Control of M_n, M_w/M_n, End-Groups, and Kinetics in Living Polymerization of Cyclic Esters

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Summary: Factors affecting molar mass, molar mass distribution, end-groups, and kinetics control in polymerization of ε-caprolactone (CL) and L,L-dilactide (LA) initiated by covalent alkylmetal alkoxides, metal alkoxides, and metal carboxylates are discussed. First, an importance of the reliable molar mass measurements of the resulting polyesters is stressed. Then, it is shown that R_2AlOR', $Al(OR)_3$, $Sn(OR)_2$, and $Sn[(O)OCR')]_2/ROH$ initiators provide living polymerization of cyclic esters, in spite of the extensive aggregation phenomena. In LA polymerization Sn(II)-alkoxides appeared to be particularly effective, allowing M_n control in the range from 10^2 up to 10^6. Conditions enabling side chain transfer reactions to be eliminated are also discussed.

Introduction

There is a large number of papers describing ring-opening polymerization of cyclic esters, particularly ε-caprolactone (CL) and lactides and claiming that these polymerizations behave as the living ones. Quite often these claims are not sufficiently proved by experimental data. The most striking is for instance an observation made sometimes (that we could not comprehend) of an agreement between the molar masses (M_n) measured by size exclusion chromatography (SEC) with polystyrene standards and M_n calculated from the ratio of [consumed monomer]/[initiator]$_0$. This coincidence is striking, because the true M_n determined for example for poly(ε-caprolactone) (PCL) is approximately 0.45 times lower than that calculated without any correction from the polystyrene standards (THF, room temperature).[1-3] For poly(L-lactide) (PLA) this correction parameter is equal to 0.58.[4,5]

In the present paper we shortly give an account on the systems defined well enough (we discuss deviations from livingness) to be convinced that M_n, polydispersity index (M_w/M_n), end-groups and kinetics have been under control. This means, that almost any

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M_n (up to 10^6), M_w/M_n (down to predicted by Poisson distribution), required end-groups, and rates of polymerization could be obtained at will. We show in this paper how and why the same system could behave within a given polymerization as a well controlled up to the certain monomer conversion and how the control could be lost when the polymerization proceeds any further. In this respect we describe polymerization of CL and/or L,L-dilactide (LA) with three different groups of initiators, namely: dialkylaluminum alkoxides, aluminum trialkoxides, and tin(II) octoate (2-ethylhexanoate) (the latter with an alcohol as coinitiator). Each of these initiators may provide a living system with fully controlled features as indicated above, provided that their function is understood and polymerization is conducted at the proper conditions. These factors are discussed in this paper.

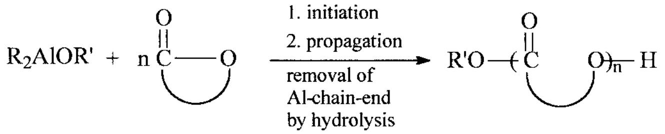
Dialkylaluminum Alkoxides

Dialkylaluminum alkoxides (R_2AlOR') were used for the first time by Chedron[6] and Hsieh[7] and then studied in more details in our group.[1,8-14] These initiators are prepared from commercial trialkylaluminums in reaction with desired alcohol. Teyssie et al.[15-17] and then Kricheldorf[18] and Hillmyer[19] have applied this opportunity to prepare a number of polymers with desired end-groups.

R_2AlOR' have two alkyl groups, being unreactive toward cyclic ester monomers (otherwise more reactive in several reactions than OR') and the alkoxide group that give the growing chains.[1,14] These compounds tend to aggregate, and the smaller R and OR' the higher the tendency of aggregation. It has been shown, however, by ^1H NMR[14] that at least for $(C_2H_5)_2AlOC_2H_5$ the exchange between various (not specified) aggregates is fast enough not to hamper the initiation and therefore, not influencing the molar mass distribution (MMD) that was found to be equal to 1.03-1.13 for CL polymerized at 25 °C in THF solvent.[1]

In order to avoid broadening of the MMD polymerization has to be stopped before broadening becomes larger than desired (cf. the last section of this paper). Actually, the narrow distribution may not be needed and as it will be shown in the next sections one may adjust the polymerization conditions to the required level in the range from Poisson distribution to the most probable one.

