. As demonstrated in two previous papers,[19,20] such cyclic initiators allow the syntheses of macrocyclic lactones, telechelic linear polylactones with two hydroxy end groups, A−B−A-triblock copolymers, and random copolyesters.

The purpose of the present work was to synthesize the spirocyclic tin compound **1** and to study its usefulness as initiator of the homo- and copolymerization of ϵ-caprolactone and β-D,L-butyrolactone.



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Experimental Section

Materials. Di-n-butyltin oxide, pentaerythritol, ϵ-caprolactone, and β-D,L-butyrolactone were purchased from Aldrich Co (Milwaukee, WI). Both lactones were distilled over freshly powdered calcium hydride prior to use.

Spirocyclic Tin Initiator 1. Pentaerythritol (0.1 mol dried over P_4O_{10}) and Bu_2SnO (0.2 mol) were suspended in dry toluene (500 mL) and refluxed until the theoretical amount of water was eliminated (and collected over a period of 25−27 h). When the clear solution was cooled, the product precipitated. The crude product was isolated by filtration. It was dissolved in hot toluene, the insoluble fraction was removed by filtration over dry Celite, and the product was isolated by cooling (in a refrigerator overnight) and filtration. Yield: 86%. M.p: 183−185 °C dec (from DSC measurements, first heating). Anal. Calcd for $C_{21}H_{44}O_4Sn_2$ (597.96): C, 42.18; H, 7.42. Found: C, 41.56; H, 7.83.

Model Reaction of 1 and γ-Thiobutyrolactone. Pentaerythritol (25 mmol) and Bu_2SnO (50 mmol) were reacted in refluxing toluene until all the water was distilled off. γ-Thiobutyrolactone (105 mmol) was then added and the reaction mixture was stirred at 100 °C for 48 h whereby most of the product separated in the form of a syrup. The ^{1}H NMR spectrum of the reaction mixture indicated complete conversion. The toluene was evaporated in vacuo and the syrupy residue was kept at 50 °C in a vacuum of 10^{-1} mbar for 24 h to remove all volatile compounds. Since the product did not crystallize even after prolonged storage in a refrigerator, the crude product was characterized. Yield 99%. Anal. Calcd for $C_{37}H_{68}O_8S_4Sn_2$ (1006.6): C, 44.15; H, 6.81; S, 12.74. Found: C, 44.50; H, 6.66; S, 12.45.

The fast atom bombardment mass spectroscopy gave a molecule peak at 1007 g/mol. The ^{13}C NMR spectrum exhibits one CO signal at 172 ppm in $CDCl_3$/TMS. A ^{119}Sn NMR spectrum recorded in $CDCl_3$ with $Sn(CH_3)_4$ for shift referencing displayed one sharp signal at 130 ppm. The ^{1}H NMR spectrum is given in Figure 1B.

Polymerizations. (A) Homopolymerizations of ϵ-Caprolactone (Tables 1 and 2). ϵ-Caprolactone (30 mmol) was weighed under nitrogen into a 25 mL Erlenmayer flask with ground glass joints and silanized glass walls (pretreated with Cl_2SiMe_2). The spiro initiator was added as a dry powder. The reaction flask was closed with glass stopper and steel spring and completely immersed into a thermostated oil bath. When the reaction time was over, the product was dissolved in CH_2Cl_2 (40−60 mL), precipitated into cold diethyl ether (600 mL), filtered off, and dried at 40 °C in vacuo.

(B) Homopolymerizations of β-D,L-Butyrolactone (Table 3). These polymerizations were conducted with 50 mmol of β-D,L-butyrolactone as described above for ϵ-caprolactone.

(C) Blockwise Copolymerizations (Table 4). β-D,L-Butyrolactone (50 mmol) was homopolymerized with the spiro initiator (1 mmol) in bulk at 75 °C for 1 day as described for A. The reaction vessel was then opened and ϵ-caprolactone (50 mmol) was added and thoroughly mixed with the poly(β-D,L-butyrolactone) by shaking of the closed reaction vessel. Finally the copolyester was dissolved in CH_2Cl_2 and precipitated into cold diethyl ether.

(D) Random Copolymerizations (Table 5). β-D,L-Butyrolactone (25 mmol) and ϵ-caprolactone (25 mmol) were weighed into a 25 mL Erlenmeyer flask and mixed. The spiro initiator **1** (1 mmol or less) was added as a dry powder. The reaction mixture was thermostated at 80 °C. Finally, the

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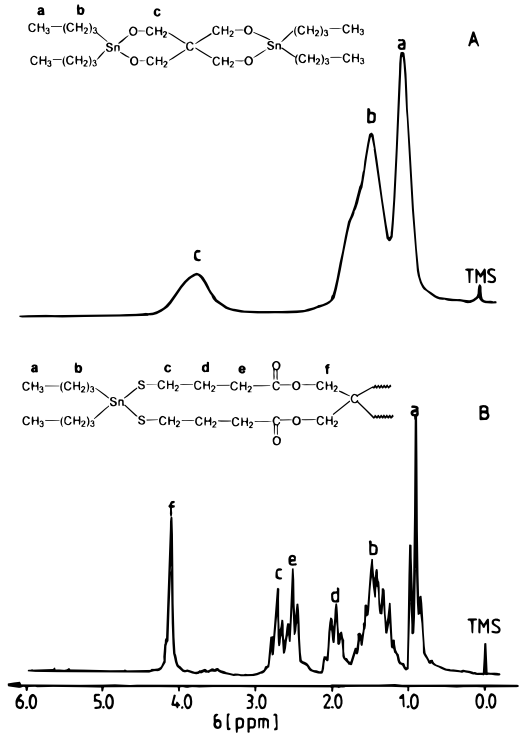


