# Living Polymerization of Cyclic Esters - a Route to (Bio)degradable Polymers. Influence of Chain Transfer to Polymer on Livingness

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**Summary:** Polymerization of cyclic esters leads to (bio)degradable polymers of the increasing industrial importance. These polymerizations are of the living nature, although chain transfer to polymer with chain scission may cause deviations from the livingness and introduce structural differences (e.g. in end-groups), important for physical properties. Two different systems are discussed. In the first one two living macromolecules react one with another and reproduce two living macromolecules, retaining the same reactivities and the same end-groups. Polymerizations of ε-caprolactone and lactide belong to this category. On the other hand, polymerization of cyclic carbonates proceeds with chain transfer, in which disproportionation of the living chains takes place: from two living macromolecules one "dead" and one "doubly active" can be formed. Conditions of retaining the livingness in terms of the ratios of the rate constants of transfer, reinitiation, and propagation are discussed.

**Keywords:** chain-transfer, L,L-dilactide, living polymerization, MALDI, polyesters

## Introduction

Polymerization of cyclic esters is not any more an area of academic curiosity but has become an important field in industrial polymers.[1] This is because on top of the previously technically important polymers like polyolefins, polymers of vinyl monomers or polymers made by ring-opening polymerization, a novel family of polymers appears, namely (bio)degradable polymers. Some are derived from the renewable resources. The major polymer based on the renewable resources is polylactide. Moreover, polylactide can be made from various wastes, as it has recently been demonstrated, and is perfectly biodegradable. Thus, polylactide is on the crossroads of three important tendencies: renewable raw materials, the use of the municipal waste, and biodegradability. Another important class of polymers is based on the polymerization of cyclic carbonates, degrading (e.g. hydrolytically) without giving accumulated acidic products.

Polymerization of cyclic esters has already been studied in detail.[2] Although some motivation to these studies may come from the above mentioned technological reasons, for a

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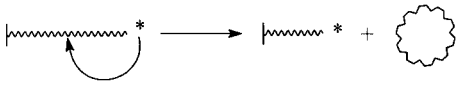
polymer chemist these processes open also a way to study novel living processes, in which there are phenomena non existing in vinyl polymerizations. One of the sources of this difference stems from the nature of the repeating units in the chains. In vinyl polymerization chains are built on the carbon-carbon linkages whereas in polymerization of cyclic esters the ester bonds are formed, the same ones as attacked in monomer and opened in the propagation step. Therefore, these repeating units are prone to similar attack and bond breaking in the chain. The understanding of these processes, apart from their fundamental importance, are also vital for the practical reasons, because depending on their nature and contribution to the overall polymerization process, polymers differing substantially in the molar mass distribution are formed. Different distributions influence the final physical properties of the involved polymers. Even more dramatic are these processes in highly branched, star-like polymers.[3]

## Results and Discussion

### (a) Chain Transfer in Polymerization of Cyclic Esters

There are two types of chain transfer to polymer with chain scission: namely the intra- and intermolecular transfers, as shown schematically below:

- intramolecular chain transfer- back biting (leading to cyclics formation):



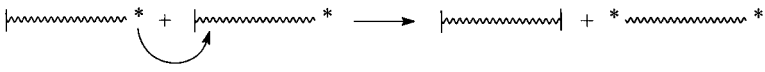
(1)

- intermolecular chain transfer:

  (a) either conserving the activities of both chains

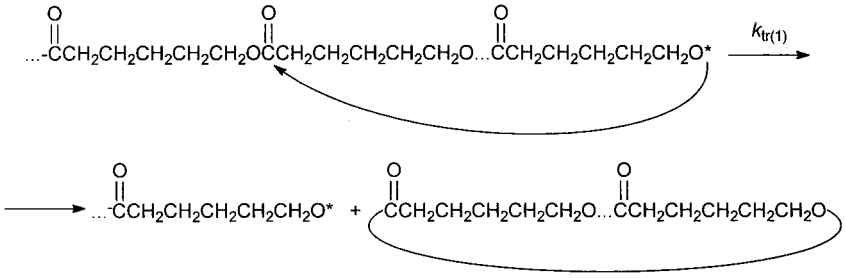
(2)

  (b) or disproportionating living chains into "dead" and "doubly active" chains



(3)

The first kind (intramolecular) of chain transfer has previously been studied quantitatively in our laboratory in the polymerization of ε-caprolactone:[4-6]

