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CONTROLLED POLYMERIZATION OF CYCLIC ESTERS. STRUCTURE OF INITIATORS AND OF ACTIVE SPECIES RELATED TO THE SELECTIVITY OF INITIATION AND PROPAGATION

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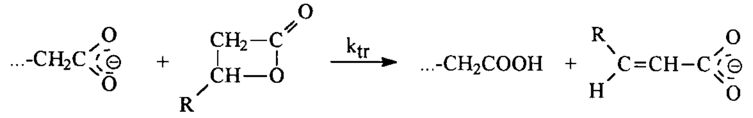
Abstract: This paper reviews mostly the already published work of our own, complemented with some new data and related to the control (i.e. selectivity) in the anionic and covalent (pseudoanionic) polymerization of cyclic esters. Ionic and covalent growing species are briefly compared in terms of their susceptibility to undergo side reactions. Then, structures of covalent initiators (mostly multivalent metal alkoxides) are discussed from the view point of their behavior in initiation and formation of active species. R_2AlOR', $(RO)_3Al$, and other metal alkoxides are discussed.

Introduction

Comparison of ionic and covalent active species in the polymerization of cyclic esters has shown that the latter ones induce less of side reactions and provide more control and selectivity of polymerization (Ref. 1-5). The major side reactions are either related to the proton transfer, known in the anionic polymerization of cyclic ethers and lactones for almost as long, as these processes are being studied (Ref. 6-8) or to the chain transfer to macromolecules followed by the chain scission (Ref. 1-5,9,10).

More recently proton transfer, accompanying propagation, was studied quantitatively for ß-propiolactone and its ß-methyl substituted counterpart (i.e. ß-butyrolactone) and the corresponding rate constants have been determined (Ref. 11). The higher rate constant of transfer for the ß-butyrolactone was observed, e.g.:



(1)

(R = H : $k_{tr} = 10^{-7}$, $k_p = 4\cdot10^{-3}$; R = CH_3 : $k_{tr} = 10^{-6}$, $k_p = 10^{-6}$ (rate constants expressed in $mol\cdot L\cdot s^{-1}$)).

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Similar reactions can take place at the stage of initiation. Then, transfer influences exclusively the structure of the end-groups. Therefore, at this stage transfer is less important, since eventually growing species are quantitatively formed. Moreover, independently of the extent of these side reactions they do not break the material chains. Usually, both initiation by addition and transfer coexist, and their relative importance depends on the ionic initiator used: more important for alcoholates, less important for carboxylates (Ref. 12-14). Sometimes the reversibility of transfer may minimize its importance. Actually, Dale has shown, that alcoholates react reversibly with higher lactones, including ϵ-caprolactone (Ref. 15). Although the quantitative data are not yet available, the importance of transfer may depend on the counterion structure and the extent of pairing. These processes are even more important for the polymerization of propylene oxide, where transfer in anionic polymerization does not allow forming of high polymers (Ref. 6).

However, these difficulties are removed, at least for cyclic esters, when covalent initiators are used; therefore the interest to the synthetic aspect of the anionic polymerization of at least ϵ-caprolactone (CL) and lactides (e.g. L,L-dilactide (LA)), vanished and became only of historical interest. Nevertheless, the extensive work on reactivities of macroions and macroion-pairs in the polymerization of cyclic esters retains its general importance (Ref. 16-18) and further work may provide ways of increasing the selectivity of ionic species. Thus, extension of research showing the importance of ligands in tuning the reactivities, as it was revealed in the carbanionic polymerization (Ref. 19), will bring a new possibilities also to the anionic ring-opening polymerization.

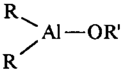
The differences described above stem from the fact, that covalent initiators, being also of alcoholate structure, are much weaker bases than alcoholate anions, paired and (particularly) the free ones. Studies of initiation with covalent alcoholates, whenever carefully performed, did not show any other products apart from the addition products of initiator and monomer.

