Macromolecular Engineering of Polylactones and Polylactides. 4. Mechanism and Kinetics of Lactide Homopolymerization by Aluminum Isopropoxide

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ABSTRACT: Aluminum isopropoxide is an effective initiator for the polymerization of lactides in toluene at 70 °C. The ring-opening polymerization proceeds through a "coordination-insertion" mechanism and selective rupture of the acyl oxygen bond of the monomer. A kinetic study has shown that the polymerization is first order in both the monomer and initiator. The polymerization is typically "living" until a molecular weight of ca. 90 000 is reached. At higher temperatures (100 °C), inter- and intramolecular transesterification reactions are responsible for a limitation in the molecular weight of the growing chains. In toluene, at 70 °C, each alkoxide of the aluminum isopropoxide participates in the polymerization. Any molecular weight below 90 000 can accordingly be predicted on the basis of the monomer/Al molar ratio, and the polydispersity is rather narrow (1.1-1.4).

Introduction

Ever increasing attention is paid nowadays to synthetic polymers for their potentialities in the design of artificial organs and the formulation of drugs. Stringent conditions must however be fulfilled for a polymer to be used in biomedical applications. Biocompatibility, which means at least the absence of toxicity, is the primary requirement. Silicone rubber (Silastic) was used very early because, in addition to that prerequisite, it provided a good permeability to many biologically active molecules. Biodegradation is an additional advantage when the polymer must be removed after an appropriate period of implantation time in a living organism.[1] In that respect, poly-ε-caprolactone, polylactides, and polyglycolide are of great interest since they are hydrolytically unstable and degraded in vitro as well as in vivo[2] with release of nontoxic byproducts. These aliphatic polyesters display a large range of biodegradability: their half-life can vary from several days to several years[3] and can be modulated by the copolymerization of the related monomers used in various molar ratios.[2]

Polymers and copolymers of ε-caprolactone, lactides, and glycolide are used in medicine as biodegradable sutures, artificial skin, and resorbable prostheses. They also contribute to the design of galenic formulations[1-6] that allow the therapeutic index of drugs to be increased (sustained drug release and targeting of tumors).

The ring-opening polymerization of lactones, lactides, and glycolide provides a direct access to the related polyesters, in contrast to the traditional step-polycondensation method. Molecular weight of polycondensates is generally limited to a few tens of thousands, byproducts are formed, and stoichiometry of the reagents must be carefully adjusted.[7] All these disadvantages are overcome by the ring-opening polymerization.

In the particular case of lactides, high molecular weights can be obtained when the polymerization of the cyclic diester (or lactide) is initiated by antimony,[8] zinc,[9] lead,[10,11] or preferably tin catalysts, e.g., tin(IV) halides,[12,13] tin octoate,[3,6,14,15] and tin tetraphenyl,[16,17] but also various metallic alkoxides.[18] Polymerization is generally carried out in bulk at high temperature (more than 130 °C). The molecular weight distribution is however broad ($\bar{M}_w/\bar{M}_n \geq 2$) and the number-average molecular weight is very different from the theoretical value predicted by the monomer/initiator molar ratio.

Several years ago, some of us reported that bimetallic (Al,Zn) μ-oxo alkoxides were very effective in the controlled polymerization of unsubstituted lactones.[19-23] Feng and Song[24] showed later that the living polymerization of lactones could be extended to D,L-lactide. It is worth noting that Inoue et al. were also able to polymerize lactones and lactides in a living manner, by using (α,β,γ,δ-tetraphenylporphinato)aluminum alkoxides as initiators.[25-27]

This paper reports the controlled synthesis of high molecular weight polylactides (PLA), which, to our best knowledge, has not been published until now. Furthermore the initiator is a common and largely available compound: aluminum isopropoxide $Al(O^iPr)_3$. The discussion will focus on the ring-opening mechanism, polymerization kinetics, and conditions for a living process. At least two stereoisomers of lactide will be considered: the D,L- and L,L-lactides. The poly(L,L-lactide) is a semicrystalline polymer, whereas an amorphous polyester results from the D,L-lactide polymerization.

Experimental Section

Monomer. Lactides (D,L and L,L) were purchased from Boehringer and recrystallized three times from dried ethyl acetate at 60 °C. The monomer was dried for 24 h at 25 °C under reduced pressure (10^{-2} mmHg) before polymerization.

Catalyst. Aluminum isopropoxide (Fluka) was distilled under vacuum (10^{-2} mmHg) and dissolved into dry toluene. The solution concentration was determined by complexometric titration of Al by EDTA.