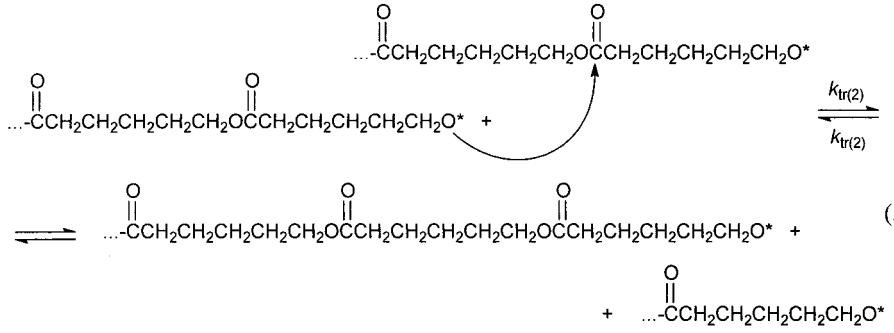


(4)

(where ...O* denotes active species, either anions (e.g. alcoholate anion with omitted cation) or ...O-Mt, i.e. covalent alcoholate bond , e.g. ...-O-$AlR_2$, ...-OSnOC(O)R etc., on which propagation proceeds by concerted addition- insertion mechanism).

It has been established that $k_p/k_{tr(1)}$ (i.e. selectivity of polymerization) depends on both reactivity of active centers (given by $k_p$) and the size (i.e. the occupied volume) of these species.[5, 6]

For the intermolecular chain transfer there are, as indicated above, two possibilities: in the first one two living macromolecules (i.e. both fitted with active species) react one with another and give back two living macromolecules. Actually, in polymerization of lactones this is the only possibility, as shown below for ε-caprolactone (CL) (independently whether the active species are carboxylate anions, like in polymerization of β-propiolactone or alcoholate anions, like in polymerization of CL):



(5)

Thus, these processes do not change the number of living macromolecules: the total number of growing macromolecules remains constant, although a given living macromolecule is

changing its size a number of times during propagation due to the chain transfer reactions. Thus, propagation is not the only process responsible for the polymerization degree.

For the intramolecular chain transfer we were able to find the relationship between the selectivity and structure of active centers. Therefore, we have also been looking for the same dependence in the intermolecular transfer. The kinetic scheme that has to be considered is given below. Schematically:

$$P_i^* + M \xrightarrow{k_p} P_{i+1}^* \quad \text{(propagation)}$$

$$P_i^* + P_j^* \underset{k_{tr(2)}}{\overset{k_{tr(2)}}{\rightleftharpoons}} P_{i+n}^* + P_{j-n}^* \qquad (6)$$

We were not able to find an analytical solution of this scheme although the corresponding differential equations could easily be formulated.[6-9] Nevertheless, we used another approach, namely we constructed nomograms, allowing to find the dependence of $k_{tr(2)}/k_p$ from the plot of $M_w/M_n$ on monomer conversion ($\alpha$), determined experimentally.[6, 7, 9, 10]

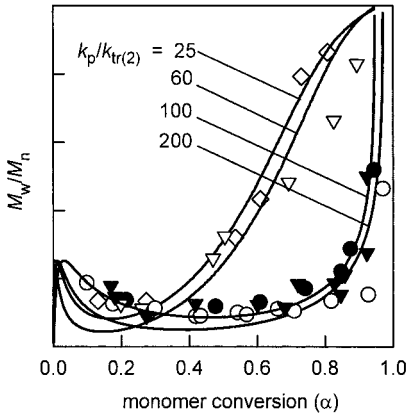



Fig. 1. Dependencies of $M_w/M_n$ on monomer conversion determined for L,L-dilactide (LA) polymerization initiated with (in brackets are given $[M]_0/[I]_0$ ratios in which $[I]_0$ denotes starting concentration of the alkoxide group): (◊, $10^2$ )$Bu_3SnOEt$, (▽, $2.4\times10^2$) $Fe(OEt)_3$, (▼, $3.3\times10^1$) $Al(O^iPr)_3$, (●, $5.6\times10^1$) $Sn(Oct)_2$, (○, $5.6\times10^1$ ) $Sn(OBu)_2$, THF solvent, 80 °C or 20 °C for $Sn(OBu)_2$. Points experimental, lines computed assuming $k_p/k_{tr(2)}$ = 25, 60, 100, and 200, respectively (ref.[11]).