We confine ourselves in this review only to the well established systems. Polymerization of cyclic esters is a very active research area, related to important large scale technologies, and almost any potential initiator was mixed with monomers, heated and sometimes claimed to be a better initiator than the other ones, although the evidence is sometimes rather weak.

Initiation with covalent initiators

(a) dialkylaluminum alkoxides

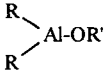
These initiators, of the general formula


$R_2Al{-}OR'$

(where R and R' are the same or different)

have been introduced over 30 years ago but studied quantitatively and understood only recently (Ref. 3,20-26).

Depending on the size of substituents (R and R') these initiators are known to exist in solution mostly as monomeric, dimeric or trimeric species (Ref. 27-29):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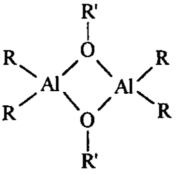
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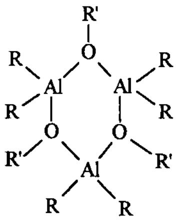
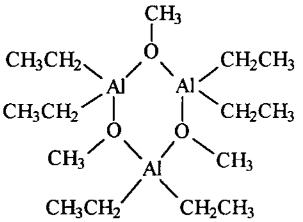
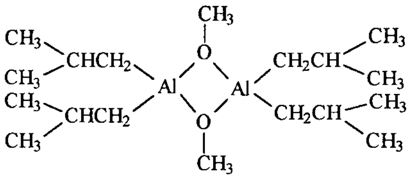


More complicated structures have also been proposed. The aggregates shown above are usually in equilibria with monomeric structures. The rate of interconversion depends on the number of factors (e.g. solvent, temperature, R and R' substituents). The same dialkylalkoxy compound may assume in one solvent the aggregated structure and deaggregated in another one. Deaggregation proceeds easier in polar and nucleophilic solvents, able to interact with Al atoms. If solvent is too strong as a complexing agent, stronger than monomer itself, the "initiator" may be exclusively monomeric, but initiation may not take place at all or become very slow. This kind of behavior was observed in our attempts of initiating the CL polymerization by Et_2AlOEt in hexamethylphosphorous triamide (HMPT) (Ref. 30).

In the dialkylalkoxy compounds R_2AlOR' there is only one oxygen atom per one Al atom, therefore the variety of structures that can be formed is much lower than in trialkoxy compounds, discussed later. The state of aggregation is a result of interplay of two opposing factors, like in other similar compounds: for enthalpic reasons the monomeric structures prefer to form an aggregate, because formation of aggregates is exothermic (Ref. 27-29). However, this is an endoentropic process, since at least translational entropy is lost when aggregates are formed. Moreover, when large substituents R and/or R' are present, then crowding causes repulsion and higher aggregates (e.g. trimers) can not be formed. Therefore, diethylaluminum methoxide forms mostly a trimer, whereas diizobutylaluminum methoxide, because of crowding, forms mostly a dimer:



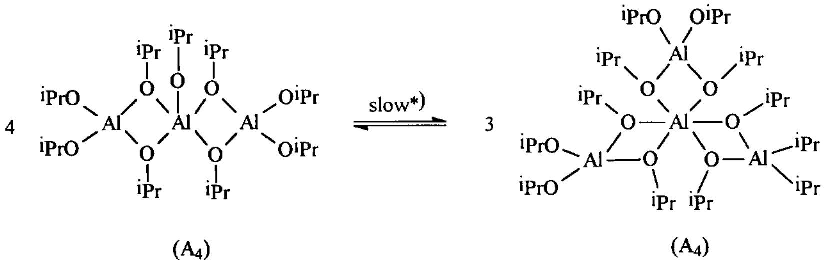


These aggregates are weaker bonded than the corresponding aggregates of trialkoxyaluminum, where (at least in some structures) Al atoms are linked to other Al atoms by not merely two, as indicated above, but by up to six oxygen atoms. The ^1H and ^{27}Al NMR spectra of higher dialkylaluminum alkoxides do not indicate a presence of isomers (cf. structures given in the next reaction), at least at or above r.t. in THF or C_6D_6 solvent, i.e. at conditions typical for cyclic esters polymerization (Ref. 30,31). The ^1H NMR spectrum of the low molecular weight oligomer, formed when a high enough ratio $[R_2AlOR']_0/[monomer]_0$ is used, shows exclusively signals expected for the 1:1 reaction product, responsible for further polymerization. The alkyl groups stay intact on Al and only the alkoxy group is involved in initiation (Ref. 31):