Figure 1. 100 MHz ^{1}H NMR spectra in $CDCl_3$: (A) spiroinitiator **1** (extracted from the powder precipitated from the original toluene solution) and (B) spiromacrocycle **5** prepared from **1** and γ-thiobutyrolactone.

copolyester was dissolved in CH_2Cl_2 (40 mL) and precipitated into cold diethyl ether.

All reaction mixtures were prepared under dry nitrogen.

Transesterification Model Reaction. Poly(β-D,L-butyrolactone (20 mmol, $T_m \sim 66$ °C, η_{inh} 0.2 dL/g) and poly(ϵ-caprolactone (20 mmol, Aldrich Co.) were dissolved together in CH_2Cl_2 (50 mL) and precipitated into cold methanol. The dry blend (25 mmol) was weighed into an Erlenmeyer flask with silanized glass walls, and the spiro initiator (0.5 mmol) was added. The transparent and seemingly homogeneous melt was thermostated at 80 °C for 5 days and then characterized by ^{13}C NMR spectroscopy in $CDCl_3$/TMS.

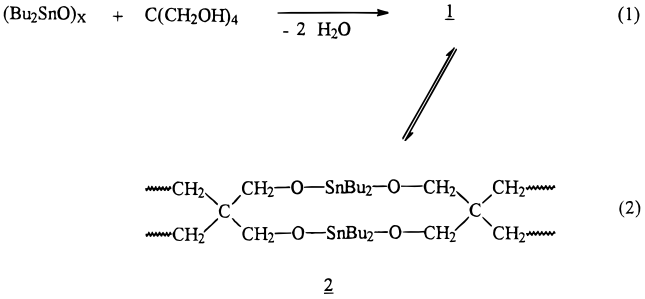
Measurements. The viscosities were measured in an automated Ubbelohde viscometer thermostated at 25 °C. The 100 MHz ^{1}H NMR spectra were recorded with a Bruker AC-100 FT-NMR spectrometer in a 5 mm o.d. sample tube. The 25.4 MHz ^{13}C NMR spectra were recorded with the same instrument in a 10 mm o.d. sample tube.

The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen.

The GPC measurements were conducted on a Kontron HPLC apparatus equipped with a Waters 410 differential diffractometer. A combination of 4 Ultrastyragel columns with pore sizes of 10^2, 10^3, 10^4, and 10^5 Å were used, and tetrahydrofuran served as eluent. The fast atom bombardment mass spectrum was recorded with a VG70−250S spectrometer using *m*-nitrobenzyl alcohol as the matrix and xenon as the ionized gas.

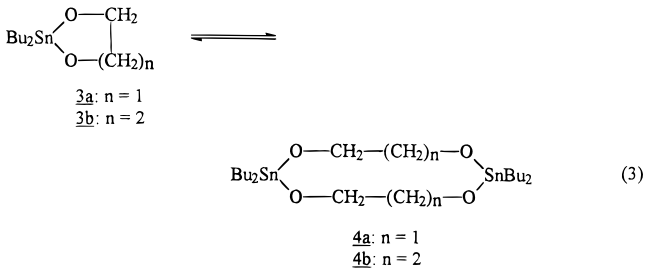
Results and Discussion

Synthesis of the Spirocyclic Initiator 1. The synthesis of the spiro initiator **1** was attempted by a method which has proved to be convenient and successful for the preparation of various five- and six-membered cyclic dibutyltin compounds.[19−21] For this purpose pentaerythritol was refluxed in toluene together with dibutyltin oxide, and the eliminated water (eq 1) was collected and measured. The suspension of the starting materials, which are entirely insoluble in toluene, finally yielded a clear solution. This clear solution and the



liberation of the theoretical amount of water prove the completion of the desired reaction. After cooling, the spiro compound **1** precipitated from the toluene solution and this process turned out to be largely irreversible. Heating of the isolated dry initiator in toluene caused a partial but never a complete dissolution.

The characterization of the spirocyclic initiator **1** is aggravated by its extremely low solubility in all common inert organic solvents. This low solubility is obviously a consequence of aggregation or polymerization processes. The aggregation of Sn−O compounds is based on the interaction of the free O-electrons with free d-orbitals of Sn-atoms. A typical example is the low solubility of $BuSn(OMe)_3$. However, it is also known from five- and six-membered 1,2,3-stannoxanes (**3a**, **3b**)[19,20] that they form cyclic dimers (**4a**,**4b**, eq 3) which



are stable enough to be detectable by mass spectroscopy[20] not only in solution. Therefore, a true polymerization of **1** yielding polycyclic oligomers of structure **2** (eq 2) should be taken into account. Considering this high aggregation/polymerization tendency, it was surprising that a sufficient concentration in $CDCl_3$ was obtained to record at least an ^{1}H NMR spectrum at room temperature (Figure 1A). All ^{1}H NMR signals are broad, in agreement with the existence of oligomerization equilibria. Somewhat sharper signals were observed in toluene at 100 °C. However, the concentration of **1** was too low for ^{13}C or ^{119}Sn NMR measurements, regardless of the solvent.

