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L-Lactide Macromonomer Synthesis Initiated by New Cyclic Tin Alkoxides Functionalized for Brushlike Structures

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ABSTRACT: L-Lactide macromonomers with an incorporated double bond were successfully synthesized by controlled ring-opening polymerization initiated by two new cyclic tin alkoxides (1,1-di-*n*-butyl-stanna-2,7-dioxacyclo-4-heptene and 9,9,20,20-tetrabutyl-8,10,19,21-tetraoxa-9,20-distanna-dispiro[5.5.5.5]docosa-2,14-diene). Initiators and crude reaction mixtures were characterized by NMR. ^{1}H NMR analysis showed that the initiators were completely reacted in the polymerization and that both tin−oxygen bonds were reactive and participated in propagation. The polymerizations were performed in chloroform at 60 °C, and the molecular weight was effectively controlled by adjusting the monomer-to-initiator ratio. The molecular weight distribution was narrow (<1.1) for both high and low molecular weights (3000−72 000 g/mol). A plot of M_n vs conversion was linear up to a conversion of 98%, showing a system propagating in a controlled manner. The kinetic investigation showed that all of the polymerizations were first order in monomer and that no termination reactions occurred during polymerization.

Introduction

L-Lactide is one of the most frequently used monomers for the synthesis of degradable and resorbable materials. The inherent properties are easily modified by varying the molecular architecture of the polymer or by copolymerization with other monomers. Thus, the polymers have applications ranging from soft and flexible materials for sutures to strong materials for bone plate screws.

The most widely used synthetic method for cyclic ester polymerization is ring-opening polymerization (ROP), and many different molecular architectures have been obtained by carefully selecting the initiator system and comonomers. Di-,[1,2] tri-,[3] and multiblock[4,5] copolymers have been synthesized as well as star-shaped structures.[6,7] Synthesis of macromonomers is another tool for developing resorbable polyesters. The incorporation of a double bond into a polylactide chain offers a wide range of possibilities for the synthesis of advanced structures such as comblike[8−10] and brushlike[11] polymers or cross-linked networks. The double bond can be used directly either for polymerization[12,13] or for further functionalization.[14]

In previous papers we have reported on the controlled ROP of 1,5-dioxepan-2-one[15] and L-lactide (L-LA)[16] initiated by a cyclic tin alkoxide (1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane) in solution at 40−60 °C. Kricheldorf and co-workers have used similar cyclic tin alkoxides for the bulk polymerization of lactones at higher reaction temperatures, yielding polymers with somewhat broader molecular weight distributions (PDI).[17,18] The reaction mechanism for tin alkoxides has been carefully investigated;[3,15−19] it proceeds through a coordination−insertion mechanism, yielding stereoregular polymers of controllable molecular weight and narrow PDI.

The aim of this study was to synthesize L-LA macromonomers with a double bond inserted into the main chain, which in a subsequent study will be used for postpolymerization into brushlike polymers. In the present work, two new cyclic tin alkoxides (six- and seven-membered rings) containing a double bond were used as initiators for the synthesis of the desired poly(L-LA) macromonomers. The initiators were characterized by NMR, and their ability to initiate ROP of L-LA was compared to that of a five-membered cyclic tin alkoxide. A series of poly(L-LA) macromonomers with molecular weights ranging from 3000 to 72 000 g/mol were synthesized and characterized by NMR and SEC.

Experimental Section

Materials. L-Lactide (L-LA) (Serva Feinbiochemica, Germany, 98%) was purified by recrystallization in dry toluene and subsequently dried under reduced pressure (10^{-2} mbar) at room temperature for at least 48 h prior to polymerization. Chloroform (Labora Chemicon, Sweden) stabilized with 2-methyl-2-butene was dried over calcium hydride for at least 24 h and distilled under reduced pressure in an inert atmosphere just before use.

Initiators. 1,1-Di-*n*-butyl-stanna-2,7-dioxacyclo-4-heptene (**2/5**) and 9,9,20,20-tetrabutyl-8,10,19,21-tetraoxa-9,20-distanna-dispiro[5.5.5.5]docosa-2,14-diene (**3/6**) were synthesized from dibutyltin dimethoxide and the corresponding diols as described in the literature.[20−22] Initiator **3/6** was recrystallized in dry toluene, and both initiators were distilled over a short-path apparatus under reduced pressure (10^{-3} mbar) before use.

Polymerization of L-Lactide with Initiator 2/5. A silanized round-bottomed flask (25 mL) equipped with a magnetic stirring bar and closed by a three-way valve was used as reaction vessel. For [M]/[I] = 50, 0.590 g (4.09 mmol) of L-LA and 0.026 g (0.082 mmol) of initiator **2/5** were weighed and transferred to a reaction vessel inside a drybox (Mbraun MB 150B-G-I). Freshly distilled chloroform (7 mL) was added to the flask under an inert atmosphere by a flamed syringe. The reaction vessel was immersed into a thermostated heating bath, preheated to 60 °C. The temperature was held constant (±1 °C) using an Ikatron ETS D3 temperature regulator. All glassware was flame-dried before use. ^{1}H NMR and SEC samples for the kinetic and mechanistic investigation were withdrawn from the polymerization mixture at given times by using a flamed syringe while flushing with inert gas (Ar). At full conversion (15 h and 26 min reaction time, conversion:

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98.4% NMR analysis), the reaction mixture was precipitated in cold methanol (or hexane for [M]/[I] < 50). The SEC analysis of the precipitated polymer gave M_n = 13 950 and PDI = 1.05. Yield was 86%.