(2)

(b) trialkoxyaluminums ($Al(OR)_3$) and related compounds ($Sn(OR)_2$, $Fe(OR)_3$, $Ti(OR)_4$)

Trialkoxyaluminum are known as initiators for a long time (Ref. 1,32). The triizopropoxyaluminum ($Al(O^iPr)_3$) has been the most often used. We have shown recently, that in all of the works published prior to our papers (Ref. 33-36) the difference in reactivities of two coexisting aggregates of ($Al(O^iPr)_3$) was overlooked. This initiator does not only consist of aggregates differing in reactivities, what was a known fact in organic chemistry (Ref. 37), not appreciated in the works concerning polymerization, but also the rate of exchange between these two forms is slow enough to highly influence the kinetics of polymerization. Thus, we have shown, that the two forms of $(Al(O^iPr)_3$, namely its trimer (A_3) and tetramer (A_4):



(3)

*) the actual reaction path - i.e.number of steps - is not yet known

due to these slow rates of exchanges (for the ^{1}H and ^{13}C NMR time scales) could separately be observed by NMR (Ref. 33,34,36). Then, we observed, also by NMR, that from a mixture of A_3 and A_4, it is A_3 that reacts fast with the CL monomer, initiating polymerization quantitatively, whereas A_4 is left almost unreacted when all of CL was already consumed in propagation (Ref. 33,34).

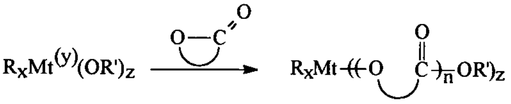
The difference in the rates of initiation with A_3 and A_4 is more dramatic for CL than with LA. This is because CL is a more discriminating monomer: it reacts much faster, not giving enough time for A_3 and A_4 to interexchange. LA reacts much slower with $Al(O^iPr)_3$ (A_3), therefore at least some A_4 can be converted into A_3 (or other reactive form of $Al(O^iPr)_3$) before it is polymerized through A_3 initiation. The recently determined $k_{i(A3)}/k_{i(A4)}$ ratios (where k_i denotes the respective rate constant of initiation) are equal to 10^5 and $4 \cdot 10^3$, whereas the apparent propagation rate constants (k_p^{app}) equal 0.5 and $7.5 \cdot 10^{-5}$ $mol \cdot L \cdot s^{-1}$ for CL and LA, respectively (THF as a solvent, 20°C) (Ref. 36). However, since polymerizations of CL and LA are reversible processes and monomer is present in the system when the *living polymer* $\rightleftharpoons$ *monomer* equilibrium is reached, then eventually, after a time long enough A_4 would also vanish, converting into growing species and chain ends.

More recently we have shown, that alkoxides of other metals (e.g. $Sn(O^nBu)_2$, $Fe(OEt)_3$ or $Ti(O^iPr)_4$) behave similarly, i.e. all of the alkoxy substituents are used in initiation and the corresponding number of chains grow "from" the metal atom (Ref. 38,39). Particularly interesting is $Sn(O^nBu)_2$, which (surprisingly) has not yet been studied, although a number of other tin compounds were screened. The latter initiator gives in a controlled way ($\overline{DP}_n = ([M]_o-[M]_{eq}/2[I]_o)$ linear polyesters with $\overline{M}_n$ from 10^3 up to 10^6 in the polymerization of LA

(Ref. 39), the range hardly accessible for any other initiator, including $Sn(Oct)_2$, for which the relationship $\overline{DP}_n = ([M]_o\text{-}[M]_{eq})/[I]_o)$ does not hold.

