Mechanism of Cyclic Ester Polymerization Initiated with Tin(II) Octoate. 2.[†] Macromolecules Fitted with Tin(II) Alkoxide Species Observed Directly in MALDI−TOF Spectra

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ABSTRACT: Polymerization of ϵ-caprolactone (CL) initiated with tin(II) octoate (tin(II) 2-ethylhexanoate, ($Sn(Oct)_2$)) in the presence of butyl alcohol (BuOH) or water and conducted in tetrahydrofuran (THF) as a solvent at 80 °C was studied using MALDI−TOF mass spectrometry. Formation of the following populations of macromolecules was revealed: $Bu[O(O)C(CH_2)_5]_nOSnOct$, $Bu[O(O)C(CH_2)_5]_nOct$, $Bu[O(O)C(CH_2)_5]_nOH$, $H[O(O)C(CH_2)_5]_nOct$, $H[O(O)C(CH_2)_5]_nOH$, macrocyclics $[O(O)C(CH_2)_5]_n$, and macrocyclics with incorporated tin(II) alkoxide moieties $[O(O)C(CH_2)_5]_nOSn$. Thus, the most rewarding has been a direct observation of species with a tin atom covalently bonded with the polyester chain, at least for two populations of macromolecules (i.e., $Bu[O(O)C(CH_2)_5]_nOSnOct$ and $[O(O)C(CH_2)_5]_nOSn$ cyclics). Identification of the tin-containing macromolecules was based not only on the agreement between the observed *m*/*z* and the calculated molar mass values but also on the particular isotopic distribution provided by the tin atom. This result is in favor of the mechanism postulating propagation on the tin(II) alkoxide as the active center.

Introduction

Covalent metal carboxylates, particularly tin(II) octoate (tin(II) 2-ethylhexanoate ($Sn(Oct)_2$), belong to the most frequently used initiators for polymerization of cyclic esters (see, for example refs 1−19). The most advocated mechanism is a direct catalytic action of $Sn(Oct)_2$.[3,5,7,12] Thus, $Sn(Oct)_2$ has been proposed to activate monomer, i.e., forming a donor−acceptor complex which further participates directly in propagation. $Sn(Oct)_2$ is liberated in every act of propagation. It follows from this mechanism that Sn(II) atoms are not covalently bound to the polymer chain at any stage of polymerization.

In another mechanism proposed, $Sn(Oct)_2$ reacts with compounds (purposely added or adventitiously present in the reacting mixture) containing hydroxide groups and gives an actual initiator, i.e., tin(II) alkoxide or hydroxide.[1,11,14,17−19] Then, the elementary reaction of the polyester chain growth was assumed to proceed via monomer insertion as for the other metal alkoxide active centers. However, neither kinetic nor spectroscopic data are available to support this mechanism, mostly proposed earlier on the basis of the secondary evidence. In our recently published preliminary paper[17] we presented, among other data, results of MALDI−TOF experiments for poly(ϵ-caprolactone) (PCL), prepared with $Sn(Oct)_2$. Various end groups were detected and their proportions depend on the ratio of components forming the actual initiator. These phenomena will be analyzed elsewhere.[20] The most awarding has been, however, direct observation of the Sn(II)-containing species incorporated at the end groups in one of the populations of macromolecules. It looks to us that this is the first observation by MALDI−TOF of the active species in polymerization. In this paper, we describe these facts in more detail as well as report the observation of cyclic macromolecules of PCL comprising in the same way the Sn(II) atoms. Mass spectra of PCL and poly(lactide)s have already been published, but in none of these papers have metal−alkoxide active centers been detected (see for example refs 21, 22 (FAB) and 14, 23, 24 (MALDI−TOF)).

Experimental Section

Substrates and Solvents. Tin octoate ($Sn(Oct)_2$) commercial product (from Sigma, Aldrich or ABCR (Karlsruhe, Germany)) containing about 4.5 wt % (i.e., 10.6 mol %) of 2-ethylhexanoic (octanoic) acid and up to 0.5 wt % (i.e., 9.5 mol %) of H_2O shows in ^1H NMR spectra the presence of acidic protons (for example from octanoic acid and H_2O) at $\delta = 11.10$ ppm. Their content, depending on the supplied sample, and calculated from the relative intensity of the NMR signals, reached 30 mol % (relative to the sum of $Sn(Oct)_2$ and octanoic acid concentrations). Two consecutive high vacuum distillations resulted in $Sn(Oct)_2$ showing in the NMR spectra 1.8 mol % of the acidic protons (fraction distilling at 140 °C/3×10^{-3} mbar). Thus, the concentration of acidic protons decreased almost 20 times. This was, in our hands, the limit of the $Sn(Oct)_2$ purity we could obtain with vacuum distillations. Further removal of the protonic impurities was based on several distillations of dry THF (20 v/v) in and out of the sample under vacuum. The content of the impurities was reduced in this way further down to 0.9 mol % (i.e., ∼40 times from the original sample). Thus, purified $Sn(Oct)_2$, kept all of the time on the vacuum line, was finally distributed directly into thin-walled vials or ampules equipped with break-seals, sealed off, and stored at −12 °C.

ϵ-Caprolactone (CL, from Aldrich) was distilled under reduced pressure (80 °C/1 mbar) from calcium hydride and stored in vacuo over 4 Å molecular sieves. Just before use, CL was purified by two consecutive distillations to ampules with fresh Na mirrors, and finally it was distributed into ampules equipped with break-seals.

***n*-Butyl alcohol** (BuOH, from Aldrich) was dried with Na metal and distributed by vacuum distillation into the thin-walled vials or ampules equipped with break-seals.

[†] For part 1 of this series: see ref 18.

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Tin(II) butoxide ($Sn(OBu)_2$) was prepared in a two-step synthesis according to the method described in ref 25. In the first step $SnCl_2$ was reacted with CH_3OH, in the presence of $(CH_3)_3N$ as the HCl scavenger. The resulting $Sn(OCH_3)_2$, insoluble in the reaction mixture, was then "transalkoxidized" with butyl alcohol, giving eventually $Sn(OBu)_2$, which finally was crystallized from toluene, dried in vacuo, and distributed into the thin-walled break-seals.

