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On the Mechanism of Polymerization of Cyclic Esters Induced by Tin(II) Octoate

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SUMMARY: Mechanism of initiation and propagation in polymerization of ε-caprolactone and L,L-dilactide induced with tin(II) octoate ($Sn(Oct)_2$) and $Sn(Oct)_2$/*n*-butyl alcohol system is presented. Tin(II) alkoxide bond formation is required in reaction of $Sn(Oct)_2$ with hydroxyl group containing compound to form a true initiator. Then tin(II) alkoxide end group is an active centre in the further propagation.

Introduction

Polymerization of cyclic esters, mostly ε-caprolactone (CL) and L,L-dilactide (LA) is gaining increasing interest since the corresponding polymers are degradable and have become industrial reality[1-7]. Therefore monomers are easier accessible and numerous blocks, grafts, hyperbranched polymers, based on these monomers are being developed[8].

There are two classes of initiators the most often used in the ring opening polymerization of cyclic esters: metal alkoxides and metal carboxylates. Initiation with the first class and further chain propagation is relatively well understood; all of the alkoxide substituents at the metal atoms start the growing chains, the rate of initiation for several metal alkoxides is comparable with the rate of propagation[9]. Tetramer of the aluminium *tris*-isopropoxide is the only well documented exception[10-12].

The side reactions revealed till now are reversible chain transfers to macromolecules with chain scission (via transesterification): either unimolecular (back biting) or bimolecular (chain transfer with chain rupture - reshuffling)[13-18]. In polymerizations with covalent metal alkoxides as active centres back-biting is suppressed kinetically[13-15], whereas reshuffling is not depriving polymerization processes from their living character[16-18]. Thus, the number of chains started does not change throughout the whole polymerization process, and all of the macromolecules initiated retain their ability to grow.

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Metal carboxylates, mostly tin(II) octoate ($Sn(Oct)_2$), and less often used zinc derivatives, are very versatile initiators[19-35]. Commercial products can be handled in the half open system (i.e. do not require high vacuum equipment) and are relatively easy to purify (at least down to ≈2 mol-% of proton containing impurities)[35] by simple distillation for the synthetic applications and for semiquantitative work. The mechanism of initiation and the details of the chain growth were however not studied carefully enough in the past and a number of explanations were proposed, found recently[34-36] to be not fully correct.

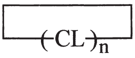
In our recent papers[34-38] we described a series of experiments that allowed description of the general mechanism of polymerization initiated with $Sn(Oct)_2$. In the present short review we summarize the most important findings of the already published papers and add some additional evidence supporting the proposed mechanism.

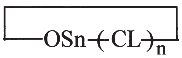
The presence of Sn atoms in the macromolecules

The major questions to be answered and being a source of a certain controversy in the past are:
- is the Sn atom located, and in which form, in the growing macromolecules ?
- is $Sn(Oct)_2$ initiating by "itself "; i.e. by a direct reaction with monomers or whether it requires a coinitiator ?

The first question was answered by studying MALDI-TOF mass spectra of poly(ε-caprolactone) (PCL) and poly(L-lactide) (PLA) prepared in the presence of $Sn(Oct)_2$ and C_4H_9OH (BuOH) or H_2O, used as coinitiators and/or transfer agents (the role of coinitiator is described below). In the case of the $CL/Sn(Oct)_2/H_2O$ system the following major populations of macromolecules have been observed (schematically)[34,36]:

$HO{-}(CL)_n{-}COOH \qquad Oct{-}(CL)_n{-}COOH$



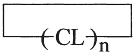


whereas for the CL/$Sn(Oct)_2$/BuOH system there was a larger number of various populations, shown below:

$$\mathrm{OctSnO}\text{-}(\mathrm{CL})_n\mathrm{COOBu}$$

$$\mathrm{HO}\text{-}(\mathrm{CL})_n\mathrm{COOBu} \qquad \mathrm{Oct}\text{-}(\mathrm{CL})_n\mathrm{COOBu}$$

$$\mathrm{HO}\text{-}(\mathrm{CL})_n\mathrm{COOH} \qquad \mathrm{Oct}\text{-}(\mathrm{CL})_n\mathrm{COOH}$$



