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Kinetics and mechanism of ε-caprolactone and L,L-lactide polymerization coinitiated with zinc octoate or aluminum acetylacetonate: The next proofs for the general alkoxide mechanism and synthetic applications

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Abstract

Following our previous papers on mechanism of cyclic esters' polymerization coinitiated by tin(II) octoate [tin(II) bis-(2-ethylhexanoate), ($Sn(Oct)_2$)] in the presence of either the low molar mass coinitiator (an alcohol, hydroxy acid, or H_2O) or a macromolecule fitted with a hydroxy end group (ROH), the present work deals with ε-caprolactone (CL) and L,L-lactide (LA) polymerizations coinitiated with zinc octoate ($Zn(Oct)_2$) or aluminum acetylacetonate ($Al(Acac)_3$). A series of kinetic measurements revealed that similarly as in the $Sn(Oct)_2$ coinitiated process, these polymerizations proceed by simple monomer insertion into the …Mt−OR bond, reversibly formed in the reaction −Mt−L + ROH ⇌ …−Mt−OR + LH (where Mt = Sn, Zn or Al; L = Oct or Acac), taking place throughout the whole polymerization process. MtL_n itself does not play an active role in the polymerization. Applicability of the commercially available $Zn(Oct)_2$ or $Al(Acac)_3$ for the aliphatic polyester ($10^3 \leq M_n \leq 4 \times 10^5$) synthesis is also discussed.

Keywords: Zinc octoate; Aluminum acetylacetonate; Cyclic ester polymerization

1. Introduction

The mechanism of initiation of cyclic esters' polymerization with stannous 2-ethyhexanoate [tin(II) octoate ($Sn(Oct)_2$)] used to be for a long time a matter of controversy. Twenty years ago it has been proposed that this polymerization starts on the tin(II)-alkoxide (…−Sn−OR) bond [1], formed by the exchange reaction of the carboxylate ligands with hydroxyl group-containing compound (ROH). ROH could be added purposely to the reacting mixture or present as a difficult to remove impurity (e.g. water (''moisture'') or hydroxyacids) from the corresponding monomer. However, this suggestion was not based on the experimental evidence. Probably this weakness prompted several other authors to propose their own ''mechanisms'' of initiation of cyclic esters' polymerization with $Sn(Oct)_2$ [2–7]. The proposed modes of initiation can be divided into the following groups:

- direct insertion mechanism;
- cationic mechanism: with formation of secondary oxonium ions (e.g. initiation with carboxylic acid);
- activated monomer mechanism;
- chain end mechanism with a direct monomer insertion assuming formation of the actual initiating species in the exchange reactions (Scheme 1).

Direct reaction of $Sn(Oct)_2$ with L,L-lactide (LA), also leading to Sn(II)-alkoxide species, although discussed was considered as an initiation path of secondary importance. One of the consequences of this ''direct reaction'' should be linear increase of polymerization rate with increasing $[Sn(Oct)_2]_0$. This is, however, not the case. Taking into account that only

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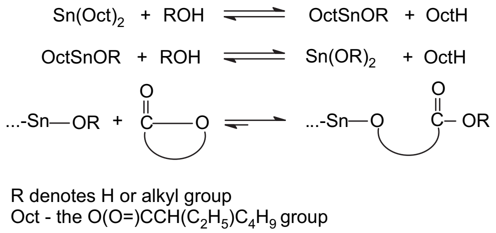
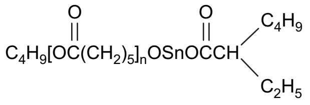


Scheme 1. Initiation with tin(II)-alkoxide formed via carboxylate–alkoxide ligand exchange reactions.

minute amounts of $Sn(Oct)_2$ were consumed, also kinetic plots should exhibit tendency to auto-acceleration, however, first-order kinetic dependencies were typically observed [8,9]. Cationic mechanism was easy to dismiss since we have shown that polymerization of ε-caprolactone (CL) and LA takes place in the presence of amines (e.g. $C_4H_9NH_2$) [9,10]. Besides, polymerization of CL and LA coinitiated with $Sn(Oct)_2$ proceeds readily also in the presence of a proton sponge/trap [11].

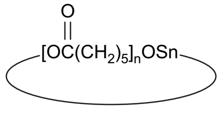
The activated monomer mechanism has finally been rejected by us on the basis of kinetic arguments [8,9], similar to these presented in the present paper (*vide infra*). Indeed, mechanism proposed by the Hamburg group [5] was the most difficult to put on the rest. These authors studied interaction of benzyl alcohol (BnOH) with $Sn(Oct)_2$ and on the basis of observed chemical shifts assumed first that $BnOH \cdot Sn(Oct)_2$ complex formation (not the reaction product) is responsible for the observed changes. Then this complex in their opinion reacts with a cyclic ester, in such a manner that the complexed molecule of the alcohol is opening the monomer molecule, giving the first linear unit with an ester tail end group and a hydroxyl head end group. $Sn(Oct)_2$ comes again to the hydroxyl end group, complexing with it, and this scenario is then repeated in every propagation step. Thus, in this mechanism Sn atoms were not bound covalently to the growing chains (later on, after our paper described below appeared [12] this opinion has been changed [13]).

Therefore, we concentrated our efforts, apart from kinetic arguments, on an attempt to directly show the presence of Sn in the growing macromolecules. Indeed, we determined by MALDI-TOF mass spectrometry, the existence of the Sn containing macromolecules (first in polymerization of CL) [12]:


$$C_4H_9[OC(=O)(CH_2)_5]_nOSnOC(=O)CH(C_4H_9)(C_2H_5)$$

[Bu-(cl)$_n$-OSnOct]

Even more remarkable was detection of cyclic molecules having Sn atoms in their structure, like:


$$[OC(=O)(CH_2)_5]_nOSn$$

[(cl)$_n$-OSn]

We have shown by this direct detection and then by kinetic experiments that tin(II)-alkoxides are the actual initiators. This conclusion, terminating the twenty years controversy, has been then supported or confirmed by results from other laboratories [13–19].

In the present work we give kinetic evidence indicating that also zinc octoate ($Zn(Oct)_2$) and aluminum acetylacetonate ($Al(Acac)_3$) initiate polymerization of CL or LA only after being converted into their alkoxide derivatives. Finally, reactivity and applicability of $Zn(Oct)_2$ and $Al(Acac)_3$ for the aliphatic polyester synthesis are compared with these of $Sn(Oct)_2$.