$BuO[C(O)(CH_2)_5O]_nH$. Butoxyhydroxytelechelic poly(ϵ-caprolactone) (PCL) of the assumed molar mass (i.e., M_n controlled by the consumed monomer to transfer agent concentrations ratio) was prepared by the CL polymerization initiated with $Sn(OBu)_2$ and with BuOH as a transfer agent. Polymerization conditions: $[CL]_0 = 2.0$ mol·L^{-1}, $[Sn(OBu)_2]_0 = 0.01$ mol·L^{-1}, $[BuOH]_0 = 0.40$ mol·L^{-1}, C_6H_6 as a solvent, and 25 °C. The resulting PCL, after deactivation of the growing species with 2 N HCl_{aq} was washed with distilled water (up to neutral pH) and lyophilized under reduced pressure.

Tetrahydrofuran (THF) (from POCh, Gliwice, Poland) was kept, after the usual purification, over liquid Na−K alloy, from which it was distilled in vacuo just before use.

Polymerization Procedures. Polymerizing mixtures were prepared in sealed glass ampules or dilatometers, using standard high vacuum techniques.

Determination of Monomer Conversion. Conversion of CL was determined using dilatometric method. Dilatometric readings were occasionally confirmed by size exclusion chromatography (SEC) measurements.

SEC traces were recorded using a LKB 2150 HPLC pump and a set of TSK Gel columns (G 2000 HXL and 6400 HXL). A Wyatt Optilab 903 interferometric refractometer and a MALLS Dawn F laser photometer (both Wyatt Technology Corp., Santa Barbara, CA) were applied as detectors in a series. Methylene chloride was used as an eluent. A flow rate of 0.8 mL·min^{-1} was applied.

Determination of Molar Masses (M_n) and of Polydispersity Indexes (M_w/M_n). The actual number-average molar masses (M_n) of PCL were determined using the calibration method described already by us[26] and based on the PCL standards prepared in our laboratory (for the molar masses up to $M_n = 2 \times 10^4$). M_n values higher than 10^4 were directly determined with a MALLS Dawn F laser photometer detector (Wyatt Technology Corp., Santa Barbara, CA) giving the actual values of molar masses.

MALDI−TOF Mass Spectrometry. Mass spectrometric measurements were performed using a Voyager-Elite (PerSeptive Biosystems, Framingham, MA) time-of-flight instrument equipped with a pulsed N_2 laser (337 nm, 4 ns pulse width) and time-delayed extraction ion source. An accelerating voltage of 20 kV was used. Mass spectra were recorded in the reflector mode. The matrix, 2,5-dihydroxybenzoic acid, was dissolved in purified THF (10 mg·mL^{-1} and the solution was mixed with the polymerizing mixture (monomer concentration in the feed: 1.0 mol·L^{-1}) in a 25:1 v/v ratio. The mixture was dried on a stainless steel covered by the gold metal target.

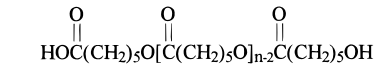
Results and Discussion

Successful observation by MALDI−TOF of Sn(II)-containing species bound to the polymer chains was preceded by a number of unsuccessful attempts. Eventually, we have understood that there are at least two prerequisites to be fulfilled. First, the starting concentration of $Sn(Oct)_2$ has to be high enough, and second, the ultimate care has to taken in preparing and handling the polymer solution. A high starting concentration of $Sn(Oct)_2$ is needed to have macromolecules with M_n low enough. Only in this instance do Sn isotopes (cf. further) introduce their fingerprint into the macromolecules. If there is too much water in the system, then the Sn(II)−O bonds would hydrolyze before the MALDI experiment is conducted.

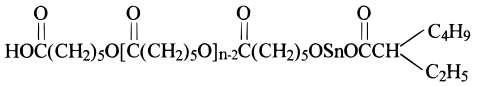
Isotopic Distribution Effect—Calculated Mass Spectra. The mass spectra of compounds containing Sn atoms are particularly easy to recognize, because they form a characteristic pattern, which cannot be mistaken for any other structure. These distinctive patterns result from the unique distribution of ten, naturally abundant, Sn isotopes which are present in comparable concentrations.[27] The carbon atoms, consisting mostly of 98.9% and 1.1% of the ^{12}C and ^{13}C isotopes, respectively, also give rise to the specific arrangement of the mass spectra peaks. On the other hand, the natural abundances of various hydrogen and oxygen isotopes are so low that they can be neglected, at least in the present analysis of the mass spectra.

Using the computer IsoPro3.0 program, available from the Internet,[28] it is possible to compute the molar mass distribution expected for a given compound containing tin atoms and then compare the resulting pattern with the experimental mass spectrum. However, the latter have to be recorded in the reflector mode, to ensure a resolution on the level of the individual isotopic peaks.

For example, in Figure 1 are compared the calculated molar mass distributions for the linear oligomers of CL: $HO(CL)_nH$ and $HO(CL)_nSnOct$ having structures as follows:



($HO(CL)_nH$)



($HO(CL)_nSnOct$)

All traces in Figure 1 have been normalized to the identical surface area; i.e., they correspond to the same concentration of the respective species. As is clearly seen, the presence of the Sn atoms causes at least two effects: splitting the signal into the higher number of peaks, in comparison with the Sn-free counterpart, and decreasing considerably the signal height. This results from a combination of the isotopic distribution of both tin and carbon atoms.

When the molar mass increases, then the influence on the total pattern resulting from the presence of Sn atom decreases. It is seen that the "multiplicity" of signals due to the presence of various Sn isotopes can be used as a tool of the quantitative analysis only for the relatively short chains, with molar masses not exceeding a few thousands. Moreover, analysis of the real spectra is complicated by the aparature broadening of the individual peaks and their deformation by the noise signals. Therefore, the detection threshold, related to the analysis of the signals shapes, is equal to the molar mass of about 2000. Further rectification of the MALDI spectrometry will certainly shift this value significantly up.