R_2AlOR' are also convenient in preparation of macromolecules with specific end-groups and in synthesis of block copolymers. Schematically it is shown in equation (1):



(1)

Thus, R_3Al can be used in the reaction with any alcohol R'OH, bearing an additional functional group. For instance, $(C_2H_5)_3Al$ + $CH_2=CHCH_2OH$ → $(C_2H_5)_2AlOCH_2CH=CH_2$.[1] The same principle was used for preparing macromolecules with other end-groups, such as $-O(CH_2)_2Br$, $-(CH_2)_3NEt_2$, $-(CH_2)_3CH=CH_2$, $-(CH_2)_2OC(O)C(Me)=CH_2$, $-(CH_2)_4-$, $-(CH_2)_2N(CH_3)(CH_2)_2-$,[15,16] geraniol, quinine, hormone moities[18] or polyisoprene and polybutadiene chains.[19] Being interested in the chain dynamics we prepared PCL macromolecules having at the chain-ends pyrenyl groups, known to give a signal when they meet.[20] These macromolecules were prepared by using difunctional initiator $R_2AlOR'OAlR_2$, which in turn was prepared from $HO(CH_2CH_2O)_3H$ and $(C_2H_5)_3Al$. Eventually, in this way PCL was prepared of the following structure:

where ∿∿∿∿ stands for the PCL chain.

The growing macromolecules initiated with R_2AlOR' also aggregate and the degree of aggregation depends on the size of the R substituents. This could clearly be observed in the dependence of the rate of polymerization on the starting concentration of initiator. The pertinent kinetic equation is simply derived from the straightforward kinetic scheme:

$$\left.\begin{array}{l} P_i^* + M \xrightarrow{k_p} P_{i+1}^* \\ mP_i^* \overset{K_{ag}}{\rightleftharpoons} (P_i^*)_m \end{array}\right\} \text{where } P_i^* \text{ and } P_j^* \text{ are growing, nonaggregated macromolecules and } (P_i^*)_m \text{ is an aggregate} \qquad (2)$$

Then $-d[M]/dt = k_p[P_i^*][M]$; and $K_{ag} = [(P_i^*)_m]/[P_i^*]^m$. Since importance of aggregation is apparent when $m[(P_i^*)_m] > [P_i^*]$ then $m[(P_i^*)_m] \approx [I]_0$ and $[P_i^*] = (mK_{ag})^{-1/m} \cdot {}^{1}/_{m}[I]_0^{1/m}$ Finally: $-d[M]/[M]dt = k_p(mK_{ag})^{-1/m} \cdot {}^{1}/_{m}[I]_0^{1/m}$ or $\ln r_p = \ln\{k_p(mK_{ag})^{1/m}\} + {}^{1}/_{m}\ln[I]_0$ (where $r_p = -d[M]/[M]dt$ denotes the relative rate of polymerization).

Plotting the left hand side as a function of $[I]_0$ the aggregation number could be determined. This dependence is shown in Figure 1 (taken from ref.[12]) for

$(C_2H_5)_2AlOPCL$ and $(^iC_4H_9)_2AlOPCL$. The first one gives the slope equal to 1/3 and the second one to 1/2.

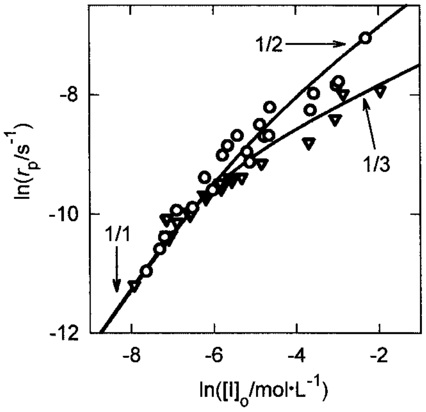
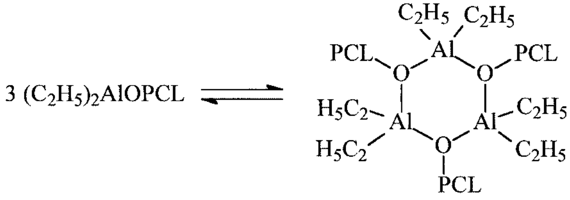


