Copolymerization of LL-Lactide at Its Living Polymer−Monomer Equilibrium with ϵ-Caprolactone as Comonomer

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Introduction. Copolymerization of a given monomer, after it has reached equilibrium with its homopolymer, is a well-known general phenomenon and was studied in the past by several authors.[1−8] The monomer in equilibrium may interact either stronger or weaker with a foreign active center than with its own. In the former instance its equilibrium monomer concentration ($[M]_{eq}$) would decrease, whereas in the latter no effect on $[M]_{eq}$ would be observed. The pertinent equations describing the dependence of the copolymer composition on the monomer feed have also been derived in the past for several systems.[9] Thermodynamic treatments of such instances have been summarized in the extensive Sawada's monograph[1] and the chapter devoted to thermodynamics of the ring-opening polymerization in *Comprehensive Polymer Science*.[10] However, we could not find in the available open literature any study of specific copolymerization with the aim of introducing a given monomer into a polymer after living polymer−monomer equilibrium was reached.

It is shown in the present paper that LL-lactide (LA) can be completely converted into polymer repeating units with the help of another monomer. This is important because the six-membered LA, as well as some other medium-strained cyclic esters, has relatively high equilibrium monomer concentrations, increasing with the increasing polymerization temperature.[11−13] Since polymerization of LA is conducted often in the monomer/polymer melt, relatively high temperatures are required. In our earlier work, devoted to the thermodynamics of LA polymerization, the corresponding dependence of the equilibrium LA concentration ($[LA]_{eq}$) on temperature was found, and then the enthalpy (ΔH_{lc}) and entropy ($\Delta S°_{lc}$) of the LA monomer to polymer transformation were determined.[11] For instance, at 180 °C, i.e., close to the polymer melting point, $[LA]_{eq}$ is equal to 0.32 mol L^{-1}. It is therefore important to find conditions to force this monomer, being in a relatively high equilibrium concentration, to enter into the polymer chains.

If lowering of the polymerization temperature cannot be applied, copolymerization looks to be the only way to achieve this goal. Indeed, lowering temperature and polymer crystallization would decrease the amount of monomer at equilibrium, but remelting of the system at higher temperature would restate the previous conditions. When copolymerization is applied, the repeating units derived from a comonomer will appear at the polymer chain end that would alter in a certain way the final polymer properties. Thus, the comonomer structure has to be chosen in a way preventing deterioration of the properties as little as possible. In another series of papers from this laboratory and related to another system of the ring-opening polymerization, it has been shown that when equilibrium is reached, it is possible by proper comonomer choice to form a periodic or alternating copolymer, depending on the structures of the given comonomers pair.[7,8]

Results and Discussion. In this preliminary communication we show that LA is able to copolymerize with ϵ-caprolactone (CL) at or below its monomer equilibrium concentration ($[LA]_{eq}$) reached in homopolymerization. We also show that even CL, known to have much lower reactivity than LA in their copolymerization carried out above equilibrium concentration for both comonomers,[14] enters even faster the chains than LA when $[LA]_{eq}$ is reached. This phenomenon has a thermodynamic origin since LA addition to the active polymer chains bearing a terminal lactide unit is counterbalanced by depropagation (thus, cannot form longer sequences). Therefore, whenever the ...-la* chain end is formed, the probability of formation of the ...-la-cl* unit prevails over that of ...-la-la*. It does not mean that the formation of the ...-la-la* unit is slower than formation of the ...-la-cl* unit (thus, LA is still more reactive monomer), but ...-la-la* depropagates much faster than the ...-la-cl* does.

To avoid or at least to minimize transesterification that would not allow achieving our goal because of constant re-formation of LA by its depropagation from the newly created PLA chain ends (for example, by attack of the ...-cl* chain ends on the ...-la-... repeating units), 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(nitrylomethilidyne)]diphenol [(*S*)-$SB(OH)_2$]. 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 CL and LA.[15] It has also been shown in the recently published papers that the A_3/(*S*)-$SB(OH)_2$ complex polymerizes LA to PLA with low polydispersity index (M_w/M_n) to high conversion, indicating only little transesterification taking place.[16,17] Thus, LA was polymerized first with (*S*)-SBO_2Al-O-..., and when the living polymer−monomer equilibrium was reached CL was added, and the dependencies of [LA] and [CL] on the copolymerization time were simultaneously measured by SEC. Experimental procedures are described in ref 18.