Thus, for both systems macromolecules with tin(II) alkoxide units were observed :

$$\ldots\text{-}Sn\text{-}O\text{-}(CH_2)_5COO\text{-}\ldots$$

In the polymerization of LA with $Sn(Oct)_2$/BuOH system macromolecules fitted with $OctSn\text{-}O\text{-}CH(CH_3)COO\text{-}\ldots$ active end groups were also observed, similary to the polymerization of CL[38)].

Thus, the first question - whether Sn atoms are on the chains has been answered.

Some elements of kinetics of polymerization with $Sn(Oct)_2$

Polymerization of CL or LA induced by $Sn(Oct)_2$ without a coinitiator purposely added is a very slow process (cf. kinetic plots in Fig. 1) and the rate clearly depends on the purity of $Sn(Oct)_2$ used. The better purity - the lower the rate of polymerization. We can safely assume (vide infra) that $Sn(Oct)_2$ alone does not initiate polymerization, at least at moderate temperatures. In a number of papers dealing with the mechanistic aspects of either CL or LA polymerization commercial $Sn(Oct)_2$ was used[23,32)]. It contains, according to our ^1H NMR measurements, up to 30 mol% of compound(s) with active protons. We were able to purify $Sn(Oct)_2$ down to 0.9 mol-% (with respect to the octoate groups content) of these compounds, including presumably octanoic acid and water[35)].

Polymerization of CL as well as LA induced by $Sn(Oct)_2$ in the presence of BuOH proceeds kinetically like a living process at least below 100°C in THF solvent and the dependence of M_n, of the resulting polyesteras a function of monomer conversion is a straight line as was described previously[35,37)].

When BuOH (or e.g. $C_4H_9NH_2$ ($BuNH_2$)) are added to the polymerizing mixture, as we have shown for both CL[34,35] and LA[38], then the rates of polymerization increases, almost linearly at the lower $[BuOH]_0/[Sn(Oct)_2]_0$ ratio. However, when the ratio $[BuOH]_0/[Sn(Oct)_2]_0$ exceeds a certain value, then the rate becomes independent on $[BuOH]_0$. Similar observation was noted when the rate of polymerization was plotted as a function of $[Sn(Oct)_2]_0/[BuOH]_0$ ratio, i.e. when for a given set of kinetic measurements starting concentration of BuOH is kept constant in all experiments and starting concentration of $Sn(Oct)_2$ varies. This results is the most instructive, and meaning, that $Sn(Oct)_2$ as such is not providing active sites. The latter are formed in a reaction with BuOH that eventually gives an actual initiator.

Reaction of an alcohol with tin(II) carboxylate can be presented in the following way:

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

$$\mathrm{RC(O)OSnOR' + R'OH \rightleftharpoons R'OSnOR' + RC(O)OH} \tag{1b}$$

Whether both equilibria (1 (a) and 1 (b)) take place at the polymerization conditions or only the former - it is not clear at the present moment.

If this is indeed this exchange that provides tin(II) alkoxides as initiator, then the rate of polymerization with a system $Sn(O(O)CR)_2$ + R'OH should be comparable to the rate of polymerization with a system $Sn(OR')_2$ + RC(O)OH since:

$$\mathrm{R'OSnOR' + RC(O)OH \rightleftharpoons RC(O)OSnOR' + R'OH} \tag{2a}$$

$$\mathrm{RC(O)OSnOR' + RC(O)OH \rightleftharpoons RC(O)OSnO(O)CR + R'OH} \tag{2b}$$

Indeed, Schemes 1 and 2 are identical although approached from opposite sides and at a certain starting ratios of $Sn(O(O)CR)_2$ to HOR' (Scheme 1) and $Sn(OR')_2$ to RC(O)OH (Scheme 2) should give identical overall compositions. In Fig.1 we show that, for example for LA polymerizations, ratios: $[Sn(Oct)_2]_0/[BuOH]_0$ and $[Sn(OBu)_2]_0/[OctH]_0$ being close to 1:2 give almost identical rates of polymerization.