Solvents. Toluene and ethyl acetate were dried by refluxing over CaH_2 and $CaCl_2$, respectively, and distilled under nitrogen atmosphere.

Polymerization Procedure. Polymerization took place with stirring, in toluene, in a previously flamed and nitrogen-purged glass reactor. The addition of the monomer into the reactor was carried out in a glovebox under a nitrogen atmosphere. Solvent and initiator were then added successively through rubber septums with syringes and stainless steel capillaries. The reaction was stopped by adding an excess (relative to initiator) of 2 N HCl solution. The initiator residues were extracted four times with a dilute acid solution. The reaction mixture was then washed with water to a neutral pH and the polymer was precipitated into an excess of methanol, filtered, and dried under vacuum to a constant weight. The filtrate was finally distilled off in order to recover oligomers possibly dissolved in methanol.

NMR Measurements. ^1H NMR spectra of PLA were recorded in $CDCl_3$ with a Bruker AM 400 apparatus at 25 °C.

IR Measurements. IR spectra were recorded on a Perkin-Elmer IR 197 apparatus.

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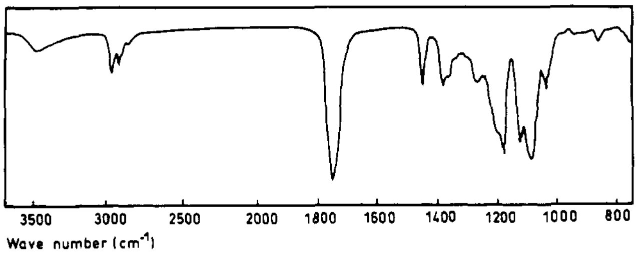


Figure 1. IR spectrum of oligo-P(L,L)LA.

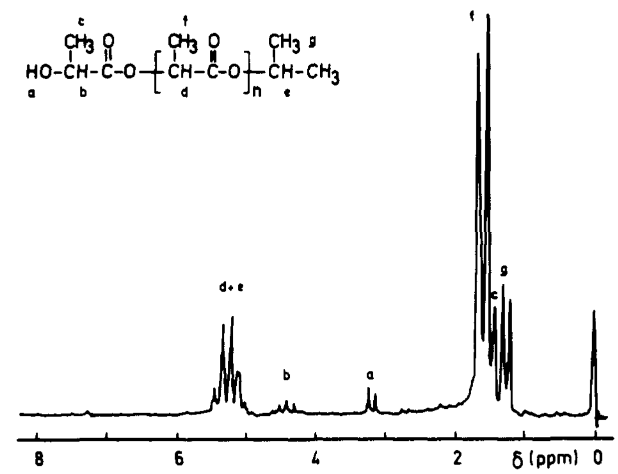


Figure 2. ^{1}H NMR spectrum of oligo-P(L,L)LA in CDCl$_3$.

Molecular Weight Determination. Molecular weight and molecular weight distribution were determined by using a gel permeation chromatograph (Waters 200) operating at 30 °C in THF and calibrated with polystyrene standards. The universal calibration method was applied for P(D,L)LA on the basis of the following viscometric relationships, valid in THF at 30 °C:[16] $[\eta] = 1.25 \times 10^{-2}\,\bar{M}^{0.717}$, PSt; $[\eta] = 5.49 \times 10^{-2}\,\bar{M}^{0.639}$, P(D,L)LA.

Low molecular weights ($\bar{M}_n < 15\,000$) were also estimated by ^{1}H NMR from comparison of the signal intensities of the isopropyl ester end group and the methine ester groups of the polyester chain. A perfect agreement was observed between $\bar{M}_n$'s obtained by GPC and NMR.