Polymerization of L-Lactide with Initiator 3/6. A silanized round-bottomed flask (25 mL) equipped with a magnetic stirring bar and closed by a three-way valve was used as reaction vessel. For [M]/[I] = 50, 1.003 g (6.97 mmol) of L-LA and 0.052 g (0.140 mmol) of initiator **3/6** were weighed and transferred to a reaction vessel inside a drybox (Mbraun MB 150B-G-I). Freshly distilled chloroform (14 mL) was added to the flask under an inert atmosphere by a flamed syringe. The reaction vessel was immersed into a thermostated heating bath, preheated to 60 °C. The temperature was held constant (±1 °C) using an Ikatron ETS D3 temperature regulator. All glassware was flame-dried before use. ^{1}H NMR and SEC samples for the kinetic and mechanistic investigation were withdrawn from the polymerization mixture at given times by using a flamed syringe while flushing with inert gas (Ar). At full conversion (reaction time: 15 h and 56 min; conversion: 95.8% NMR analysis), the reaction mixture was precipitated in cold methanol (or hexane for [M]/[I] < 50). The SEC analysis of the precipitated polymer gave M_n = 11 700 and PDI = 1.08. Yield was 83%.

Instrumental Methods. a. Nuclear Magnetic Resonance. The conversion and the molecular weight of L-LA were determined using ^{1}H NMR spectroscopy. The measurements were performed using a Bruker Avance 400 Fourier transform nuclear magnetic resonance spectrometer (FT-NMR) operating at 400 MHz, T = 25 °C, with chloroform-d_1 ($CDCl_3$) as solvent. The samples (25 mg) were prepared in sample tubes with a diameter of 5 mm and dissolved in 0.5 mL of $CDCl_3$. Nondeuterated chloroform was used as an internal standard (δ = 7.26 ppm). ^{1}H NMR spectra of initiator **2/5** were acquired at −13, +7, and +25 °C.

Using a Bruker DMX 500, 2D ^{1}H−^{13}C heteronuclear multiple quantum coherence−gradient selected (invieagssi) spectra were acquired and processed with a standard Bruker microprogram. A total of 256 experiments were accumulated using one scan with a relaxation delay of 2 s. The spectrum was obtained with 9 ppm spectral width over the F_2 (proton) axis and 200 ppm for ^{13}C along the F_1 (carbon) axis at −13 °C.

b. Size Exclusion Chromatography. The changes in molecular weight and PDI during polymerization were determined by size exclusion chromatography (SEC). The analysis was performed at room temperature using a Waters 717plus autosampler and a Waters model 510 apparatus equipped with three PLgel 10 μm mixed-B columns, 300 × 7.5 mm (Polymer Labs., UK). Spectra were recorded with an PL-ELS 1000 evaporative light scattering detector (Polymer Labs., UK) connected to an IBM-compatible PC. Millenium[32] version 3.20 software was used to process the data. Chloroform was used as eluent at a flow rate of 1.0 mL/min. Narrow polystyrene standards in the 1700−706 000 g/mol range were used for calibration.

Results and Discussion

Initiators. The cyclic tin alkoxides **2/5** and **3/6** have been mentioned briefly in the literature.[23] No NMR spectra were reported, although a ^{119}Sn NMR analysis on these initiators showed that the unimer form of initiator **2/5** predominates at room temperature whereas initiator **3/6** is mainly present as a dimer.

In the present work, tin alkoxides **2/5** and **3/6** were characterized by NMR spectroscopy and used for controlled ring-opening polymerization (ROP) of L-LA, yielding L-LA macromonomers. The kinetics of the reactions was compared to earlier reported kinetics of L-LA polymerization initiated with **1/4**. The reaction conditions and the results of the polymerizations are summarized in Tables 1 and 2.

To estimate the differences in steric hindrance of the active Sn−O bond for the two new initiators, the geometries of the unimer forms were optimized using the hybrid density functional method B3LYP[24] using the basis set LANL2DZ as implemented in the Gaussian98 program.[25] This method produces reliable geometries. The geometries were compared with that of the earlier investigated initiator **1/4**. All three tin alkoxides have a tetrahedral geometry, and no major difference in steric hindrance of the active Sn−O bond could be seen (Figure 1), although a more detailed study is needed. The reason for choosing the unimeric forms for optimization is that, at the chosen reaction temperature (60 °C), the three initiators are probably present as unimers.[15]

