

## Copolymerization of Cyclic Esters at the Living Polymer-Monomer Equilibrium

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**Summary:** This paper gives a short review of our findings related to the copolymerization of  $\gamma$ -butyrolactone (**B**) and L,L-lactide (**L**) with  $\epsilon$ -caprolactone (**C**) at or below **B** and **L** equilibrium concentrations in homopolymerization. We show, contrary to the commonly established opinions, that: (i) **B** effectively undergoes ring-opening reaction and therefore is able to high molar copolymers formation containing up to 50 mol-% repeating units derived from **B** and (ii) in conditions eliminating transesterification living poly(**L**) does initiate polymerization of **C** leading to poly(**L**)-*block*-poly(**C**) copolymer.

**Keywords:**  $\gamma$ -butyrolactone;  $\epsilon$ -caprolactone; copolymerization; kinetics (polym.); L,L-lactide; ring-opening polymerization; thermodynamics (polym.)

### Introduction

The large majority of unsaturated compounds polymerize leaving relatively low monomer concentration when it comes to equilibrium. Indeed, if we take non-solvent, bulk polymerization of monomers such as ethylene,<sup>[1]</sup> methyl acrylate or styrene<sup>[2]</sup> then we have at 25 °C the following equilibrium monomer concentrations ( $[M]_{eq}$ ):  $\approx 10^{-10}$ ,  $10^{-9}$  or  $10^{-6}$  mol  $\cdot$  L<sup>-1</sup>, respectively. When unsaturated monomers providing steric hindrance in the polymer units are considered, then homopolymerization may be hampered, and 1,1-diphenylethylene is the best example, since joining of two consecutive units is prohibited. Introduction of the second, even small, substituent increases  $[M]_{eq}$  considerably. For instance, for methyl methacrylate or  $\alpha$ -methylstyrene  $[M]_{eq} = 10^{-3}$  or 2.2 mol  $\cdot$  L<sup>-1</sup> at 25 °C has been determined.<sup>[2]</sup>

In the group of cyclic compounds the Gibbs' energy of polymerization at the given temperature depends mostly on the enthalpy of polymerization, given by the ring strain.

Thus, the three- and four membered cyclic ethers and four membered cyclic esters polymerize practically to completion. From this view point ethylene oxide ( $[M]_{eq} \approx 10^{-15} \text{ mol} \cdot \text{L}^{-1}$  at  $25^\circ\text{C}$ ) and even the four-membered  $\beta$ -propiolactone ( $[M]_{eq} = 3 \times 10^{-10} \text{ mol} \cdot \text{L}^{-1}$  at  $25^\circ\text{C}$ ) do resemble unsaturated monomers.<sup>[3]</sup> Cyclic ethers and esters with larger rings, particularly the five- and six-membered ones are less strained and their equilibrium monomer concentrations are much higher and therefore the ceiling temperatures are much lower. The ceiling temperature ( $T_c$ ), is the lowest temperature, at which the equilibrium monomer temperature is equal to the starting monomer concentration ( $[M]_0$ ), i.e. at which no high polymer is formed. Since:<sup>[4]</sup>

$$\ln[M]_{eq} = \Delta H_p / RT - \Delta S_p^\circ / R \quad (1)$$

$T_c$  is given by:

$$T_c = \Delta H_p / (\Delta S_p^\circ + R \ln[M]_0) \quad (2)$$

where  $\Delta H_p$ ,  $\Delta S_p^\circ$ ,  $T$ , and  $R$  denote enthalpy of polymerization, the standard entropy of polymerization, the absolute temperature, and the gas constant, respectively. Some thermodynamic parameters of polymerization determined for several cyclic esters ( $\beta$ -propiolactone (**P**),  $\gamma$ -butyrolactone (**B**), L,L-lactide (**L**), 1,4-dioxan-2-one (**D**), and  $\epsilon$ -caprolactone (**C**)) are given in Table 1.

Table 1. Thermodynamic parameters of cyclic esters polymerization.

