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Polylactones 54: ring-opening and ring-expansion polymerizations of ϵ-caprolactone initiated by germanium alkoxides

Hans R. Kricheldorf, Dennis Langanke

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

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Abstract

Et_3GeOMe-initiated polymerizations of ϵ-caprolactone were studied at six different temperatures, but even at 180 °C the conversion was below 50% after two days. $Ge(OEt)_4$ proved to be more reactive and a temperature of 120 °C was found to allow for a nearly quantitative conversion after two days. All four ethoxy groups were active in the initiation process, but a broad molecular weight distribution was found and a low percentage (presumably <1 mol%) of cyclic oligomers was formed. Ring-expansion polymerization initiated with a spirocyclic germanium alkoxide was feasible at 140 °C and yielded a molecular weight distribution quite different from that obtained with $Ge(OEt)_4$. The monomer/initiator (M/I) ratio was varied, and it was found that the average degree of polymerization ($\overline{DP}$) did not agree with the M/I ratio for M/I's above 200. Addition of 4-nitrobenzoyl chloride to the hot virgin reaction mixtures yielded poly(ϵ-CL) chains having functional endgroups but the degree of functionalization never exceeded 80%.

Keywords: Polymerizations; Germanium alkoxides; Transesterification

1. Introduction

Most biodegradable polymers studied and technically produced are polyesters prepared by ring-opening polymerization of lactones and cyclic diesters. For fundamental research aluminum alkoxides and tin alkoxides or tin salts were the most widely used initiators so far. For the technical production of polylactides and copolyesters of lactic acid tin salts are preferentially used as initiators [1]. However, tin compounds are rather toxic and they are excellent transesterification catalysts [2,3] causing rapid 'back-biting' degradation and scrambling of regular sequences of copolymers. Therefore, other initiators being less toxic and less active in transesterification are of interest. In this connection, it was the purpose of the present work to elaborate first-hand information about the properties and usefulness of germanium alkoxides as initiators. Germanium compounds are somewhat less toxic than comparable tin compounds and they are less reactive in transesterification. To the best of our knowledge, polymerizations of lactones initiated by germanium alkoxides have never been reported before.

Three Ge-alkoxides should be studied and compared: Et_3GeOMe as an example of a monofunctional initiator, $Ge(OEt)_4$ as an example of a tetrafunctional initiator and a spirocyclic compound of structure **1** which should allow for ring-expansion polymerizations of lactones. Analogous spiroalkoxides of other elements such as titanium, zirconium and tin are insoluble in all inert solvents [4], and thus, are difficult to synthesize in a pure form and useless for controlled polymerizations of lactones. Also in the case of germanium spirocyclic alkoxides derived from α-ω-diols with even numbers of CH_2 groups are insoluble [5]. Therefore, the spirocyclic **1** is the only soluble spirocyclic alkoxide (with a central metal atom) known so far [5].

2. Experimental

Materials: ϵ-Caprolactone (ϵ-CL) was purchased from Aldrich Co. (Milwaukee, WI, USA) and distilled over freshly powdered calciumhydride. $Ge(OEt)_4$ and Et_3GeOMe were purchased from ABCR Co. (Karlsruhe, Germany) and used as received. Aromatic solvents, CH_2Cl_2 and chloroform (including $CDCl_3$) were distilled over P_4O_{10}. The 1,3-propane diol (Aldrich Co.) was azeotropically dried with toluene and distilled in vacuo.

2.1. Polymerization

(A) *With Et_3GeOMe as initiator*: ϵ-CL (40 mmol) was weighed into an Erlenmeyer flask (50 ml) with silanized

E-mail address: kricheld@chemie.uni-hamburg.de (H.R. Kricheldorf).