Table 1. Ring-Opening Polymerization of L-LA with Tin Alkoxide 2/5 as Initiator; Reaction Was Conducted at 60 °C in Chloroform with $[M]_0$ = 0.5 M

polymer	[M]/[I][a]	time (h)	M_n[b]	M_n[c]	M_n[d]	PDI[d]	conv (%)[c]	yield (%)[e]
1	20	6	3 200	3 000	5 900	1.06	98	72
2	50	16	7 520	7 500	14 400	1.07	98	86
3	100	28	14 720	19 700	29 200	1.05	90	83
4	250	71	36 320	39 000	41 800	1.10	78	68
5	500	140	72 320	79 000	104 400	1.09	83	76

[a] Molar feed ratio calculated from the unimeric species. [b] Value calculated assuming living polymerization. [c] Calculated from ^{1}H NMR on crude reaction mixture. [d] Determined by SEC analysis calibrated with polystyrene standards. [e] Amount of polymer formed after precipitation in methanol.

Table 2. Ring-Opening Polymerization of L-LA with Tin Alkoxide 3/6 as Initiator; Reaction Was Conducted at 60 °C in Chloroform with $[M]_0$ = 0.5 M

polymer	[M]/[I][a]	time (h)	M_n[b]	M_n[c]	M_n[d]	PDI[d]	conv (%)[c]	yield (%)[e]
6	20	8	3 250	3 000	4 800	1.07	95	40
7	50	16	7 570	7 300	11 700	1.11	96	83
8	100	32	14 770	14 400	21 300	1.11	95	78
9	500	160	72 370	72 500	52 200	1.08	65	63

[a] Molar feed ratio calculated from the unimeric species. [b] Value calculated assuming living polymerization. [c] Calculated from ^{1}H NMR on crude reaction mixture. [d] Determined by SEC analysis calibrated with polystyrene standards. [e] Amount of polymer formed after precipitation in methanol.

NMR Analysis of Initiators. The ^{1}H NMR spectrum (T = 25 °C) with assignments of initiator **2/5** is shown in Figure 2 together with two ^{1}H NMR spectra obtained at lower temperatures (7 and −13 °C). The peak at δ = 5.82 was assigned to the protons of the double bond. The peak appearing at δ = 4.49 originated from the two $-O-CH_2-$ groups in the initiator. Peaks a and b appeared to be broad single peaks, but on lowering the temperature both peaks split. To fully understand this behavior, a ^{1}H−^{13}C hmqc-gs spectrum was recorded (Figure 3), from which it became clear that the splitting of the signals originated from a fast equilibrium between **2** and **5**. At room temperature, the rate of exchange between the monomeric and dimeric forms was too fast for the signals to be resolved.

The ^{1}H NMR spectrum (T = 25 °C) of initiator **3/6** with assignments is shown in Figure 4. The two peaks emerging at δ = 5.65 and δ = 5.60 originated from the $-CH{=}CH-$ group. The broad peaks c and c′ appearing at δ = 3.60−3.72 were assigned to the diastereotopic protons in the $-O-CH_2-$ group in the initiator. The signal from the two protons closest to the double bond was assumed to be the most downfield shifted signal. Higher oligomers are probably also present to a less extent, causing the broadening to the left of the two peaks. Two additional spectra were recorded at lower