Monomer	Ring size	Monomer Polymer States <sup>a)</sup>	$\frac{\Delta H_p}{\text{kJ/mol}}$	$\frac{\Delta S_p^\circ}{\text{J/mol K}}$	$\frac{[M]_{eq}^{e)}}{\text{mol/L}}$	$\frac{T_c^{g)}}{\text{K}}$
<b>P</b> <sup>[5]</sup>	4	lc	-82.3 <sup>b)</sup>	-74 <sup>b)</sup>	$3.9 \times 10^{-10 \text{ b)}}$	1112
<b>B</b> <sup>[6]</sup>	5	lc	5.1 <sup>b)</sup>	-29.9 <sup>b)</sup>	$3.3 \times 10^{-3 \text{ b)}}$	- 171
<b>L</b> <sup>[7]</sup>	6	ss	-22.9 <sup>c)</sup>	-41 <sup>c)</sup>	$5.5 \times 10^{-2 \text{ c, f)}}$	914
<b>D</b> <sup>[8]</sup>	6	ll	-13.8 <sup>d)</sup>	-45 <sup>d)</sup>	2.5 <sup>d, f)</sup>	520
<b>C</b> <sup>[9]</sup>	7	lc	-28.8 <sup>b)</sup>	-53.9 <sup>b)</sup>	$5.3 \times 10^{-2 \text{ b)}}$	534
( $\approx 0$ ) <sup>f)</sup>						

<sup>a)</sup> l – liquid, c – condensed, s – solution; <sup>b)</sup> at 298 K, <sup>c)</sup> at 353 K, <sup>d)</sup> at 373 K; <sup>e)</sup> calculated from equation 1, on the basis of  $\Delta H_p$  and  $\Delta S_p^\circ$  determined thermochemically, if not indicated otherwise; <sup>f)</sup> determined experimentally; <sup>g)</sup> calculated from equation 2 assuming bulk polymerization

## Homo- and Copolymerization of $\gamma$ -Butyrolactone

$[M]_{eq}$  of the five-membered non-strained  $\gamma$ -butyrolactone (**B**) is equal to  $3.3 \times 10^3 \text{ mol} \cdot \text{L}^{-1}$  at room temperature, whereas its concentration at the same temperature equals to  $12.9 \text{ mol} \cdot \text{L}^{-1}$ . The  $[M]_{eq}$  was calculated by us from equation 1, from  $\Delta H_p$  and  $\Delta S_p^\circ$  determined thermochemically on the basis of **B** and poly(**B**) combustion and specific heats.<sup>[6]</sup> Oligomeric polyester having  $M_n$  up to  $3.5 \times 10^3$  was prepared for this purpose but only at high temperatures and pressures (e.g.:  $160^\circ\text{C}$ ,  $2 \times 10^3 \text{ MPa}$ ).<sup>[10, 11]</sup> Therefore, several authors of the polymer chemistry textbooks claimed that homopolymerization of **B** and/or its ring-opening at ambient conditions is not possible. Some of these statements are quoted as follows: "...Carothers found that neither  $\gamma$ -butyrolactone... is able to polymerize..." (Sawada<sup>[12]</sup>), "...most lactones...from polyesters...with the exception of a five membered  $\gamma$ -butyrolactone, which resists ring-opening..." (Stevens<sup>[13]</sup>), "...among the simple lactones, only the five membered  $\gamma$ -butyrolactone does not polymerize under conventional conditions" (Kučera<sup>[14]</sup>), "For the lactones, the 5-membered ring,  $\gamma$ -butyrolactone, is not polymerizable..." (Lenz a.o.<sup>[15]</sup>), "While the five-membered ring ( $\gamma$ -butyrolactone) is not readily cleaved, the smaller rings readily polymerize..." (Seymour and Carraher, Jr.<sup>[16]</sup>), and "... $\gamma$ -butyrolactone, which contains a five-membered ring, apparently does not polymerize..." (Allcock a.o.<sup>[17]</sup>).

In this section our earlier results, mostly coming from papers published under references<sup>[18-20]</sup> are put together, quoted and discussed de novo, taking into account results from these works. Comprehensive listing of the literature references related to **B** homo- and copolymerization has recently been published by Keul and Höcker.<sup>[21]</sup>