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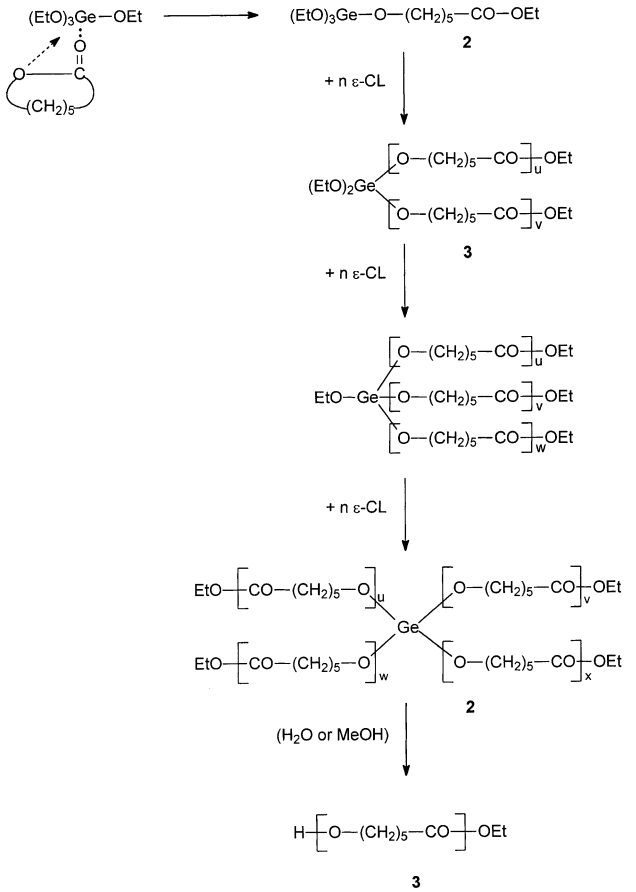
glass walls, the initiator was added in the form of a 1 M solution in dry chlorobenzene, the reaction vessel was closed with glass stopper and steel spring and immersed into a preheated oil bath. After two days, the conversion was determined by ^{1}H-NMR spectroscopy in $CDCl_3$.

(B) *With Ge(OEt)$_4$ as initiator*: ϵ-CL (60 mmol) was weighed into an Erlenmeyer flask (60 ml) having silanized glass walls and the initiator was added in the form of a 1 M solution in dry chlorobenzene (0.3 ml). The reaction vessel was closed with glass stopper and steel spring and immersed into a thermostated oil bath. After 48 h the conversion was checked by ^{1}H-NMR spectroscopy. The cold virgin reactor products were characterized by MALDI-TOF mass spectroscopy. The product was then dissolved in CH_2Cl_2, precipitated into cold methanol and dried at 40 °C in vacuo.

(C) *Initiation with the spirocycle* **1**: psi;-Caprolactone (50 mmol) was weighed into a 25 ml Erlenmeyer flask having silanized glass walls and the initiator was injected in a 1 M solution in CH_2Cl_2 by means of syringe. The reaction vessel was closed by a glass stopper and steel spring and immersed into an oil bath preheated to 140 °C. After cooling the reaction product was dissolved in 40 ml CH_2Cl_2, and precipitated into cold methanol and dried at 20–25 °C in vacuo.



Scheme 1.

Table 1
Et_3GeOMe-initiated polymerizations of ϵ-caprolactone in bulk (M/I = 100)

Temperature (°C)	Time (d)	Conversion (%)
80	2	0
100	2	0
120	2	2
140	2	5
160	1	5
160	2	30
160	4	95
180	2	45

2.2. Measurements

The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer thermostated at 20 °C.

The ^{1}H-NMR spectra were recorded with a Bruker AM-400 FT NMR spectrometer in 5 mm outer diameter sample tubes. $CDCl_3$ containing TMS served as solvent and shift reference.

The MALDI-TOF mass spectra were recorded with a Bruker Biflex III in the reflection mode. The irradiation targets were prepared from solutions of polylactone and dithranol in tetrahydrofuran and doped with potassium trifluoroacetate.

3. Results and discussion

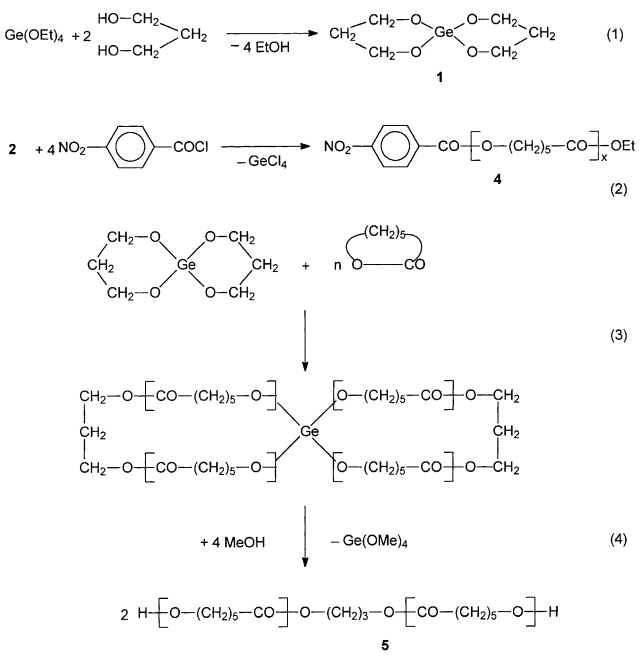
3.1. Initiation with Et_3GeOMe or $Ge(OEt)_4$

