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COMMUNICATION

L-Lactide polymerization catalysed by Tin(II) 2-ethylhexanoate. A deeper look at chain transfer reactions

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The mechanism of segmental exchange in the polymerization of L-lactide catalysed by tin(II) 2-ethylhexanoate/alcohol system was studied as model system. It was shown by analysis of MALDI-TOF spectra and modelling by Monte Carlo that the carbonyl group closest to tin atom is at least 100 times more reactive than another carbonyl group along chain.

Segmental exchange reactions (also called redistribution, reshuffling, or chain transfer reactions) are important in many processes involving macromolecules. These reactions proceed via an attack by a chain end of one polymer on a labile bond inside a chain of a separate polymer chain, leading to a transfer of monomeric units from one chain to another.^{1,2} As a result a distribution of molecular weight (MWD) changes (and therefore the weight average molar mass (M_w) and dispersity (D)) though the number average molar mass (M_n) remains intact. In case of copolymers the sequences of constitutional repeating units also rearrange.

Polymerization of L-lactide (LL) catalysed by tin(II) 2-ethylhexanoate (SnOct_2) has been the subject of intense interest in the literature.³⁻⁶ Thus the mechanism of this process was intensively studied in order to understand better the mechanism and kinetics of the segmental exchange reactions. The experimental evidence of the exchange reactions is broadening of molar mass distribution which can be detected by Size Exclusion Chromatography (SEC) at the late polymerization stages.⁷⁻¹¹ Penczek, et. al. conducted kinetic studies and numerical modelling of the segmental exchange reactions, leading to the introduction of a selectivity/reactivity parameter for this system. This value, expressed as the ratio of rate constants of propagation to chain transfer reactions, is determined assuming equal reactivity of all monomeric units in the polymer chain.⁷ The approach was later used by Morbidelli in case of polymerization in bulk.^{8,9}

Another experimental evidence of the segmental exchange reactions is presence of a population of chains composed of an odd number of lactoyl units (later called in short odd chains), accompanying the population of chains composed of even number of

lactoyl units (even chains) formed initially by the propagation-depropagation reactions. Significant amount of odd chains was detected by MALDI-TOF spectrometry from very beginning of the polymerization, when dispersity is still very low.^{12,13} Szymanski proposed splitting of cyclic lactoyl trimer by back-biting reaction as a possible explanation of this observation.¹⁴

In the present work it will be shown, that a difference of reactivity of last carbonyl group in a chain should be taken into account in order to explain all experimental findings observed in polymerization of LL catalysed by SnOct_2 .

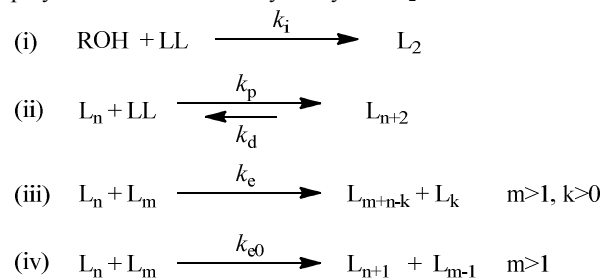
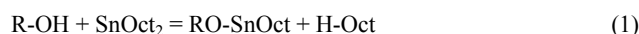


Fig. 1 Model of the polymerization process: (i) irreversible initiation, (ii) reversible propagation, (iii) specific redistribution (attack of active centres on the last lactoyl unit in another chain), (iv) nonspecific redistribution (attack of an active centre on any lactoyl unit of another chain). k , m , n stand for the number of constitutional repeating lactoyl units in a chain.

Since the equilibrium (1) between the active tin alkoxylates and inactive hydroxyl ends existing in processes initiated by alcohol/ SnOct_2 systems has been omitted in our model, all rate constants in the scheme should be understood as the apparent ones.



Justification of the model, Monte Carlo algorithm and executable program for simulation, polymerization details, and characteristics of

synthesized poly(L-Lactide) PLA samples (SEC and ^1H NMR) are given in the Electronic Supplementary Information (ESI).