It has been shown in our work, that **B** does give lower molar mass oligomers in homopolymerization. The corresponding results are illustrated in Figure 1.<sup>[20]</sup> Homopolymerization of **B** at room temperature results in a series of short oligomers; chains up to degree of polymerization equal to 10 could be directly observed. Oligomerization of **B** was conducted in THF solvent and was initiated with  $\text{Al}(\text{O}^i\text{Pr})_3$  at  $80^\circ\text{C}$ . In mass spectrum (chemical ionization) a series of oligomers with structure  $\text{H}[\text{OCH}_2)_3\text{C}(\text{O})]_n\text{O}^i\text{Pr}$  were detected. This discrepancy between the quoted above opinions from reviews and textbooks and the presented here results has apparently its origin in two facts. The first is purely experimental. These low molar mass oligomers could easily be overlooked, since attempts to precipitate the polymer were not successful,

due to its low molar mass. The second fact has its origin in the theoretical value of  $[B]_{eq} = 3.3 \times 10^3 \text{ mol} \cdot \text{L}^{-1}$  calculated on the basis of  $\Delta H_p$  and  $\Delta S_p^\circ$  (cf. discussion above).

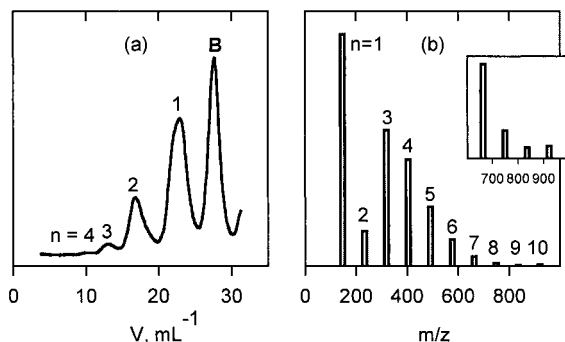
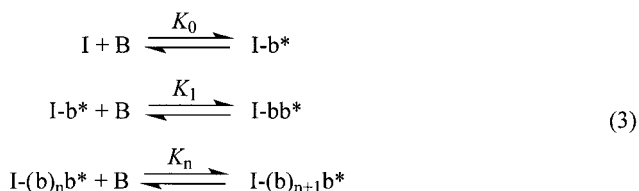


Figure 1. Oligomerization of  $\gamma$ -butyrolactone (**B**) initiated with  $\text{Al}(\text{O}^i\text{Pr})_3$ . SEC trace (a) and mass spectrum (chemical ionization) (b) of the isolated series of the linear oligomers:  $\text{H}-[\text{O}(\text{CH}_2)_3\text{C}(\text{O})]_n-\text{O}^i\text{Pr}$ . Conditions of oligomerization:  $[\text{BL}]_0 = 3.8 \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{Al}(\text{O}^i\text{Pr})_3]_0 = 0.2 \text{ mol} \cdot \text{L}^{-1}$ , THF solvent,  $80^\circ\text{C}$  (Reprinted with permission from ref.<sup>[20]</sup>).

However, it has been forgotten, that the equilibrium constants differ with the chain length (in Scheme 3 below, I stands for initiator, B for  $\gamma$ -butyrolactone monomer and b for a repeating unit derived from B):



where  $K_0 \neq K_1 \neq K_2 \neq K_n$ ; only after a certain value of  $n$  the equality holds:  $K_n = K_{n+1}$ .

For a given  $n$  we have:

$$\Delta G_n = \Delta H - T(\Delta S^\circ + R \ln ([B][\text{I-(b)}_n\text{b}^*] / [\text{I-(b)}_{n+1}\text{b}^*])) \tag{4}$$

where  $\Delta G_n$  denotes Gibbs' energy of oligomerization. When  $[\text{I-(b)}_n\text{b}^*] > [\text{I-(b)}_{n+1}\text{b}^*]$  the second positive term in brackets may outweigh the negative  $\Delta S^\circ$ , and since  $\Delta H \approx 0$  the value of  $\Delta G_n$  becomes negative for this given value of  $n$ , allowing thus formation of the corresponding  $n$ -mer.

Although homopolymerization of **B** gives, as shown above, only low molar mass



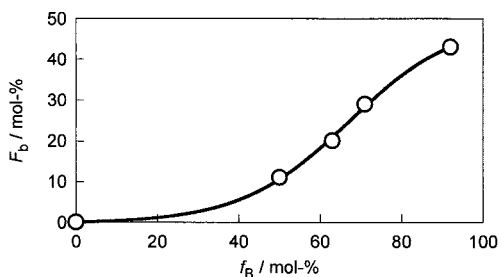
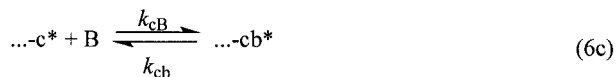