The initiation of the ring-opening polymerization of ϵ-CL with Et_3GeOMe or $Ge(OEt)_4$ served three purposes. Firstly, the minimum temperature required for an almost quantitative conversion within a time period of two days should be determined. Secondly it should be elucidated, if all four ethoxy groups participate in the initiation process when $Ge(OEt)_4$ was used. Thirdly, it should be found out, if cyclic oligolactones are formed by back-biting degradation from the active chain end.

Table 2
$Ge(OEt)_4$-initiated polymerizations of ϵ-caprolactone conducted in bulk with M/I = 200

Temperature (°C)	Conversion[a] (%)	$\eta_{inh.}$[b] (dl/g)
60	3	–
80	10	–
100	20	–
120	97	0.21
140	99	0.23
160	99	0.26
180	99	0.26
200	99	0.25

[a] Determined after two days from 400 MHz ^{1}H-NMR spectra of the virgin reaction mixtures.
[b] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.



Eight experiments were conducted with Et_3GeOMe at reaction times up to four days. The temperatures were varied from 60 to 180 °C in steps of 20 °C and the virgin reaction mixtures were examined by ^{1}H-NMR spectroscopy. No significant conversion was observed from 60 to 120 °C within two days, and a temperature of 160 °C was needed along with a reaction time of four days to achieve more than 90% conversion (Table 1). Therefore, these experiments clearly demonstrate that Et_3GeOMe is not reactive enough to serve as a useful initiator for preparative purposes. When compared to Bu_3SnOMe [2,6], it may be said that the temperature should be at least 100 °C higher to obtain similar polymerization rates with Et_3GeOMe.

In the case of $Ge(OEt)_4$ again eight polymerization experiments were performed with an M/I ratio of 200:1 beginning at a temperature of 60 °C. Higher temperatures were selected in steps of 20 °C (Table 2). After two days the reaction mixtures were analyzed on the basis of 400 MHz NMR spectra. From the conversions listed in Table 2 it was learnt that at least a temperature of 120 °C is needed for a polymerization in bulk to obtain more than 95% conversion. These NMR spectra also revealed that at temperatures $\geq$120 °C the typical O–CH_2 signal of the initiator (3.55 ppm) had disappeared. This observation means that all four ethoxy groups were active in the coordination–insertion mechanism (Scheme 1), so that the resulting polyester initially had the structure of a four armed star (**2**). This interpretation is in perfect agreement with the results obtained previously from $Ti(OnBu)_4$ and $Zr(OnPr)_4$-initiated polymerizations of lactones [2].

Furthermore, the virgin reaction mixtures obtained at temperatures $\geq$120 °C were subjected to MALDI-TOF mass spectroscopy. It was found quite analogous to tin alkoxide initiated polylactones that either moisture or the OH-groups of the matrix materials cleaved the Ge–OCH_2 bonds. As shown in Fig. 1 the MALDI-TOF mass spectra revealed a series of intensive peaks corresponding to polylactones of structure **3**. A series of weak peaks was found to originate from cyclic oligomers. However, these cycles were not detectable in the GPC elution curve and a comparison with tin-alkoxide initiated poly(ϵ-CL) samples