It has also to be noted that the mass spectrum signals, obtained in the reflector mode, are marked usually at the peak of the maximum intensity, which position (M_{max}) in general, does not correspond to the average molar mass ($M_{av} = \sum w_i M_i$, where w_i and M_i denote the weight fraction and molar mass of the ith isotope, respectively). The respective M_{max} value can be pre-

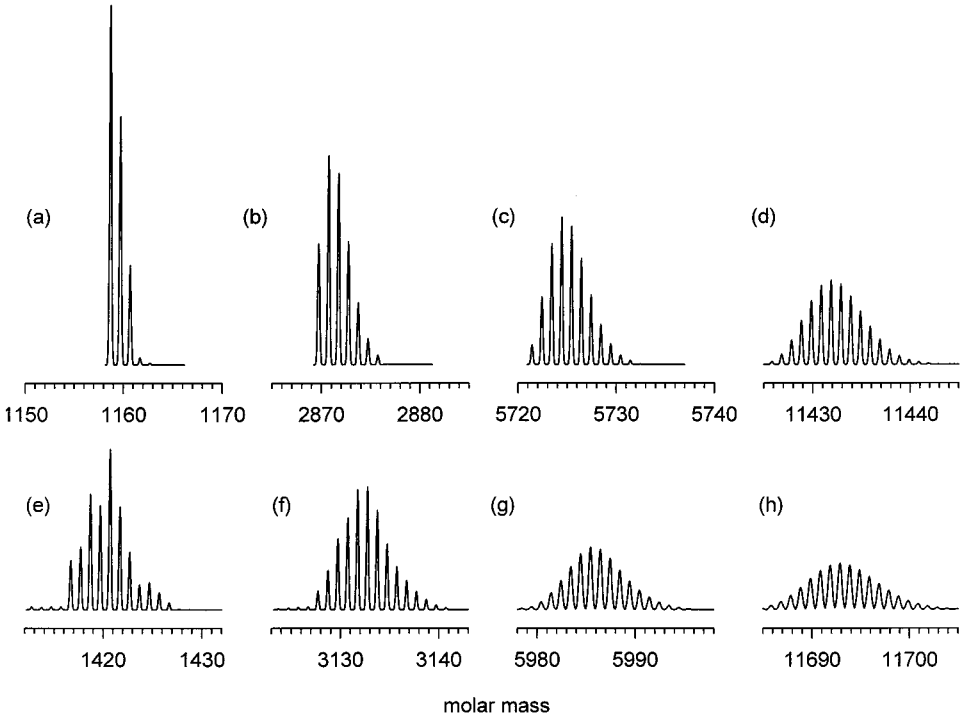


Figure 1. Comparison of the computed molar masses distribution for the ϵ-caprolactone oligomers: (a−d) HO $[(O)C(CH_2)_5O]_nH$ and (e−h) $HO[(O)C(CH_2)_5O]_nSnOct$ chains; (a, e) $n = 10$, (b, f) $n = 25$, (c, f) $n = 50$, and (g, h) $n = 100$.

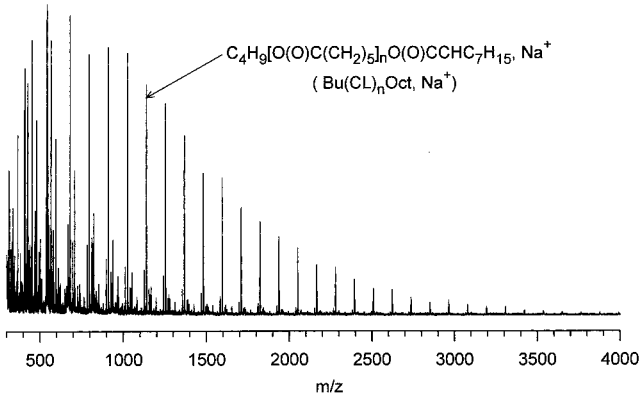


Figure 2. MALDI−TOF spectrum of the ϵ-caprolactone/tin octoate/butyl alcohol reacting mixture. Polymerization conditions: $[CL]_0 = 0.95$ mol·L^{-1}, $[Sn(Oct)_2]_0 = 1.0$ mol·L^{-1}, and $[BuOH]_0 = 0.15$ mol·L^{-1}; in THF solvent, at 80 °C.

dicted from the isotopic distribution computed for a given compound. This fact has to be taken into account during the calibration procedure of the spectrometer; i.e., it is necessary to introduce the M_{max} value for the standard compound used for the calibration.

MALDI−TOF Analysis of the Living CL/Sn(Oct)$_2$/BuOH System. Figures 2 and 3 show the MALDI−TOF mass spectra of PCL, prepared with $Sn(Oct)_2$/BuOH initiating system in THF solvent (a similar spectrum was already presented in our preliminary note[17]). For this sample of PCL, $M_n = 800$ and $M_w/M_n = 1.78$ were determined by the size exclusion chromatography (SEC), whereas $M_{CL}[CL]_0/[BuOH]_0 + M_{BuOH} + M_{Oct} = 924$ (the latter calculation does not take into account formation of the cyclic oligomers fraction).

In the full spectrum, given in Figure 2, a series of signals dominate, which can be ascribed to the Bu-$(CL)_n$Oct oligomers doped with Na^+ ions. A more detailed picture, presented on the fragment of the spectrum for molar masses from 1000 to 1550, revealed