An important result of the ^{1}H NMR measurements is the chemical shift of 3.6 ppm found for the OCH_2 protons in $CDCl_3$ (Figure 1A). For tetrakis(trimethylsilyl)pentaerythritol a chemical shift of 3.4 ppm was observed in $CDCl_3$/TMS. In contrast, the tetraacetyl pentaerythrite shows a ^{1}H NMR signal at 4.1 ppm in $CDCl_3$/TMS. Thus the acetylation causes a downfield shift of 0.5−0.7 ppm. This is a quite normal shift effect for an alkyl ester group relative to the corresponding alkyl ether. The knowledge of these chemical shifts is important for the discussion of the polymerization mechanism (see below).

The characterization of the initiator **1** was also aggravated by its low thermostability. Upon attempted melting above 180 °C, decomposition took place. This low thermostability in combination with the oligomeric

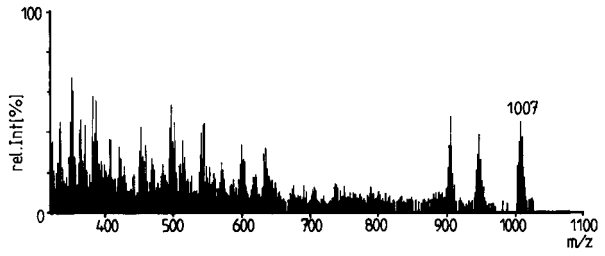
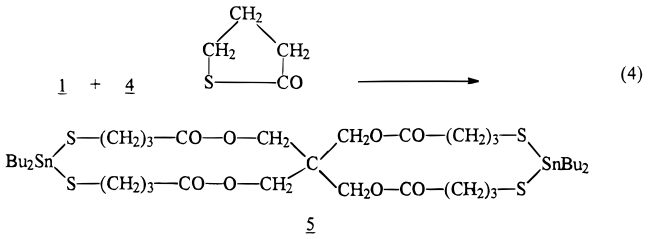
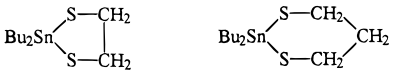


Figure 2. Fast atom bombardment mass spectrum of the spirocycle **5**.

character prevented a successful characterization by mass spectroscopy. In order to improve the characterization of **1** and to find a model reaction of the polymerizations discussed below, a freshly prepared solution of **1** in hot toluene was reacted with γ-thiobutyrolactone (eq 4). γ-Thiobutyrolactone is a commerical compound



which for thermodynamical reasons does not polymerize under atmospheric pressure. The driving force for its reaction with **1** is the formation of Sn−S bonds which are more stable than Sn−O bonds. The spiro macrocycle **5** was isolated as a monomeric syrupy material soluble in several inert solvents such as $CHCl_3$ or tetrahydrofuran. The monomeric character is in full agreement with the structure **5**, because other 2-stanna-1,3-dithianes, such as **6** or **7** are also monomeric in



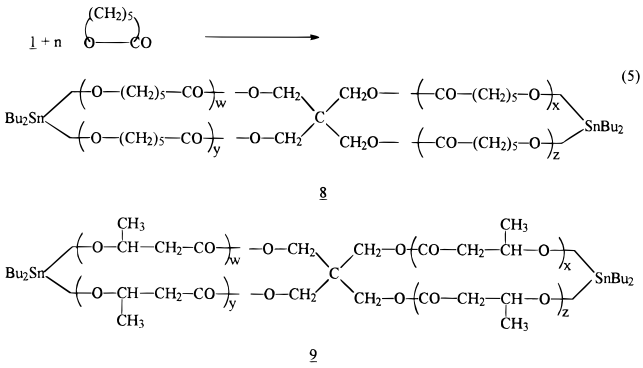
contrast to **3a** or **3b**.[20,21] The spirocycle **5** was characterized by elemental analyses, ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy (eg. Figure 1B), and by fast atom bombardment mass spectroscopy (Figure 2). The ^{1}H NMR spectrum displayed in Figure 1B exhibits a singlet signal at 4.15 ppm as expected for a quantitative acylation of all four $SnOCH_2$ groups. Furthermore, a ^{119}Sn NMR spectrum showed one signal at 130 ppm, which agrees well with the ^{119}Sn NMR signal of the 1,3-dithiane **7** (150 ppm). In contrast, the 1,3-dioxane **3b** absorbs at −203 ppm (relative to $SnMe_4$). A more detailed description of **5** and analogous model compounds will be published separately.[22] The almost quantitative formation of **5** from **1** does not only prove the structure of freshly prepared **1**, it also represents a model reaction of the insertion of lactones into all four Sn−O bonds of **1**.

Homopolymerizations of ϵ-Caprolactone. In previous studies all polymerizations initiated with cyclic tin initiators (e.g. **3a**,**b**/**4a**,**b**) were conducted in bulk, because all attempts to initiate the polymerizations of lactide and lactones in solution below 80 °C had failed. Whether this failure is a consequence of a low reactivity or of the low solubility of the initiators is an open question in the case of **3b**/**4b**, whereas the solubility was high enough in the case of **3a**/**4a**. Anyway, all polymerizations of the present work (eq 5) were conducted in bulk, and the spiro initiator **1** was added in the form of a fine powder.