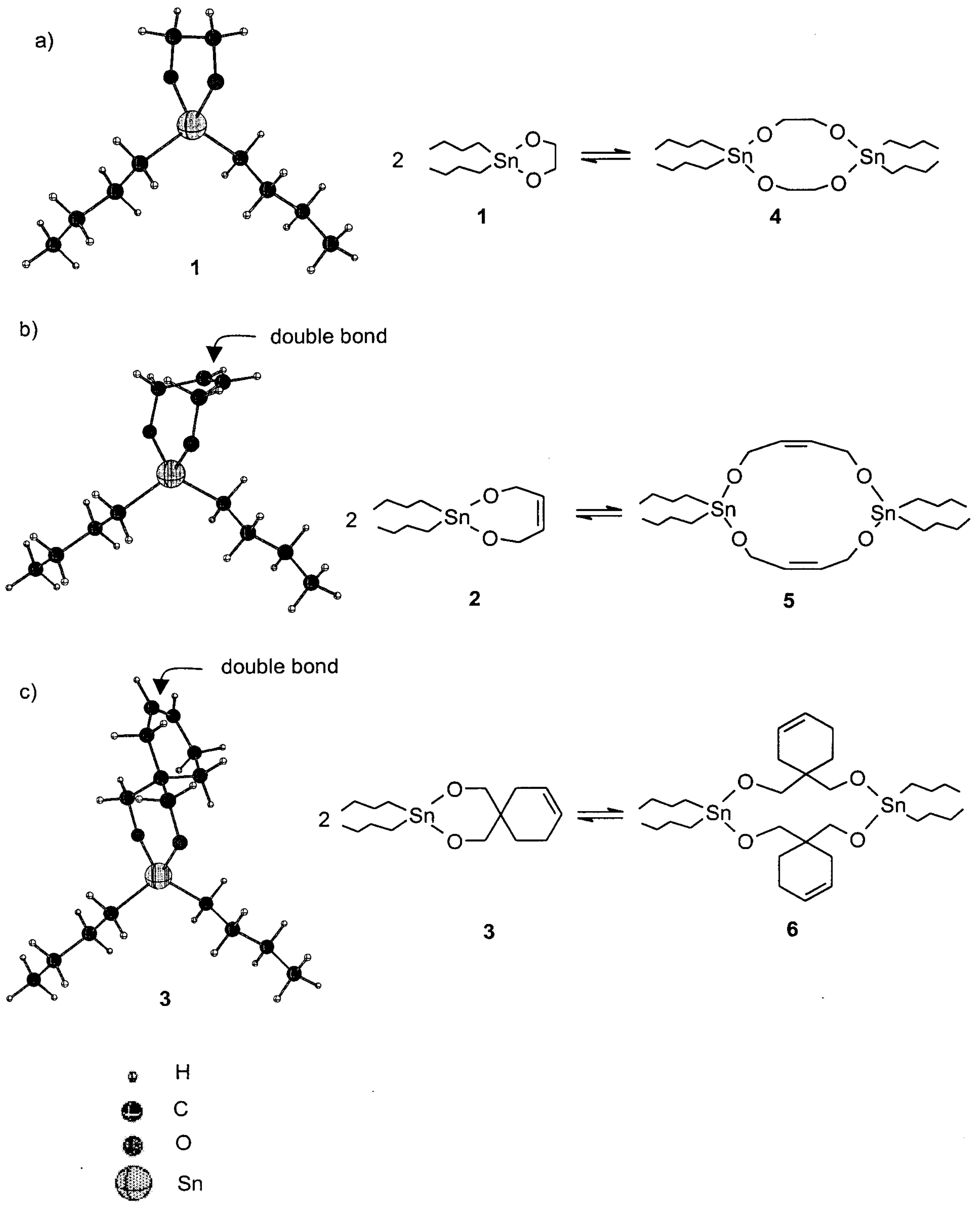
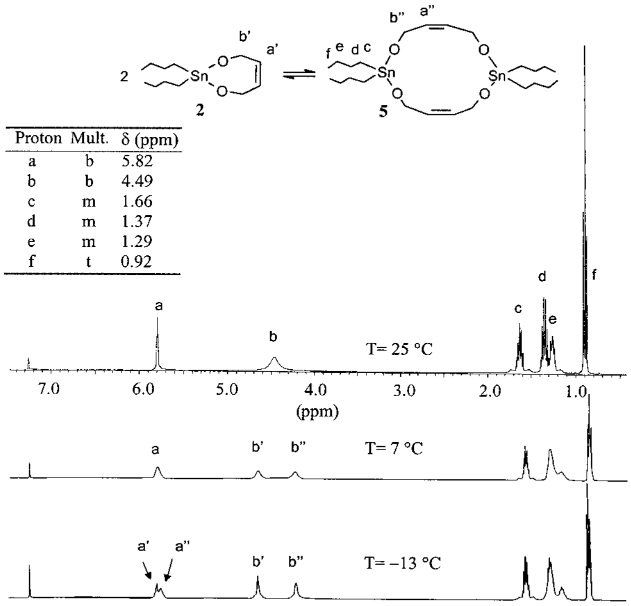


Figure 1. Optimized geometries of the unimer forms of cyclic tin initiators together with their molecular structure.

temperatures, +7 and −13 °C, but this lowering of the temperature did not affect the spectrum as it did with initiator **2/5**. This is because the rate of exchange between **3** and **6** is slow enough for the peaks to be resolved at 25 °C. Kricheldorf has reported the same observation for similar cyclic tin alkoxides.[17]

The dimerization equilibrium of **1/4** results from conformational strain in the five-membered ring of **1** due to an almost ecliptic position of the CH_2 groups in the ring and the bond angle deformation at tin. However, this argument does not hold for the unsaturated initiators. Instead, the possibility for initiator **2/5** and **3/6** to dimerize is most likely due to the favorable Sn−O donor−acceptor interactions, known for all tin alkoxides.[26]

Polymerizations. A series of polymerizations of L-LA with initiator **2/5** and initiator **3/6** were carried out in chloroform at 60 °C with an initial monomer concentration of 0.5 M. The monomer-to-initiator ratio ([M]/[I]) was varied from 20/1 up to 500/1 for both initiators. Samples were withdrawn regularly from the reaction mixtures and analyzed by ^{1}H NMR and SEC



Proton	Mult.	δ (ppm)
a	b	5.82
b	b	4.49
c	m	1.66
d	m	1.37
e	m	1.29
f	t	0.92

Figure 2. ^{1}H NMR spectrum of initiator **2/5** at different temperatures: (a) 25, (b) 7, and (c) −13 °C.