Thus, a general conclusion for the initiation with metal alkoxides is as follows:

- all of the comprehensively studied metal alkoxides (including alkylalkoxides) initiate polymerization by a simple and quantitative reaction of the alkoxy groups:



$$R_xMt^{(y)}(OR')_z \xrightarrow{O-C(=O)} R_xMt(\!(O\ \overset{\overset{O}{\|}}{C})_{\overline{n}}OR')_z \qquad (4)$$

(where z = y-x and y = 2,3 or 4)

- when $R_xMt(OR')_z$ exists in different aggregated states exchanging slowly enough:

$$p[R_xMt(OR')_z]_q \rightleftharpoons q[R_xMt(OR')_z]_p \qquad (5)$$

then it may happen, that one of these forms is so much less reactive, that polymerization initiated by the more reactive form, comes to the polymer ⇌ monomer equilibrium before the less reactive form does react at all.

The simple solution for a bench chemist, is to use exclusively the most reactive form, when two or more isomeric forms of an initiator coexist. Then, the full control of polymerization is possible, i.e. $\overline{DP}_n$ of the polymer is equal to $([M]_o\text{-}[M]_{eq})/[I]_o$ and the end-groups are as required. For instance, separation of A_3 from A_4 is relatively simple. A_3 is soluble in pyridine, whereas A_4 is not. The pertinent description of the involved procedure is given in Ref. 32.

There was a number of studies of other authors on the related systems. The unequivocal results were published at least for the tin(IV) based initiators (Ref. 5,40,41), conforming the general conclusions described in this chapter. There are also some other systems that are not yet fully understood at present (as e.g. the lanthanoide derivatives) and we refrain from discussing the related polymerizations. Strange enough, the most often used tin octanoate ($Sn(OC(O)CH(C_2H_5)C_4H_9)_2$, ($Sn(Oct)_2$)), belongs to this group. However, on the basis of our recent, unpublished work, this salt of octanoic acid is converted first into the corresponding alcoholate in reaction with ROH compounds present in the system, and only active as initiator in this form (Ref. 39). ROH (R = alkyl, aryl, or H) may either be an impurity or is introduced intentionally.

Propagation

(a) dialkylaluminum alkoxides

Structures and behavior of active species in propagation reflect the properties of initiators, described in the preceding section. The "only" difference, when an initiator like dialkylaluminum alkoxide, is used is related to the size of alkoxy substituent, becoming during propagation a polymer chain (cf. equation (2)). Indeed, propagation initiated with R_2AlOR' proceeds exclusively on the aluminum-oxygen bond $R_2Al—OR'$, therefore during propagation the size of the alkoxy substituent increases. This certainly creates additional steric hindrance. The influence of the size of the polymer chain on the rate constant of propagation is not yet known, neither for dialkylalkoxy nor trialkoxyaluminum initiators. The ester bond appear in the polymer repeating units, with their electron donating oxygen atoms from carbonyl groups, providing an additional source of coordination of aluminum atoms. However, the ability to coordinate with metal atoms (since this behavior is not unique for aluminum) depends on the structure of the repeating unit and electronic structure of the metal atom. Information on the state of aggregation of the growing species comes from kinetics, whereas the information on the degree of solvation was obtained from the NMR studies.

In the studies of kinetics of polymerization of CL initiated with R_2AlOR' it was established, that one molecule of initiator (I) gives one macromolecule (Ref. 22,23). It was also observed, that the rate of polymerization is directly proportional to the first power of concentration of the active species $[P_i^*]$ only at the low enough $[P_i^*]$ (under the living polymerization conditions $[P_i^*] = [I]_o$). At higher concentration the rate is either proportional to $[I]_o^{1/2}$ when R = ^{i}Bu or to $[I]_o^{1/3}$, when R = Et (Ref. 23-25). It follows from these kinetic data, that aggregation of active species takes place into dimers ($[I]_o^{1/2}$) or trimers ($[I]_o^{1/3}$) and that only the deaggregated species propagate, whereas the aggregated ones are dormant. At these conditions only a certain fraction of chains are instantaneously active; they become dormant upon aggregation and restore their reactivity when deaggregate. The rates of this aggregation - deaggregation processes are not yet known.