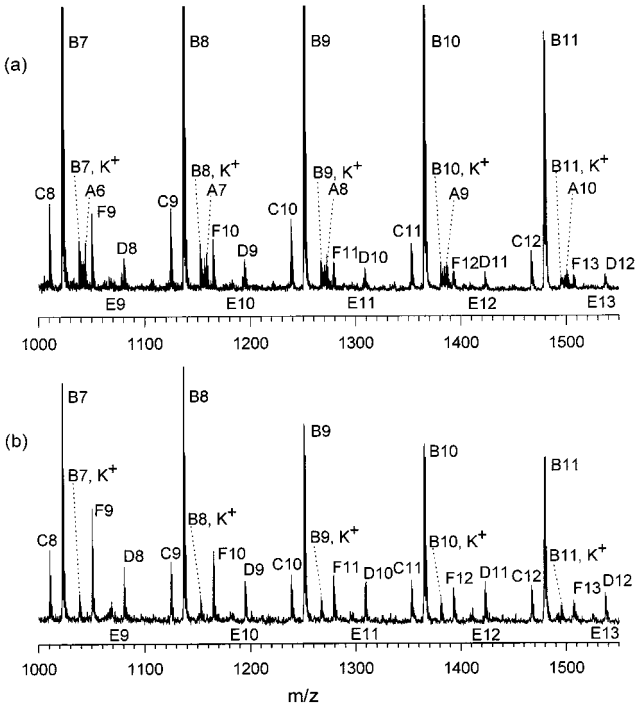


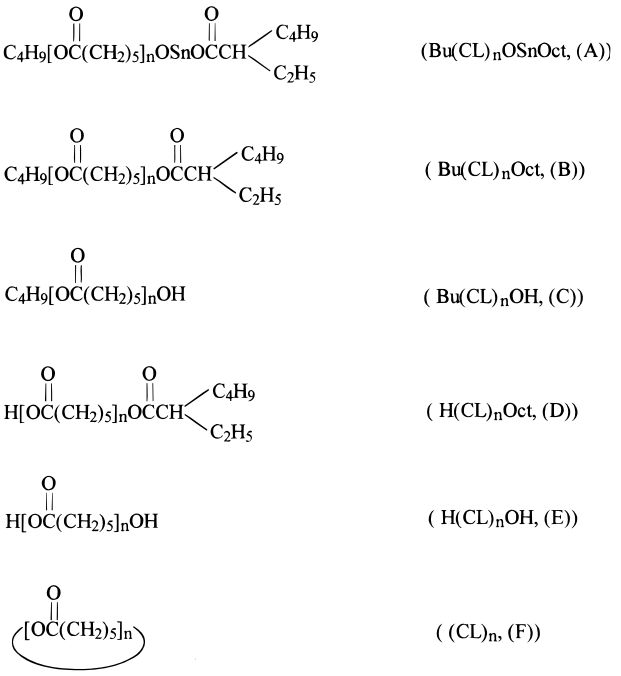
Figure 3. Comparison of the 1000−1550 *m/z* fragments of the MALDI−TOF spectra the ϵ-caprolactone/tin octoate/butyl alcohol reacting mixture recorded under the living conditions (a) and after the HCl_{aq} treatment (b). Polymerization conditions are given in the caption for Figure 2. If the cation is not shown, then the corresponding macromolecule is doped with Na^+.

formation of at least six different populations of macromolecules in the CL/$Sn(Oct)_2$/BuOH reacting system (Figure 3, where trace a was recorded for the virgin reacting mixture and trace b for the reacting mixture treated with 2 N HCl_{aq}).

Assignments are given directly in the mass spectra, according to the notation given below. All signals

marked in Figure 3 correspond to the macromolecules doped with Na^+, except for one series coming from the K^+ adducts (i.e., B, K^+), which is indicated separately.

Besides, in Table 1 are given (for two representative series of A−F oligomers) the calculated average (M_{av}) molar masses and these computed[28] for the isotopic peak of the maximum intensity (M_{max}). Thus, the obtained M_{av} and M_{max} are compared with molar masses determined experimentally (M_{exp}) from the MALDI spectrum as the *m*/*z* value for the isotopic peak of the maximum intensity in a given signal. There is a very good agreement between M_{max} and M_{exp}, taking into account that the accuracy of the *m*/*z* measurement, given in the technical specification of the spectrometer, is equal to 0.01%.



The origin of signals from B to F, their relative proportions as a function of polymerization conditions, and a similar analysis for lactide polymerization will be published separately.

In Figure 4 one of the signals from population A, namely $Bu(CL)_6OSnOct$, Na^+ (A6, Na^+), is expanded and shown separately by a bold line. It is, however, overlapped partially with the signal of the $Bu(CL)_7Oct$, K^+ (B7, K^+) species. The computed isotopic distributions for signals A6, Na^+ and B7, K^+ are given in the same figure by thin lines. A sum of the calculated traces reproduces the experimental signal almost perfectly.

After hydrolysis, the mass spectrum (Figure 3b) still contains all of the peaks from B to F, however, peaks A assigned to macromolecules containing Sn atoms disappear. The proportion between the peak heights changed slightly, but the spectrum remains (for populations from B to F) essentially the same.

MALDI−TOF Analysis of the $Bu[O(O)C(CH_2)_5]_nOH$/$Sn(Oct)_2$ System. To ascertain that the tin-containing compounds of structure A are not formed, in a direct reaction from species C and $Sn(Oct)_2$ during the MALDI−TOF analysis, we recorded the spectrum for the artificial C/$Sn(Oct)_2$ mixture. The oligomeric CL of structure C was prepared separately in the CL polymerization initiated with tin(II) alkoxide ($Sn(OBu)_2$) with BuOH as a transfer agent (cf. Experimental Section). Concentrations of the PCL repeating units, hydroxyl groups, and $Sn(Oct)_2$ were close to these in the CL/BuOH/$Sn(Oct)_2$ reacting mixtures analyzed above. We observed only one population of macromolecules: $Bu(CL)_nOH$, devoid of Sn atoms. Therefore, the tin(II) alkoxide species ($Bu(CL)_nOSnOct$) are not formed during the sample preparation for the MALDI−TOF measurement as well as during accumulation of the MALDI spectra.

On the other hand, comparison of the MALDI TOF traces for CL/BuOH/$Sn(Oct)_2$ and $Bu(CL)_nOH$/$Sn(Oct)_2$ systems for the *m*/*z* range below 1000 (Figure 5) reveals presence of additional signals not detected above *m*/*z* =

Table 1. Comparison of the Experimentally Determined Molar Masses (M_{exp}) with the Computed Ones (IsoPro 3.0) for the Isotopic Peak of the Maximum Intensity (M_{Max}) and with the Calculated Average (M_{av}) Molar Masses for the Species Detected in the CL/$Sn(Oct)_2$/BuOH Reacting Mixture[b]

		no. of repeating units in the PCL chain	
		9	10
A, Na^+	M_{exp}	1385.62	1499.72
	M_{max}	1385.68	1499.75
	M_{av}	1385.32	1499.47
B, Na^+	M_{exp}	1249.74	1363.80
	M_{max}	1249.78	1363.85
	M_{av}	1250.61	1364.85
B, K^+	M_{exp}	1265.72	1379.80
	M_{max}	1265.75	1379.82
	M_{av}	1266.72	1380.87
C, Na^+	M_{exp}	1123.54	1237.70
	M_{max}	1123.68	1237.74
	M_{av}	1124.41	1238.56
D, Na^+	M_{exp}	1193.67	1307.71
	M_{max}	1193.72	1307.79
	M_{av}	1194.51	1308.65
E, Na^+	M_{exp}[a]	1067.59	1181.77
	M_{max}	1067.61	1181.68
	M_{av}	1068.31	1182.45
F, Na^+	M_{exp}	1049.56	1163.67
	M_{max}	1049.60	1163.67
	M_{av}	1050.29	1164.44

[a] M_{exp} values for E, Na^+ species are taken from the spectrum presented in Figure 3b. [b] The values of M_{exp} are taken from the spectrum presented in Figure 3a.