2. Experimental

2.1. Materials

Tin(II) bis-(2-ethylhexanoate) [tin(II) octoate ($SnOct_2$)] (Aldrich, 95% according to our determinations) was purified two times by high-vacuum distillation ($\approx 10^{-3}$ mbar, 180 °C) [8]. Zinc bis-(2-ethylhexanoate) [zinc octoate ($ZnOct_2$)] (ABCR, 98%) was purified in a similar way. Aluminum tris-acetylacetonate [$Al(Acac)_3$] (Aldrich, 99%) was sublimated in vacuum (150 °C/10^{-3} mbar). L,L-Lactide (LA) (Boehringer Ingelheim, Germany, 99%) was crystallized consecutively from dry 2-propanol and toluene and purified just before use by vacuum sublimation (10^{-3} mbar, 85 °C). ε-Caprolactone (CL) (Aldrich, 99%) was stirred over CaH_2 for several hours at room temperature and distilled under reduced pressure ($\approx 10^{-2}$ mbar, 90 °C) into ampoule covered inside with a Na mirror. Purified LA and CL monomers were finally distributed into ampoules equipped with breakseals and sealed in vacuo. Butyl alcohol (BuOH) (Aldrich, +99.4%) was purified by distillation from Na metal under reduced pressure at room temperature. Tetrahydrofuran (THF) (POCh, Gliwice, Poland, 99%) kept several days over KOH pellets, filtered off, distilled, degassed, and stored over liquid Na/K alloy (blue solution) was distilled into the reaction vessel just before use.

2.2. Measurements

Conversion of LA into polymer units was determined using size exclusion chromatography (SEC) and/or polarimetry. SEC traces were recorded using a LKB 2150 HPLC pump, two sets of TSK Gel columns (G 2000 H_{XL} and 4000 H_{XL} or G 3000 H_{HR} and G 6000 H_{HR} with pore sizes 2.5×10^2 and 10^6 or 1.5×10^3 and 10^6 Å, respectively) at 20 °C. Wyatt Optilab 903 interferometric refractometer and MALLS Dawn F Laser Photometer, equipped with He–Ne laser emitting at 632.8 nm, (both Wyatt Technology Corp., Santa Barbara, CA) were applied as detectors in series. Methylene chloride was used as an eluent at flow rate of 0.8 mL min^{-1}. Polarimetric measurements were performed with a Perkin Elmer 241 MC Polarimeter at 20 °C. The polymerization mixtures were prepared and transferred into optical cells under high-vacuum conditions and then the cells were sealed off.

Conversion of CL was followed by dilatometry and occasionally by SEC. The polymerization mixtures were prepared and transferred into the all-glass dilatometers or ampoules under high-vacuum conditions and then the dilatometers or ampoules were sealed off.

The actual number-average molar masses (M_n's) of the living poly(CL) (PCL) and poly(LA) (PLA) were determined

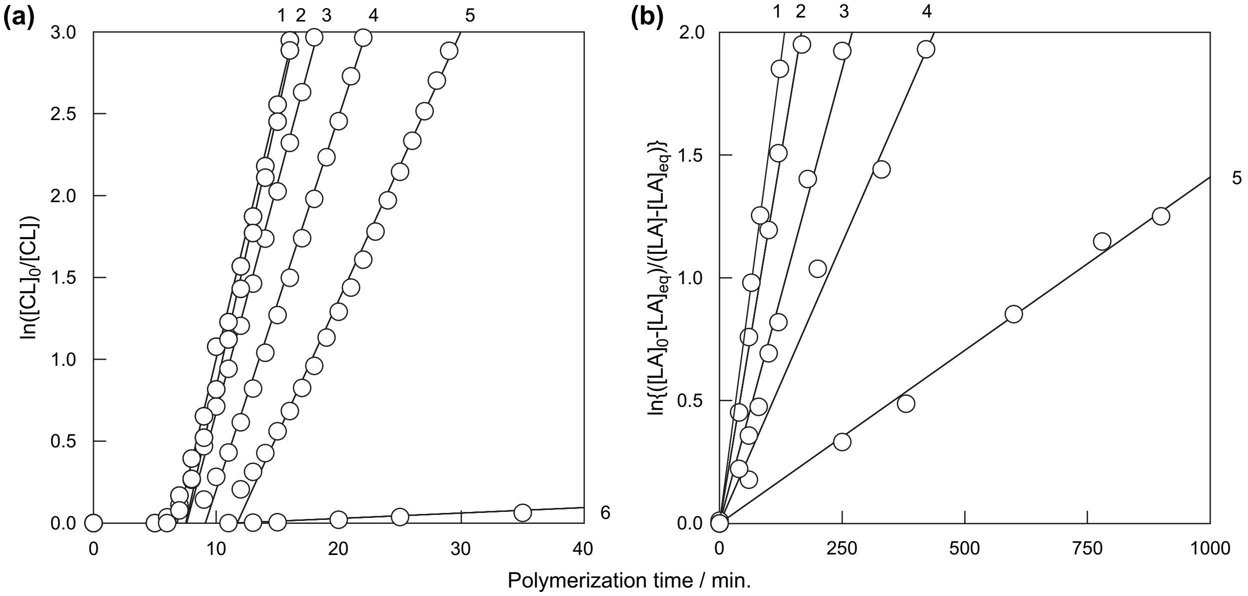


Fig. 1. Kinetics of ε-caprolactone (CL) (a) and L,L-lactide (LA) (b) polymerization initiated with $Zn(Oct)_2$/BuOH system. $[CL]_0 = 2.0$ mol L^{-1}, $[BuOH]_0 = 0.01$ mol L^{-1}, $[Zn(Oct)_2]_0$ (in mol L^{-1}) = 0.40 (1), 0.30 (2), 0.20 (3), 0.10 (4), 0.05 (5), 0.01 (6) (a). $[LA]_0 = 1.0$ mol L^{-1}, $[Zn(Oct)_2]_0 = 0.05$ mol L^{-1}, $[BuOH]_0$ (in mol L^{-1}) = 0.175 (1), 0.1 (2), 0.044 (3), 0.01 (4), 0 (5); ($[LA]_{eq} = 5.5 \times 10^{-2}$ mol L^{-1} [24]) (b); THF solvent, 80 °C.

using the PCL and PLA standards prepared in our laboratory ($M_n \leq 2 \times 10^4$) or with a MALLS Dawn F Laser Photometer and using ASTRA v 4.70 program (Wyatt Technology Corp., Santa Barbara, CA) ($M_n > 10^4$). The actual M_n's of the deactivated and isolated PLA or PCL were occasionally determined with Knauer Osmometers: vapor pressure or high speed membrane osmometers for $M_n \leq 3.5 \times 10^4$ or $\geq 3.5 \times 10^4$, respectively, in dry chloroform as solvent. The M_w/M_n ratios were determined from the SEC traces.