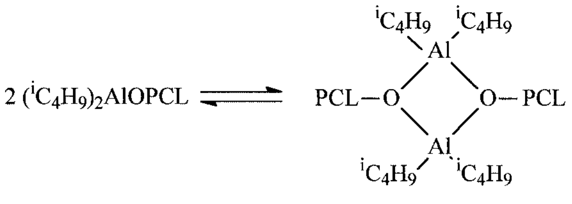
Figure 1. Bilogarithmic dependencies of the relative polymerization rates (r_p) against the starting concentrations of initiator ($[I]_0$). Polymerization of ε-caprolactone initiated with dialkylaluminum alkoxides: (▽)-$(C_2H_5)_2AlOC_2H_5$, (○)-$[(CH_3)_2CHCH_2]_2AlOCH_3$, (▼)-$(C_2H_5)_2AlOCH_2CH{=}CH_2$. Conditions: $[CL]_0$ = 2.0 mol·L^{-1}, THF solvent, 25 °C. Points experimental; curves plotted on the basis of the computer simulation of aggregation-deaggregation equilibrium with experimentally determined K_{ag} (Reproduced from ref.[12]).

Thus, growing macromolecules aggregate in the following way into the inactive ones:



(3 a)

active non-active



(3 b)

active non-active

These reversible, temporary deactivation reactions preserve however the livingness, since a given macromolecule restores its activity in the full integrity of the previously growing chain. When LA is polymerized by the same initiators, then aggregation is less apparent. In all these systems the polymerization degrees are equal to the ratio of the reacted monomer to the used initiator and the semilogarithmic plots: instantaneous monomer concentration vs. polymerization time are linear, fulfilling this way the requirement of living polymerization.

Besides the R_2AlOR'initiator tin(IV) alkylalkoxides ($R_xSn(OR')_{4-x}$) were also successfully used.[21-24]

Metal alkoxides

In the family of metal alkoxides (fully "alkoxylated" - $Mt(OR)_x$) the most often used and the most thoroughly studied is aluminum *tris*-isopropoxide ($Al(O^iPrO)_3$),[21,25-32] although the highest reported molar mass, obtained in fully controlled conditions, belongs to the tin(II) alkoxide, namely $Sn(OC_4H_9)_2$.[24] This is shown in Figure 2. Besides, as shown in Figure 3 all of the macromolecules have expected end-groups (after killing the living chains by hydrolysis). The only observed structure, as documented by MALDI-TOF mass spectrometry, is HO-PLA-C_4H_9. Similar structures, namely HO-PCL-C_4H_9 were observed by MALDI-TOF mass spectrometry in CL polymerization.

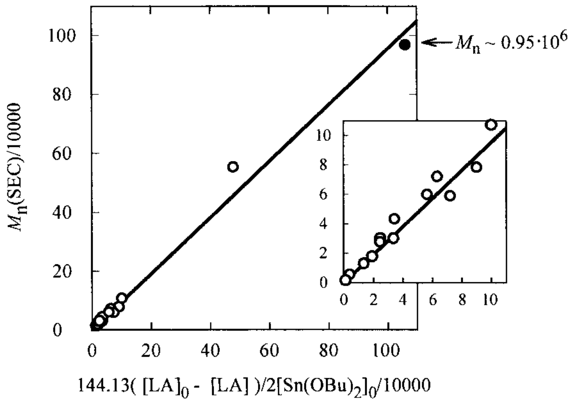


Figure 2. Depende :C on M_n calculated from the feed composition; M_n(calcd) = 144.13($[LA]_0$ - [LA])/2$[Sn(OBu)_2]_0$. Conditions of polymerization: (○) $[LA]_0$ from 1.0 to 3.0 mol·L^{-1}, THF solvent, 80°C; (●) polymerization in bulk, 120°C. (Reproduced from ref.[24]).

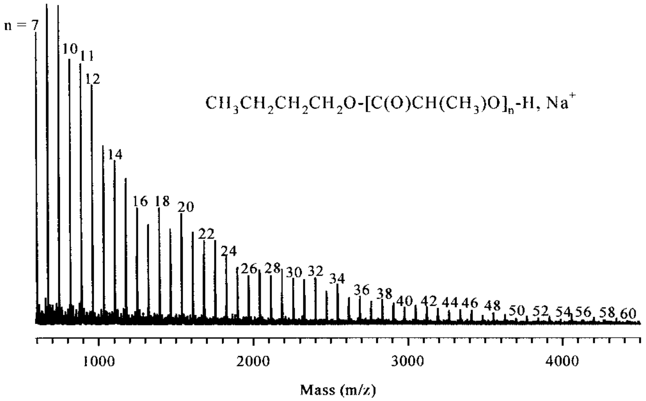


Figure 3. MALDI-TOF spectrum of living poly(L-lactide). Mass(m/z) = M_{BuOH} + nM_{la} + $M_{\mathrm{Na+}}$ (where $M_{\mathrm{BuOH}} = 74$, $M_{\mathrm{la}} = 72$, $M_{\mathrm{Na+}} = 23$. Conditions of polymerization: $[\mathrm{LA}]_0 = 1.0$ mol·L^{-1} $[\mathrm{Sn(OBu)_2}] = 3.75 \cdot 10^{-2}$ mol·L^{-1}, C_6D_6 solvent, 80°C. (Reproduced from ref.[24]).

