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POLYMERIZATIONS OF ε-CAPROLACTONE AND L,L-DILACTIDE INITIATED WITH STANNOUS OCTOATE AND STANNOUS BUTOXIDE - A COMPARISON

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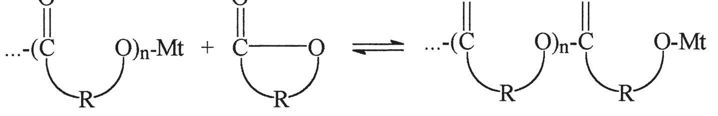
SUMMARY: Polymerizations of ε-caprolactone (CL) and L,L-dilactide (LA) initiated with stannous octoate ($Sn(O(O)CCH(C_4H_9)C_2H_5)_2$ ($Sn(Oct)_2$), $Sn(Oct)_2/C_4H_9OH$, stannous butoxide ($Sn(OC_4H_9)_2$), and $Sn(OC_4H_9)_2/C_2H_5(C_4H_9)CHC(O)OH$ were studied. It is shown, on the basis of the pertinent kinetic data and MALDI-TOF evidence, that polymerization of cyclic esters initiated by $Sn(Oct)_2$ in the presence of ROH as coinitiator proceeds on the tin(II) alkoxide (...-Sn-OR) active centres. $Sn(OC_4H_9)_2$ initiator behaves as other covalent metal alkoxides, i.e.: initiation is fast and quantitative, every alkoxide group in $Sn(OC_4H_9)_2$ starts growth of one macromolecule, and monomer addition proceeds with the acyl-oxygen bond scission. Polymerization in the $LA/Sn(OC_4H_9)_2$ system is a living process and can be controlled in a wide range of molar masses, from $M_n = 10^3$ to 10^6. Kinetic convergence of the polymerizations initiated with $Sn(Oct)_2/C_4H_9OH$, and $Sn(OC_4H_9)_2/C_2H_5(C_4H_9)CHC(O)OH$ points to an identity of growing species in both systems.

Introduction

Covalent metal alkoxides studied till now (for example: $Al(OR)_3$, R_2AlOR', $Fe(OR)_3$, $Ti(OR)_4$, $Sn(OR)_2$, $R_2Sn(OR')_2$, R_3SnOR') provide ring opening polymerization of cyclic esters practically devoid of termination and with quantitative initiation. Polyester chain growth proceeds via monomer insertion into the metal-alkoxide bond with the acyl-oxygen bond scission, e.g.:



$$\ldots\text{-(}\overset{\overset{O}{\|}}{C}\underset{R}{\smile}O)_n\text{-Mt} + \overset{\overset{O}{\|}}{C}\underset{R}{\smile}O \rightleftharpoons \ldots\text{-(}\overset{\overset{O}{\|}}{C}\underset{R}{\smile}O)_n\text{-}\overset{\overset{O}{\|}}{C}\underset{R}{\smile}O\text{-Mt} \qquad (1)$$

where R: $(CH_2)_5$ (,-caprolactone), $CH(CH_3)C(O)OCH(CH_3)$ (lactides); Mt: Al<, Fe<, Sn-, -Sn<, -Ti<, etc.

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This process is a preferable method for the controlled synthesis of the poly(aliphatic ester)s. Contribution of our laboratory to this field is reviewed briefly in the paper of Penczek et al[1)] in the present volume; for the other most recent reviews see Refs. 2 and 3.

Covalent metal carboxylates have been used even more frequently than metal alkoxides, but there was no clear cut evidence how do they induce polymerization[4-12)]. However, we have recently shown, using MALDI-TOF mass spectrometry, that macromolecules having OctSn-O-polyester end groups are formed, appearing as such in the spectrum of polyester prepared with $Sn(O(O)CCH(C_4H_9)C_2H_5)_2$ ($Sn(Oct)_2$)[13,14)]. To the similar conclusion leads analysis of the pertinent kinetic data[13,15)]. It has become, therefore, interesting to compare polymerization conducted with Sn(II) alkoxide and Sn(II) carboxylate. If Sn(II) carboxylate functions as an initiator when converted into Sn(II) alkoxide, one should be able to create conditions when these two initiators, due to the interconversions shown below become indistinguishable, e.g.:

$$Sn(Oct)_2 + C_4H_9OH \rightleftarrows OctSnO\,C_4H_9 + C_2H_5(C_4H_9)CHC(O)OH \qquad (2\,(a))$$

$$OctSnO\,C_4H_9 + C_4H_9OH \rightleftarrows Sn(O\,C_4H_9)_2 + C_2H_5(C_4H_9)CHC(O)OH \qquad (2\,(b))$$

In the present paper, summarizing results of our recent studies, polymerizations of ε-caprolactone and L,L-dilactide initiated with $Sn(Oct)_2$, $Sn(Oct)_2/C_4H_9OH$, $Sn(OC_4H_9)_2$, and $Sn(OC_4H_9)_2/C_2H_5(C_4H_9)CHC(O)OH$ systems are compared, mostly from the point of view of their kinetic behaviour.