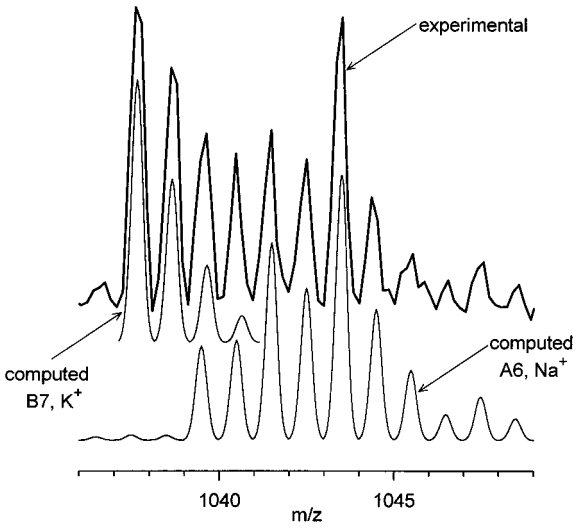


Figure 4. Comparison of the 1036−1049 *m*/*z* fragment of the MALDI−TOF spectrum shown in Figures 2 and 3a (bold line) with the isotopic distribution computed for the following species: $Bu(CL)_7Oct$, K^+ (B7, K^+) and $Bu(CL)_6OSnOct$, Na^+ (A6, Na^+) (thin lines). The experimental multiplet results from superposition of the B7, K^+ and A6, Na^+ signals.

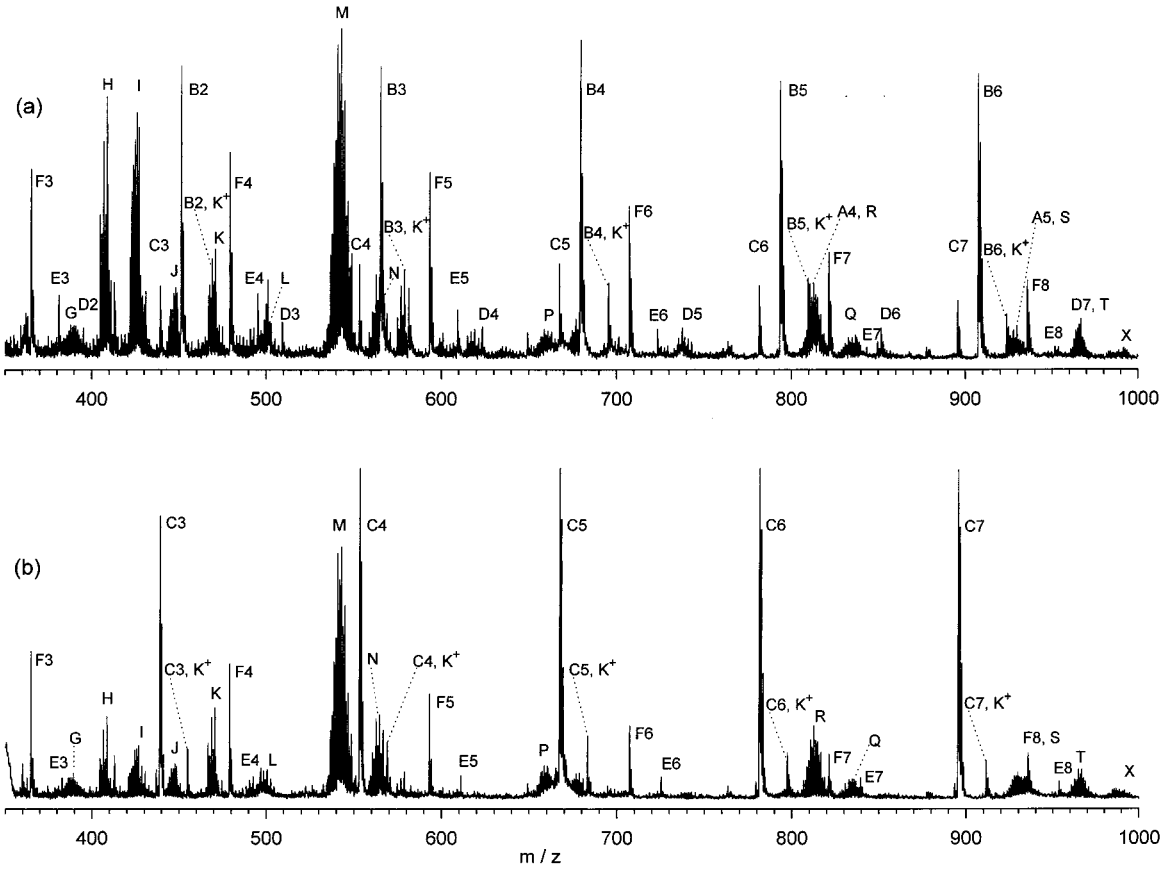


Figure 5. Comparison of the 350−1000 *m*/*z* fragments of the MALDI−TOF spectra for (a) the ϵ-caprolactone/tin octoate/butyl alcohol reacting mixture with polymerization conditions given in the caption for Figure 2a and (b) for the $HO[(CH_2)_5C(O)O]_nBu$ ($M_n = 640$)/tin octoate/THF mixture with conditions as follows: $[PCL\ repeating\ units]_0 = 1.0\ mol{\cdot}L^{-1}$ and $[Sn(Oct)_2]_0 = 1.0\ mol{\cdot}L^{-1}$, at 20 °C.