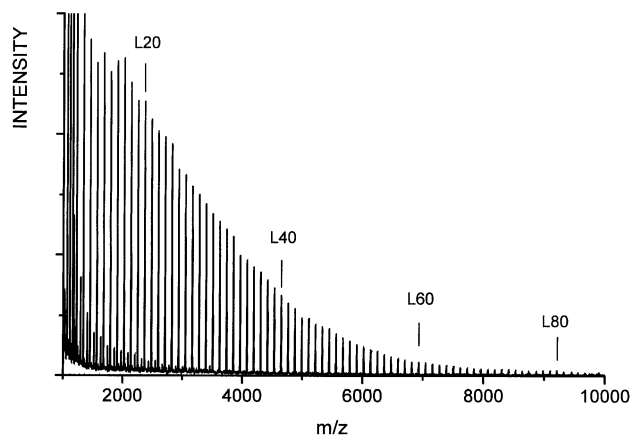


Fig. 1. MALDI-TOF mass spectrum of a poly(ϵ-caprolactone) initiated with $Ge(OEt)_4$ at 120 °C/48 h (C is cycles, L is linear chains of structure **3**).

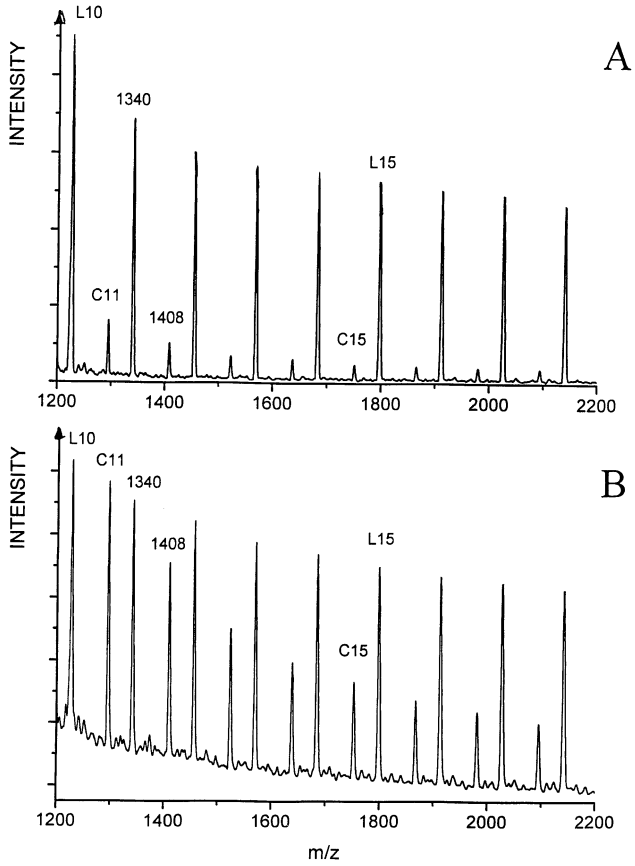


Fig. 2. MALDI-TOF mass spectra (segments) of a poly(ϵ-caprolactone) initiated with $Ge(OEt)_4$ (Table 2): (A) 120 °C/48 h, (B) 180 °C/48 h (C is cycles, L is linear chains of structure **3**).

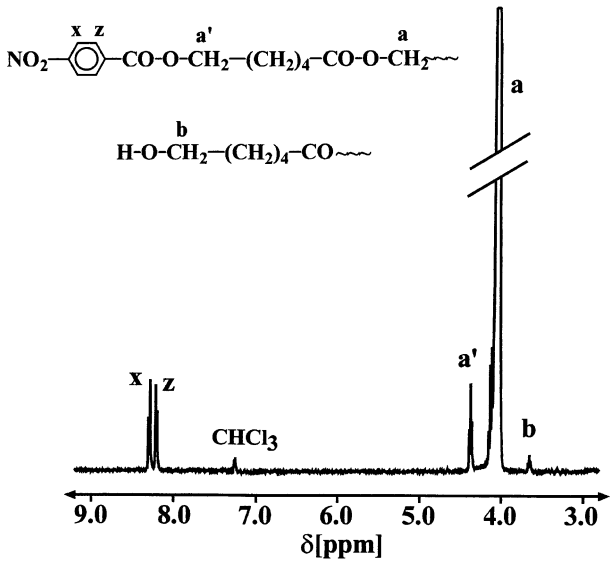


Fig. 3. 400 MHz ^{1}H-NMR spectrum of a poly(ϵ-caprolactone) initiated $Ge(OEt)_4$ at 120 °C (M/I = 100) and reacted with 4-nitrobenzoyl chloride at 120 °C/20 h.