to study the mechanism and kinetics of the two different polymerization systems. The conversions were nearly complete for all polymers, especially at the lower [M]/[I] ratios. In the NMR analysis, the molecular weight was determined by comparing the integrals of the peak from the $-CH{=}CH-$ group of the initiator ($\delta = 5.8$ ppm for **2/5** and $\delta = 5.6-5.7$ ppm for **3/6**) with the peak from the methine protons in the PLLA chain ($\delta = 5.1-5.2$ ppm). In Figure 5 the absolute number-average molecular weight, M_n, is plotted vs the [M]/[I] feed ratio for L-LA polymerization initiated by **2/5**. The relationship was linear over the entire range of [M]/[I] ratios and the increase in monomer-to-initiator is proportional to the increase in M_n. For both systems, the mild reaction conditions resulted in controllable molecular weight and a narrow molecular weight distribution (PDI) (Tables 1 and 2). This agrees with our earlier reported results on solution polymerization initiated with **1/4**[15,16] but is contrary to previously reported results on bulk polymerization.[17] There is a discrepancy between M_n values determined by SEC and by NMR in Tables 1 and 2, which is explained by the use of polystyrene standards for SEC calibration. The values from the SEC analysis are mainly used for monitoring the change in molecular weight and PDI with conversion. The NMR analysis gave M_n values very close to the calculated M_n, even though there were some minor deviations at higher molecular weights due to detection limitations in the NMR analysis.

Mechanism and Kinetics. The crude reaction mixtures were analyzed by ^{1}H NMR to investigate whether the initiators were completely reacted during the polymerization. The crude reaction mixture spectra together with the spectrum of pure initiator are shown in Figures 6 and 7. In both cases, the signal from the unreacted initiator ($\delta = 4.49$ and $\delta = 3.60$) rapidly disappeared and was no longer detectable after 15 min of reaction. In Figure 6, the peak from the incorporated

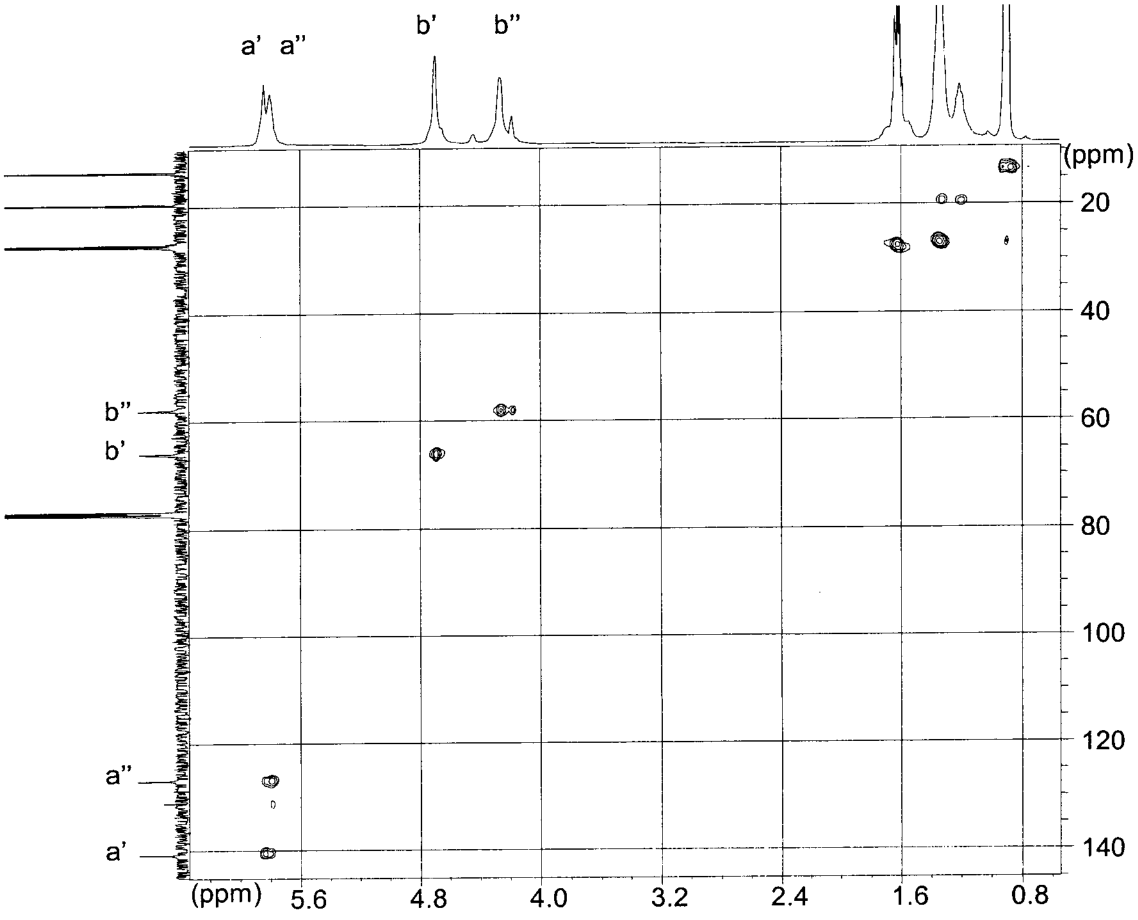
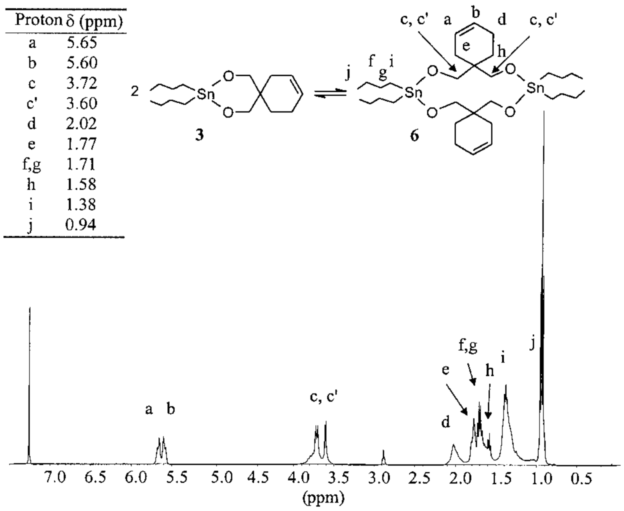