MALDI-TOF 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 obtained in the reflector and/or linear mode. The matrix, 2,5-dihydroxybenzoic acid, was dissolved in THF or methylene chloride in concentration equal to 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 plate covered by the gold metal target.

3. Results and discussion

3.1. Polymerization coinitiated with zinc octoate [$Zn(Oct)_2$]

Zinc compounds were exploited as initiators and/or catalysts in cyclic esters' polymerization in a much lower extent in comparison with their tin counterparts (see e.g. Refs. [20–23]). This could be surprising since some Zn derivatives, such as $Zn(Oct)_2$, are available commercially and show negligible cytotoxicity, at least when used in the catalytic amounts. Therefore we decided to check a general applicability of $Zn(Oct)_2$ for aliphatic polyester synthesis and to answer a question whether the initiation route with this carboxylate conforms to the scheme established by us for $Sn(Oct)_2$.

The representative kinetic plots for CL and LA polymerizations initiated with $Zn(Oct)_2$/alcohol mixtures are shown in Fig. 1 in semilogarithmic coordinates. Their linearity indicates that concentration of the active species is invariable throughout the whole polymerization process (at least up to ≈95% of monomer conversion) – thus, there is no termination. However, for the relatively fast CL polymerization the induction period is clearly seen (Fig. 1a). The lower the starting concentration of $Zn(Oct)_2$ ($[Zn(Oct)_2]_0$) the longer is the induction period. This effect is, most probably, related with a rearrangement of zinc octoate aggregates during the initial reactions with alcohol (BuOH) molecules.

The molar masses (M_n's) of the resulting polyesters (PCL and PLA) have been found to be practically equal to M_n (calcd) $= M_M([M]_0 - [M])/[BuOH]_0 + M_{BuOH}$ in polymerizations initiated with $Zn(Oct)_2$/BuOH system, independently of the concentration of $Zn(Oct)_2$ used (Table 1).

When no BuOH is used polymerization is considerably slower and molar masses are very high. A few examples are given in Table 2.

These results clearly indicate that this is the $Zn(Oct)_2$ itself introducing some amount of the impurities playing a role of the coinitiator, starting the polyester chain growth. For example, the M_n of poly(CL) equal to 3×10^5 means $DP_n \approx 2600$, which corresponds to concentration of active centers P_n* (assuming no termination or transfer) equal to $[CL]_0/DP_n = 2.0$ mol L^{-1}/2600 $= 7.7 \times 10^{-4}$ mol L^{-1} and being much lower than $[Zn(Oct)_2]_0$. This is the concentration, at which the adventitiously present impurities may govern the final molar mass. Similar results have been obtained for the $Sn(Oct)_2$ coinitiated polymerization [8,9,25].

Table 1
Molar masses (M_n's) for PCL and PLA prepared with $Zn(Oct)_2$/BuOH system[a]

Monomer	$[Zn(Oct)_2]_0$/ mol L^{-1}	$[BuOH]_0$/ mol L^{-1}	M_n[b] (calcd)	M_n[c,d] (SEC)	M_n[e] (osm)
CL	0.05	0.010	2.29×10^4	2.5×10^4[c]	2.2×10^4
	0.40	0.010	2.29×10^4	2.3×10^4[c]	–
	0.05	0.120	1.97×10^3	1.9×10^3[d]	1.4×10^3
	0.05	0.210	1.16×10^3	1.1×10^3[d]	0.9×10^3
	0.05	0.430	0.60×10^3	–	0.7×10^3
LA	0.01	0.008	1.71×10^4	1.5×10^4[c]	–
	0.05	0.050	2.62×10^3	2.8×10^3[d]	–
	0.01	0.120	1.14×10^3	1.2×10^3[d]	–

[a] Polymerization carried out in THF solvent, at 80 °C; $[CL]_0 = 2$ mol L^{-1}, $[LA]_0 = 1$ mol L^{-1}.

[b] $M_n = M_M([M]_0 - [M]_{eq})/[BuOH]_0 + M_{BuOH}$, where M_M and M_{BuOH} denote molar masses of monomer and BuOH, respectively; $[M]_0$, $[BuOH]_0$ – the corresponding starting concentrations; $[M]_{eq}$ – monomer equilibrium concentrations (≈0 and 0.055 mol L^{-1} for CL and LA, respectively).

[c] Determined with laser light scattering (LLS) detector.

[d] Determined with refractive index (RI) detector and calibration on polyester standards for the crude reacting mixtures.

[e] Determined with vapor pressure osmometer for the isolated polyester samples.

It is interesting to note that in this series of experiments such a high molar masses could be achieved with a simple, commercially available initiator.

In the molar mass region where M_n could be determined without ambiguity the calculated M_n was found to be equal to the measured M_n. Ineed, as it follows from Fig. 2, giving the MALDI-TOF traces of the oligomeric PCL and PLA the calculated M_n's are equal to 2356 (PCL) and 2091 (PLA) whereas M_n (MALDI) = 2500 and 2100, respectively (see caption of Fig. 2). This is a satisfactory result taking into account the expected experimental error. The spectrogram for PCL (Fig. 2a) is particularly clean, it almost exclusively shows peaks, being apart of 114.14 m/z and corresponding to the linear BuO–$(cl)_n$–H [where cl stands for the ε-caproyl ($C(=O)(CH_2)_5O$) repeating unit] chains without any trace of the macrocyclic oligomers at the complete monomer conversion. In the LA polymerization the macrocyclics are also absent and the peaks being apart of $\Delta m/z = 144.13$ and corresponding to the linear BuO–$(la)_{2n}$–H [where la stands for the lactoyl ($C(=O)CH(CH_3)O$) repeating unit] chains prevail in the spectrogram. However, already at the 70% monomer conversion a peak series of lower intensity, corresponding to the BuO–$(la)_{2n+1}$–H chains (i.e. containing odd number of la units), is clearly seen pointing to the intermolecular transesterification (Fig. 2b).