containing more cycles [7] suggests that the cyclic oligomers in the $Ge(OEt)_4$-initiated poly(ϵ-CL) amount to less than 1 mol%. The fraction of cyclic oligomers increased with higher reaction temperatures (Fig. 2). However, when the MALDI-TOF mass spectra of these $Ge(OEt)_4$-initiated polylactones were compared to those Bu_2Sn alkoxide-initiated polymerizations at 60 or 80 °C [8] it seems that the extent of back-biting is considerably lower with $Ge(OEt)_4$ as initiator. This is another characteristic consequence of the lower reactivity of Ge alkoxides. The MALDI-TOF mass spectra also revealed a broad molecular weight distribution similar to that of polycondensates. This result may be explained by the assumption that the four ethoxide groups attached to one Ge atom react at different times, because the increasing number of polylactone chains growing out from one Ge atom represent a higher and higher steric hindrance for the initiation of a new chain. In other words, the four kinds of active species depicted in formulas of Scheme 1 should have different rate constants of the initiation process.

Finally, three polymerizations were repeated at 120 °C with a M/I ratio of 100 and 4-nitrobenzoyl chloride was added after almost complete polymerization of ϵ-CL. The purpose of these experiments was to find out, if a quantitative acylation of the active Ge–O–CH_2 chain ends is feasible to allow for an in situ synthesis of monofunctional oligomers (Eq. (2)). The reaction mixtures were examined by ^{1}H-NMR spectroscopy, and after 4 h a degree acylation around 45% was achieved. After 8 h the acylation reacted 75% and after 20 h 80%. The signal assignments of the isolated polylactone **4** are shown in Fig. 3. These results demonstrate again that the reactivity of the germanium alkoxides is far lower than that of Sn-alkoxides so that a quantitative acylation is much more difficult to obtain.

3.2. Synthesis and use of a spirocyclic initiator *1*

The spirocyclic germanium alkoxide **1** was described as a viscous liquid soluble in inert organic solvents and distillable in a high vacuum [5]. It was prepared by an interchange reaction of $Ge(OEt)_4$ with 1,3-propane diol, but a detailed description of the procedure was not given. In this work $Ge(OEt)_4$ was initially heated with the double molar amount of dry 1,3-propane diol to 160 °C, but even after 6 h the conversion did not exceed 80%. Therefore an excess of 20 mol% of 1,3-propane diol was added and the heating at 160 °C was continued for 6 h. At this point more than 95% of the ethoxy groups were replaced by the 1,3-propane diol. After application of vacuum of 10^{-3} bar the excess of 1,3-propane diol was completely removed. Yet, in contrast to the literature the product did not distill over a short path apparatus, even when the temperature was raised to 180 °C. After cooling a yellowish transparent viscous oil was obtained which was completely soluble in $CDCl_3$. Elemental analyses, ^{1}H and ^{13}C NMR spectra agreed with the expected structure, but around 3 mol% of the ethoxy groups were still present. This crude product was then used as an initiator for the ring-expansion polymerization of ϵ-CL.

Considering the results obtained with $Ge(OEt)_4$ as initiator the first polymerizations initiated with the spirocycle **1** were performed at 120 °C. However, it turned out that **1** was slightly less reactive than $Ge(OEt)_4$, and thus, the temperature was raised to 140 °C. The M/I ratio was varied from 50 to 400 and the reaction time was varied to achieve more than 90% conversion in all experiments (Table 3). In the first

Table 3
Polymerizations of ϵ-caprolactone in bulk at 140 °C initiated by spirocyclic Ge-bis(trimethylene dioxide)

Polymer number	Monomer/Init.	Time (d)	Yield (%)	$\eta_{inh.}$ [b] (dl/g)	Conversion[a] (%)
1	50	1	65	0.16	~ 95
2	100	2	70	0.23	~ 95
3	200	3	85	0.33	≥ 98
4	300	4	80	0.28	≥ 98
5	400	4	84	0.23	≥ 98

[b] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.
[a] Determined by ^{1}H-NMR spectroscopy.