Polymerization Initiated With Tin(II) Octoate

Purification of the initiator. The commercially available $Sn(Oct)_2$ contains about 4.5 wt-% (i.e. 10.6 mol-%) of 2-ethylhexanoic acid (OctH) and up to 0.5 wt-% (i.e. 9.5 mol-%) of H_2O. Our ^1H NMR spectra show the presence of the acidic protons (e.g. from OctH 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 OctH concentrations). This value corresponded to the content of acidic protons calculated on the basis of the composition claimed by the supplier. Two consecutive high vacuum distillations resulted in $Sn(Oct)_2$ showing in NMR spectra 1.8 mol-% of the acidic protons (fraction distilling at $140^{\circ}C/3\cdot10^{-3}$ mbar). Thus, the concentration of "acidic protons" decreased almost 20 times. This was, in our hands, a 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 THF (20 v/v) in and out of the sample under vacuum. The content of the impurities was reduced in this way down to 0.9 mol-% (i.e. about 40 times from the starting commercial sample).

Kinetics of propagation and dependencies of molar masses on monomer conversion. Kinetics of polymerization of ε-caprolactone (CL) and L,L-dilactide (LA) was followed either by size exclusion chromatography (SEC) or by dilatometry and polarimetry, respectively. Typical semilogarithmic dependencies of monomers concentrations as a function of time, for polymerizations, initiated with $Sn(Oct)_2$, (purity: 98.2 mol-%), are presented in Fig. 1. Both experimental plots give straight lines, indicating, that initiation is fast and quantitative and concentrations of active species are invariable throughout polymerization.

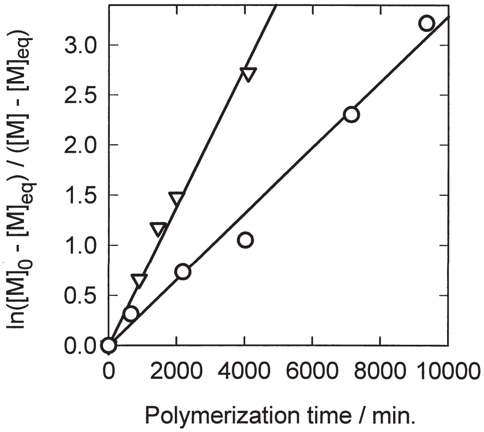


Fig. 1: Kinetics of ε-caprolactone (○) and L,L-dilactide (▽) polymerization initiated with tin octoate. Conditions: $[CL]_0 = 2.0$ mol·L^{-1}, $[Sn(Oct)_2]_0 = 0.15$ mol·L^{-1}, 80°C; $[LA]_0 = 1.0$ mol·L^{-1}, $[Sn(Oct)_2]_0 = 0.05$ mol·L^{-1}, 50°C; THF solvent$^{15,16)}$.

Linear evolution of molar masses (M_n) with monomers conversion (Fig. 2; the same polymerization conditions as in Fig. 1) points to an absence of the unimolecular transfer (transesterification). Figs. 1 and 2 taken together indicate that these polymerizations are living, at least within an accuracy of the measurements. Eventually, for the full monomer conversions, poly(CL) and poly (LA) were formed having M_n's equal to $1.8 \cdot 10^5$ and $1.3 \cdot 10^5$, respectively. These values correspond to the following concentrations (in mol·L^{-1}) of the macromolecules: $1.2 \cdot 10^{-4}$ (poly(CL)) and $1.1 \cdot 10^{-3}$.(poly(LA)) and most probably are equal to the concentrations of the hydroxyl group containing impurities, adventitiously present in the polymerizing mixture and playing a role of coininitiators and/or transfer agents. Using the standard high vacuum technique and $Sn(Oct)_2$ of the highest purity of we were able to obtain (0.9 mol-% of "$H^{\oplus}$") we prepared both poly(CL) and poly(LA) with M_n reaching 10^6 (as determined by SEC with the laser light scattering detector). The latter value looks to be a limit of M_n of the poly(aliphatic ester)s prepared by the ring opening polymerization, and is related to the impurities concentration level. Similar threshold value ($M_v \approx 10^6$) was already reported by Pennings$^{4)}$.