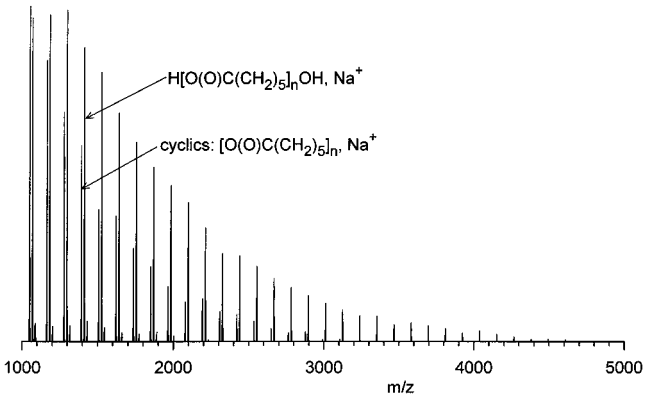
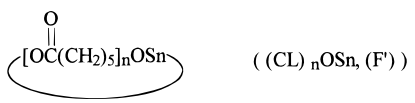


Figure 6. MALDI−TOF spectrum ($m/z \geq 1000$) of the ϵ-caprolactone/tin octoate/H_2O reacting mixture. Polymerization conditions: $[CL]_0 = 1.0\ mol{\cdot}L^{-1}$, $[Sn(Oct)_2]_0 = 0.05\ mol{\cdot}L^{-1}$, $[H_2O]_0 = 0.05\ mol{\cdot}L^{-1}$; THF solvent, 80 °C.

1000. At least some of these signals were identified as related to the following structures: $Sn(Oct)_2$, H^+ (H), $Sn(Oct)_2$, Na^+ (I), OctSnOSnOBu, H^+ (K), OctSnOSnOct, H^+ (M), OctSnOSnOct, Na^+ (N), and OctSnOSn$(CL)_3$OBu, H^+ (P). For others, such as G, J, L, Q, R, S, T, and X, the pertinent structures have not been ascribed yet. Interaction of $Sn(Oct)_2$ with the matrix cannot be ruled out. The use of another matrix could answer this question, but none of the others gave a clearer spectrum in the low molar mass material range. Thus, the spectra given in Figure 5 reveal presence of the unreacted $Sn(Oct)_2$ and several distannoxane species, which apparently could be formed after completion of the polymer chain growth, for example during the MALDI−TOF analysis, and therefore these species will not be discussed in more detail as they are not relevant to the polymerization mechanism.

MALDI−TOF Analysis of the Living CL/$Sn(Oct)_2$/H_2O System. The commercially available tin octoate contains an admixture of H_2O (cf. Experimental Section), which may play the role of the co-initiator. It was therefore of interest to study also the $Sn(Oct)_2/H_2O$ initiating system.

MALDI−TOF mass spectra of PCL prepared with $Sn(Oct)_2/H_2O$ mixture were recently published by Storey and Taylor.[14] Under the applied conditions, detection of Sn atoms in macromolecules could not be possible due to the low $[Sn(Oct)_2]_0$. Indeed, for the low starting concentration of $Sn(Oct)_2/H_2O$ initiating system we observed (Figure 6) essentially two populations of the PCL macromolecules, namely E and F (i.e., $H(CL)_nOH$ and $(CL)_n$ cyclics, respectively). However, when the starting concentration of $Sn(Oct)_2$ was much higher, then we observed an additional population of Sn-containing species. The corresponding spectrum is shown in Figure 7. The population of $[O(O)C(CH_2)_5]_n$ (F) is identical to that shown in Figure 6. However, the most interesting is the population of cyclics containing Sn atoms, and having the structure as shown below:



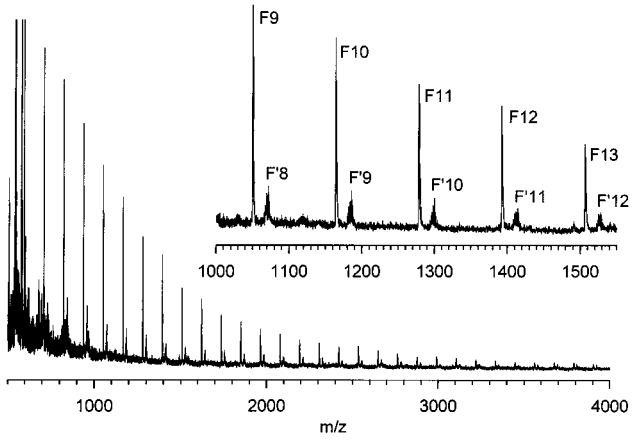


Figure 7. MALDI−TOF spectrum ($m/z \geq 1000$) of the ϵ-caprolactone/tin octoate/water reacting mixture. Polymerization conditions: $[CL]_0 = 1.0$ mol·L^{-1}, $[Sn(Oct)_2]_0 = 1.0$ mol·L^{-1}, and $[H_2O]_0 = 0.03$ mol·L^{-1}; in THF solvent, at 80 °C.

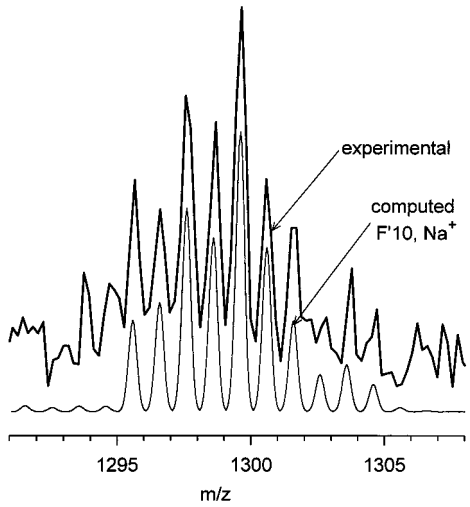


Figure 8. Comparison of the 1291−1308 m/z fragment of the MALDI−TOF spectrum shown in Figure 6 (bold line) with the isotopic distribution computed for the cyclic species: SnO-$(CL)_{10}$, Na^+ (F′10, Na^+) (thin line).