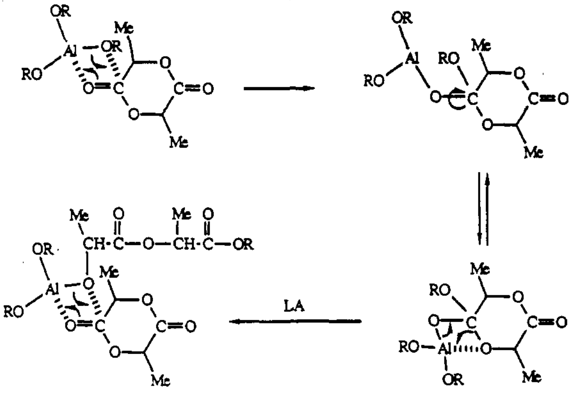
Results and Discussion

It has been shown previously that aluminum isopropoxide is very effective in promoting the living polymerization of ε-caprolactone (ε-CL) in toluene at 0 °C.[28] The polymerization mechanism proceeds through coordinative insertion of the monomer into an aluminum alkoxide bond of the initiator. That insertion involves selective cleavage of the acyl oxygen bond of the monomer and controls accordingly the nature of the polyester end groups, i.e., an ester and a hydroxyl group, respectively. As a result of the living character of the propagation step, the number-average molecular weight is predictable. It is thus of great interest to investigate whether these characteristics could be imparted to the lactide polymerization and to possibly define experimental conditions preventing any secondary reactions from occurring.

Mechanism of Polymerization. Preliminary experiments have shown that D,L- and L,L-lactides could be polymerized to completion in toluene with aluminum isopropoxide as an initiator. In contrast to ε-caprolactone, which polymerizes at 0 °C in that solvent, lactide polymerization proceeds properly only above 70 °C since the monomer is insoluble in toluene below that temperature. This is in agreement with observations published by Kricheldorf et al.[18]

In order to determine unambiguously the mechanism of the lactide-opening polymerization, stoichiometric amounts of Al(O^{i}Pr)$_3$ and (L,L)LA were reacted in toluene at 70 °C. After hydrolysis of the reaction medium, the final products were quantitatively recovered by solvent evaporation, purified (see Experimental Section), and analyzed by IR and ^{1}H NMR spectroscopies. The IR spectrum (Figure 1) shows a broad absorption in the region of 3500 cm^{-1}, which is characteristic of the hydroxyl functions. Furthermore, the absorption at 935 cm^{-1} of the lactide monomer has completely disappeared. According to ^{1}H NMR (Figure 2), the reaction product comprises one hydroxyl and one isopropoxyl ester whereas no carboxylic acid proton is present: $\delta(CH(Me)OH) = 4.4$ ppm, $\delta(CO_2CH(Me)_2) = 5.2$ ppm.

These observations clearly show that the insertion of the lactide into the Al–O bond of the initiator involves the selective acyl oxygen cleavage of the LA. The final product has thus the following structure:



(1)

On that basis and by analogy with the mechanism accepted for ε-CL polymerization by aluminum alkoxide functions, eq 1 schematizes the lactide ring-opening polymerization. This proposal, which requires the coordination of the monomer to the initiator, is in agreement with observations reported by Feijen et al.[17] These authors have concluded that aluminum tribromide or aluminum triisobutyl form complexes with lactide and glycolide through coordinative bonds between Al and the acyl oxygen of the cyclic monomers.

Kinetics. Kinetics of the (D,L)LA polymerization by aluminum isopropoxide has been investigated in toluene at 70 °C. After an induction period, the polymerization becomes first order in monomer (Figure 3). That the polymerization does not start as soon as monomer and initiator are mixed has already been observed in ε-CL polymerization. This feature has been attributed to a rearrangement of the coordinative aggregates of the initiator in toluene upon addition of the polar monomer. It is known indeed that aluminum isopropoxide tends to associate in bulk and in solution in an apolar solvent.[28–30] The mean degree of association is of course controlled by the polarity and the coordination capability of the solvent or any additives, as well as by the bulkiness and electronic structure of the R groups.

The (D,L)LA polymerization is also first order in initiator as shown by Figure 4, which indicates the linear dependence of ln ([LA]$_0$/[LA])/t on [Al(O^{i}Pr)$_3$].

In conclusion, except the induction period, the polymerization proceeds according to a simple overall kinetics law of the form

$$\frac{-d[LA]}{dt} = k[LA][Al(O^iPr)_3] \qquad (2)$$

where the kinetic constant, $k = 0.6$ L mol^{-1} min^{-1} ([LA]$_0$ = 1 mol L^{-1}). This equation is exactly the same as that

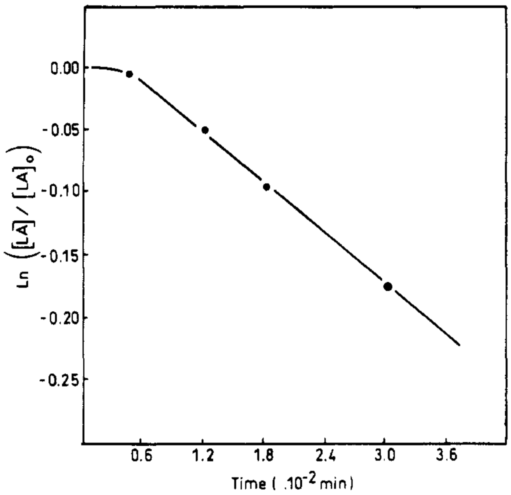


Figure 3. Determination of the order in monomer for the polymerization of (D,L)LA at 70 °C promoted by $Al(O^iPr)_3$ in toluene ($[LA]_0 = 5.6 \times 10^{-1}$ mol L^{-1}; $[LA]_0/[Al] = 417$).