The corresponding kinetic scheme reads:

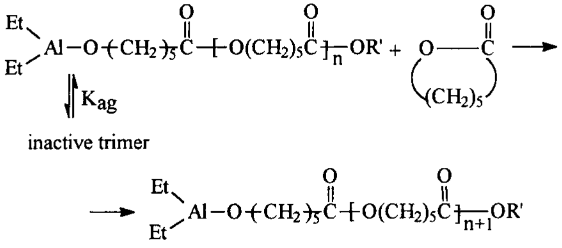
$$\ldots\text{-}P_i^* + M \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \ldots\text{-}P_{i+1}^* \tag{6a}$$

$$x \ldots\text{-}P_i^* \underset{k_{dag}}{\overset{k_{ag}}{\rightleftharpoons}} (\ldots\text{-}P_i^*)_x \tag{6b}$$

(where k_p, k_d, k_{ag}, and k_{dag} denote the rate constants of propagation, depropagation, aggregation, and deaggregation, respectively; $x = 2$ for $R = {}^iBu$ and $x = 3$ for $R = Et$)

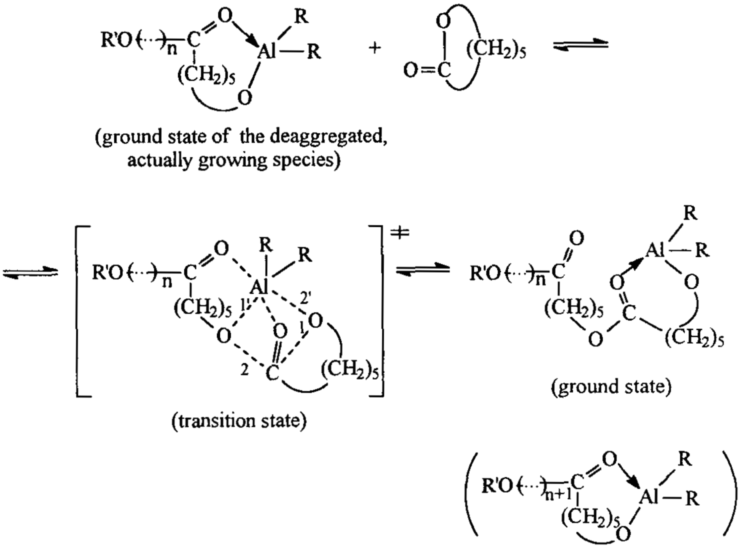
This scheme gives eventually: $d[M]/dt = k_p^{app}[M][I]_o^{1/x}$, where x is the aggregation degree and encompasses both the absolute rate of propagation and equilibrium constant $K_{ag} = k_{ag}/k_{dag}$. It was, however, possible to determine from kinetic data k_p, k_d, and the k_{ag}/k_{dag} ratio. We could also compute the proportion of the aggregated and deaggregated species as a function of a total concentration of the growing chains (Ref. 23-25).

Thus, for instance, propagation of CL initiated with diethylaluminum alkoxide can be visualised in the following way:



(7)

Although there is no detailed work on the stereelectronic factors involved in the actual propagation step, one can propose the following tentative picture of the transformation of the ground state to the transition state:

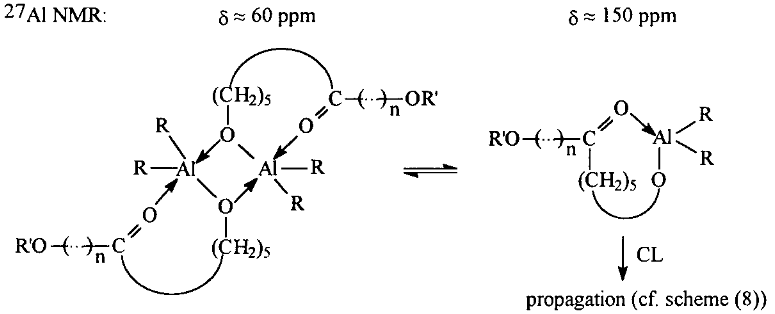


(8)