Figure 1 shows plots of LA and CL concentration changes during the copolymerization time. Before copolymerization was started, LA already has reached its equilibrium concentration, i.e., $[LA]_0 = [LA]_{eq} = 0.055$ mol L^{-1} (at 80 °C, THF solvent). It is clearly seen that at these conditions, in contrast to what is known on the copolymerization of the LA/CL, CL is a "faster monomer", as mentioned already above. This is simply because LA at these conditions is unable to homopolymerize. Thus, the kinetic equations for such a copolymerization may be written as in Scheme 1.

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Scheme 1. Kinetic Scheme of the Reversible LA/CL Copolymerization in the Absence of Transesterification[a]

$$\text{...-la* + LA} \underset{k_{lala}}{\overset{k_{laLA}}{\rightleftharpoons}} \text{...-la-la*} \qquad (k_{laLA}\,[\text{...-la*}][\text{LA}] \ll k_{lala}\,[\text{...-la-la*}]) \tag{1a}$$

$$\text{...-la* + CL} \underset{k_{lacl}}{\overset{k_{laCL}}{\rightleftharpoons}} \text{...-la-cl*} \qquad (k_{laCL}\,[\text{...-la*}][\text{CL}] > k_{lacl}\,[\text{...-la-cl*}]\,) \tag{1b}$$

$$\text{...-cl* + LA} \underset{k_{clla}}{\overset{k_{clLA}}{\rightleftharpoons}} \text{...-cl-la*} \qquad (k_{clLA}\,[\text{...-cl*}][\text{LA}] > k_{clla}\,[\text{...-cl-la*}]) \tag{1c}$$

$$\text{...-cl* + CL} \underset{k_{clcl}}{\overset{k_{clCL}}{\rightleftharpoons}} \text{...-cl-cl*} \qquad (k_{clCL}\,[\text{...-cl*}][\text{CL}] \gg k_{clcl}\,[\text{...-cl-cl*}]) \tag{1d}$$

[a] la and cl denote the monomer units derived from LA and CL comonomers, i.e., two lactoyl [C(O)CH(CH_3)O−C(O)-CH(CH_3)O] units and one caproyl [C(O)(CH_2)$_5$O] unit, respectively; la* and cl* are the corresponding active species.

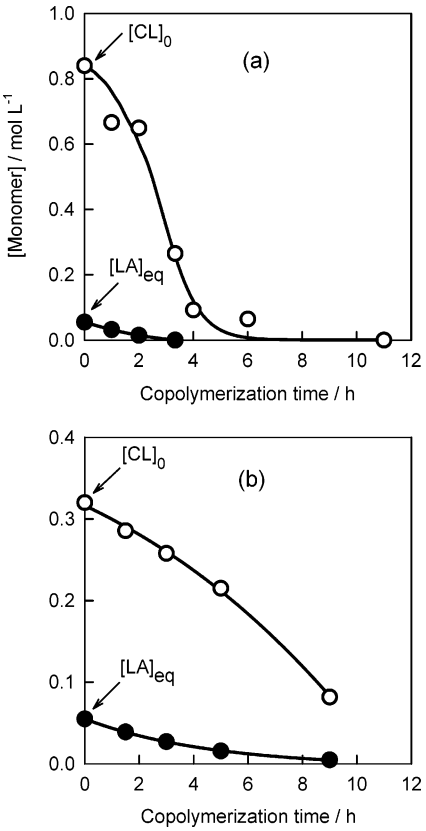

Figure 1. Plots of the change of concentration of LL-lactide (LA) (●) and ϵ-caprolactone (CL) (○) on the copolymerization time when (a) $[CL]_0/[LA]_{eq} = 15.3$, $[CL]_0 = 0.89$ mol L^{-1} and (b) $[CL]_0/[LA]_{eq} = 5.8$, $[CL]_0 = 0.32$ mol L^{-1}. Other conditions: $[(S)\text{-SBO}_2\text{Al-O-...}]_0 = 4.3 \times 10^{-3}$ mol L^{-1}, 80 °C, THF as solvent; M_n(living PLA) = 4780.