Figure 3. 2D hmqc-gs spectrum of initiator **2/5** at −13 °C. F1 = conventional ^{13}C NMR spectrum; F2 = conventional ^{1}H NMR spectrum.



Proton	δ (ppm)
a	5.65
b	5.60
c	3.72
c'	3.60
d	2.02
e	1.77
f,g	1.71
h	1.58
i	1.38
j	0.94

Figure 4. ^{1}H NMR spectrum of initiator **3/6** at 25 °C.

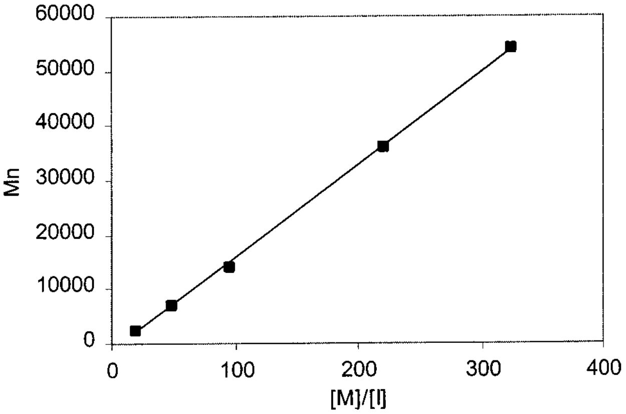
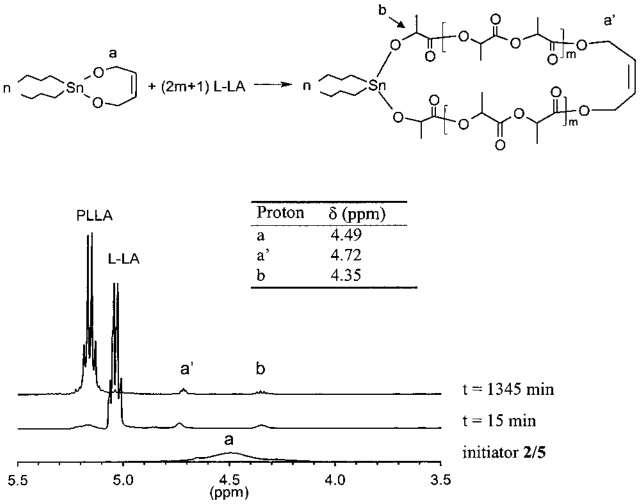


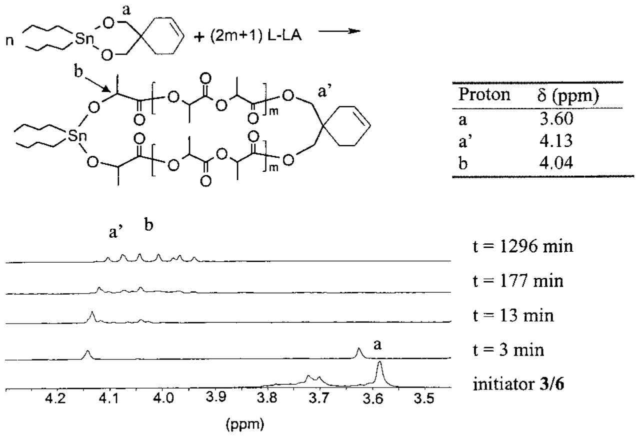
Figure 5. Number-average molecular weight (M_n) determined by ^{1}H NMR as a function of [M]/[I] for L-LA polymerization initiated by **2/5**. [M]/[I] has been corrected for conversion.



Proton	δ (ppm)
a	4.49
a'	4.72
b	4.35

Figure 6. ^{1}H NMR spectrum of L-LA polymerization initiated with **2/5** in chloroform, [M]/[I] = 20, and $[M]_0 = 0.5$ mol L^{-1}.