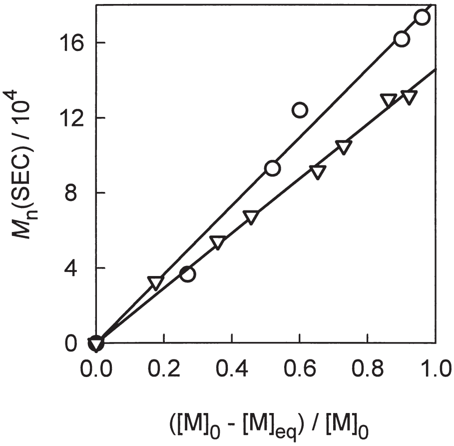
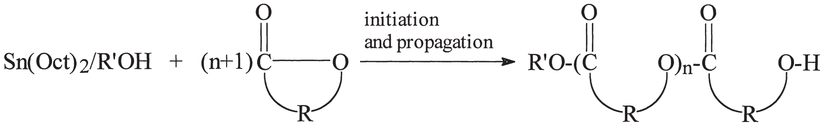


Fig. 2: Dependence of molar masses (absolute M_n, measured by SEC with the laser light scattering detector) of poly(ε-caprolactone) (○) and poly(L,L-dilactide) (▽) on monomer conversion in the polymerization of ε-caprolactone and L,L-dilactide initiated with tin octoate$^{15,16)}$. Conditions as in the caption for Fig. 1

However, in the experiments such as described above molar mass of the polyester could hardly be controlled and strongly depends on the purity of the components of the reacting mixture. Molar mass control with $Sn(Oct)_2$ can only be achieved with the purposely introduced coinitiator (and/or transfer agent), for example with butyl alcohol (C_4H_9OH), which we applied in the present work. Indeed, as it is illustrated in Fig. 3a on the example of CL polymerization, initiated with well purified $Sn(Oct)_2$, M_n does not depend on $[Sn(Oct)_2]_0$, when the latter is changing over one hundred times. The independence of M_n on $[Sn(Oct)_2]_0$ was mentioned in a few other papers, but non conclusive results appeared also, because $Sn(Oct)_2$ if not sufficiently purified may contain impurities acting as coinitiators$^{9,11)}$.

On the other hand, M_n increases linearly with decreasing butyl alcohol concentration in the feed and can be predicted from the $[CL]_0/[C_4H_9OH]_0$ ratio as shown in Fig. 3b. Thus, every molecule of C_4H_9OH gives rise of one macromolecule; schematically:



(3)

where R'OH denotes coinitiator and/or transfer agent; $DP_n = ([M]_0 - [M]_{eq})/[R'OH]_0$.

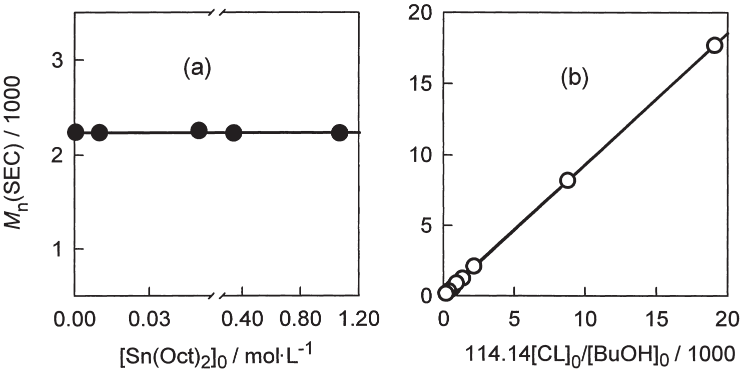


Fig. 3: Molar masses (M_n) of poly(ε-caprolactone)s, obtained in the polymerization of ε-caprolactone initiated with tin octoate. (a) Influence of the starting concentration of $Sn(Oct)_2$; $[C_4H_9OH]_0 = 0.1$ mol·L^{-1}. (b) Influence of the starting concentration of C_4H_9OH (114.14 is the molar mass of poly(CL) repeating unit); $[Sn(Oct)_2]_0 = 0.05$ mol·L^{-1}. Conditions: $[CL]_0 = 2.0$ mol·L^{-1}, THF, 80°C. M_n(SEC) determined with poly(CL) standards and RI detection[15,16)].