The observed consumption of LA above its equilibrium concentration means that reactions ...-cl* + LA → ...-cl-la* and ...-la* + CL → ...-la-cl* are faster than depropagation back to ...-cl*, i.e., ...-cl-la* → ...-cl* + LA. Finally, according to Figure 1a, LA is completely reacted, although the conditions are far from the optimal ones since complete conversion of LA required almost 10 units of CL per one unit of LA. In another experiment (Figure 1b) an almost 3 times lower starting concentration of CL was used, namely, 0.32 mol L^{-1} for $[LA]_{eq}$ = 0.055 mol L^{-1} (the latter as in the previous experiment). At these conditions LA reacted completely when ≈0.25 mol L^{-1} of CL reacted; this means that the ratio of concentrations [CL]/[LA] reacted is now equal to ≈5.0, and the proportion of CL units in the final polymer falls twice compared to the previous experiment (Figure 1a). More research is needed to further decrease this ratio. Thus, for polymerization conducted in bulk close to the polymer melting point (≈180 °C), if an alternating copolymer would be obtained, the proportion of the second monomer added could further fall down to less than 4 mol %; in these calculation we used $[LA]_{eq}$ (in bulk, at 180 °C) as equal to 0.32 mol L^{-1} (this proportion does not depend on the molar mass of the starting PLA).

We refrain in this short communication from detailed analysis of the copolymerization process and, particularly, from determining the involved rate constants. It suffices to say that a system has been found in which addition of the comonomer (CL) is reducing $[LA]_{eq}$ and eventually allows complete conversion of LA. The molecular origin is related to the repulsion of the methyl groups in ...-la-la-... repeating units whereas in the diad ...-cl-la-... such a repulsion does not take place.

From the thermodynamic point of view, the equilibrium LA concentration is lower than in homopolymerization because the cross-propagation decreases the ratios of the concentration of the corresponding active centers.

For a binary system in our study (Scheme 1)

$$[\text{LA}]_{eq} = [\text{...−la-la*}]_{eq}/(K_{laLA}\,[\text{...−la*}]_{eq}) \tag{2}$$

where $K_{laLA} = k_{laLA}/k_{lala}$ (eq 1a).

In homopolymerization $[\text{...−la*}]_{eq} \approx [\text{...−la-la*}]_{eq}$, whereas in copolymerization $[\text{...−la*}]_{eq} = [\text{...−la-la*}]_{eq} + [\text{...-cl-la*}]_{eq}$.

Thus, an expression for the equilibrium concentration in homopolymerization reads

$$([\text{LA}]_{eq})_{homo} \approx 1/K_{laLA} \tag{3}$$

whereas in copolymerization (transesterification depressed)

$$([\text{LA}]_{eq})_{co} = [\text{...-la-la*}]_{eq}/K_{laLA}([\text{...−la-la*}]_{eq} + [\text{...-cl-la*}]_{eq}) \tag{4}$$

Dividing eqs 3 and 4 leads, after slight rearrangement, to a final equation:

$$([\text{LA}]_{eq})_{co} = \frac{1}{1 + \dfrac{[\text{...-cl-la*}]_{eq}}{[\text{...-la-la*}]_{eq}}} \times ([\text{LA}]_{eq})_{homo} \tag{5}$$

Equation 5 shows that, except for [...-cl-la*] = 0, the equilibrium concentration of lactide in copolymerization would always be lower than that in homopolymeriza-

tion. Our research should thus be directed toward comonomers, giving as high as possible ratio of active centers resulting from cross- and homopropagations: [...-cl-la*]/[...-la-la*].

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Supporting Information Available: Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) See the Supporting Information.

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