Table 1. Reaction Conditions and Results of 1-Initiated Polymerizations of ϵ-Caprolactone in Bulk at 70 °C

no.	M/I	time (h)	yield (h)	η_{inh}[a] (dL/g)	M_v[b] ($\times 10^3$)	M_n[c] ($\times 10^3$)	M_w[c] ($\times 10^3$)
1	25	24	94	0.33		10	22
2	50	24	96	0.47	24	12	28
3	100	24	97	0.63		22	42
4	200	24	97	0.85	43	35	62
5	400	24	90	1.52	74	34	88
	400	24	91	1.46			
6	800	24	90	2.52	133	56	164
	800	24	87	2.44			
7	1500	96	95	0.90		25	72
	1500	192	93	1.00	49	27	71

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [b] Calculated from intrinsic viscosities: $[\eta] = 1.395 \cdot 10^{-4} \times M_w^{0.786}$ (ref 23). [c] From GPC measurements and equ.: $[\eta] = 1.395 \cdot 10^{-4} \times M_w^{0.786}$ (ref 23).



Due to the fact that poly(ϵ-caprolactone) has a melting temperature in the range of 60−65 °C, 75 °C was selected as the lowest temperature for a first series of polymerizations (Table 1). The monomer/initiator (M/I) ratio was varied from 25/1 up to 1500/1 and yields ≥90% were found in all cases. Considering the high yields and high molecular weights obtained at a M/I of 800/1 within 24 h (nos. 7 and 8, Table 1), it may be concluded that the spiro initiator **1** is highly efficient and reactive despite its initial insolubility. In order to check the reproducibility of these results, those polymerizations with the highest M/I ratios were repeated (nos. 5, 7, and 9) and a satisfactory agreement was found. A conspicuous phenomenon is the relatively low viscosities obtained for M/I = 1500/1, when compared to M/I's = 400 and 800. The long reaction time of experiment no. 10 (Table 1) and the high yield prove that this is not a consequence of incomplete conversion. Possibly, the lower rate of conversion, which is a necessary consequence of a higher M/I ratio, allows side reactions (e.g. chain transfer to the monomer) to interfere with the polymerization process.

The high efficiency of the spiro initiator **1** was also illustrated by the results of polymerizations conducted at 120 °C (Table 2). Yields ≥90% were obtained even at a reaction time of only 4 h. Again the viscosities increase with higher M/I ratios, but at M/I = 800, a reduction takes place. Obviously this reduction corresponds to the lower viscosities obtained with M/I = 1500/1 at 75 °C (nos. 9 and 10, Table 1). Absolute molecular weights were determined for the polycaprolactone samples of Table 1 in two ways. Firstly, viscosity average molecular weights were determined

Table 2. Results of 1-Initiated Polymerizations of ϵ-Caprolactone in Bulk at 120 °C/4 h

no.	M/I	yield (%)	η_{inh}[a] (dL/g)
1	25	94	0.44
2	50	95	0.52
3	100	96	0.77
4	200	96	0.82
5	400	89	1.68
6	800	90	1.53

[a] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2.

Table 3. Homopolymerizations of β-D,L-Butyrolactone in Bulk, Initiated with the Spiro Initiator 1

no.	M/I	temp (°C)	time (d)	yield (%)	η_{inh}[a] (dL/g)
1	50/1	50	5	91	0.15
2	50/1	75	1	51	0.14
3	100/1	75	1	81	0.20
4	100/1	75	5	74	0.20
5	200/1	75	1	88	0.23
6	200/1	75	5	72	0.25
7	300/1	75	1	84	0.26
8	300/1	75	5	80	0.27
9	400/1	75	5	86	0.29
10	400/1	75	10	75	0.26
11	800/1	75	5	0	
12	800/1	75	10	11	

[a] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2.

from intrinsic viscosities via the Mark−Houwink equation (6).[23] Secondly, GPC measurements were conducted in THF, and number-average molecular weights (M_n) and the weight-average molecular weights (M_w) were determined by means of the *a* and *K* values of eq 6. Equation 6 has been published by Schindler et al.[23] for solutions of poly(ϵ-caprolactone) in tetrahydrofuran.

$$[\eta] = 1.395 \cdot 10^{-4} \times M_w^{0.786} \quad (6)$$

The molecular weight data suggest the following interesting conclusions: Firstly, the molecular weight distributions are broad with M_w/M_n ratios around 3. Secondly, the molecular weights (M_n's) obtained at low M/I ratios are much higher than expected from these M/I ratios. A consistent explanation of both phenomena can be given on the basis of the following assumptions. Firstly, the entire initiation process is slow relative to the propagation due to the slow and gradual dissolution of **1** in the liquid monomer. Secondly, even after dissolution, the initiator molecules do not react immediately all at the same time. This assumption is supported by the finding that in the case of other cyclic tin initiators (e.g. **3a**/**4a** and **3b**/**4b**) the propagation steps are faster than the initiation steps. Thirdly, it is unlikely that all Sn−O bonds of a spiro initiator react all at the same time. Unfortunately, detailed kinetic studies by ^{1}H NMR spectroscopy are hampered by the fact that the OCH_2 signal of the acylated (incorporated) initiator is obscured by the OCH_2 signal of the repeating units of ϵ-caprolactone.