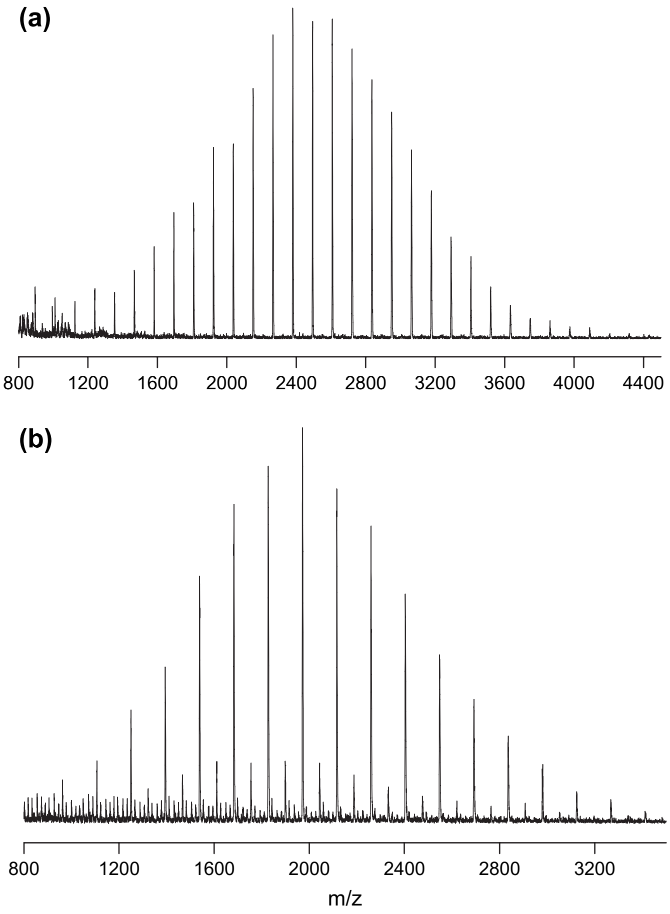


Fig. 2. MALDI-TOF traces of PCL (a) and PLA (b) prepared with $Zn(Oct)_2$/BuOH system (THF solvent, 80 °C). Concentrations (in mol L^{-1}): (a) $[CL]_0 = 2.0$, $[Zn(Oct)_2]_0 = 0.12$, $[BuOH]_0 = 0.1$ (conversion ≈ 100%); (b) $[LA]_0 = 1.0$, $[Zn(Oct)_2]_0 = 0.05$, $[BuOH]_0 = 0.05$ (conversion ≈ 70%).

Having established the livingness of polymerization of both CL and LA with $Zn(Oct)_2$/BuOH initiating system, we measured the dependencies of the relative (i.e. normalized to the

Table 2
Molar masses (M_n's) and their dispersities (M_w/M_n) for poly(ε-caprolactone) and poly(L-lactide) prepared with "pure" $Zn(Oct)_2$[a]

Monomer	$[Zn(Oct)_2]_0$/mol L^{-1}	Monomer conversion/%	$\tau_{1/2}$ [b]/min	M_n[c] (SEC)	M_w/M_n[c]	M_n[d] (osm)
CL	0.02	≈100	220	4.4×10^5	1.04	3.6×10^5
	0.03	84	127	3.3×10^5	1.05	3.0×10^5
	0.04	96	71	2.9×10^5	1.10	2.5×10^5
	0.05	≈100	46	3.0×10^5	1.17	2.6×10^5
	0.20	≈100	16	2.1×10^5	1.08	2.4×10^5
LA	0.05	95	500	1.3×10^5	1.18	–
	0.02	92	2400	2.1×10^5	1.21	–

[a] Polymerization carried out in THF solvent, at 80 °C; $[CL]_0 = 2$ mol L^{-1}, $[LA]_0 = 1$ mol L^{-1}.

[b] $\tau_{1/2}$ – time of the 50 mol% monomer conversion.

[c] Determined with LLS detector for the crude reacting mixtures.

[d] Determined with high speed membrane osmometer for the isolated polyester samples.

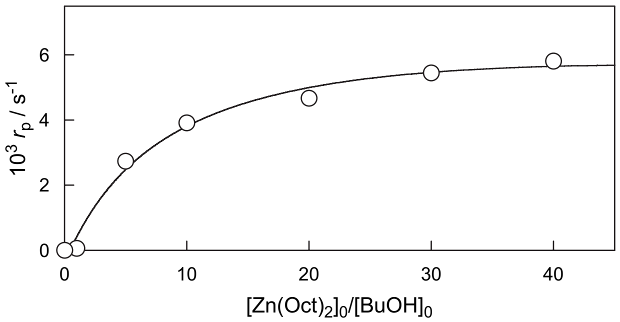


Fig. 3. Dependence of the relative rate of polymerization ($r_p = -d[CL]/[CL]dt = t^{-1}\ln([CL]_0/[CL])$) of CL coinitiated with $Zn(Oct)_2$ on $[Zn(Oct)_2]_0/[BuOH]_0$ ratio with $[BuOH]_0 = 0.01\ mol\ L^{-1}$ constant through this series of experiments; THF solvent, 80 °C.

unitary monomer concentration) polymerization rate (r_p) on the ratio $[Zn(Oct)_2]_0/[BuOH]_0$ when $[BuOH]_0$ is kept constant. The corresponding plots for CL and LA are shown in Figs. 3 and 4a. Additionally, in Fig. 4b is given r_p dependence on $[BuOH]_0/[Zn(Oct)_2]_0$ ratio when $[Zn(Oct)_2]_0$ is kept constant. These plots are formally the same as observed for our studies with $Sn(Oct)_2$ and the same monomers [8,9].

The above reported results show that the rate first increases and then levels off. Such a kinetic behavior indicates that $Zn(Oct)_2$ is neither a catalyst nor the initiator exclusively by itself; rather these results indicate that $Zn(Oct)_2$ must react with an alcohol in order to produce the true initiator. The rate of polymerization increases with added alcohol as long as there is sufficient $Zn(Oct)_2$ in the system to provide the initiator (Fig. 4b). The same argument holds when $[BuOH]_0$ is kept constant and $[Zn(Oct)_2]_0$ is incrementally increased in every next experiment (Figs. 3 and 4a). When all of the BuOH is already used as coinitiator in reaction with $Zn(Oct)_2$ its further addition no longer increases the rate. Thus the $Zn(Oct)_2$ coinitiated polymerization proceeds according to Scheme 2.