The course of these lines depends also on the starting $[M]_0/[I]_0$ ratio (where $[M]_0$ and $[I]_0$ stand respectively for starting concentrations of monomer and initiator). This is clearly

indicated in Figure 1, where two sets of lines (and corresponding experimental data) are related to different ratios $[M]_0/[I]_0$.

Another way to observe the rate of transfer, particularly in polymerization of lactide (LA), is to monitor the MALDI TOF mass spectrometry. When there is no transfer only macromolecules with even number of repeating units appear (LA is a dimer of lactic acid). Transfer leads to macromolecules with uneven number of units. This is illustrated in Figure 2a and b.

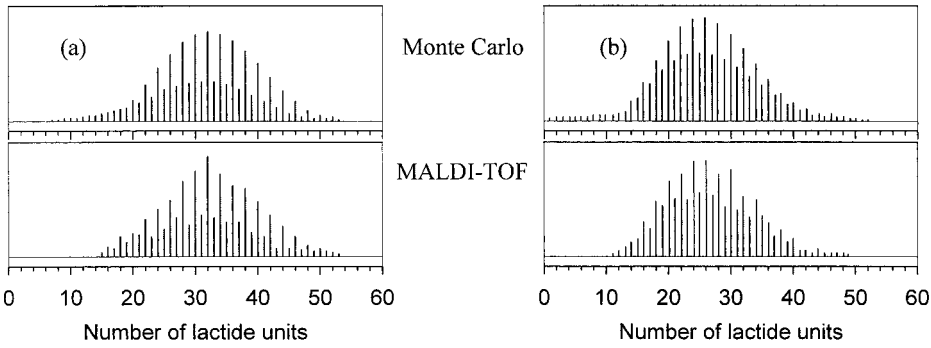



Fig. 2. Relative concentrations of oligomers in L,L-dilactide (LA) polymerization as observed by MALDI TOF and obtained by Monte Carlo computations. $[LA]_0$ = 1.2 mol/L, [Sn(II) octanoate]$_0$ = 0.05 mol·L$^{-1}$, [Butanol]$_0$ = 0.01 (a), 0.03 (b) mol·L$^{-1}$, solvent THF. Conversions, $DP_n$, and $DP_w/DP_n$, respectively: 76%, 30.1, 1.108 (a); 86%, 25.4, 1.116 (b). The estimated kinetic parameters: $k_p/k_{tr(2)}$ = 83.3, $k_{tr(1)}/k_{tr(2)} = 1.07\times10^{-3}$ mol·L$^{-1}$.[12]

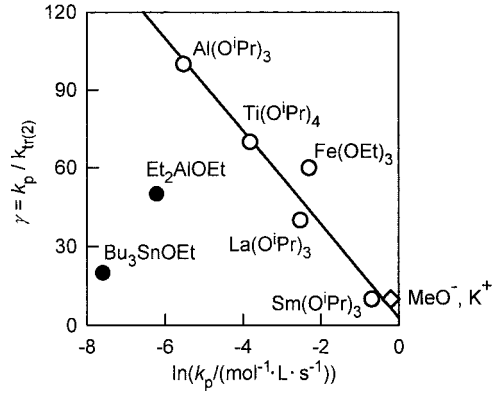
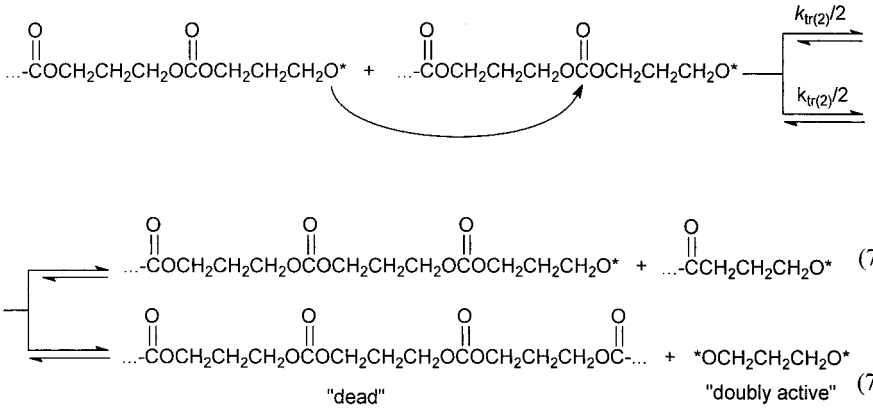



Fig. 3. Dependence of $\gamma = k_p/k_{tr(2)}$ on ln $k_p$ determined in polymerizations of L,L-dilactide initiated by metal alkoxides. Covalent alkoxides: (○, ●); ionic alkoxide - MeOK: (◊). Conditions: $[LA]_0$ = 1.0 mol·L$^{-1}$, THF solvent, 80°C (MeOK initiated polymerization - at 20°C) (ref.[6]).