Homopolymerization of β-D,L-Butyrolactone. All but one of the homopolymerizations of β-D,L-BL were conducted at 75 °C (Table 3). Significantly higher reaction temperatures are not possible due to the low boiling point of this monomer, and they are not attractive due to side reactions which cause termination steps. Temperatures below 50 °C are unfavorable, because previous studies with other tin alkoxide initiators[15,25] have demonstrated that polymerizations of β-D,L-BL below 50 °C are so slow that several weeks are required for complete conversion. However, lower reaction temperatures have the advantage that the stereoselectivity is higher, and thus, one polymerization was conducted at 50 °C (no. 1, Table 3). The isolated poly(β-D,L-BL) was indeed a semicrystalline material with a main melting endotherm at 78 °C and a glass-transition temperature of 11 °C (Figure 3). However, in contrast to polymerizations initiated by $Bu_2Sn(OMe)_2$,[15] no fraction with higher melting temperature was found. Melting temperatures in the range of 110−130 °C are characteristic for long blocks having a syndiotactic configuration.[15] The ^{13}C NMR spectrum measured in $CDCl_3$ indicated only 60−65% of syndiotactic diads, in agreement with the low melting temperature. Hence, it may be concluded that the spiro initiator **1** is not particularly interesting from the view point of its stereoselectivity.

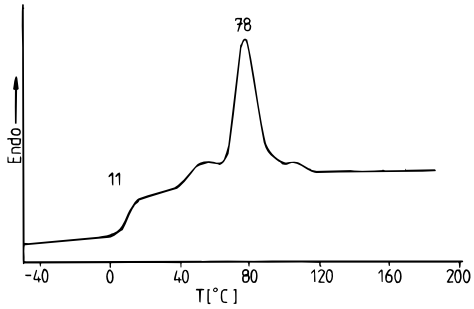


Figure 3. DSC measurements of poly(β-D,L-butyrolactone) initiated with **1** at 50 °C (no. 1, Table 3).

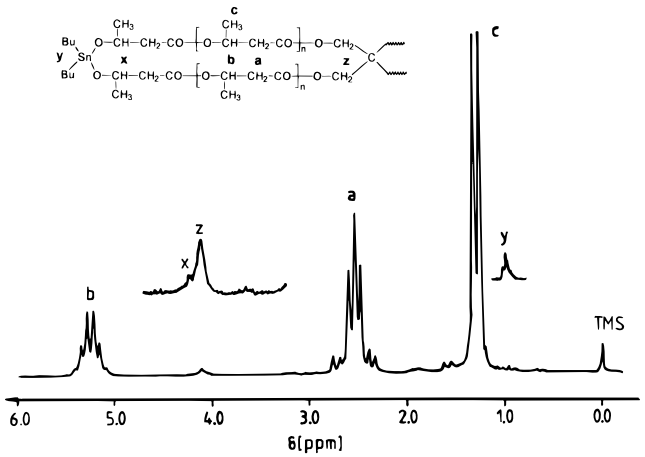


Figure 4. 100 MHz ^{1}H NMR spectrum of poly(β-D,L-butyrolactone) initiated with **1** at a M/I ratio of 50/1 (no. 1, Table 3).

Particularly noteworthy are the ^{1}H NMR spectra of poly(β-D,L-butyrolactone) because they display one singlet signal at 4.15 ppm (Figure 4). This is exactly the position expected for a tetraacylated pentaerythritol, as demonstrated by the aforementioned chemical shift of tetraacetylpentaerythritol. The same signal also shows up in the ^{1}H NMR spectrum of model compound **5**, and thus, the ^{1}H NMR spectrum of Figure 4 clearly supports the formation of spiromacrocycles of structure **9**.

When the polymerizations were conducted at 75 °C, the M/I ratio was varied between 50/1 and 800/1 (Table 3). A higher M/I ratio proved to be useless, because even the polymerizations conducted with M/I = 800/1 failed almost completely. This failure agrees well with previous results based on other tin alkoxides. It is difficult to polymerize β-D,L-BL at M/I ratios ≥400. At each M/I ratio two polymerizations were conducted, one with a short reaction time and another with a long one. In all but one case a slightly higher yield was obtained at the

Table 4. Synthesis of Block Copolyesters by Batchwise Copolymerization of β-D,L-Butyrolactone[a] and ϵ-Caprolactone in Bulk at 80 °C

no.	M/I	time (d) β-D,L-BL	time (d) ϵ-CL	yield (%)	ϵ-CL[b]/ β-D,L-BL	η_{inh}[c] (dL/g)	T_m[d] (°C)
1	50	1	1	75	2.3	0.51	
2	100	1	1	71	2.2	0.67	63.0
3	200	1	1	76	1.3	0.54	
4	400	5	3	85	1.3	0.50	66.0

[a] β-D,L-Butyrolactone was homopolymerized first and the ϵ-caprolactonewas added. [b] Molar composition of the isolated block copolyester as determined by ^{1}H NMR spectroscopy. [c] Measured at 20 °C in CH_2Cl_2 with $c = 2$ g/L. [d] From the first heating curve of DSC measurements (heating rate, 20 °C/min).

short time. At least at M/I ratios ≤300 a reaction time of 1 day is sufficient to reach nearly complete conversion. The finding that all yields were below 90% is mainly a consequence of the low molecular weights and of the amorphous character of all samples. Upon precipitation of the crude reaction products into diethyl ether, the oligomers remained in solution (detected after evaporation of the diethyl ether).