Like in the already discussed R_2AlOR' also $\mathrm{Mt(OR)_x}$ are known to be aggregated. However, in contrast to the studied R_2AlOR' initiators, that are weakly aggregated , the $\mathrm{Al(OR)_3}$ form strongly bound aggregates. This was shown for $\mathrm{Al(O^iPr)_3}$, for which for a long time it was assumed, that it participates as a single species in initiation.[25] However, it was shown that in the case of $\mathrm{Al(O^iPr)_3}$, known to form trimeric (A_3) and tetrameric (A_4) aggregates, A_3 initiates fast both polymerization of CL as well as LA whereas at least at room temperature A_4 is practically inactive. Therefore, it is sufficient to remove A_4 from the sample of initiator, in which A_3 and A_4 are present simultaneously, in order to start polymerization giving, like for R_2AlOR' discussed in the previous paragraph, the degree of polymerization and kinetics in a full agreement with the requirements for livingness. This observation is important also for other initiators when the polymerization kinetics is studied. The molar masses in the region close to 10^6 have never been recorded for $\mathrm{Al(O^iPr)_3}$ in contrast to polymerizations initiated with $\mathrm{Sn(OC_4H_9)_2}$. The reason is not clear; it could be related to the presence of impurities (on the level of a few ppm).

In the metal alkoxide initiators all of the alkoxide groups initiate polymerization. This is documented in Figure 4, where the determined and calculated M_n are plotted one against another. M_n were calculated, assuming that every alkoxide group gives one chain.

Thus, $\mathrm{Al(O^iPr)_3}$ and other fully alkoxylated initiators give living polymerizations. The proper substitution of the Mt atom provides the required end-groups.

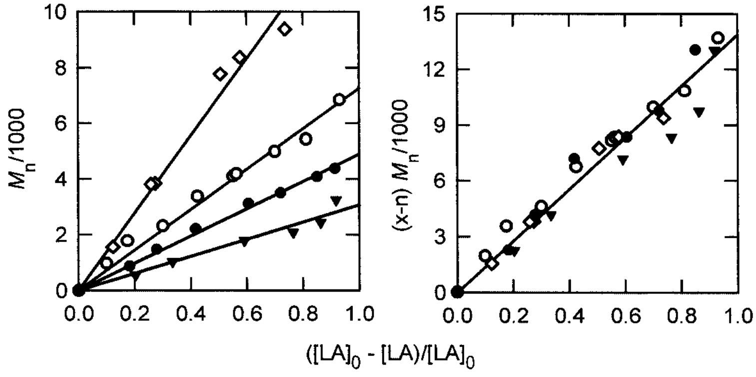
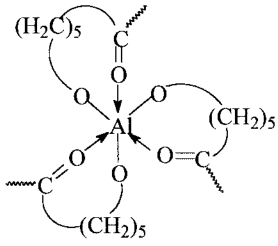


Figure 4. Dependence of M_n of poly(L-lactide) on the monomer conversion degree. Polymerization of L,L-dilactide initiated with metal alkoxides ($R_nMt(OR')_{x-n}$): Bu_3SnOEt (◇), $Sn(OBu)_2$ (○), $Al(O^iPr)_3$ trimer (A_3) (●), and $Ti(O^iPr)_4$ (▼). Conditions: $[LA]_0 = 1.0$ mol·L^{-1}, $[R_nMt(OR')_{x-n}]_0 = 10^{-2}$ mol·L^{-1}, THF solvent, 80 °C (except $Sn(OBu)_2$ for which polymerization was conducted at 25 °C) (Reprinted from ref.[33]).

$Al(O^iPr)_3$ is only aggregated as such (cf. above), but it does not give aggregated macromolecules. Studies of the ^{27}Al NMR spectra revealed that in the polymerizing mixtures hexacoordinated Al atoms prevail at least for CL [30, 33]:



The existence of this structure was confirmed by a direct reaction of $Al(O^iPr)_3$ with $HO-(CH_2)_5C(O)OC_2H_5$. After displacing the $-O^iPr$ substituents by the hydroxyester, being identical to the first repeating unit in the polymer chain, the observed ^{27}Al NMR spectrum of this species was identical to the ^{27}Al NMR spectrum recorded during polymerization. The spectrum consists of one, sharp singlet at $\delta = 1.7$ ppm, characteristic for the symmetrically hexacoordinated Al atom.