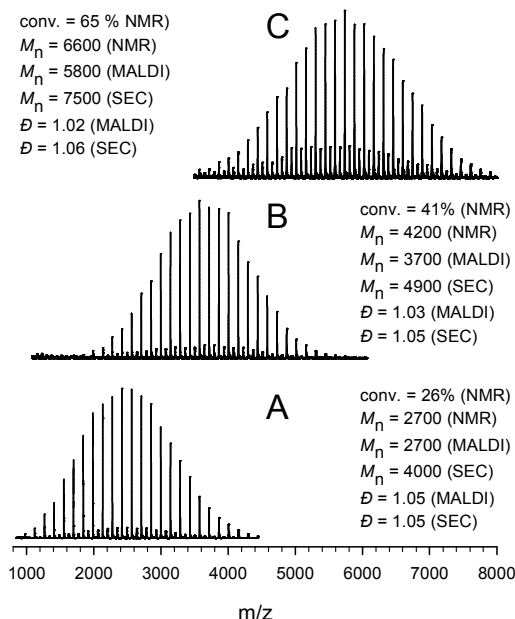


Fig. 2 Collected MALDI-TOF mass spectra of synthesized PLA samples.

On MALDI-TOF spectra (shown in Figure 2) two series of signals with the bell-shaped distribution of intensities are present, both centred around the same maximal value of m/z . Signals of higher intensities were ascribed to even chains and signals of lower intensities placed between them to odd chains. Progress of polymerization increases M_n and contribution of odd chains, with only negligible change of dispersity, which confirms results obtained by Prud'homme.¹²

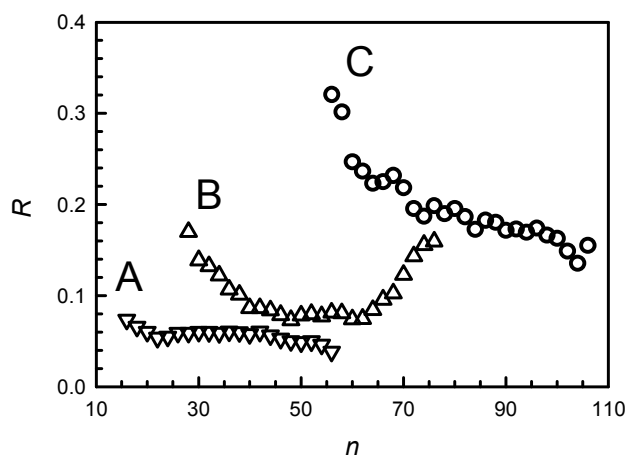


Fig. 3 Plots of the function R for synthesized PLA samples.

For qualitative interpretation of MALDI-ToF spectra a function R has been introduced:

$$R(n) = \frac{I(2n-1) + I(2n+1)}{2 \times I(2n)} \quad (2)$$

Where n is a natural number, $2n$ is number of lactoyl units in an even chain, and $I(2n)$, $I(2n-1)$, $I(2n+1)$ mean integrations of signals

ascribed respectively to an even chain and two odd chains placed on its left and its right sides.

Properties of the normal distribution assures (cf. Figure S5 in ESI) that the R is horizontal straight line when distributions of odd and even chains have the same standard deviations and centres. When standard deviations differ, the line becomes concave or convex (but still symmetric) and when distribution centres do not match line becomes skewed.

In Figure 3 we present plots of R for synthesized PLA samples. Large values of R at plots' ends may suggest that the odd chains' lengths distributions are wider than distributions of the lengths of the even chains, though an overestimation of small signal integrations gives similar effects. On the other hand, linear middle parts of plots indicate proportionality of distributions in these ranges of chain lengths. The skewed plot for sample C indicates a small reduction of the lengths of the odd chains.