The viscosity measurements revealed one analogy to those of poly(ϵ-caprolactone). The viscosities increased with higher M/I ratios. However, in contrast to poly(ϵ-caprolactone), only low viscosities and molecular weights were obtained in all experiments. In the case of sample no. 9 of Table 3, a GPC curve was recorded and evaluated by means of eq 6. A M_n of 26 000 and a M_w of 39 000 were found. These values indicate a somewhat lower degree of polydispersity than in the case of poly(ϵ-caprolactone). Furthermore, they illustrate by comparison with those of poly(ϵ-caprolactone) that the polymerizations of β-D,L-BL is affected by side reactions causing termination steps. From this point of view, the behavior of the spiro initiator completely agrees with that of other dibutyltin alkoxides.[13,15,24]

Copolymerizations. Two series of copolymerizations were conducted to synthesize either copolyesters with a blocky or with a random sequence. The blocky sequences were prepared by a batchwise copolymerization in a one-pot procedure. At first β-D,L-BL was homopolymerized in bulk at 80 °C. The M/I ratio was varied between 50/1 and 400/1. The reaction time was limited to 1 or 5 days in the case of M/I = 400/1 (Table 4). According to the results listed in Table 3, these reaction times were sufficient for a nearly complete conversion of the monomer. Furthermore, the conversion was monitored by ^{1}H NMR spectroscopy and ≥95% conversion was found in all four cases. An equimolar amount of ϵ-caprolactone was then added to the reaction mixture and the polymerizations were continued for another day or 3 days (Table 4). In the case of polymerizations 1 and 3 (Table 4), a sample was taken immediately before the addition of the ϵ-caprolactone and immediately before the entire copolymerizations were stopped. Both samples were compared by GPC measurements, and a significant increase of the molecular weight was found after copolymerization of the ϵ-caprolactone (Figure 5). Finally, the copolyesters were isolated after precipitation into diethyl ether.

The molar composition was determined by ^{1}H NMR spectroscopy and in all cases a β-D,L-BL/ϵ-CL ratio below unity was found (Table 4). This result is somewhat difficult to explain considering the high conversion of β-D,L-BL in the initial homopolymerizations. However, similar results were obtained with another cyclic initiator (**3b**/**4b**).[19] This result is at least partially a consequence of the fractionation which takes place upon precipitation into diethyl ether. The copolymers with the longer rapidly crystallizing blocks of poly(ϵ-caprolactone) are certainly less soluble than those chains containing long amorphous poly(β-D,L-BL) blocks. The blocky character of all four copolyesters was confirmed by ^{13}C NMR spectra (Figure 6A), which display only two CO signals. The signal of the β-DL-butyrolactone blocks is split due to the tacticity. Furthermore, DSC measurements were conducted (Figure 7) which prove in combination with WAXS powder patterns that all block copolyesters contain long crystallizing blocks of ϵ-caprolactone units. However, it should be mentioned that, in the case of no. 1 of Table 4, the ^{13}C NMR spectrum displays at high signal-to-noise ratio tiny signals of the crossover steps (β-BL → ϵ-CL and ϵ-CL → β-BL).

The second series of copolymerizations was conducted in such a way that equimolar amounts of both lactones were mixed and polymerized at 80 °C with variation of the M/I ratio (Table 5). In this series the molar composition was closer to unity, regardless of the M/I ratio. The random character of the sequences is evident from the ^{13}C NMR spectra of all samples (Figure 6B). These results are in agreement with a previous study

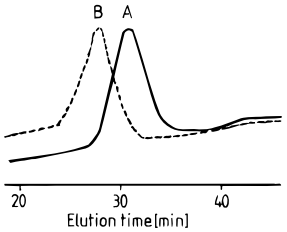


Figure 5. GPC curves of (A) poly(β-D,L-butyrolactone used for the synthesis of the block copolymer (no. 2, Table 4) and (B) the isolated block copolymer from run no. 2, Table 4.

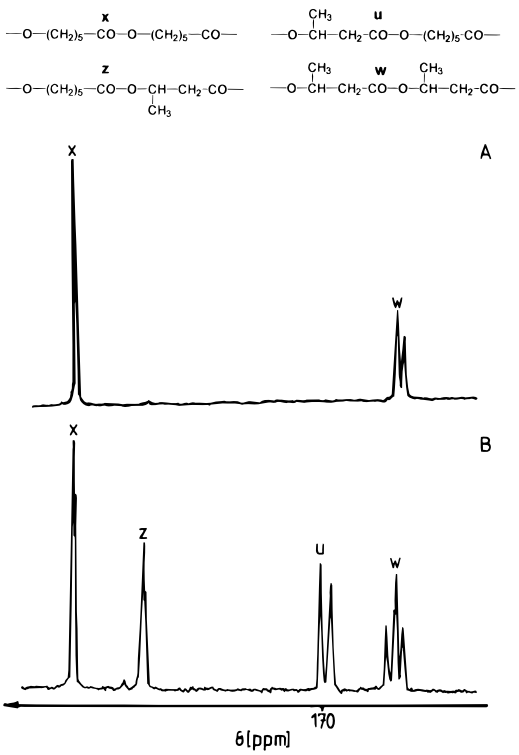


Figure 6. 25.4 MHz ^{13}C NMR spectra (CO signals only) of (A) the block copolyester from run no. 3, Table 4 (the splitting of signal "w" represents the syndiotactic and isotactic diads) and (B) the random copolyester from run no. 3, Table 5.