Then in Figure 3 (taken from ref.[6]), the dependence of $k_{tr(2)}/k_p$ on $k_p$ is given. It follows that, this dependence holds only for a series of active species relatively similar in "size". Particularly low $k_{tr(2)}/k_p$ has been observed for aluminum *tris*-acetylacetonate (already mentioned in ref.[14] but not quantitatively studied). This preliminary result indicates, that the actual dependence of $k_{tr(2)}/k_p$ on the structure of active centers should include simultaneously reactivity and steric features. Similar phenomena have been observed in the polymerization of CL, where $k_{tr(1)}$ (for back-biting) depended on both $k_p$ and the size of active centers.[4-6] The most striking example could be given by comparing ...-O-Al$(C_2H_5)_2$ and ...-OAlO$^i$Bu$_2$ active centers, that propagate CL with identical $k_p$ but $k_{tr(2)}/k_p$ is for the former higher almost two times than for the latter.

**(b) Chain Transfer with Disproportionation of Active Centers**

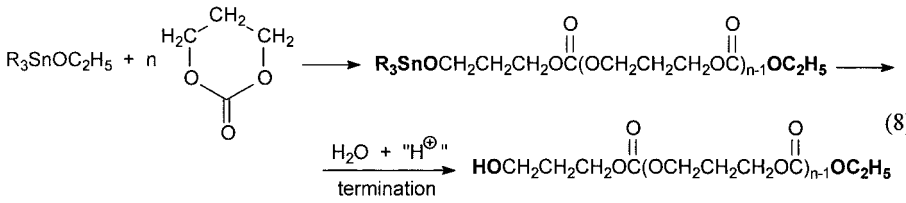
In the previous paragraph chain transfer to polymer with chain scission and retention of activities in both interacting living macromolecules was discussed. However, as it has already been mentioned, this is only characteristic for some polyesters. In polycarbonates an additional reaction takes place as illustrated by Equation 3. Polycarbonates are "symmetrical esters" and in these symmetrical structures chain transfer with chain scission may proceed in an additional way: two living macromolecules, with one active center each, may react one with another, giving (cf. Equation 3) one "dead" macromolecule and one macromolecule with two active centers. For example, for trimethylene carbonate:




For the first time the evidence of the existence of the process according to Equation 7b in the polymerization of cyclic esters has recently been given on the basis of the analysis of the

MALDI TOF spectra of poly(trimethylene carbonate) obtained with $(n\text{-}C_4H_9)_2SnOC_2H_5$ as initiator.[13]

According to the present knowledge, if the polymerization process were without any chain transfer with reshuffling of structures, then the end-groups should exclusively be **HO-** and **$-OC_2H_5$** as shown below:




(8)

Chain transfer according to Equation 7a would provide exclusively end-groups formed in initiation and termination. However, chain transfer according to Equation 7b (with disproportionation) would introduce two more sets of macromolecules, derived from "dead" and "doubly active" macromolecules containing either two $-OC_2H_5$ or two –OH end-groups. The existence of macromolecules with these end-groups is clearly seen in the MALDI TOF spectrum given in Figure 4, where for every polymerization degree there are three different kinds of macromolecules, namely HO~~~~$OC_2H_5$ (1), $C_2H_5O$~~~~$OC_2H_5$ (2), and HO~~~~OH (3). This particular variety of the end-groups has never been observed in polymerization of either CL or LA, where there is no way for disproportionation during chain transfer to occur. Because of equal probabilities of breaking of two ester bonds of the carbonate moieties the equilibrium constant of the reaction 7b is equal to ¼. Consequently the concentration of monofunctional chains in equilibrium is twice as high as the concentration of "dead" or "doubly reactive" chains.

Comparison of the Monte-Carlo computations of the chain transfer with and without disproportionation revealed surprisingly small difference between these two mechanisms in their influence on the dependence of $M_w/M_n$ on monomer conversion ($\alpha$). This small difference can be explained by formation in the chain transfer reactions of new chains with the same molar mass distribution (MMD) for the processes with or without disproportionation (the only difference is in the structure of chain ends). The existing differences in total MMD of polymers stem from the two times faster propagation on the "doubly active" chains then on the "normal " chains (the dead chains, of course, do not propagate at all). However, the MMD of the sum of dead and "doubly reactive" chains is not much different from the MMD of the

monofunctional chains. The difference between these MMDs decreases with increasing the rate of reshuffling of the polymer segments.