Carboxylates

The mechanism of polymerization with this group of initiators was a subject of major controversies.[34-39] It has recently conclusively been shown, that initiator like $Sn[OCOCH(C_2H_5)C_4H_9$ (abbreviated as $Sn(Oct)_2$) or its Zn analogue initiate polymerization when at least one carboxylic ligand is replaced by an alkoxide substituent: $Sn(Oct)_2 + ROH \rightleftharpoons OctSnOR + HOct$.[40-43]

Nevertheless, there are still papers appearing assuming that polymerization proceeds on the monomer-metal carboxylate complex, thus with a mechanism that has already been put on rest.

In principle, the system $Sn(Oct)_2$ + ROH (or H_2O) resembles the $Sn(OR)_2$ initiator. In the former system the hydroxyl group containing coinitiators are either present in the polymerization system as impurities (e.g. lactic acid in LA) or added intentionally in order to increase the rate of polymerization, since $Sn(Oct)_2$ alone does not initiate. Thus, the only difference between the $Sn(OR)_2$ and $Sn(Oct)_2$/ROH system is the presence of the octanoic acid in the polymerization medium. The role of octanoic acids has been studied[40-42] and it has been shown, that it:

- decreases the rate of polymerization
- does not influence the molar mass
- can form octanoic ester end groups

The inhibiting effect is due to the reversible conversion of the active and inactive states of the growing species (cf. above). Hydroxyl chain-end esterification may be observed only when the time of polymerization is much longer than time needed to complete polymerization. It has also been shown, that addition of the proton sponges or traps to this system increases the rate, due to the “chemical immobilization” of the octanoic acid, whereas they do not change the molar mass.[43] Therefore, this system may also provide living polymerization with a full control of kinetics and the end-groups.

Chain transfers

There are two kinds of chain transfer, both stemming from the presence of the ester bonds in the backbones.[5,8,44] This is an intramolecular transfer (back-biting) (eq. 4 a) and intermolecular chain transfer with chain rupture (eq 4 b).

$$\ldots\text{-(m)}_n\text{-m}^* + \text{M} \underset{k_{p(x)}}{\overset{k_{tr(1)}}{\rightleftharpoons}} \ldots\text{-(m)}_{n\text{-}x}\text{-m}^* + \text{(m)}_x \tag{4 a}$$

$$\ldots\text{-(m)}_n\text{-m}^* + \ldots\text{-(m)}_p\text{-m}^* \underset{k_{tr(2)}}{\overset{k_{tr(2)}}{\rightleftharpoons}} \ldots\text{-(m)}_{n+q}\text{-m}^* + \ldots\text{-(m)}_{p\text{-}q}\text{-m}^* \tag{4 b}$$

The first one results in formation of new cyclic molecules and therefore changes the number of the formed macromolecules; the number becoming larger than the number of molecules of initiator used. The latter does not change the number of macromolecules but changes the distribution of molar masses. The extent of this transesterification depends on the monomer conversion and on the structure of the active sites.

The formation of cyclics is thermodynamically inevitable for polyesters but kinetic conditions can be found for both CL and LA to prepare linear macromolecules almost free of cyclics. Polymerization of CL is inherently more prone on backbiting than the polymerization of LA. This is most probably related to the steric hindrance in cyclization for the substituted rings. Although more comprehensive studies on the ratio of the rate constants of propagation and transfer (k_p/k_{tr}) have only been done for the intermolecular transfer,[44] but it can safely be assumed, that the same relationship is valid for both kinds of transfers. The k_p/k_{tr} (selectivity), determined for LA polymerization, decreases in the following order for the initiators studied till now: $Sn(Oct)_2 \approx Sn(OBu)_2 > Al(O^iPr)_3 > Ti(O^iPr)_3 > Fe(OEt)_3 > La(O^iPr)_3 > Sm(O^iPr)_3 > MeO^-K^+$. Some not yet quantitative and preliminary data indicate, that high selectivity can also be reached with aluminum *tris*-acetylacetonate.[45] Thus, as it was indicated in Introduction, polymerization may proceed to a certain monomer conversion as a living one, and then is loosing this feature.

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