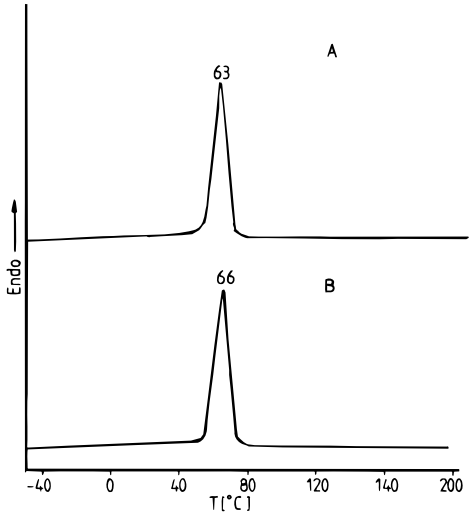


Figure 7. DSC measurements (heating rate 20 °C/min) of (A) block copolyester from run no. 2, Table 4, 1st heating and (B) block copolyester from run no. 4, Table 4, 1st heating.

Table 5. Copolymerization of ϵ-Caprolactone and *β*-D,L-Butyrolactone in Bulk at 80 °C

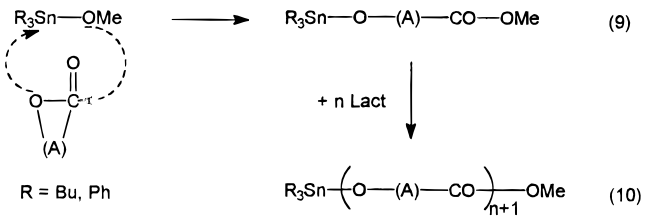
no.	M/I	time (d)	yield (%)	ϵ-CL[a]/*β*-D,L-BL	η_{inh}[b] (dL/g)
1	50/1	1	53	1.15	0.41
2	100/1	1	50	1.05	0.58
3	200/1	5	49	1.05	0.64
4	400/1	10	~10		

[a] Molar composition as determined by ^{1}H NMR spectroscopy. [b] Measured at 25 °C in CH_2Cl_2 with c = 2 g/L.

based on initiator **3b**/**4b**.[19] It was found that the reactivity ratios of both monomers are nearly equal when copolymerizations were conducted in bulk. A significant contribution of ester interchange reactions can be excluded for two reasons. The first reason is the blocky sequences of the copolyesters listed in Table 4. Secondly, a molecular blend of poly(*β*-D,L-BL) and poly(ϵ-CL) was prepared by dissolution of both polyester in CH_2Cl_2 and coprecipitation into methanol. This blend was doped at 80 °C with the spiro initiator **1** and examined by ^{13}C NMR spectroscopy after 3 and 5 days. Not the faintest indication of transesterification was found.

Mechanistic Aspects. This study has not been designed to make a substantial contribution to the elucidation of polymerization mechanisms, in as much as mechanistic studies concerning tin-based initiators have been published in previous parts of this series.[12,25] Nonetheless, a short discussion of the polymerization mechanism initiated by the spiro initiator **1** should be presented here.

The basis of this mechanistic discussion is previous results which demonstrate that butyltin alkoxides initiate a so-called "insertion mechanism" (eqs 9 and 10).



This "insertion mechanism" involves a rearrangement of polarized covalences, but is free of ionic species. In the simple case this mechanism consists of two steps:

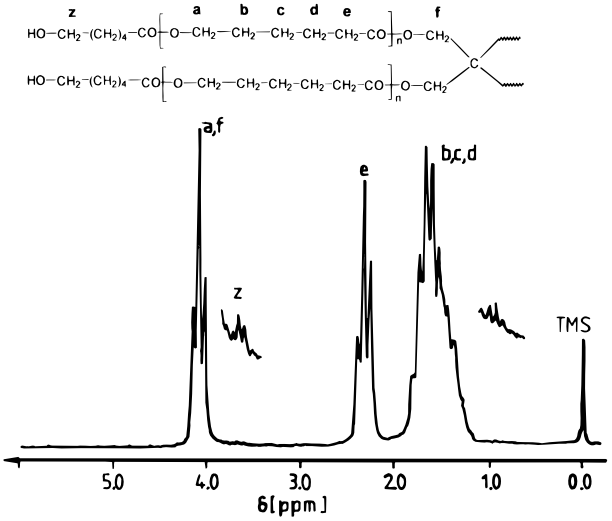
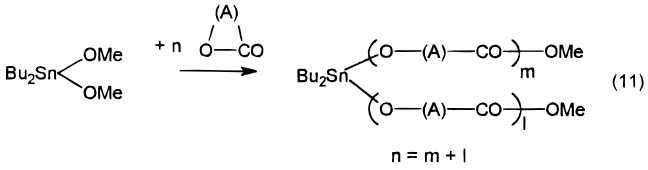
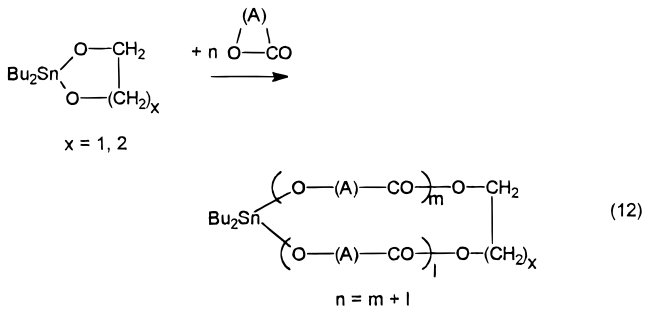