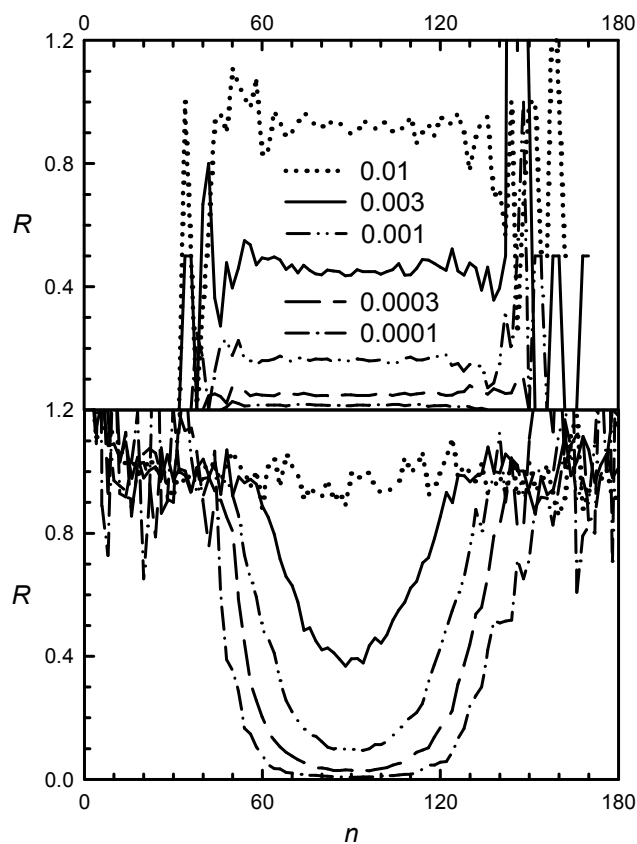


Fig. 4 Dependence of R on n at time 11 500 s (conv.=65%). Top: specific redistribution, k_{e0} shown on the plot. Bottom: nonspecific redistribution; k_e : (---) $3 \cdot 10^{-6}$, (--) $1 \cdot 10^{-5}$, (-.-) $3 \cdot 10^{-5}$, (—) $1 \cdot 10^{-4}$, (···) $3 \cdot 10^{-4}$, all in $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

Figure 4 presents dependences of R on n obtained from modelling of kinetics of the polymerization process shown in the Figure 1, for various redistribution rate constants at LL conversion equal to 65%. For the specific redistribution, which assumes an attack on the last lactoyl unit, R is independent upon n . Since nonspecific redistribution yields strongly concave plots, domination of specific redistribution during those stages of polymerization could explain the experimentally observed linear dependence R on n .

Computed changes of dispersity D vs time for different rate constants of both types of redistribution reactions are shown in Figure 5. Comparison of results presented in Figures 4 and 5 indicate

that increase of the value of R function is associated with significant increase of dispersity in case of the non-specific redistribution, whereas \mathcal{D} remains low in case of the specific redistribution. Hence, only intensive specific redistribution reaction could be responsible for the high content of odd chains and the low value of \mathcal{D} just from beginning of the polymerization process.