Structure of growing species. In our already published work[13,15)] we have shown, that addition of C_4H_9OH to $Sn(Oct)_2$ in coinitiating polymerization of CL first increased the rate, and then the rate levelled off for higher $[C_4H_9OH]_0/[Sn(Oct)_2]_0$ ratios, giving dependence with the inflection point between $[C_4H_9OH]_0/[Sn(Oct)_2]_0 = 1$ and 2 (Fig. 4). Moreover, small quantity of the 2-ethylhexanoic acid (about 10 mol-% with respect to the $Sn(Oct)_2$ content) inhibited CL polymerization almost completely[15)]. These results suggest, that the real initiator is formed in the reactions given by Eqs. 2. More recently, similar dependencies for LA monomer have also been obtained[16)].

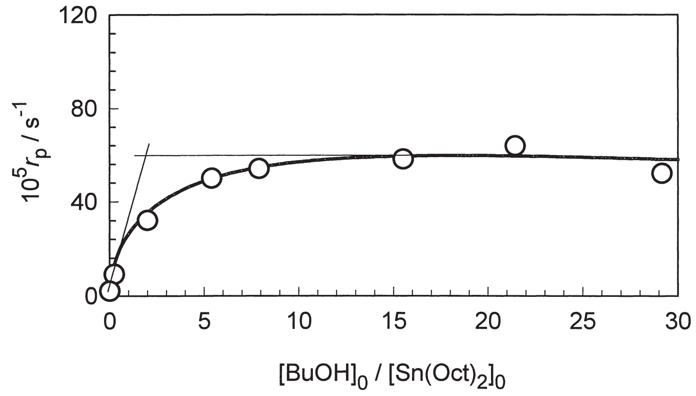


Fig. 4: Dependence of the rate of polymerization (r_p = -d[CL]$_0$/[CL]dt = (1/t)·ln([CL]$_0$/[CL])) of ε-caprolactone initiated with tin octoate on the starting concentrations of butyl alcohol to tin octoate ratio $[C_4H_9OH]_0/[Sn(Oct)_2]_0$ with $[Sn(Oct)_2]_0$ = 0.05 mol·L^{-1} kept constant. Conditions: $[CL]_0$ = 2.0 mol·L^{-1}, THF solvent, 80°C[15].

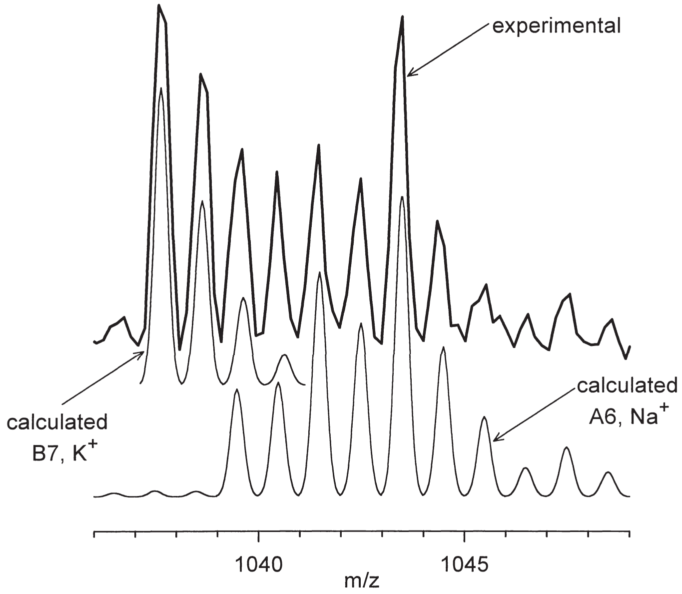


Fig. 5: Comparison of the 1036-1049 m/z fragment of the MALDI-TOF spectrum (bold line), recorded for the ε-caprolactone/tin octoate/butyl alcohol reacting mixture, with the isotopic distribution calculated for species: $C_4H_9O[C(O)(CH_2)_5O]_7(O)CCH(C_4H_9)C_2H_5$, $K^{\oplus}$, (B7, $K^{\oplus}$) and $C_4H_9O[C(O)(CH_2)_5O]_6$-SnO(O)CCH$(C_4H_9)C_2H_5$, $Na^{\oplus}$ (A6, $Na^{\oplus}$) (thin lines). The experimental "multiplet" results from superposition of B7, $K^{\oplus}$ and A6, $Na^{\oplus}$ signals. Polymerization conditions: $[CL]_0$ = 0.95mol·L^{-1}, $[Sn(Oct)_2]_0$ = 1.0 mol·L^{-1}, $[BuOH]_0$ = 0.15 mol·L^{-1}; THF solvent, 80°C[14].