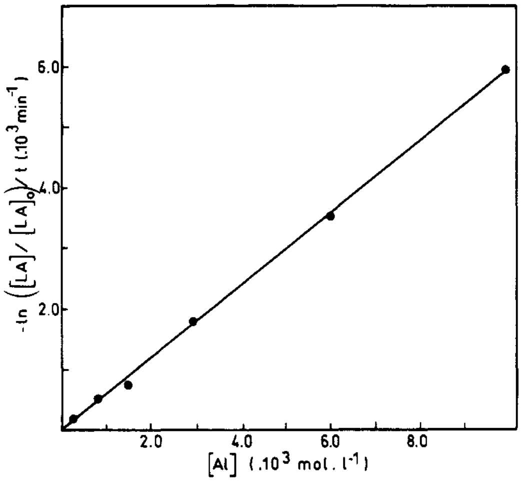


Figure 4. Determination of the order in initiator for one polymerization of (D,L)LA at 70 °C promoted by $Al(O^iPr)_3$ in toluene ($[LA]_0 = 6.0 \times 10^{-1}$ mol L^{-1}).

derived by Ouhadi[28] for polymerization of ε-CL in toluene at 0 °C, the k value being much higher in the latter case (36.6 L mol^{-1} min^{-1}).

Living Character of the Polymerization. The (D,L)-LA polymerization is a perfectly "living" process when initiated by aluminum isopropoxide in toluene at 70 °C. This characteristic is supported by polymerization resumption experiments and by the linear relationship between the experimental $\overline{DP}$ of the polymer and the monomer/initiator molar ratio calculated for the actual monomer conversion [($[LA]_0/[Al]x/100$, where x is the monomer conversion] (Figure 5). It is worth noting that this linearity is no longer observed at the highest values of the monomer/initiator molar ratio ($[LA]_0/[Al] > 1600$). Transesterification reactions could be responsible for that phenomenon, which will be discussed later. The same conclusions are valid for the (L,L)LA polymerization.

The Number of Active Centers (*n*). From the slope of the linear dependence of the degree of polymerization and the monomer/initiator molar ratio (Figure 5), it can easily be calculated that one initiator unit $Al(O^iPr)_3$ initiates three polylactide chains, at least as far as $[LA]_0/[Al] < 1600$. Now the molecular weight of PLA can be predicted on the basis of eq 3, where MM is the molecular mass of LA (144 g mol^{-1}).

Table I compares the mean number of active polymerization sites per aluminum when ε-caprolactone and lactides are polymerized by $Al(O^iPr)_3$ in toluene at 0 and 70 °C, respectively. Although all the aluminum alkoxide bonds are active in the polymerization of LA at 70 °C, only one of them contributes to the polymerization of ε-CL at 0 °C. This discrepancy cannot be attributed to the difference in the polymerization temperature. Indeed the average number of active sites in the ε-CL polymerization does not exceed 1.4, when the temperature is increased from 0 to 100 °C.

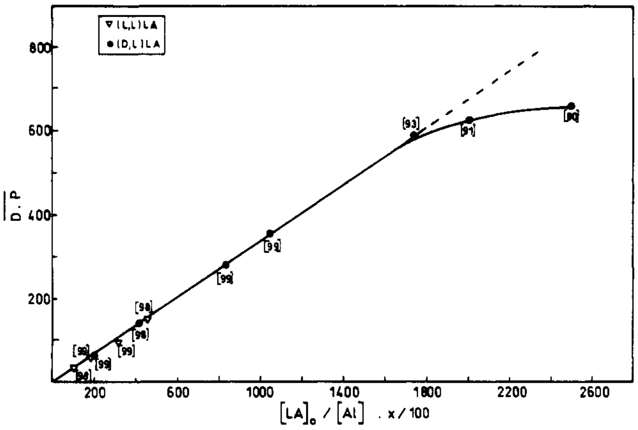


Figure 5. Dependence of the $\overline{DP}$ on the monomer/initiator molar ratio, taking account of the conversion for the polymerization of (D,L)LA at 70 °C promoted by $Al(O^iPr)_3$ in toluene ($[LA]_0 = 6.0 \times 10^{-1}$ mol L^{-1}). Conversion to high molecular weight polymer (%) is noted in brackets.