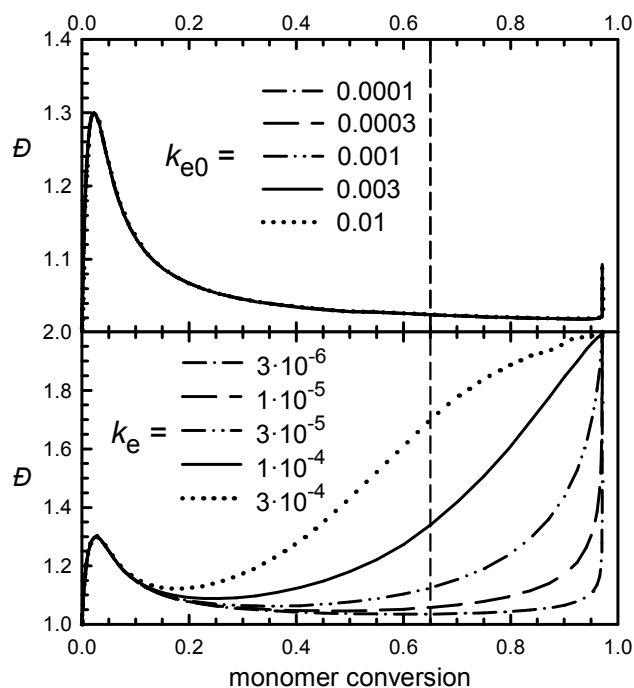


Fig. 5 Dependence of \mathcal{D} on monomer conversion. Top: specific redistribution, bottom: nonspecific redistribution. k_{e0} and k_e (in $\text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) are specified on plots.

At late stages of LL polymerization the increasing of dispersity requires also participation of the nonspecific redistribution, since the specific redistribution alone changes \mathcal{D} too slowly. In fact, the propagation-depropagation reactions changing chain lengths by two lactoyl units increase dispersity more effectively than the specific redistribution reaction.

We can relate the specific redistribution initial rate $r_{e0}(0)$ and the initial rate of propagation $r_p(0)$ according to following formula (derivation given in the Supporting Information):

$$\frac{r_{e0}(0)}{r_p(0)} = \frac{k_{e0}[\text{ROH}]_0}{k_p[\text{LL}]_0} = \frac{k_{e0}}{k_p DP_n} \quad (3)$$

Where $[\text{LL}]_0$ is initial concentration of L-Lactide and DP_n is the number average polymerization degree calculated for complete monomer conversion.

Thus, the ratio of odd chains formation to propagation rates should be inversely proportional to DP_n , what was indeed observed by Prud'homme et al. (cf. Figure 9 in the ref. 12).

Rate of the nonspecific redistribution reaction $r_e(0)$ is equal:

$$r_e = \frac{d[\text{O}]}{dt} = -\frac{d[\text{E}]}{dt} = k_e([\text{E}] - [\text{O}])([\text{LL}]_0 - [\text{LL}]_t) \quad (4)$$

where $[\text{LL}]_t$ is instantaneous concentration of L-Lactide.

The equation (4) predicts an acceleration of odd and even chains inter-conversion rate with increase of monomer conversion in time for nonspecific redistribution reaction, illustrated by solid lines in

Figure 6. The Figure 6 shows also that any rate constant does not give good fit to our experimental data when only the nonspecific redistribution is taken into account. The best fit (to data obtained for three experimental samples) was obtained using $k_e=2.6\cdot 10^{-6} \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $k_{e0}=1.05\cdot 10^{-3} \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. This means, that the carbonyl group closest to the active centre of polymerization is at least 100 times more reactive than another groups inside chain.

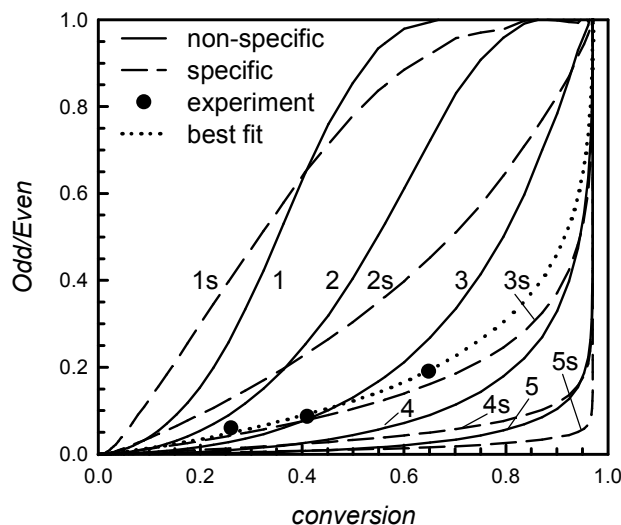


Fig. 6 Changes of total fractions of odd and even chains in time. k_e : (1) $3\cdot 10^{-6}$, (2) $1\cdot 10^{-5}$, (3) $3\cdot 10^{-5}$, (4) $1\cdot 10^{-4}$, (5) $3\cdot 10^{-4}$; k_{e0} : (1s) $1\cdot 10^{-4}$, (2s) $3\cdot 10^{-4}$, (3s) $1\cdot 10^{-3}$, (4s) $3\cdot 10^{-3}$, (5s) $1\cdot 10^{-2}$, all in $\text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$.