Another, more direct evidence of formation of the tin(II) alkoxide species in the CL/Sn(Oct)$_2$/C_4H_9OH reacting mixture comes from the MALDI-TOF mass spectrometry. Fig. 5 shows 1036-1049 m/z fragment extracted from the MALDI-TOF spectrum given in our recent paper[13,14] "Multiplet" in Fig. 5 was ascribed by us to two overlapping signals coming from the following CL oligomers: $C_4H_9O[C(O)(CH_2)_5O]_7(O)CCH(C_4H_9)C_2H_5$, K$^{\oplus}$, (B7, K$^{\oplus}$, m/z = 1037.64) and $C_4H_9O[C(O)(CH_2)_5O]_6$-SnO(O)CCH$(C_4H_9)C_2H_5$, Na$^{\oplus}$ (A6, Na$^{\oplus}$, m/z = 1043.51). The respective m/z values calculated for these structures are almost identical to the experimental ones and are equal to 1037.61 and 1043.47, respectively. Moreover, we observed in the m/z range from 300 to 4000 appearance of the whole series of signals being apart of m/z = 114.14 (molar mass of the poly(CL) repeating unit) corresponding to $C_4H_9O[C(O)(CH_2)_5O]_n$-SnO(O)CCH$(C_4H_9)C_2H_5$ tin(II) monoalkoxide species.

The mass spectra of compounds containing Sn atoms are particularly easy to recognise, 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[17]. The carbon atoms, consisting mostly of 98.9% and 1.1% of the ^{12}C and ^{13}C isotopes, respectively, give also rise to the specific arrangement of the mass spectra peaks of the individual species. On the other hand, the natural abundance of various hydrogen and oxygen isotopes is so low that can be neglected, at least in the present analysis of the mass spectra.

Using the IsoPro3.0 program[18] 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, providing that the latter was recorded in the reflector mode, in order to ensure a resolution on the level of the individual isotopic peaks. Such comparison is presented in Fig. 5 on the example of A 6, Na$^{\oplus}$ and B7, K$^{\oplus}$ oligomers, showing good agreement of the experimental and computed traces.

Applicability of the MALDI-TOF mass spectrometry to detecting the tin-containing macromolecular species was confirmed more recently on the example of the poly(ϵ-caprolactone) macrocycles ($\overparen{\text{poly(CL)-S}(C_4H_9)_2\text{SnS-poly(CL)}}$)[19].

It is still an open question whether active species have exclusively the monoalkoxide structure: $C_4H_9O[C(O)(CH_2)_5O]_n$-SnO(O)CCH$(C_4H_9)C_2H_5$ or the second 2-ethylhexanoate group substitution could take place as it is shown in Eq. 2b 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 the MALDI-TOF were unsuccessful not only in the living CL/Sn(Oct)$_2$/C_4H_9OH system described above but also in the Sn(OC_4H_9)$_2$ initiated polymerization of CL (cf. below). This result may indicate, that the tin(II) dialkoxide species are so much unstable, that do not survive the present procedure of the MALDI-TOF experiment. It does not preclude, however, that these species are not present in the Sn(Oct)$_2$ initiated polymerization.

Polymerizations Initiated With Tin(II) Butoxide

Preparation of the initiator. Tin(II) butoxide (Sn(OC_4H_9)$_2$) was prepared in the two step synthesis according to the method described in Ref. 20.

$$SnCl_2 + 2\,CH_3OH + 2\,(C_2H_5)_3N = Sn(OCH_3)_2\downarrow + (C_2H_5)_3HN^{\oplus}Cl^{\ominus} \qquad (4\,(a))$$

$$Sn(OCH_3)_2 + 2\,C_4H_9OH = Sn(OC_4H_9)_2 + 2\,CH_3OH\uparrow \qquad (4\,(b))$$

In the first step $SnCl_2$ was reacted with CH_3OH, in the presence of $(C_2H_5)_3N$ as HCl scavenger. The resulting $Sn(OCH_3)_2$ was then ”transalkoxidized” with the higher boiling butyl alcohol, giving eventually $Sn(OC_4H_9)_2$. Quantitative substitution of the butoxide groups for the methoxide groups in $Sn(OCH_3)_2$ was confirmed by the MALDI-TOF spectra, showing an exclusive presence of signals coming from the ...-OC_4H_9 end groups in the resulting polyester (cf. Eqs. 5).