CL presumably solvates fast the monomeric R_2AlOR'. The carbonyl oxygen atom is the most nucleophilic one and in the actual transition state it coordinates with the Al atom. The other oxygen atom from the ester bond additionally coordinates with the Al atom, which forms up to six partial coordination sites in the transition state. At or close to the transition state this monomer - initiator (and then monomer - active species) complex may form the structure represented with two trigonal pyramids with three oxygen atoms at one base, two alkyl groups and one oxygen atom at the second base, and aluminum atom at both tops. One of the pyramids has to be "upside down" if the other one is upright. Two of the oxygen atoms come from the monomer molecule and two from the polymer chain end to which Al atom has been attached. At the transition state two covalent bonds brake simultaneously, namely bonds 1 and 1', i.e. the acyl-oxygen bond in the monomer molecule and the oxygen-Al bond at the active chain end. These two bonds are replaced by newly formed bonds, namely 2 and 2' (all shown in Scheme (8)). Bond 2 is incorporating a monomer molecule into the chain and bond 2' forms new active Al-alcoholate active chain end. Thus, the new ground state is formed. Each propagation step repeats this sequence.

The Al atoms in diethylaluminum ethoxide are tetracoordinated, whereas after conversion of initiator into the growing species they become mostly pentacoordinated, as it follows from the

^{27}Al NMR (Ref. 30). The pentacoordination may result from the additional, internal coordination, involving the carbonyl oxygen atoms as described above. There is also a smaller peak in the area of the tetracoordinated species, presumably the actually growing ones. The proportion of the tetracoordinated, as measured from NMR, corresponds well to the proportion calculated from kinetics. Similar ^{27}Al NMR spectra were observed in polymerization initiated with diizobutylaluminum methoxide. Therefore, we can assume the following structure of the inactive, aggregated (e.g.dimeric) species, being in equilibrium with the active deaggregated ones:



(9)

(b) trialkoxyaluminum

Propagation with trialkoxyaluminum, and particularly triizopropoxyaluminum was a matter of controversy for some time, as already discussed in this and our previous papers. Authors, worked (without realizing this fact) with different proportions of the trimer: $[Al(O^iPr)_3]_3$ (A_3) and tetramer: $[Al(O^iPr)_3]_4$ (A_4), depending on conditions of preparation of $Al(O^iPr)_3$. Therefore, if all three alkoxy groups initiate from A_3 and none from A_4, then the calculated number of growing macromolecules depends on the starting ratio concentrations $[A_3]_o/[A_4]_o$. Of course, a prolonged contact of A_4 with CL, left at the living polymer-monomer equilibrium will eventually lead to the complete consumption of A_4. This was demonstrated by us in a number of ways: ^{1}H, ^{13}C, and ^{27}Al NMR, kinetics of monomer conversion and GPC (Ref. 33-36).

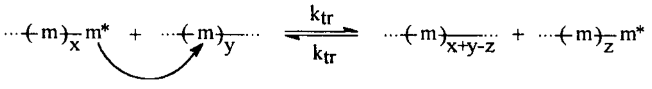
It was also shown, that indeed three chains grow from one Al atom: first the $\overline{M}_n$ was measured for a living polymer (after the complete monomer conversion) by MALLS and then "arms" were cut-off by hydrolysis and $\overline{M}_n$ measured again. The $\overline{M}_n$ of the starting, living polymer was found to be three times higher than $\overline{M}_n$ of the individual arms. These results were then confirmed in other laboratory by means of the ^{1}H NMR and viscometric measurements (Ref.42).