This sample of PCL was prepared with $[CL]_0 = 1.0$ mol·L^{-1}, $[Sn(Oct)_2]_0 = 1.0$ mol·L^{-1}, and $[H_2O]_0 = 0.03$ mol·L^{-1} at 80 °C in THF solvent, and it is necessary to note that the main polymer fraction had $M_n \approx 6 \times 10^4$ as determined by SEC (MALLS detector) and that the MALDI TOF spectrum comes from the low molar mass tail observed also by SEC (RI detector). It has to be stressed that in these model experiments we used intentionally high $[Sn(Oct)_2]_0$ in order to be able to observe Sn atoms linked to the short chains. Sn atoms should also be present on the longer chains/larger cycles, but then the influence of Sn atoms on the pattern of the corresponding spectra would not be sufficient in order to distinguish between macromolecules containing Sn and devoid of this atom. The absence of $H(CL)_nOH$ oligomers (population E) at high $[Sn(Oct)_2]_0$ is a result of a position of the equilibrium 3b (see next section), which is shifted onto the right-hand side.

A more detailed picture, for molar masses from 1000 to 1550, is given as an insert in Figure 7. Assignments are given directly in the mass spectrum, according to the notation introduced above. All signals marked in Figure 7 correspond to the macromolecules doped with Na^+. In Figure 8 the enlarged signal F′10 is given (solid line) with a superposition on it of the computed peaks for species having the composition $[O(O)C(CH_2)_5]_{10}OSn$. The agreement of both traces shows once again all of the powers of MALDI−TOF in identifying the single macromolecules.

Mechanism of Formation of Sn-Containing Macromolecules. It is a well established fact that six- and seven-membered cyclic esters could hardly be opened both by the ionic[29] and covalent[22,30] metal carboxylates. On the other hand, metal alkoxides provide perfectly controlled polymerization of these monomers.[31] The mechanism of formation of Sn-containing macromolecules, linear and cyclic, observed in this work directly should therefore be based on the exchange reaction leading to the formation of the tin alkoxide active species and further propagation on the tin alkoxide bond, e.g.

$$\mathrm{RC(O)OSnO(O)CR + R'OH} \leftrightarrows \mathrm{RC(O)OSnOR' + RC(O)OH} \quad (1a)$$

$$\mathrm{RC(O)OSnOR' + \mathbf{n}M} \rightleftharpoons \mathrm{RC(O)OSnO{-}(m)_n{-}R'} \quad (1b)$$

(where R stands for $C_4H_9(C_2H_5)CH$ and R′ for H or alkyl group; M denotes the cyclic ester monomer, and m indicates the polyester repeating unit derived from M).

Of course, a reaction similar to eq 1a can take place at any stage of polymerization:

$$\mathrm{RC(O)OSnO{-}(m)_n{-}R' + RC(O)OH} \leftrightarrows \underset{\text{dormant}}{\mathrm{RC(O)OSnO(O)CR + HO{-}(m)_n{-}R'}} \quad (2)$$

Therefore, to speed up the reaction, RC(O)OH should be either trapped or removed from the reaction mixture. A less complete scheme was already given as an explanation of results of our kinetic results, published recently.[17,18] It has to be added that conversion of Sn-$(Oct)_2$, inactive per se, into the RC(O)OSnOR′ in its reaction with an alcohol was proposed several times,[1,10,14] but the experimental evidence from earlier papers was quite weak. Only recently Storey and Taylor, reported the NMR data showing that $Sn(Oct)_2$ reacts directly with hydroxyl groups (of ethylene glycol) giving eventually the respective 2-ethylhexanoate ester.[14] We observed a similar reaction between $Sn(Oct)_2$ and BuOH.[17,18] Therefore, the polymerization scheme (eqs 1 and 2) has to be supplemented with reaction 3:

$$\mathrm{RC(O)OH + R'OH} \overset{\mathrm{Sn(Oct)_2}}{\rightleftharpoons} \mathrm{RC(O)OR' + H_2O} \quad (3a)$$

$$\mathrm{RC(O)OSnO(O)CR + H_2O} \rightleftharpoons \mathrm{RC(O)OSnOH + RC(O)OH} \quad (3b)$$

$$\mathrm{RC(O)OSnOH + NM} \rightleftharpoons \mathrm{RC(O)OSnO{-}(m)_n{-}H} \quad (3c)$$

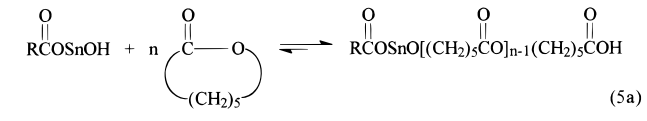
Esterification may also proceed with the already formed (cf. eqs 2 and 4) hydroxy−PCL, e.g.:

$$\mathrm{RC(O)OH + HO{-}(m)_n{-}R'} \overset{\mathrm{Sn(Oct)_2}}{\rightleftharpoons} \mathrm{RC(O)O{-}(m)_n{-}R' + H_2O} \quad (3d)$$

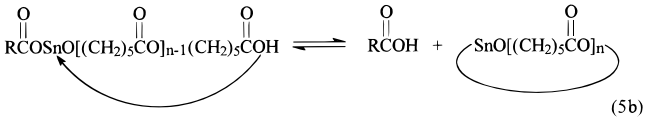
Moreover, as was already established for other polymerizing systems,[30,32−34] R′OH may act not only as a coinitiator but also as a transfer agent, e.g.:

$$RC(O)OSnO{-}(m)_n{-}R' + R'OH \rightleftharpoons RC(O)OSnOR' + HO{-}(m)_n{-}R' \quad (4)$$

When polymerization is conducted in the presence of $Sn(Oct)_2/H_2O$ system, formation of cyclics can be explained by the scheme involving reactions 3b and 3c. In the case of CL we have further:



(5a)



(5b)

Cyclic macromolecules may either be formed by an end-to-end reaction, as shown above, or by backbiting usually occurring in cyclic esters polymerization.

It is still an open question whether active species have exclusively the monoalkoxide structure (population A) or the second 2-ethylhexanoate group substitution could take place, e.g.