Kinetics of propagation and dependencies of molar masses on monomer conversion. Semilogarithmic anamorphoses of the kinetic data obtained in the polymerization of CL and LA initiated with $Sn(OC_4H_9)_2$ give straight lines (Fig. 6), suggesting that initiation is fast and quantitative, and that termination is practically absent. Polymerizations initiated with $Sn(OC_4H_9)_2$ are considerably faster than these with Sn(Oct)$_2$ (cf. Fig. 1). Agreement of the polarimetric and SEC readings indicate that there is no LA monomer racemization. Molar masses (M_n) measured by SEC in the polymerization of LA increase linearly with monomer conversion (Fig. 7a) and are in close agreement with the molar masses calculated from the feed composition: $M_n = 144.13([LA]_0 - [LA]_{eq})/2[Sn(OC_4H_9)]_0$ (Fig. 7b), showing that intramolecular transeterification can also be excluded (at least in the LA polymerization).

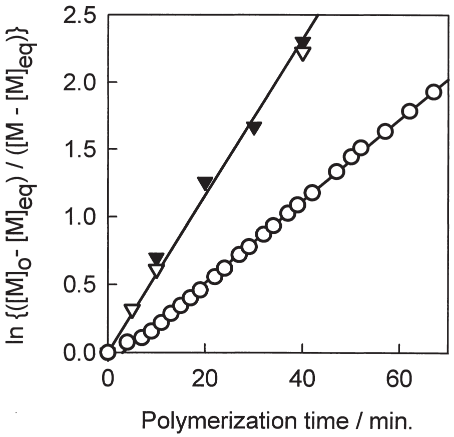


Fig. 6: Kinetics of ε-caprolactone (O, dilatometry) and L,L-dilactide (∇, polarimetry; ▼, SEC) polymerization initiated with tin butoxide. Conditions: $[CL]_0 = 2.0$ mol·L^{-1}, $[Sn(OC_4H_9)_2]_0 = 3.3 \cdot 10^{-3}$ mol·L^{-1}, 80°C; $[LA]_0 = 1.0$ mol·L^{-1}, $[Sn(OC_4H_9)_2]_0 = 1.2 \cdot 10^{-3}$ mol·L^{-1}, THF, 80°C; [16].

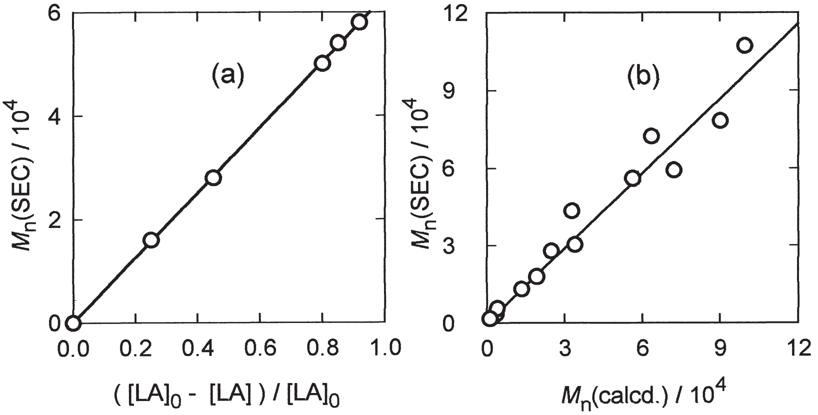
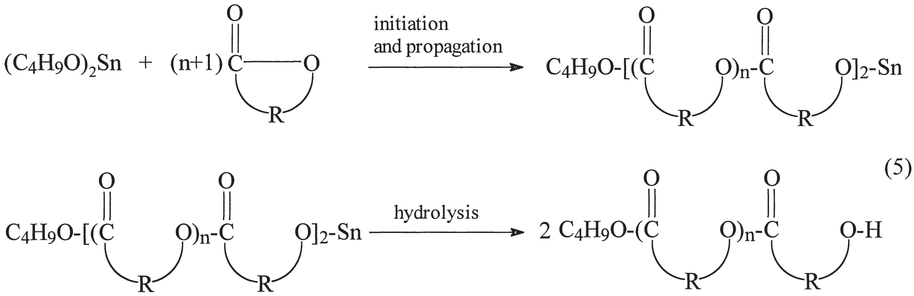