Figure 8. 100 MHz ^{1}H NMR spectrum of the poly(ϵ-caprolactone) (no. 1, Table 1) after treatment with 1,2-dimercaptoethane.

the association of the lactone with a free d-orbital (or sp^3d^2-orbital) of the tin atom followed by an insertion step. NMR end group analyses have proven that in the case of dibutyldimethoxytin both methoxy groups initiate a chain (eq 11), although not necessarily at the



same time.[12] Cyclic tin alkoxides such as **3a**,**b** initiated an analogous mechanism, yielding macrocyclic polylactones (eq 11).[19,20] On the basis of all these results, it



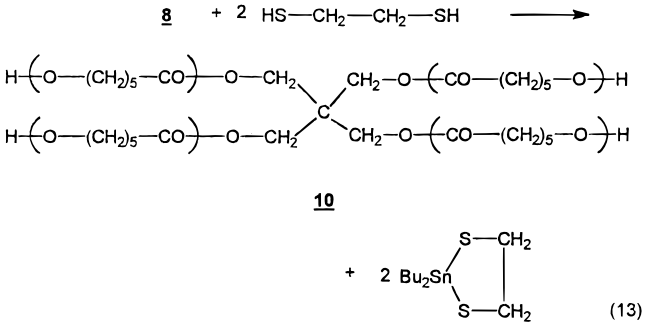
may be assumed that polymerizations initiated by the spiro initiator **1** will follow the same route, so that spirocyclic polylactones such as **8** or **9** are initially formed. As discussed above, the gradual dissolution of the initiator **1** in the lactone and the gradual reaction of all four Sn−O bonds have the consequence of broad molecular weight distributions and of degrees of polymerization which may be higher than the M/I ratio. However, finally, a complete acylation of all four $SnOCH_2$ groups takes place, which can be proven by ^{1}H NMR spectroscopy. In agreement with the model compound pentaerythritol tetraacetate, a singlet signal around 4.1 ppm (in $CDCl_3$) is detectable in the ^{1}H NMR spectra of **1**-initiated poly(*β*-D,L-BL) (Figure 4). The presence of the Bu_2Sn groups in the crude reaction product can be seen from the triplet signal of the CH_3 groups at 0.9 ppm.

Table 6. GPC Measurements of Poly(ϵ-caprolactone) Initiated with 1 (M/I = 200/1) in Bulk at 80 °C

	GPC elution times (min)[a]		
no.	untreated	DME 2:1/20 h[b]	DME 4:1/1 h[c]
1	25.58	25.50	25.52
2	26.06	26.00	25.94
3	25.80	25.71	25.69

[a] Measured after precipitation into dry diethyl ether. [b] Precipitated 20 h after addition of a double molar amount of 1,2-dimercaptoethane. [c] Precipitated 1 h after addition of the 4-fold molar amount of 1,2-dimercaptoethane.

As described for macrocyclic polylactones initiated by **3a** or **3b**,[19,20] it is possible to remove the Bu_2Sn group selectively by means of 1,2-dimercaptoethane (DME) at room temperature. In the present work, two samples of spirocyclic poly(ϵ-caprolactone) prepared with a M/I = 100/1 were treated with an excess of DME in CH_2Cl_2 at 25 °C. The GPC curves recorded before and after the treatment indicate that indeed a selective ring-opening took place without chemical degradation (Table 6). These results also prove that the spirocyclic polylactones of structure **8** or **9** are not severely aggregated or dimerized via Sn−O bonds. The free CH_2OH group of the four-armed star polyesters thus obtained (eq 13)



(13)

were detectable as triplets at 3.6 ppm in the ^1H NMR spectra (Figure 8). Analogously, a four-armed star was prepared from β-D,L-BL (with a M/I ratio of 100/1), by treatment of a spirocycle of structure **8** with DME. Again, the GPC measurements indicated that the treatment with DME at room temperature did not cause any reduction of the molecular weight.

Conclusion

In continuation of previous studies of macrocyclic polylactones, the present work allows the following conclusions. A spirocyclic initiator (**1**) can be prepared from pentaerythritol and Bu_2SnO. This initiator enables the homopolymerization of ϵ-caprolactone and β-D,L-butyrolactone with high yields and, in the former case, with high molecular weights. Furthermore, block copolyesters and random copolyesters can be prepared by proper adjustment of the reaction conditions. Prior to precipitation into an alcohol, all of these polyesters possess a spirocyclic structure. Treatment with dimercaptoethane allows a selective removal of the Bu_2Sn groups, so that four-armed star polyesters with free OH end groups are formed.

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