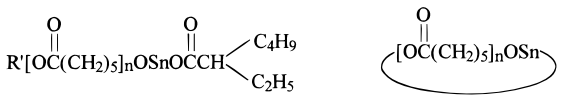
$$RC(O)OSnO(O)CR + R'OH \leftrightarrows RC(O)OSnOR' + RC(O)OH \quad (6a)$$

$$RC(O)OSnOR' + R'OH \leftrightarrows R'OSnOR' + RC(O)OH \quad (6b)$$

and the polyester chain growth proceeds then also on the resulting tin(II) dialkoxide species. Our attempts to detect the dialkoxide active centers by means of MALDI−TOF were unsuccessful not only in the living $CL/Sn(Oct)_2/BuOH$ system described above but also in the $Sn(OBu)_2$-initiated polymerization of CL. This latter system strongly indicates that the dialkoxy species are so unstable that they do not survive the present protocol of the MALDI−TOF experiment. It does not preclude, however, that these species are present in the $Sn(Oct)_2$-initiated polymerization.

Conclusions

MALDI−TOF mass spectrometry of macromolecules prepared by ring-opening polymerization of ϵ-caprolactone with $Sn(Oct)_2$, in the presence of R′OH (water or alcohol) as co-initiator, revealed that there is a certain population of macromolecules having Sn atoms in the chains, either linear and/or cyclic ones:



According to the kinetic analysis of this system, polymerization proceeds by the "active chain end" mechanism, i.e., on the Sn−alkoxide bonds present at the chain ends.[18,19]

The presence of the Sn atoms in macromolecules in the form shown above is the next strong argument for polymerization proceeding with Sn−alkoxides as active species. Thus, $Sn(Oct)_2$ and most probably any other covalent metal carboxylates have to be first converted into the an alkoxide or related compound in order to be able to initiate polymerization. These observations are the first ones when active species are detected directly by mass spectrometry.

Then, polymerization proceeds on the metal (tin(II)) alkoxide bond by insertion, like in other metal alkoxide initiators.

As we already indicated we confine ourselves in the present paper to the discussion of the appearance of Sn-containing macromolecules and to the mechanistic implications of this observation.

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References and Notes

(1) Leenslag, J. W.; Pennings, A. J. *Makromol. Chem.* **1987**, *188*, 1809.
(2) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419.
(3) Doi, Y. J.; Lemstra, P. J.; Nijenhuis, A. J.; van Aert, H. A. M.; Bastiaansen, C. *Macromolecules* **1995**, *28*, 2124.
(4) Chabot, F.; Vert, M.; Chapelle, S.; Granger, P. *Polymer* **1983**, *24*, 53.
(5) Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *J. Polym. Chem., Part A: Polym. Chem.* **1997**, *35*, 3431.
(6) Jamshidi, K.; Eberhard, R. C.; Hyon, S.-H.; Ikada, Y. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28* (1), 236.
(7) Kricheldorf, H. R.; Kreiser-Saunders: I.; Boettcher, C. *Polymer* **1995**, *36*, 1253.
(8) Kricheldorf, H. R.; Damrau, D.-O. *Makromol. Chem.* **1997**, *198*, 1753; **1997**, *198*, 1767.
(9) Dahlman, J.; Rafler, G. *Acta Polym.* **1993**, *44*, 103.
(10) Zhang, X.; MacDonald, D. A.; Goosen, M. F. A.; McAuley, K. B. *J. Polym. Sci., Part A: Polymer. Chem.* **1994**, *32*, 2965.
(11) Zhang, X.; Wyss, U. P.; Pichora, D.; Goosen, M. F. A. *Polym. Bull. (Berlin)* **1992**, *27*, 623.
(12) In't Veld, P. J. A.; Velner, E. M.; van de Witte, P.; Hamhuis, J.; Dijkstra, P. J.; Feijen, J. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 219.
(13) Schindler, A.; Hibionada, Y. M.; Pitt, C. G. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 319.
(14) Storey, R. F.; Taylor, A. E. *J. Macromol. Sci.—Pure Appl. Chem.* **1998**, *A35*, 723.
(15) Degee, Ph.; Dubois, P.; Jacobsen, S.; Fritz, H.-G.; Jerome, R. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2413.
(16) Duda, A.; Penczek, S. *Macromolecules* **1990**, *23*, 1636.
(17) Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39* (2), 74.
(18) Kowalski, A.; Duda, A.; Penczek, S. *Macromol. Rapid Commun.* **1998**, *19*, 567.
(19) Penczek, S.; Duda, A.; Kowalski, A.; Libiszowski, J. *Polym. Mater. Sci. Eng.* **1999**, *80*, 95.
(20) Kowalski, A.; Duda, A.; Penczek, S.; Pasch, H.; Rode, K. Manuscript in preparation.
(21) Hamaide, T.; Spitz, R.; Letourneux, J. P.; Claverie, J.; Guyot, A. *Macromol. Symp.* **1994**, *88*, 191.
(22) Tortosa, K.; Miola, C.; Hamaide, T. *J. Appl. Polym. Sci.* **1997**, *65*, 2357.
(23) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Anal. Chem.* **1994**, *66*, 4366.
(24) Montaudo, M.; Puglisi, C.; Samperi, F.; Spassky, N.; LeBorgne, A.; Wisniewski, M. *Macromolecules* **1996**, *29*, 6461.
(25) Gsell, R.; Zeldin, M. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1133.
(26) Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczek, S. *Macromolecules* **1990**, *23*, 1940.
(27) Davies, A. G. *Organotin Chemistry*; VCH Verlagsgesellschaft mbH: Weinheim, Germany, 1997; p 16.
(28) http://member.aol.com/msmssoft.
(29) Sosnowski, S. Ph.D. Thesis, Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland, 1990.
(30) Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982.
(31) Mecerreyes, D.; Jerome, R.; Dubois, P. *Adv. Polym. Sci.* **1998**, *147*, 1.
(32) Jacobs, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1991**, *27*, 3027.
(33) Duda, A. *Macromolecules* **1994**, *27*, 574; **1996**, *29*, 1399.
(34) Miola-Delaite, Ch.; Hamaide, T.; Spitz, R. *Macromol. Chem. Phys.* **1999**, *200*, 1771.

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