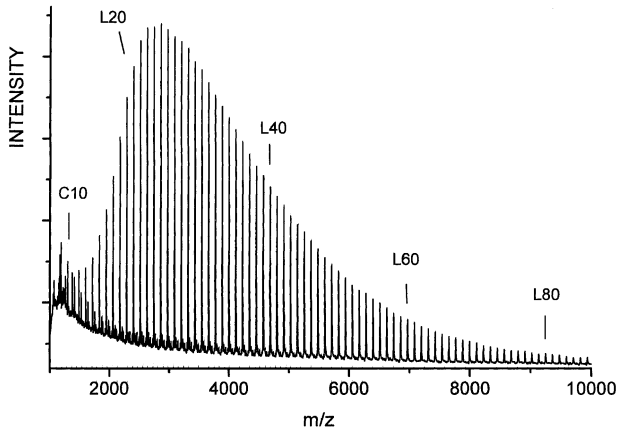


Fig. 4. MALDI-TOF mass spectrum of a poly(ϵ-caprolactone) initiated with the spirocycle **1** (M/I = 100) at 140 °C/24 h (C is cycles, L is linear chains of structure **5**).

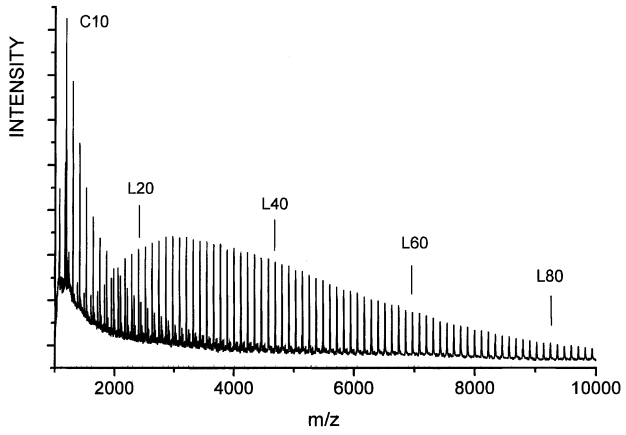


Fig. 5. MALDI-TOF mass spectrum of a poly(ϵ-caprolactone) initiated with the spirocycle **1** (M/I = 200) at 140 °C/48 h (C is cycles, L is linear chains of structure **5**).

three polymerizations the viscosity increased with the M/I ratio as expected for a stoichiometric ring-expansion polymerization according to Eq. (3). However, the viscosities were lower for the last two polymerizations. At least a partial explanation for this result was extracted from the MALDI-TOF mass spectra. As shown in Figs. 4 and 5, these mass spectra indicate that the fraction of cyclic oligomers (resulting from back-biting degradation) dramatically increases with longer reaction times. Another important result of the MALDI-TOF mass spectra is the confirmation that the linear chains have the structure **5** as expected from the ring-expansion polymerization (Eq. (3)) followed by hydrolysis or methanolysis of $Ge–OCH_2$ chain ends (Eq. (4)). The third and most interesting information disclosed by the MALDI-TOF mass spectra are the molecular weight distribution (MWDs) which are quite different from those obtained with $Ge(OEt)_4$ as initiator (Fig. 4). The shape of these MWD curves suggests that all chains were initiated at almost the same time and that the rate constant of the initiation step was similar or somewhat higher than the rate constant of the polymerization steps.

4. Conclusion

The results obtained from three different germanium alkoxides clearly demonstrate that these initiators are far less reactive than tin alkoxides. This conclusion is in perfect agreement with the fact that silicon alkoxides do not show any transesterification activity at all. Hence, germanium shows the expected intermediate position between Si and Sn. This trend is a consequence of the energy difference between LUMO and HOMO which decreases in a group of the periodic table with higher order numbers. This lower energy difference has, in turn, the consequence that the energy of activation for an exchange between a substituent in the HOMO (e.g. OR) and a nucleophic reaction partner coordinated via the LUMO is lower.

The lower reactivity of Ge-alkoxides in the initiation and polymerization processes is paralleled by a lower reactivity in 'back-biting degradation' so that Ge-alkoxide-initiated polylactones contain lower concentrations of cyclic oligolactones than Sn-alkoxide-initiated ones. On the other hand, the lower reactivity of Ge-alkoxides is paralleled by a lower reactivity towards acid chlorides, so that it is difficult to prepare functionalized telechelic oligomers by an in situ combination of ring-opening polymerization and condensation steps. However, the usefulness of a new class of spirocyclic initiator for the ring-expansion polymerization of lactones was demonstrated for the first time and in future publications more reactive spirocyclic initiators of similar structure will be described.

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