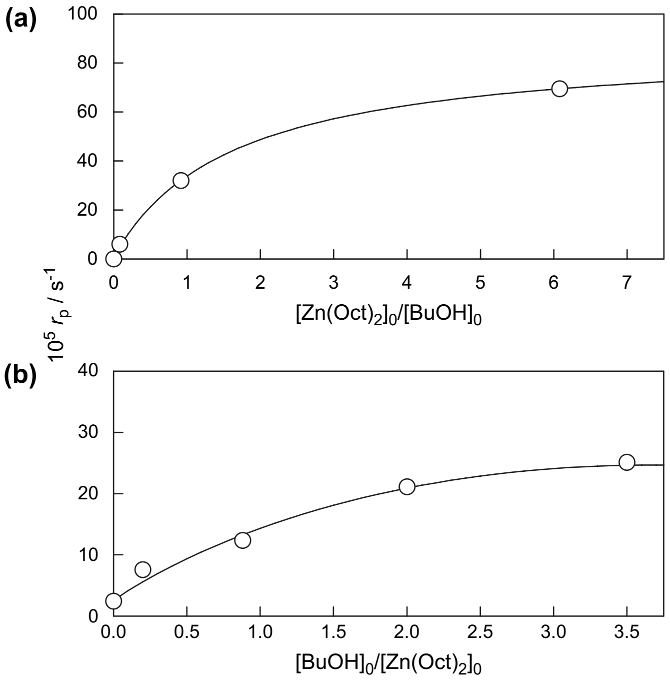
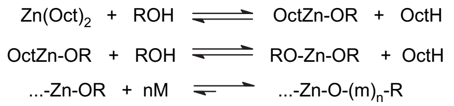


Fig. 4. Dependencies of the relative rate ($r_p = -d([LA] - [LA]_{eq})/([LA] - [LA]_{eq})dt = t^{-1}\ln\{([LA]_0 - [LA]_{eq})/([LA] - [LA]_{eq})\}$) of LA polymerization coinitiated with $Zn(Oct)_2$ on: (a) $[Zn(Oct)_2]_0/[BuOH]_0$ ratio with $[BuOH]_0 = 0.05\ mol\ L^{-1}$ kept constant, (b) $[BuOH]_0/[Zn(Oct)_2]_0$ ratio with $[Zn(Oct)_2]_0 = 0.05\ mol\ L^{-1}$ kept constant; THF solvent, 80 °C.



R denotes H or alkyl group, OctH - the 2-ethylhexanoic acid,
M - the LA or CL molecules, and m - the polyester repeating unit

Scheme 2. Initiation with zinc-alkoxide formed via carboxylate–alkoxide ligand exchange reactions.

In our works [8,9] and in the works of others polymerization rate was sometimes proportional to $[\text{"}Sn(Oct)_2\text{"}]_0$. This simply means that some coinitiator is present in $Sn(Oct)_2$ already and its reaction with $Sn(Oct)_2$ gives true initiator. Similar phenomenon we observed in the present work (Table 2). Another possibility is that coinitiator is present in monomer and/or solvent. Then, the increase of $[Zn(Oct)_2]_0$ (or $[Sn(Oct)_2]_0$) would give the same result as observed in Figs. 3 and 4a before plateau is reached.

3.2. Polymerizations coinitiated with aluminum tris-acetylacetonate

Metal (e.g. Al, Ca, Sn(II), Zr) acetylacetonates appear to be useful initiators/catalysts employed for the ring-opening homo- and copolymerization of cyclic esters [2,26–28]. Since structure of these compounds resembles to a certain extent the carboxylates structure, as it is schematically shown in Fig. 5, we decided to check whether the initiation route with these derivatives conforms to a general scheme established by us for the carboxylates.

As a model initiator from this family of compounds we have chosen aluminum tris-acetylacetonate ($Al(Acac)_3$). The representative kinetic plots for CL and LA polymerizations initiated with $Al(Acac)_3$/BuOH mixtures (THF solvent, 80 °C) are shown in Fig. 6 in semilogarithmic coordinates. Again, linearity of these plots indicates that concentration of the active species is invariable throughout the whole polymerization process, pointing to the absence of termination. However, in the absence of coinitiator (BuOH) the polymerization is extremely slow (Fig. 6b, plot 5) and the 50% conversion requires more than 100 h. M_n of

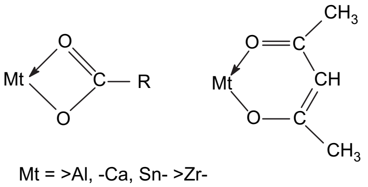


Fig. 5. Schematic presentation of the carboxylate and acetylacetonate structures.

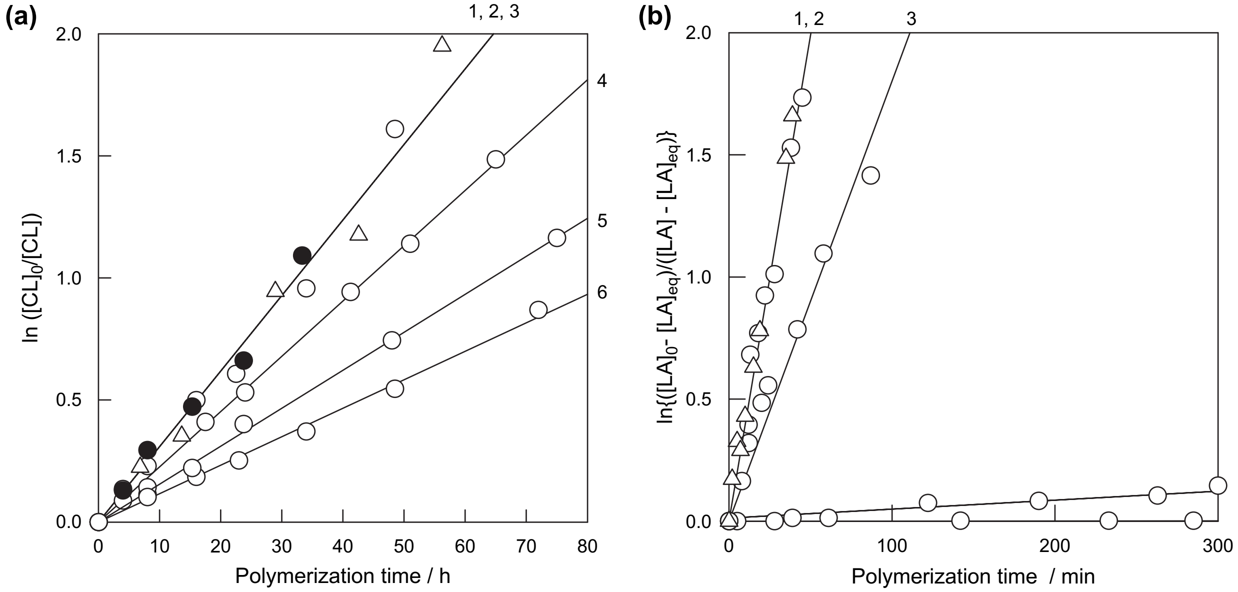


Fig 6. Kinetics of CL (a) and LA (b) polymerization initiated with $Al(Acac)_3$/BuOH system. $[CL]_0 = 2.0$ mol L^{-1}, $[BuOH]_0 = 0.05$ mol L^{-1} $[Al(Acac)_3]_0$ (in mol L^{-1}) = 0.40 (1), 0.30 (2), 0.20 (3), 0.15 (4), 0.10 (5), 0.05 (6) (a); $[LA]_0 = 1.0$ mol L^{-1}, $[Al(Acac)_3]_0 = 0.05$ mol L^{-1}, $[BuOH]_0$ (in mol L^{-1}) = 0.76 (1), 0.50 (2), 0.23 (3), 0.10 (4), 0 (5) (b); THF solvent, 80 °C.

the resulting PLA exceeds 10^5 what corresponds to the concentration of the growing and/or temporary dormant macromolecules equal to $\approx 7 \times 10^{-4}$ mol L^{-1}, whereas $[Al(Acac)_3]_0 = 5 \times 10^{-2}$ mol L^{-1} that is almost 100 times higher. Thus, most probably, M_n is governed by impurities, as it was shown above for $Zn(Oct)_2$.