Figure 3. Dependence of polymer units b content in copolymer ( $F_b = 100[b]/([b] + [c])$ ), on the **B** monomer content in the feed ( $f_B = 100[B]_0/([B]_0 + [C]_0)$ ). Data taken from ref.<sup>[18]</sup>

The set of kinetic equations for such a copolymerization is shown in Scheme 6:



where  $k_{bb}[\text{...-bb}^*] \gg k_{bB}[\text{...-b}^*][\text{B}]$ ,  $k_{cb}[\text{...-cb}^*] \leq k_{cB}[\text{...-c}^*][\text{B}]$ , and  $k_{bc}[\text{...-b}^*][\text{C}] \approx k_{bb}[\text{...-bb}^*]$ . There are two essential points in this scheme indispensable to explain the results; the first is the much higher rate of back reaction (depropagation) once the  $\text{...-bb}^*$  unit is formed than the rate of  $\text{...-bb}^*$  formation. Second, that addition of **B** to the active species  $\text{...-c}^*$  is faster than the reverse reaction - otherwise there would be no way for **B** to enter the polymer chains. On the other hand it does not matter whether the rate of addition of **C** to  $\text{...-b}^*$  is higher or lower than the rate of  $\text{...-bb}^*$  depropagation. An interesting phenomenon would be observed if the rate of **C** addition to  $\text{...-bb}^*$  were much higher than the rate of  $\text{...-bb}^*$  depropagation, but lower than the rate of  $\text{...-bbb}^*$  depropagation. In such an instance the periodic copolymer with repeating units  $\text{...-(bbc)-...}$  exclusively at  $[\text{B}]/[\text{C}] \rightarrow \infty$  should be formed. Such a phenomenon, was observed in cationic copolymerization of THF with 3,3-bis(chloromethyl)oxetane (BCMO) above the ceiling temperature of THF homopolymerization.<sup>[23]</sup>

## Copolymerization of L,L-Lactide (L) with $\epsilon$ -Caprolactone (C) after L has Reached its Equilibrium Concentration

A monomer which is reaching its equilibrium concentration in a homopolymerization is thermodynamically and kinetically in a similar situation as a monomer which at given conditions is unable to homopolymerize at all. The copolymerization at these conditions should allow complete conversion of this monomer. This is the case of L,L-lactide (L), as it is shown below.

One of the technical methods to polymerize L industrially is based on bulk polymerization at the relatively high temperature ( $\approx 180^\circ\text{C}$ ). At these conditions there is a few percent of monomer at the living polymer monomer equilibrium ( $0.32\text{ mol} \cdot \text{L}^{-1}$ , i.e. 3.7 wt-%). When, however, copolymerization is applied, in order to introduce L completely into the polymer chain, the repeating units, derived from a comonomer will appear at the polymer chain-end, provided that no transesterification takes place.

We have first chosen  $\epsilon$ -caprolactone (C) as a model comonomer, to copolymerize with L. As it is shown in Figure 4<sup>[24]</sup>, C was introduced into the system when L reached already its equilibrium concentration ( $[\text{L}]_{\text{eq}}$ ).

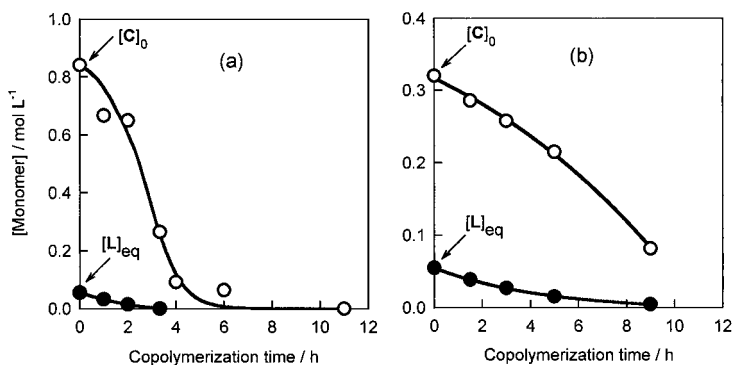


Figure 4. Plots of the change of concentration of L,L-lactide (L) (●) and  $\epsilon$ -caprolactone (C) (○) on the copolymerization time when: (a)  $[\text{C}]_0/[\text{L}]_{\text{eq}} = 15.3$  and  $[\text{C}]_0 = 0.89\text{ mol} \cdot \text{L}^{-1}$ ; (b)  $[\text{C}]_0/[\text{L}]_{\text{eq}} = 5.8$  and  $[\text{C}]_0 = 0.32\text{ mol} \cdot \text{L}^{-1}$ . Other conditions:  $[(S)\text{-SBO}_2\text{Al-O-poly(L)}]_0 = 4.3 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$ ,  $80^\circ\text{C}$ , THF as solvent;  $M_n(\text{living poly(L)}) = 4780$ . (Reproduced with permission from ref.<sup>[24]</sup>).