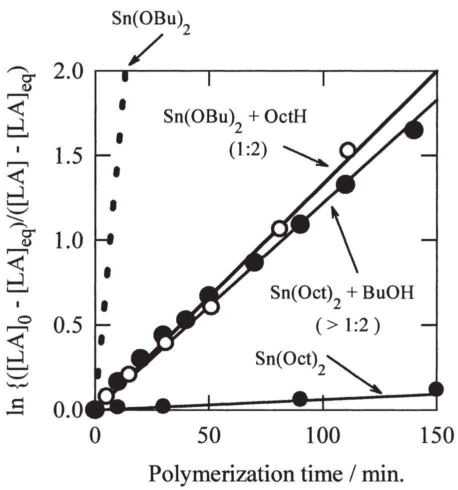


Fig.1: Kinetic convergence of $Sn(OBu)_2$/OctH and $Sn(Oct)_2$/BuOH initiating systems in the polymerization of LA. Polymerization conditions: $[Sn(Oct)_2]_0 = [Sn(OBu)_2]_0 = 0.05$ mol·L^{-1}, $[LA]_0 = 1.0$ mol·L^{-1}, THF solvent, 50°C (ref.[38]).

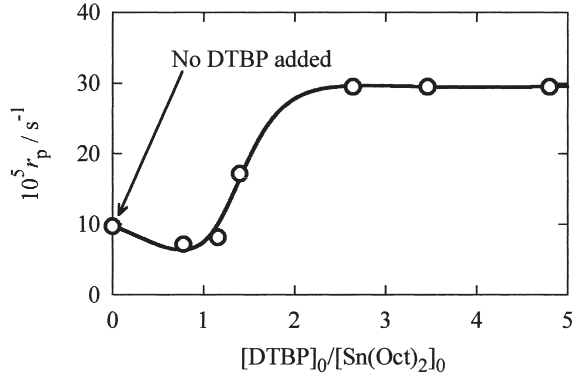


Fig.2: Infuence of 2,6-di(*tert*-butyl)pyridine (DTBP), used as a "proton trap", on the rate of polymerization of LA initiated with $Sn(Oct)_2$. Polymerization conditions: $[LA]_0 = 1.0$ mol·L^{-1}, $[Sn(Oct)_2]_0 = 0.05$ mol·L^{-1}, in THF solvent at 80°C (ref.[38]).

On the other hand, existence of these equilibria, providing a steady-state concentration of the actually growing macromolecules, should be sensitive to the addition or removal of one of the component. Thus, for Scheme 1 , addition of RC(O)OH into the system should reduce the rate, whereas removal of RC(O)OH should increase the rate. Both phenomena were experimentally verified[35,38].

In Fig.2 the influence of a "proton trap" on the rate of polymerization is shown. After a sharp original decrease, there is an increase of rate until further addition of the hindered amine is no more influencing the rate. This result means that in Scheme1 equilibrium is shifted to the right hand side, because the acid is removed by complexing with the proton sponge. Whether both equilibria (1 (a) and 1 (b)) are involved - again it is not yet clear.

These are the most important kinetic results for the polymerization of CL and LA induced by $Sn(Oct)_2$ with coinitiators.

Mechanism of cyclic esters polymerization induced with $Sn(Oct)_2$

Kinetic and structural results (MALDI-TOF) taken together allowed to proposing the following mechanism of initiation, propagation, and formation of the end groups.