M_n is a direct function of the $[M]_0/[BuOH]_0$ ratio, as it could be expected. Fig. 7 shows two examples of MALDI-TOF spectra of cyclic ester/$Al(Acac)_3$/BuOH polymerizing mixtures for which, on the basis of feed composition and monomers' conversion, the calculated M_n's are equal to 1215 and 1425 for PCL and PLA, respectively (M_n (calcd) = $M_M([M]_0 - [M])/[BuOH]_0 + M_{BuOH}$). The corresponding values measured from the spectra are equal to 1290 and 1410.

MALDI-TOF spectra point also to the strong depression of the intra- and intermolecular transesterification, since the signals corresponding either to the PCL macrocyclic fraction (Fig. 7a) or to the population of PLA chains containing odd number of the lactoyl repeating units (Fig. 7b) are almost absent.

Similarly as in the case of $Zn(Oct)_2$ initiation studies, after making sure that the $Al(Acac)_3$/BuOH system leads to living polymerization we measured the dependencies of the polymerization rate on the ratios: $[Al(Acac)_3]_0/[BuOH]_0$ ($[BuOH]_0$ = const.) and $[BuOH]_0/[Al(Acac)_3]_0$ ($[Al(Acac)_3]_0$ = const.) Results for CL and LA are shown in Figs. 8 and 9, respectively. The reported results of the kinetic measurements show that the rate first increases and then levels off. Such a kinetic behavior indicates that $Al(Acac)_3$, like $Sn(Oct)_2$ or $Zn(Oct)_2$, is neither a catalyst nor the initiator exclusively by itself. As for the carboxylates, these results indicate that $Al(Acac)_3$ must react with an alcohol in order to produce the true initiator.

The rate of polymerization increases with added alcohol as long as there is sufficient $Al(Acac)_3$ in the system to provide actual initiator (Fig. 9b). The same argument holds when

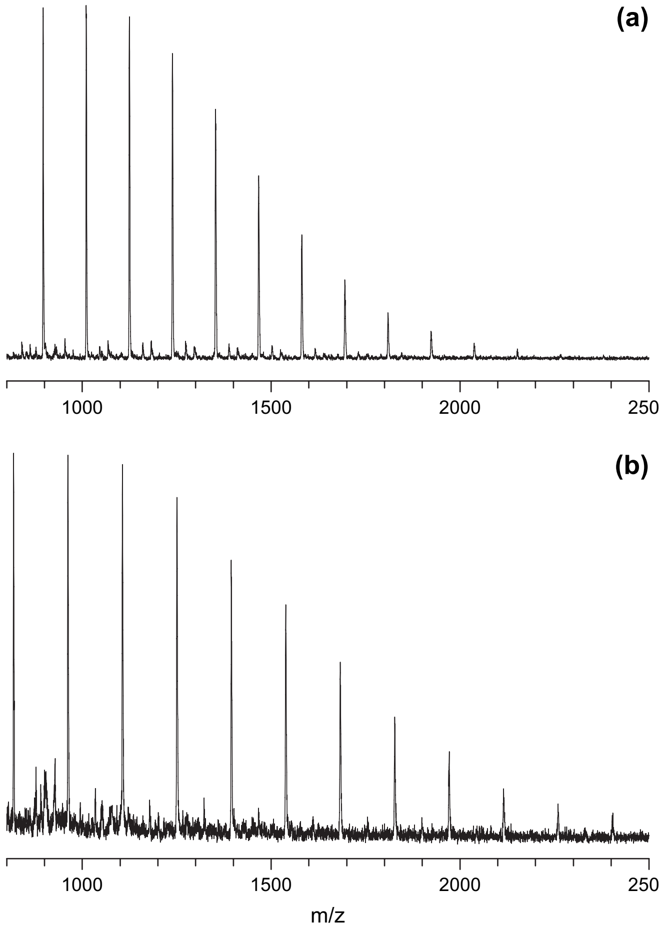


Fig. 7. MALDI-TOF traces of PCL (a) and PLA (b) prepared with $Al(Acac)_3$/BuOH system. Concentrations (in mol L^{-1}): (a) $[CL]_0 = 2.0$, $[Al(Acac)_3]_0 = 0.05$, $[BuOH]_0 = 0.20$ (monomer conversion ≈ 100%); (b) $[LA]_0 = 1.0$, $[Al(Acac)_3]_0 = 0.05$, $[BuOH]_0 = 0.10$ (monomer conversion ≈ 0.94%); THF solvent, 80 °C.

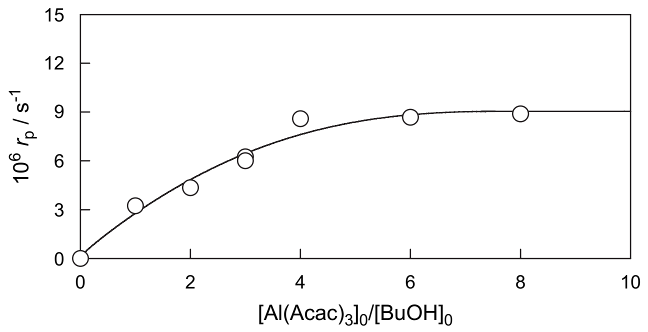


Fig. 8. Dependencies of the rate of CL polymerization r_p ($r_p = -\mathrm{d[CL]}/\mathrm{[CL]d}t$) coinitiated with $\mathrm{Al(Acac)_3}$ on $[\mathrm{Al(Acac)_3}]_0/[\mathrm{BuOH}]_0$ ratio with $[\mathrm{BuOH}]_0 = 0.05\ \mathrm{mol\ L^{-1}}$ kept constant; THF solvent, 80 °C.