Fig. 7: Dependence of M_n (measured by SEC) of poly(L,L-dilactide) in the polymerization of L,L-dilactide initiated with tin(II) butoxide: (a) on LA conversion. Conditions as in the caption for Fig. 6. (b) on M_n(calcd.) = $144.13([LA]_0 - [LA]_{eq})/2[Sn(OBu)_2]_0$. Conditions: $[LA]_0$ from 1.0 to 3.0 mol·L^{-1}, THF, 80°C[16].

Thus, polymerization of LA initiated with $Sn(OC_4H_9)_2$ reveals features of the typical living process and therefore can be fully controlled. Fig. 7a gives an example of the M_n control in the range from 10^3 to 10^5 in polymerizations carried out in THF solution and at relatively low temperature. However, in the bulk process, at 120°C we were able to prepare poly(LA) with the controlled M_n as high as ≈ 10^6. For example, starting from $[LA]_0 = 8.1$ mol·L^{-1},

$[Sn(C_4H_9)_2]_0$ = $5.5 \cdot 10^{-4}$ mol·L^{-1} (i.e. M_n(calcd.) = $1.06 \cdot 10^6$) we obtained after 19 hours polymer having M_n(SEC) = $9.68 \cdot 10^5$ (the absolute value, laser light scattering detector) and $M_w/M_n = 1.36$; membrane osmometry gave $M_n = 9.53 \cdot 10^5$.

Structure of growing species. More detailed ^{1}H and ^{119}Sn NMR, and MALDI-TOF analysis of the growing and isolated polyesters prepared with $Sn(OC_4H_9)_2$ will be published elsewhere$^{16)}$. These spectroscopic and spectrometric data, together with the molar mass data described above, reveal that polymerization of cyclic esters initiated with $Sn(OC_4H_9)_2$ proceeds as with other covalent metal alkoxides studied till now. Namely, initiation is fast and quantitative, every alkoxide group in $Sn(OC_4H_9)_2$ starts growth of one macromolecule. Active centres of the polyester chain growth have the tin(II) macroalkoxide structure. In the propagation step monomer is inserted into the tin(II)-oxygen bond of the alkoxide end group with the acyl-oxygen bond scission, schematically:



(5)

Kinetic Convergence of Polymerizations Initiated with Tin(II) Octoate/Butyl Alcohol and with Tin(II) Butoxide/2-Ethylhexanoic Acid Systems

Comparison of the kinetics of CL polymerization initiated by $Sn(Oct)_2/C_4H_9OH$ and by $Sn(OC_4H_9)_2/C_2H_5(C_4H_9)CHC(O)OH$ systems is given in Fig. 8. In all of these experiments the starting concentrations of $Sn(Oct)_2$ and $Sn(OC_4H_9)_2$ were kept constant and equal to 0.05 mol·L^{-1}. Polymerization with $Sn(Oct)_2$ with no alcohol added is very slow because it is coinitiated by the hydroxyl group containing impurities present in low concentrations. If we assume that every molecule of impurity starts growth of one macromolecule then concentration of these impurities can be calculated from the molar mass of the resulting poly(CL). Because $M_n = 2.8 \cdot 10^5$ was measured in this polymerization the estimated concentration of impurities is equal to $8 \cdot 10^{-4}$ mol·L^{-1}. The latter value is very close to the concentration of the protonic impurities introduced with $Sn(Oct)_2$ (cf. purification of the initiator), namely: 1.8 mol-% from $[Sn(Oct)_2]_0 = 0.05$ mol·L^{-1} gives $9 \cdot 10^{-4}$ mol·L^{-1}.