Initiation:

(a) preinitiation - formation of the true initiator:

$$\mathrm{RC(O)OSnO(O)CR} + \mathrm{R'OH} \overset{\text{fast}}{\rightleftharpoons} \mathrm{RC(O)OSnOR'} + \mathrm{RC(O)OH} \qquad (3)$$

(only the first equilibrium is shown from Scheme 1)

(b) first monomer addition:

$$\mathrm{RC(O)OSnOR'} + \mathrm{M} \rightleftharpoons \mathrm{RC(O)OSnO\text{-}m\text{-}R'} \qquad (4)$$

(where M denotes the cyclic ester and m – the polyester repeating unit derived from M)

Propagation:

$$\mathrm{RC(O)OSnOR'} + \mathrm{nM} \rightleftharpoons \mathrm{RC(O)OSnO\text{-}(m)_n\text{-}R'} \qquad (5)$$

Reversible chain transfer

(to the ROH which has been not used in initiation, before the chain transfer takes place):

$$\mathrm{RC(O)OSnO\text{-}(m)_n\text{-}R'} + \mathrm{R'OH} \rightleftharpoons \mathrm{RC(O)OSnOR'} + \mathrm{HO\text{-}(m)_n\text{-}R'} \qquad (6)$$

(starts a new chain)

Chain transfer with chain rupture (transesterification)

These processes are described in detail in our works devoted polymerization of CL and LA with metal alkoxides[13-18)]. There is no difference when $Sn(Oct)_2$ is used, since polymerization proceeds eventually on similar active species.

Esterification of the hydroxyl end groups

Esterification of the hydroxyl end groups was documented by observation of the corresponding populations of PCL and PLA in MALDI-TOF[34,36,38)]. The pertinent reactions, followed by propagation, read:

$$\mathrm{OctH} + \mathrm{ROH} \xrightleftharpoons{Sn(Oct)_2} \mathrm{OctR} + H_2O \qquad (7a)$$

$$Sn(Oct)_2 + H_2O \rightleftharpoons \mathrm{OctSnOH} + \mathrm{OctH} \qquad (7b)$$

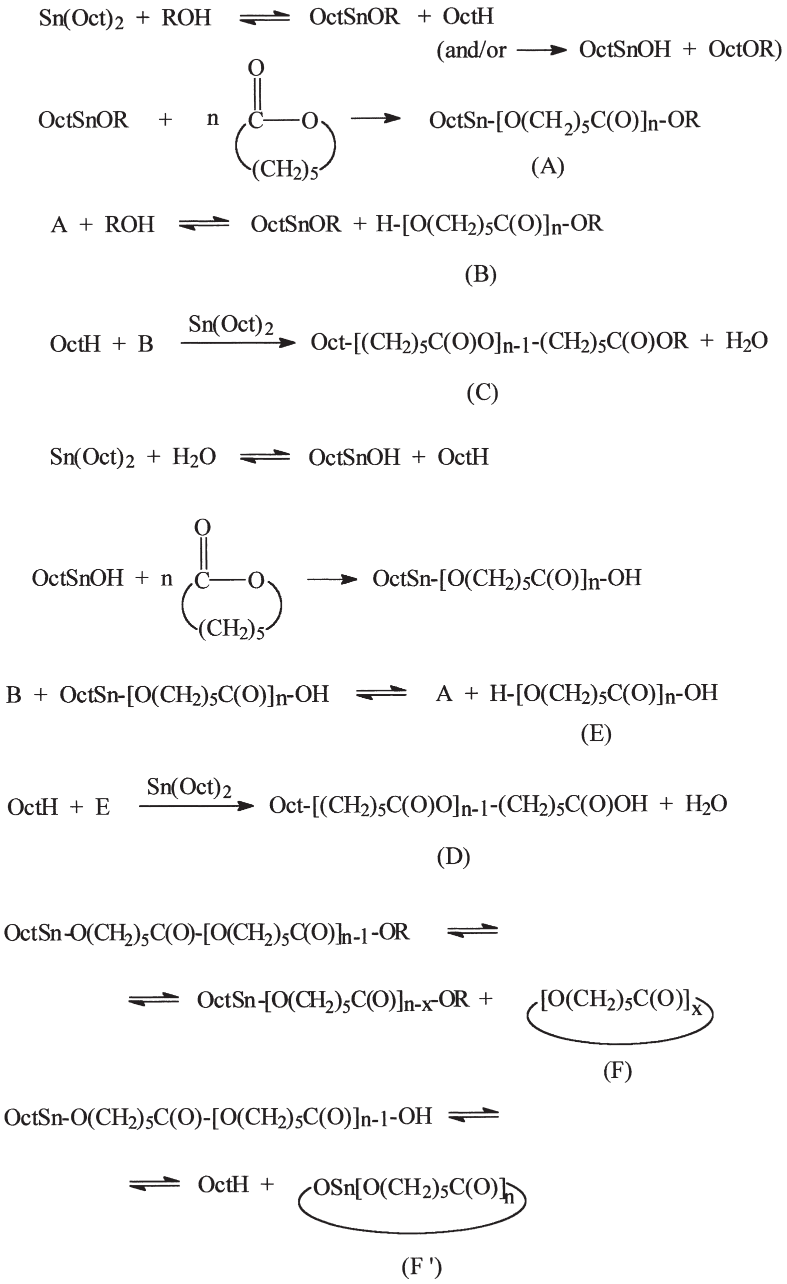
$$\mathrm{OctSnOH} + n\mathrm{M} \rightleftharpoons \mathrm{OctSnO\text{-}(m)_{n}\text{-}H} \qquad (7b)$$