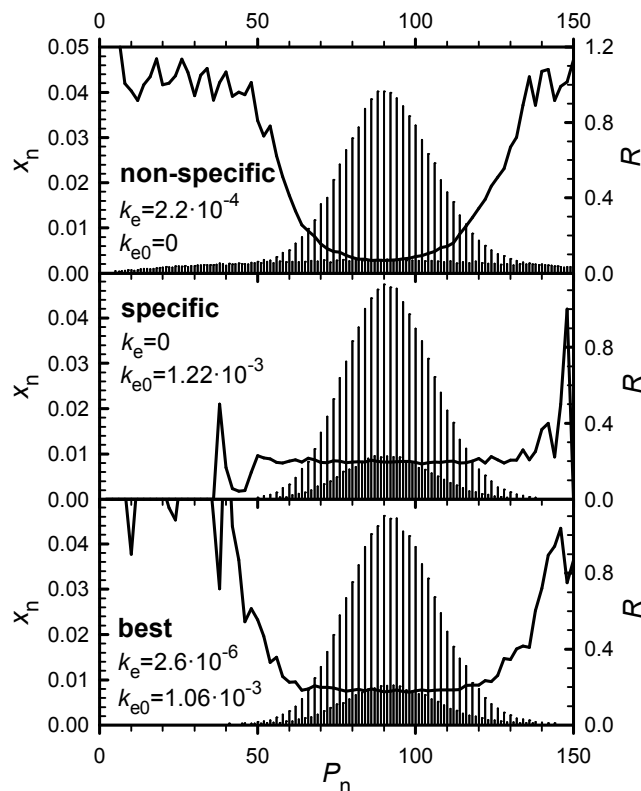
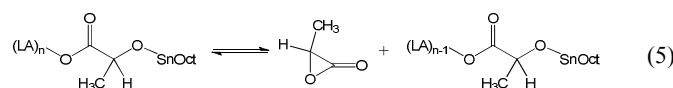


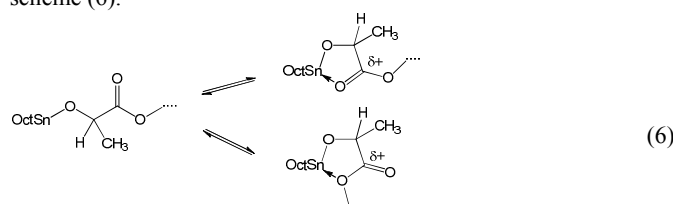
Fig. 7 MALDI-ToF spectra and R function modelled with different values of k_e and k_{e0} (in $\text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) for time 11 500 s (conv.=0.65).

Figure 7 presents MALDI-ToF spectra and plots of R function obtained for only nonspecific, only specific, and both simultaneous reactions of segmental exchange (from top to bottom of the figure, respectively). Values of k_c and k_{co} were adjusted for the best fit of the calculated ratio of odd/even total chains fractions to the experimental one determined for sample C (equal to 0.191). These plots prove that the nonspecific redistribution alone gives distribution pattern non consistent with experiment and the specific redistribution dominates at the early stage of the polymerization process.