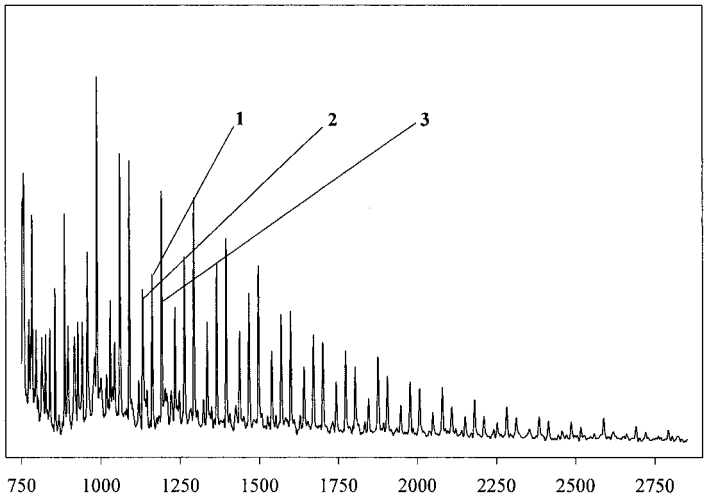



Fig. 4. MALDI-TOF-ms spectrum of poly(trimethylene carbonate) obtained in polymerization of trimethylene carbonate (TMC). Conditions: $[TMC]_0$ = 1 mol·L$^{-1}$, initiated with $Bu_3SnOEt$ ($[Bu_3SnOEt]_0$ = 0.01 mol·L$^{-1}$) at 80°C in THF; conversion 12%; $M_n$ = 1200, $M_w/M_n$ = 1.09. Numbers: 1, 2, and 3 indicate signals of polymer chains differing in end-groups: HO~~OEt, EtO~~OEt, and HO~~OH, respectively.

**(c) Chain Transfer and "Livingness" in Polymerization of Cyclic Esters.**

According to the provisional IUPAC definition, living polymerization takes place when irreversible chain transfer or termination is absent. Thus, the reversible chain transfer is allowed; it means, that active center is transferred from a living macromolecule to another molecule, which starts sooner or later the growth of another chain (reinitation with rate constant $k_{ri}$). If the rate constant of reinitiation is high enough (i.e. $k_{ri} \geq k_p$), than chain transfer is "ideal" and no retardation is observed. If $k_{ri} < k_p$ then the chain transfer is of degradative character. It looks that in the polymerization of cyclic esters, at least without disproportionation, chain transfer is ideal, no chain carriers die: all macromolecules are living all the time and all of the end-groups are the same. Therefore, this process belongs to living polymerizations. When disproportionation takes place then polymerization is on the borderline of livingness and whether all the macromolecules retain or not the ability to grow

depends on the $k_p/k_{tr}$ ratio. If $k_{tr} << k_p$ then transfer is ineffective but the "dead" macromolecules also ineffectively come back to propagation, making in this way polymerization nonliving. If, however, $k_{tr} >> k_p$ then the dead macromolecules are quickly transformed into the living ones, and then the polymerization belongs to the living category.

## Conclusion

In polymerization of cyclic esters, like ε-caprolactone (CL), lactides (LA), or cyclic carbonates (e.g. trimethylene carbonate (TMC)), taken as examples, chain transfer to polymer molecules with their scission takes place. This transfer, independently of the actual mechanism, broadens the molar mass distribution. When two living macromolecules react one with another in polymerization of CL or LA two other living macromolecules emerge and their ability to grow is identical to this of the parent ones. This behavior stems from the "unsymmetrical" structure of the ester bonds in contrast to the "symmetrical" (-OC(O)O-) in the case of polycarbonates. This symmetrical structure is responsible for two ways of breaking of the attacked chain. One way is identical to the way of breaking in "unsymmetrical" esters and the other one leads to disproportionation. In the latter reaction two living macromolecules give one "dead" (at least temporarily) and one "doubly active", i.e. with two active centers. This mechanism was for the first time established for the polymerization of cyclic carbonates by applying MALDI TOF analysis. Three different populations of macromolecules were observed with end-groups clearly indicating the presence of structural disproportionation of macromolecules undergoing chain transfer.

## Acknowledgement

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