As it is known, C is homopolymerizing much faster than L,<sup>[25]</sup> but in copolymerization this is L that first is forming the product and before polymerization of L comes to

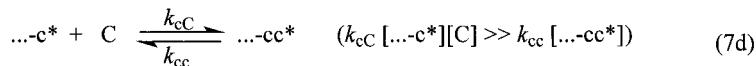
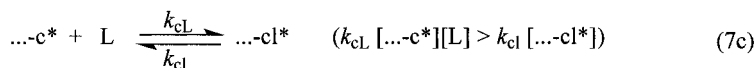
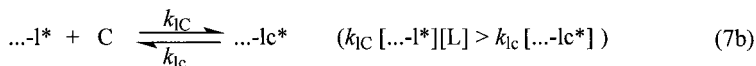
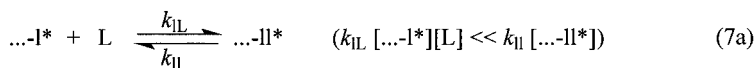
equilibrium there is no substantial amount of **C** reacted.<sup>[26]</sup> Actually, several authors (including papers published recently) claim, that block polymerization of **C** on the preformed living poly(**L**) is not possible.<sup>[27-34]</sup> This opinion is just wrong. As it is shown from Figure 4, when **L** monomer is at its equilibrium concentration (in homopolymerization,  $[L]_{eq,h}$ ), then introduced **C** polymerizes with a clear acceleration: the lower the  $[L]$  left in the system, the higher the rate of **C** polymerization (until the virtual depletion of **C**, even if **L** is already not present in the system). These phenomena have the kinetic origin, since **L** addition to the active polymer chain bearing terminal  $\dots-l^*$  unit is counterbalanced by depropagation (thus, effectively, there is no homopropagation of **L**). Therefore whenever the  $\dots-l^*$  chain end is formed the probability of the  $\dots-lc^*$  unit formation prevails over that of  $\dots-l^*l$ . It does not mean that the formation of the  $\dots-l^*l$  unit is slower than formation of the  $\dots-cl^*$  unit (thus, **L** is still more reactive monomer), but  $\dots-l^*l$  depropagates much faster than the  $\dots-cl^*$  does. Formation of copolymer at these conditions has been revealed by  $^{13}C$  NMR spectra analysis.<sup>[35]</sup>

In order to avoid or at least to minimize transesterification that would not allow block copolymer formation, because of the continuous reformation of **L** by its depropagation from the newly created poly(**L**) chain-ends ( $\dots-l^*$  units) (for example by attack of the  $\dots-cl^*$  or  $\dots-lc^*$  chain ends on the  $\dots-(l)_n\dots$  repeating units, where  $n > 1$ ), we used as an initiator the reaction product of  $Al[OCH(CH_3)_2]_3$  trimer ( $A_3$ ) with (*S*)-(+)-2,2'-[1,1'-binaphthyl-2,2'-diylbis(nitrylomethylidyne)]diphenol [(*S*)-SB(OH)<sub>2</sub>]. This choice was based on results of our earlier studies on the relationship of the selectivity of polymerization, on the structure of the growing chain-end in the polymerization of **C** and **L**.<sup>[36]</sup> It has also been shown in the recently published papers, that  $A_3/(S)$ -SB(OH)<sub>2</sub> complex polymerizes **L** to poly(**L**) with low polydispersity index ( $M_w/M_n$ ) to high conversion indicating only little transesterification taking place.<sup>[37, 38]</sup> Thus, **L** was polymerized first with (*S*)-SBO<sub>2</sub>Al-O-... and when the living polymer – monomer equilibrium was reached **C** was added and the dependencies of  $[L]$  and  $[C]$  on the copolymerization time were simultaneously measured by SEC.<sup>[24]</sup>