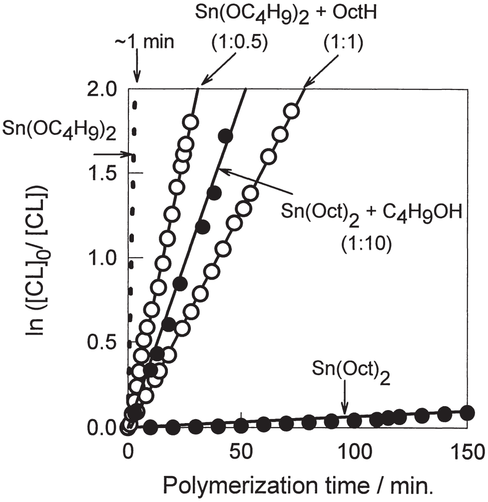


Fig. 8: Comparison of ε-caprolactone polymerizations initiated with $Sn(OC_4H_9)_2$ and conducted in the presence of 2-ethylhexanoic (octanoic) acid (OctH) (○), and $Sn(Oct)_2$ conducted in the presence of butyl alcohol (C_4H_9OH) (●). Polymerization conditions: $[CL]_0 = 2.0$ mol·L^{-1}, $[Sn(OC_4H_9)_2]_0 = [Sn(Oct)_2]_0 = 0.05$ mol·L^{-1}, THF solvent, 80°C[16)].

In the next experiment 0.5 mol·L^{-1} of C_4H_9OH was added and the polymerization rate (r_p) increased considerably (about 200 times; further increasing of $[C_4H_9OH]_0$ does not lead to the r_p increase - cf. Fig. 4).

In another series of experiments we began with measurements using $Sn(OC_4H_9)_2$ without any additive introduced purposely. This polymerization was completed within approximately 1 min., thus 10^4 times faster than with $Sn(Oct)_2$, under the otherwise identical conditions. Then, we observed that polymerization initiated with $Sn(OC_4H_9)_2$ was slowing down in the presence of $C_2H_5(C_4H_9)CHC(O)OH$ (OctH)) - the stronger the higher was the starting concentration of OctH.

At certain ratios $[Sn(OC_4H_9)_2]_0/[OctH]_0$ and $[Sn(Oct)_2]_0/[C_4H_9OH]_0$ the polymerization rates are becoming equal one to another. This results suggests that an effective interchange equilibrium takes place as given in Eq. 2. The corresponding equilibrium constants are yet unknown, but most probably the equilibria 2 are shifted onto the left hand side. Comparing polymerization rates in processes initiated with $Sn(Oct)_2$ and $Sn(OC_4H_9)_2$, and assuming similar reactivities of tin(II) alkoxide active centres derived from $Sn(OC_4H_9)_2$ and from $Sn(Oct)_2/ROH$ impurity one can estimate concentration of the actually growing species in the polymerization with $Sn(Oct)_2$ and without any purposely introduced coinitiator. This concentration in our system is equal to 10^{-5} mol.L^{-1}, whereas the total concentration of the adventitiously present coinitiator was estimated above 8.10^{-4} mol.L^{-1}, what would mean that the equilibrium constants of the interchange reactions (Eqs. 2) are of the order of 10^{-2}.

Conclusions

-Results of our kinetic studies on cyclic esters polymerization initiated with $Sn(Oct)_2$, $Sn(Oct)_2/C_4H_9OH$, and $Sn(OC_4H_9)_2/C_2H_5(C_4H_9)CH(O)OH$ systems, complemented with the MALDI-TOF observations, strongly speak for mechanism in which $Sn(Oct)_2$, does not directly initiate (or catalyse) polymerization. The real, tin(II) alkoxide, initiator is formed in the interchange reactions between $Sn(Oct)_2$ and the hydroxyl group containing compound (Eqs. 2). Then, further steps of polymerization proceed as with other covalent metal alkoxides. Other proposed mechanisms[5,6,9-11)], assuming that $Sn(Oct)_2$ activates merely the cyclic ester molecule and survives polymerization being not converted into any species chemically different from $Sn(Oct)_2$, are not consistent with the behaviour of the cyclic ester/$Sn(Oct)_2$/ROH system revealed in the present work.

-The $Sn(Oct)_2/ROH$ initiator allows preparation of the poly(aliphatic ester)s with molar masses (M_n) up to 10^6. However, M_n can practically be adjusted by the $[monomer]_0/[ROH]_0$ ratio only in the range from 10^2 to 10^4; polyesters with the exact value of the higher molar masses have to be prepared by the more tedious trial-and-error procedure.
In the synthesis of polylactide with M_n from 10^3 to 10^6 $Sn(OC_4H_9)_2$ can advantageously be used. This system provides the first example of the fully controlled polymerization of cyclic ester in a such wide range of molar masses.

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