$[\mathrm{BuOH}]_0$ is kept constant and $\mathrm{Al(Acac)_3}$ is added (Fig. 9a). When all of the BuOH is already used as coinitiator in reaction with $\mathrm{Al(Acac)_3}$ its further addition no longer increases the rate.

Interesting in the discussed kinetic data is the observation that the polymerization rate for the sufficiently high $[\mathrm{BuOH}]_0/[\mathrm{Al(Acac)_3}]_0$ ratio is close to the corresponding values determined some time ago for the $\mathrm{Al(O^{\mathit{i}}Pr)_3}$ initiated LA polymerization ($[\mathrm{Al(O^{\mathit{i}}Pr)_3}]_0 = 0.05\ \mathrm{mol\ L^{-1}}$, THF solvent, 80 °C) [29]. Namely, $r_p = 3.5 \times 10^{-4}\ \mathrm{s^{-1}}$ has been measured for the aggregated Al(O–PLA)$_3$ species, whereas for the deaggregated species the value of $12 \times 10^{-4}\ \mathrm{s^{-1}}$ could be expected. The plateau r_p value observed in the present system for $[\mathrm{Al(Acac)_3}]_0 = 0.05\ \mathrm{mol\ L^{-1}}$ is equal to $\approx 7 \times 10^{-4}\ \mathrm{s^{-1}}$ (Fig. 9b) and falls within a range of r_p's determined for $\mathrm{Al(O^{\mathit{i}}Pr)_3}$.

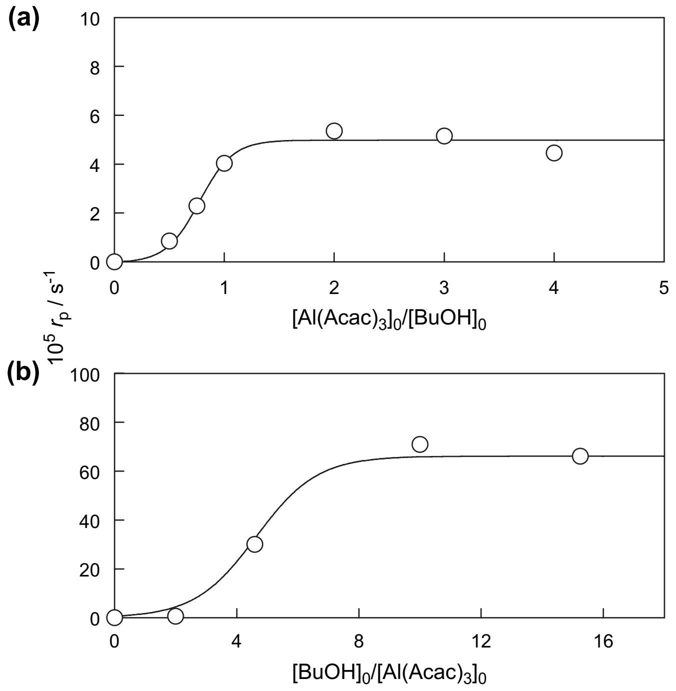
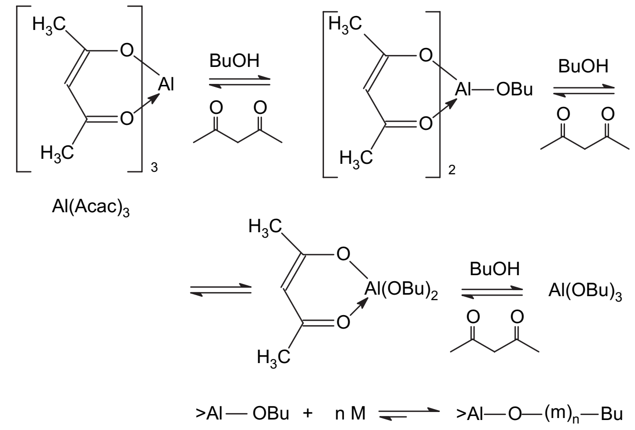


Fig. 9. Dependencies of the rate of LA polymerization r_p ($r_p = -\mathrm{d}([\mathrm{LA}] - [\mathrm{LA}]_{\mathrm{eq}})/([\mathrm{LA}] - [\mathrm{LA}]_{\mathrm{eq}})\mathrm{d}t$) coinitiated with $\mathrm{Al(Acac)_3}$ on: (a) $[\mathrm{Al(Acac)_3}]_0/[\mathrm{BuOH}]_0$ ratio with $[\mathrm{BuOH}]_0 = 0.05\ \mathrm{mol\ L^{-1}}$ kept constant, (b) $[\mathrm{BuOH}]_0/[\mathrm{Al(Acac)_3}]_0$ ratio with $[\mathrm{Al(Acac)_3}]_0 = 0.05\ \mathrm{mol\ L^{-1}}$ kept constant; THF solvent, 80 °C.



Scheme 3. Initiation with aluminum-alkoxide formed via acetylacetonate-alkoxide ligands exchange reactions.

These are strong arguments suggesting that the $\mathrm{Al(Acac)_3}$ coinitiated polymerization involves dynamic and reversible exchange of acetylacetonate and alkoxide ligands at the Al atom (Scheme 3).

Thus, most probably, the polymerization initiated with $\mathrm{Al(Acac)_3}$/BuOH system eventually proceeds as the aluminum tris-alkoxide initiated process, but only if the concentration of the added alcohol is high enough.

3.3. Comparison of $\mathrm{Sn(Oct)_2}$, $\mathrm{Zn(Oct)_2}$, and $\mathrm{Al(Acac)_3}$ coinitiated polymerizations

Since for polymerizations initiated with two-component MtL_n/ROH (Mt = Al, Sn, Zn; L = Acac, Oct) mixtures the absolute rate constants of propagation and the instantaneous concentrations of active centers are not known therefore we decided to discuss the corresponding reactivities in terms of the relative rates of propagation (r_p's). First-order kinetic plots obtained in CL and LA polymerizations coinitiated with $\mathrm{Sn(Oct)_2}$, $\mathrm{Zn(Oct)_2}$, and $\mathrm{Al(Acac)_3}$, under the identical starting concentrations and polymerization conditions, are compared in Fig. 10. Slopes of these plots give directly the r_p's values. Because $r_p = t^{-1} \ln\{([\mathrm{M}]_0 - [\mathrm{M}]_{\mathrm{eq}})/([\mathrm{M}] - [\mathrm{M}]_{\mathrm{eq}})\} = k_p[P_n^*]$ (where k_p is the absolute propagation rate constant and $[P_n^*]$ the concentration of the alkoxide active centers) the relative propagation rate depends on a position of L ligand–alkoxide group interexchange equilibria (Scheme 4).