Assuming that eventually this process is irreversible (water is consumed) the proportion of the esterified end groups has a limit given by $[Sn(Oct)_2]_0$. In the technology of PLA the amount of $Sn(Oct)_2$ is low (tens of ppm) and the molar masses of the resulting polymer are close to 10^5. The starting concentration of monomer is equal to ≈ 8 mol·L^{-1} (polymerization in bulk). Thus, ≈ 1 % of macromolecules would have esterified end groups, provided, that the system is kept long enough in order to consume all of octanoic acid.

However, in some synthetic work, i.e. in preparation of block copolymers, starting from the long blocks, fitted with hydroxyl groups , one has to be aware that important part of these hydroxyl groups could be not accessible due to esterification. If, e.g. 1 mol-% of $Sn(Oct)_2$ is used, starting block of, e.g. α,ω-dihydroxy poly(ethylene oxide) has $M_n = 10^4$ and then $Sn(Oct)_2$ is introduced first, and kept for a long time before the monomer is added, then only 80 mol-% of these -OH groups is expected to be used in the polyester block formation.

End groups

Besides the octoate end groups, formed from one end of macromolecules, and discussed in the previous paragraph, there are other end groups, in several populations of macromolecules. Below, in Scheme 8 the mechanisms responsible for the formation of these populations are given:



(8)

The kinetics and thermodynamics of the first equilibrium is still under study.

Conclusions

According to the kinetic data and direct observation of the macromolecules fitted with OctSn-O-polyester active end groups, polymerization of cyclic esters induced by $Sn(Oct)_2$ requires a preliminary formation of the tin(II) alkoxide bond, on which propagation proceeds. This course of reaction was either proposed or merely mentioned earlier in a number of papers[19,28,32] but clear cut evidence (like MALDI-TOF spectra provided by our work) was not available. Some recently published papers described another mechanisms shown in our recent paper to be unacceptable[38]. Thus, the major reaction, responsible for initiation is fast established equilibrium (first step):

$$\mathrm{RC(O)OSnO(O)CR} + \mathrm{R'OH} \xrightleftharpoons{\text{fast}} \mathrm{RC(O)OSnOR'} + \mathrm{RC(O)OH} \qquad (9)$$

which is shifted to the left hand side.

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