Set of kinetic equations, summarizing the above described kinetic phenomena, is given in Scheme 7. The observed consumption of **L** above its equilibrium concentration means that reactions  $\dots-c^* + L \rightarrow \dots-cl^*$  and  $\dots-l^* + C \rightarrow \dots-lc^*$  are faster than depropagation back to  $\dots-c^*$ , i.e.  $\dots-cl^* \rightarrow \dots-c^* + L$ . Finally, according to Figure 4 (a), **L** is eventually



completely reacted, although the conditions are far from the optimal ones, since complete conversion of **L** required, almost 10 units derived from **C** per one unit from **L**. In another experiment (Figure 4 (b)) almost three times lower starting concentration of **C** was used, namely  $0.32 \text{ mol} \cdot \text{L}^{-1}$  for  $[\text{L}]_{\text{eq}} = 0.055 \text{ mol} \cdot \text{L}^{-1}$  (the latter as in the previous experiment). At these conditions **L** reacted completely when  $\approx 0.25 \text{ mol} \cdot \text{L}^{-1}$  of **C** reacted; this means that the ratio of concentrations  $[\text{C}]/[\text{L}]$  reacted at the poly(**L**) chain-end was equal to  $\approx 5.0$ .



In Scheme 7 **l** and **c** denote the monomer units in the polymer chain derived from **L** and **C** comonomers, i.e. two lactoyl  $[\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{O}-\text{C}(\text{O})\text{CH}(\text{CH}_3)\text{O}]$  and one caproyl  $[\text{C}(\text{O})(\text{CH}_2)_5\text{O}]$  units, respectively;  $\dots\text{-l}^*$  and  $\dots\text{-c}^*$  denote the corresponding active species; transesterification was not shown in the scheme due to its virtual elimination.

More research is needed, however, to further decrease this ratio. Thus for polymerization conducted in bulk close to the polymer melting point ( $\approx 180^\circ\text{C}$ ), if an alternating copolymer would be obtained, the proportion of the second monomer added could further fall down to less than 4 mol-% at the chain-end block; in these calculation we used  $[\text{L}]_{\text{eq}}$  (in bulk, at  $180^\circ\text{C}$ ) as equal to  $0.32 \text{ mol} \cdot \text{L}^{-1}$ . This proportion does not depend on the molar mass of the starting poly(**L**). Even more advantageous situation may occur, when (like in THF/BCMO system)<sup>[23]</sup> two **l** repeating units would be separated by only one unit coming from the successfully found comonomer.

Thus, from the thermodynamic view point the equilibrium **L** concentration is lower in copolymerization than in homopolymerization, because the cross-propagation decreases the ratios of the concentration of the involved in equilibrium active centers. Indeed, for a binary system in our study (cf. Scheme 7):

$$[\text{L}]_{\text{eq}} = [\dots\text{-ll}^*]_{\text{eq}} / (K_{\text{ll}} [\dots\text{-l}^*]_{\text{eq}}) \quad (8)$$

where  $K_{IL} = k_{IL}/k_{II}$  (equation 7a). In homopolymerization:  $[...-l^*]_{eq} \approx [...-ll^*]_{eq}$ , whereas in copolymerization:  $[...-l^*]_{eq} = [...-ll^*]_{eq} + [cl^*]_{eq}$ . Thus, expression for the equilibrium concentration in homopolymerization reads:

$$([L]_{eq})_{homo} \approx 1/K_{IL} \quad (9)$$

whereas in copolymerization:

$$([L]_{eq})_{co} = [...-ll^*]_{eq}/K_{IL}([...-ll^*] + [...-cl^*]_{eq}) \quad (10)$$

Dividing equations 9 and 10 leads, after slight rearrangement, to a final equation:

$$([L]_{eq})_{co} = \frac{1}{1 + \frac{[...-cl^*]_{eq}}{[...-ll^*]_{eq}}} \times ([L]_{eq})_{homo} \quad (11)$$

Equation 11 shows, that except if  $[...-cl^*] = 0$ , the equilibrium concentration of lactide in copolymerization would always be lower than that in homopolymerization. The molecular origin of the phenomena described in this paper is related to the repulsion of the methyl groups in  $...-ll-...$  repeating units whereas in the diad  $...-cl-...$  such a repulsion does not take place.

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