There are two possible mechanisms of the specific redistribution. In the first one the three-membered α -lactone ring is formed (reaction 5) and consumed instantly due to its high ring strain (169 kJ·mol⁻¹ from ab initio molecular orbital calculations).¹⁵ Thus in real systems it can exist only at extremely low concentration.^{16,17} However, as it was shown by Monte Carlo modelling, this reaction also explains some aspects of the process kinetics.¹⁴



The second mechanism relies on reaction of two chain ends. Both mechanisms need some activation of the terminal carbonyl group, possible by coordination of Sn atom, as is illustrated by scheme (6).



Possibility of tin coordination by carbonyl or alkoxy oxygen atoms of an ester group and formation of five-membered complex has been shown for organotin trichlorides.¹⁸ Moreover, Kricheldorf observed a large change of chemical shift of ¹¹⁹Sn nuclei in solution of SnOct₂ in presence of ethyl lactate and ascribed it to coordination of the Sn atom by carbonyl oxygen atom.¹⁹

Increase of positive charge on carbonyl carbon atom makes it more susceptible to attack of the OctSn-O-... active centre and could also facilitate splitting of the three-membered ring. At the given moment we have not stronger arguments to accept or reject any of above mechanisms, although Prud'homme experimental data support the bimolecular mechanism.¹² More kinetic experiments and molecular modelling of possible structures are needed for a more substantial conclusion.

It should be noted, that in the anionic polymerization of cyclic siloxanes it was stated that silicone terminal atom is several times more susceptible to reaction of chain transfer than atoms placed inside a chain.²⁰⁻²³ An enhanced reactivity of the ultimate carbonyl group was observed also in process of acidic hydrolysis of poly(lactides).²⁴⁻²⁶ These two examples indicate that position-dependent reactivity can be a general rule in segmental exchange or hydrolysis processes.

Conclusions

In polymerization of LA initiated with the alcohol/SnOct₂ system a population of chains with odd number of repeating units is detected by MALDI-ToF spectrometry just from the very beginning of the process. The balance between the odd and even chains populations is attained very quickly without a

significant increasing of dispersity. At late stages of process increase of the dispersity can be observed in the SEC chromatograms and finally the thermodynamic equilibrium can be achieved with the most probable MWD. All observed experimental results can be explained by simple model of the process consisting of initiation, propagation, depropagation, and two types of segmental exchange reactions (specific and nonspecific ones). At the studied conditions the apparent rate constant of the specific reaction is at least 100 times higher than the apparent rate constant of the nonspecific reaction. The reactivity enhancement of the ultimate ester groups could be induced by formation of a coordination bond between their carbonyl or alkoxy oxygen and tin atoms.

As it was shown here, MALDI-ToF allows easily detect of products of specific and nonspecific redistribution reactions in case of L-Lactide and it can be easily adopted also for studies of polymerizations of other monomers composed of few constitutional units, like glycolide or cyclic siloxanes. In case of simple monomers the specific redistribution reaction also can be very intensive, although MALDI-ToF spectra will not be affected.

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Notes and references

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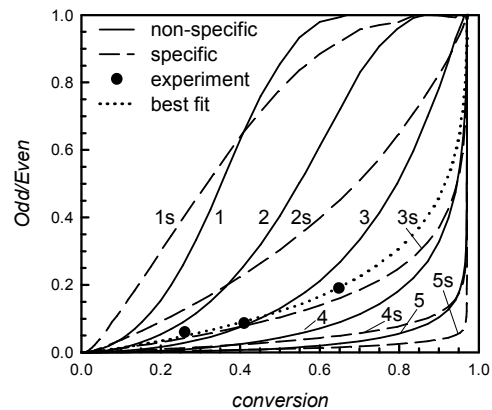
Electronic Supplementary Information (ESI) available: experimental procedures, NMR and SEC data, description of Monte Carlo algorithm with executable interactive program, derivation of differential equations. See DOI: 10.1039/c000000x/

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ToC



Segmental exchange reactions in L-lactide polymerization catalysed by Tin octoate yield chains with even and odd numbers of lactoyl units. The efficiency of the reactions depends on position of the attacked unit in chain. Terminal units are at least 100 times more reactive than other.