Controlled Synthesis of Poly(ϵ-Caprolactone) and Poly(L,L-Dilactide)

We first used dialkylaluminum alkoxides in our quantitative synthetic studies. This was at the time, when the difference of A_3 and A_4 reactivites were not yet apparent. Thus, "puzzling results" (expression taken from Ref. 43) of other authors working with $Al(O^iPr)_3$ forced us to look into initiators giving a known number of macromolecules per one molecule of initiator. This criteria were met by dialkylaluminum alkoxides. Thus, we prepared with these initiators a large number of well defined macromolecules with well controlled size, architecture, and the end-groups (Ref. 3,22,44).

Simple macromolecules with one desired end were synthetized first (Ref. 22) Then initiator $R_2Al\text{-}OR'O\text{-}AlR_2$, giving macromolecules growing in two directions was prepared and used in the syntehsis of "two ended" macromolecules (Ref. 44). Then, these and similar initiators were used a number of times by others (e.g. Ref. 26, 45-48). After understanding, a difference between A_3 and A_4 reactivities, the isolated A_3 has become the most versatile one for the controlled polymerization of cyclic esters, particularly of poly(ϵ-caprolactone) (PCL). It provides a relatively fast and quantiative initiation, moderately fast propagation and relatively good selectivity (Ref. 31,34,38). Selectivity in the polymerization of CL has been expressed by a ratio of the rate constant of propagation and the rate constant of unimolecular transfer.

In all of the polymerizations of cyclic esters there is an inevitable side reaction - transesterifiaction: one growing chain attacks another chain and segmental exchange takes place (schematically):



$$\cdots\!\left(m\right)_x\!-m^* + \cdots\!\left(m\right)_y\!\!\cdots \underset{k_{tr}}{\overset{k_{tr}}{\rightleftharpoons}} \cdots\!\left(m\right)_{x+y-z}\!\!\cdots + \cdots\!\left(m\right)_z\!-m^* \qquad (10)$$

Thus, the number of macromolecules does not change, but the molecular weight distribution (MWD) does. We have recently compared the dependence of the efficiency of this bimolecular transfer and structure of active species in the polymerization of LA, expressing the efficiency (mostly undesirable) as the ratio of k_{tr}/k_p. This ratio increases in the following order (Ref. 38):

$$\mathbf{Al(OR)_3 < Ti(O^iR)_4 < Fe(OR)_3 < Et_2AlOR < La(OR)_3 < Bu_3SnOR < Sm(OR)_3 < K^{\oplus}, {}^{\ominus}OR}$$

(where R denotes the growing macromolecule of poly(L,L-dilactide) (PLA)).

Thus, $Al(O^iPr)_3$ (in the form of A_3 (Ref. 36) looks to be ideally suited for the PLA synthesis, since apart from a good selectivity it provides, in contrast to $Sn(Oct)_2$, a direct control of the molecular weight of the resulting PLA, by simply adjusting the $([LA]_0-[LA]_{eq})/[Al(O^iPr)_3]_0$ ratio (Ref. 36,49,50). On the other hand, there is a certain limit of $\overline{M}_n$ of PLA, which can be obtained with $Al(O^iPr)_3$, equal to about 10^5. Reasons of this result are not yet well-understood (Ref. 50) and the kind of transfer taking place has to be identified.
As already mentioned in the section related to initiation, the best results in the PLA synthesis have recently been obtained with $Sn(O^nBu)_2$ as an initiator. Both low molecular weight oligomers and hmw PLA (up to $\overline{M}_n \approx 10^6$) were prepared in a controlled way (Ref. 39).

Besides the linear macromolecules also the cyclic polyesters can be prepared. Either by back-biting (unimolecular transfer) or by intentional synthesis with properly constructed initiators. Indeed, it has been known, that ß-lactones give a high concentration of cyclics, when initiated with the catalytic system: 2,2-dibutyl-1,3,2-dioxastannolane/dibutyltin dichloride (Ref. 51,52). Similar approach has been used more recently to prepare larger cyclics from lactides with 2,2-dibutyl-1,3,2-dioxastannolane alone or its thia derivatives (Ref. 53).

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