$-\mathrm{C}H_2\mathrm{CH{=}CHC}H_2-$ group from initiator **2/5** appeared at $\delta = 4.72$ together with an additional peak at $\delta = 4.35$ originating from the $-\mathrm{O}-\mathrm{CH_2}-$ group directly attached to the tin atom. In Figure 7, the signal from the incorporated alkene chain originating from initiator **3/6** appeared at $\delta = 4.13$ together with an additional peak at $\delta = 4.04$ originating from the $-\mathrm{O}-\mathrm{CH_2}-$ groups directly attached to the tin atom. These results confirm that the alkoxide groups in both initiators were completely reacted under these reaction conditions, which is consistent with earlier investigations with the similar initiator **1/4**.[16]



Proton	δ (ppm)
a	3.60
a'	4.13
b	4.04

Figure 7. ^{1}H NMR spectrum of L-LA polymerization initiated with **3/6** in chloroform, [M]/[I] = 20, and $[M]_0 = 0.5$ mol L^{-1}.

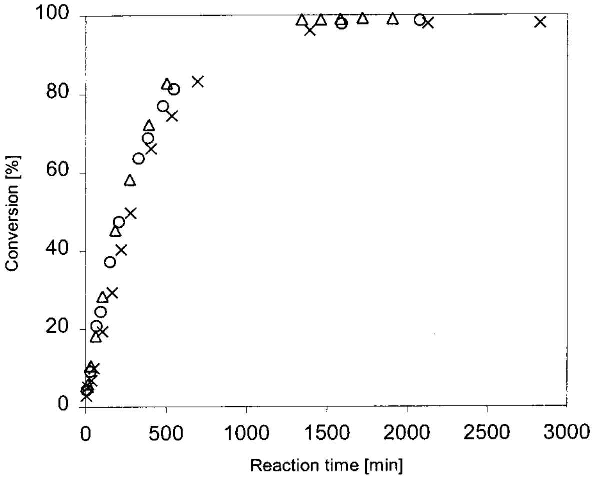


Figure 8. Conversion of L-LA as a function of reaction time. [M]/[I] = 50. Polymerization initiated with initiator **1/4** (△), initiator **2/5** (○), and initiator **3/6** (×).

The L-LA macromonomer formed should contain a double-bond residue from the initiator in the middle of the backbone chain. ^{1}H NMR analysis of all of the precipitated macromonomers revealed that the double bond had been incorporated into the polymer chain, resulting in a peak emerging at $\delta = 5.72$ from the residue of initiator **2/5** and at $\delta = 5.67$ from the residue of initiator **3/6**. This double bond is well-suited for postpolymerization into a brushlike polymer.

The conversion of L-LA is plotted in Figure 8 against the reaction time for polymerizations initiated by the three different initiators **1/4**, **2/5**, and **3/6** under identical reaction conditions. No induction period could be observed for any of the polymerizations, and the rates of the different polymerizations are very similar. No severe backbiting seemed to occur after the reaction was completed in any of the three cases. A more thorough investigation of the reaction after full conversion was performed on the polymer initiated by **2/5**. The crude reaction mixture was kept at 60 °C after full conversion, and samples were withdrawn regularly and analyzed by SEC to monitor any depolymerization or transesterification reactions. The investigation did not show any major change in molecular weight for the first 10 h

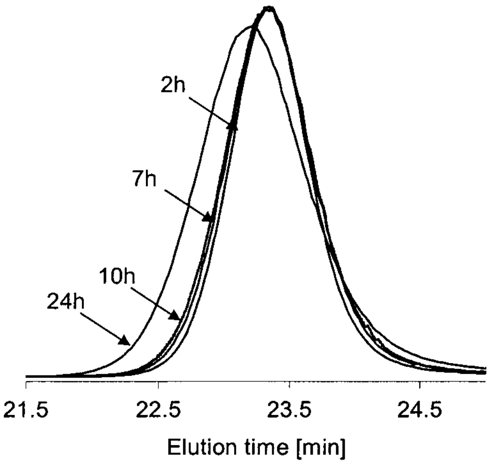


Figure 9. SEC chromatograms of continued polymerization initiated by **2/5** after 2, 7, 10, and 24 h of full conversion.

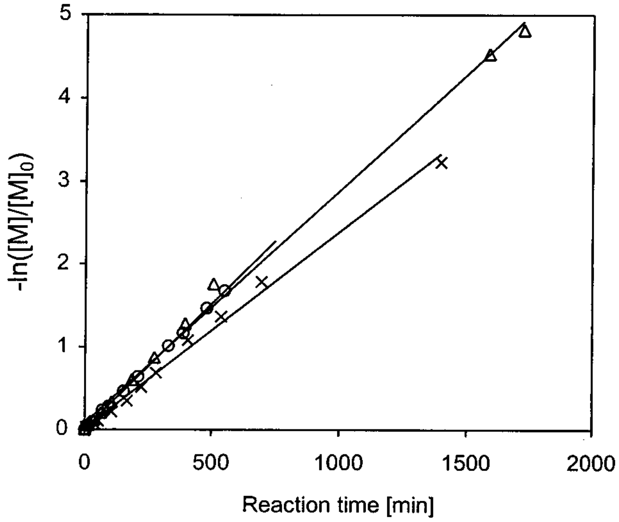


Figure 10. Semilogarithmic plots of L-LA monomer conversion expressed as $-\ln([M]/[M]_0)$ vs reaction time for polymerization initiated with (△) initiator **1/4**, [M]/[I] = 50 (○) initiator **2/5**, [M]/[I] = 50 (×) initiator **3/6**, and [M]/[I] = 50 as monitored by ^{1}H NMR spectroscopy in $CDCl_3$.

of full conversion, showing that under these mild reaction conditions the depolymerization and transesterification reactions are less pronounced. After an additional 14 h, however, the elution curve is broadened and shifted to higher molecular weights (Figure 9) as a result of transesterification reactions. The monomer (or oligomer) content did not increase during these 24 h; in other words, no backbiting was detected. The results were similar for polymerization initiated with **3/6**.