Thus, comparing r_p's in the present system allows only a discussion of the apparent reactivities, depending on the given polymerization conditions. However, the kinetic relationships shown in Fig. 10 are typical for $[\mathrm{MtL}_n]_0 \leq 0.05\ \mathrm{mol\ L^{-1}}$ and $[\mathrm{BuOH}]_0 \leq 0.1\ \mathrm{mol\ L^{-1}}$ concentration ranges, that is, in the conditions allowing controlled synthesis of polyesters with $10^3 \leq M_n \leq 10^5$.

We can see that, independently of the monomer (CL or LA) used, polymerizations coinitiated with $\mathrm{Al(Acac)_3}$ are considerably slower than those with $\mathrm{Sn(Oct)_2}$ or $\mathrm{Zn(Oct)_2}$. Therefore synthesis of the high molar mass (hmm) polyesters with $\mathrm{Al(Acac)_3}$ becomes impractical (at least at 80 °C) since it requires

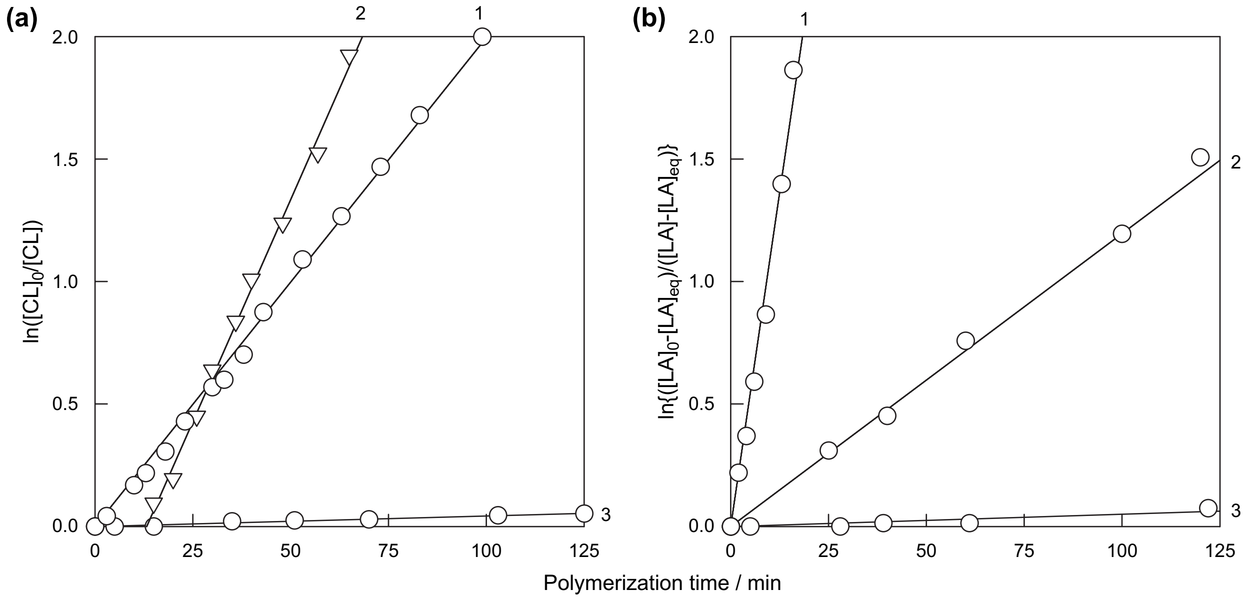


Fig. 10. Kinetics of CL (a) and LA (b) polymerization initiated with $Sn(Oct)_2$/BuOH (1), $Zn(Oct)_2$/BuOH (2), and $Al(Acac)_3$/BuOH (3) mixtures. Concentrations (in mol L^{-1}): $[CL]_0 = 2.0$, $[LA]_0 = 1.0$, $[BuOH]_0 = 0.10$, $[Sn(Oct)_2]_0 = [Zn(Oct)_2]_0 = [Al(Acac)_3]_0 = 0.05$; THF, 80 °C.

$$\mathrm{MtL_n} \underset{\text{-LH}}{\overset{\text{ROH}}{\rightleftharpoons}} \mathrm{L_{n-1}Mt\text{-}OR} \underset{\text{-LH}}{\overset{\text{ROH}}{\rightleftharpoons}} \mathrm{L_{n-2}Mt(OR)_2} \underset{\text{-LH}}{\overset{\text{ROH}}{\rightleftharpoons}} \text{etc}$$

Scheme 4. L ligand–alkoxide group interexchange equilibria at Mt atom.

very long polymerization times, even at high $[Al(Acac)_3]_0$. In contrast, $Zn(Oct)_2$ appears particularly convenient for the hmm PCL synthesis with M_n reaching 4×10^5 – in the relatively mild conditions ($[CL]_0 = 2$ mol L^{-1}, THF, 80 °C) it takes 21 h (Table 2). Similar results were obtained for $Sn(Oct)_2$/CL system [8], although the polymerization was ≈3 times slower, when compared to that with $Zn(Oct)_2$. Under the comparable conditions PLA's reaching M_n's $= 2 \times 10^5$ were prepared (Table 2 and Ref. [9]), although polymerization coinitiated with $Zn(Oct)_2$ was relatively slow and required ≈ 200 h at 80 °C for the complete monomer conversion (i.e. it was ≈6 times slower than that with $Sn(Oct)_2$).

However, it is interesting to note that selectivity, with regard to the intermolecular transesterification, of the $Al(Acac)_3$ initiated polymerization exceeds remarkably these initiated with $Sn(Oct)_2$ or $Zn(Oct)_2$. Using an approach developed earlier [30] the following k_p/k_{tr2} ratios (where k_{tr2} denotes the rate constant of the intermolecular transesterification) have been determined: 200 ($Sn(Oct)_2$, $Zn(Oct)_2$) and 350 ($Al(Acac)_3$) at the polymerization conditions given in the caption of Fig. 10. This result agrees with the observed intensities of signals in the MALDI-TOF spectra corresponding to population of PLA chains containing odd number of the lactoyl repeating units (Figs. 2b and 7b). Relatively high selectivity of the $Al(Acac)_3$ initiated polymerization can be explained by a structure of active centers dominating at $[BuOH]_0/[Al(Acac)_3]_0 = 2$. Most probably, these species bear two Acac substituents at the Al atom ($(Acac)_2Al{-}O{-}\ldots$, cf. Scheme 3), what results in a steric hindrance depressing transesterification. Thus, $Al(Acac)_3$ could be applicable for the oligomeric or medium molar mass polyesters synthesis, particularly in the processes requiring elimination of the segmental exchange (e.g. preparation of the block copolymers).

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