Figure 10 shows the semilogarithmic plot of $-\ln([M]/[M]_0)$ vs the reaction time *t* for polymerizations initiated by the different initiators, where $[M]_0$ is the initial monomer concentration and [M] is the monomer concentration at reaction time *t*. The plot shows that all of the polymerizations are first order in monomer when initiated at 60 °C in chloroform. For the three different initiators, [M]/[I] = 50 was used. The linearity of the plot for all polymerizations shows that no termination reaction occurred during polymerization; i.e., the number of propagating chains was constant throughout the reaction.

The influence of monomer conversion on molecular weight and PDI for polymerizations initiated with **2/5** and **3/6** is illustrated in Figures 11 and 12, respectively.

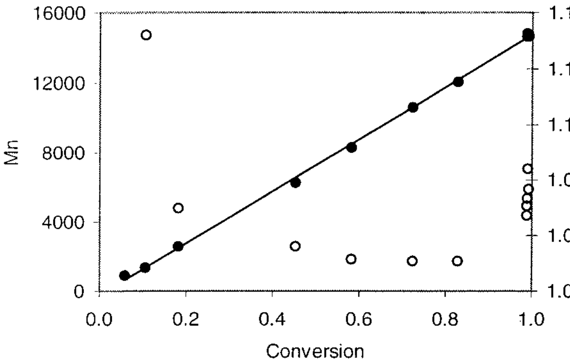


Figure 11. Relationship between the number-average molecular weight (M_n), polydispersity (PDI), and the degree of monomer conversion for the polymerization of L-LA in chloroform at 60 °C, $[M]_0$ = 0.5 M initiated by **2/5**. (●) Represents M_n, and (○) represents PDI, determined by SEC analysis calibrated with polystyrene standards.

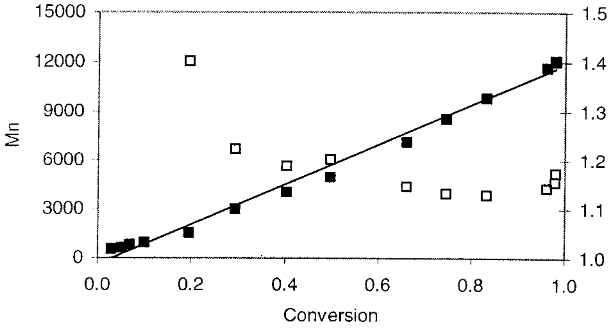


Figure 12. Relationship between the number-average molecular weight (M_n), polydispersity (PDI), and the degree of monomer conversion for the polymerization of L-LA in chloroform at 60 °C, [M]0 = 0.5 M initiated by **3/6**. (■) Represents M_n, and (□) represents PDI, determined by SEC analysis calibrated with polystyrene standards.

A plot of M_n vs conversion was linear up to a conversion of 98%, illustrating a system propagating in a controlled manner. The same behavior has been reported for L-LA polymerization with **1/4** and for ϵ-caprolactone initiated with zinc alkoxides.[27] Polymerization initiated with **2/5** had a very narrow PDI throughout the reaction, PDI ~1.05, whereas the PDI of the polymerization initiated with **3/6** was slightly broader, ~1.1–1.2. Polymerization initiated with **1/4** has been reported to have PDI ~1.1.[16] The difference between initiator **2/5** and **3/6** is more pronounced at higher [M]/[I], which demands longer reaction times, and in this case initiator **3/6** seems to be less hydrolytically stable than **1/4** and **2/5**.

Conclusion

The new cyclic tin alkoxides **2/5** and **3/6** were used to initiate controlled ring-opening polymerization (ROP) of L-LA, yielding a series of L-LA macromonomers. Both initiators contained a double bond, which was successfully incorporated into the synthesized macromonomers. This double bond is well-suited for postpolymerization into a brushlike polymer and will be investigated in the near future. The mild reaction conditions resulted in controllable molecular weight and in narrow molecular weight distributions with both initiators.

No induction period was observed, and the rates of the different polymerizations were all very similar. The kinetic investigation showed that all polymerizations were first order in monomer and that no termination reactions occurred during polymerization. A plot of M_n

vs conversion was linear up to a conversion of 98%, illustrating a system propagating in a controlled manner. No major change in molecular weight or PDI could be detected during the first 10 h after reaching full conversion. This showed that under these mild reaction conditions the depolymerization and transesterification reactions were less pronounced. The new initiators investigated in this study have essentially the same characteristics as initiator **1/4** for initiating L-LA polymerization.

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