Table I
Average Number of Active Sites (*n*) per $Al(O^iPr)_3$ Molecule in the Polymerization in Toluene of Lactides and ε-CL[a]

monomer	*n*	temp, °C	polym rate const (*k*), L mol^{-1} min^{-1}	IR freq $\nu_{C=O}$, cm^{-1}
(D,L)LA	3.0	70	0.6	1770 (17)
(L,L)LA	3.0	70	0.6	1770 (17)
ε-CL	0.9	0	36.6	1725 (31)

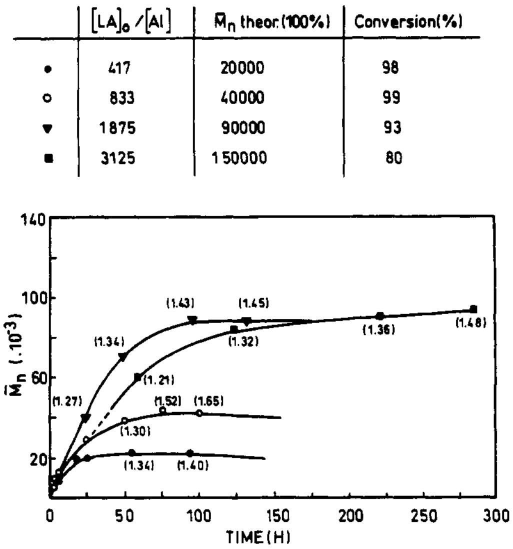
[a] $[CL]_0 = [(L,L)LA] = 1.0$ mol L^{-1}; $[(D,L)LA] = 6.0 \times 10^{-1}$ mol L^{-1}.

$$\bar{M}_{n\ \mathrm{theoretical}} = \frac{[LA]_0 MM x}{3[Al] \times 100} \qquad (3)$$

It might be assumed that the initiator is less associated in the presence of the most electron donating monomer. According to the experimental values of *n*, D,L- and L,L-lactides should be more electron donating compounds then ε-CL. This is in disagreement with IR data, which indicate that ε-CL is better able to coordinate Al than lactides (Table I).

Data of Table I could be accounted for by the dynamic character of the coordinative association of aluminum isopropoxide. The reorganization of the initiator aggregates could be slower than the polymerization and only the initially free alkoxide groups would contribute to the polymerization. This might be the case for ε-CL. In contrast, the polymerization rate constant (k) of D,L- and L,L-lactides is 60 times smaller than that of ε-CL, and bridged and free alkoxide groups could be completely exchanged during the polymerization period, allowing all of the "Al-OR" bonds to be active.

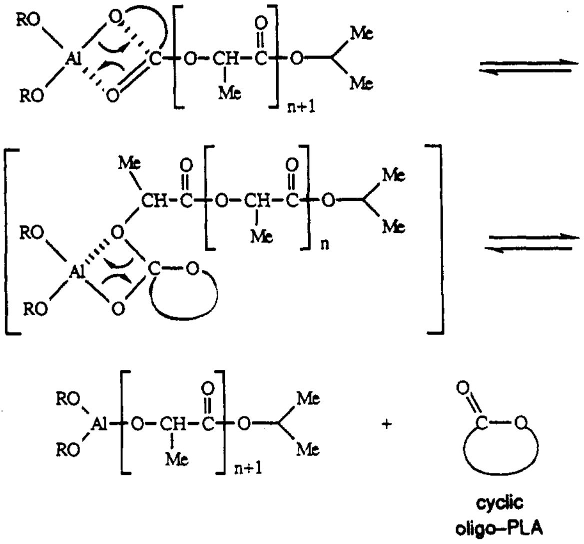
Transesterification Reactions. As already mentioned, the polymerization of (D,L)LA in toluene at 70 °C is no longer quantitative when the theoretical molecular weight exceeds ca. 90 000. Beyond that limit, the experimental molecular weight does not correspond anymore to the theoretical value, calculated from eq 3. Furthermore, Figure 6 shows that the polydispersity increases versus time.



	$[LA]_0/[Al]$	$\bar{M}_n$ theor.(100%)	Conversion(%)
●	417	20000	98
○	833	40000	99
▼	1875	90000	93
■	3125	150000	80

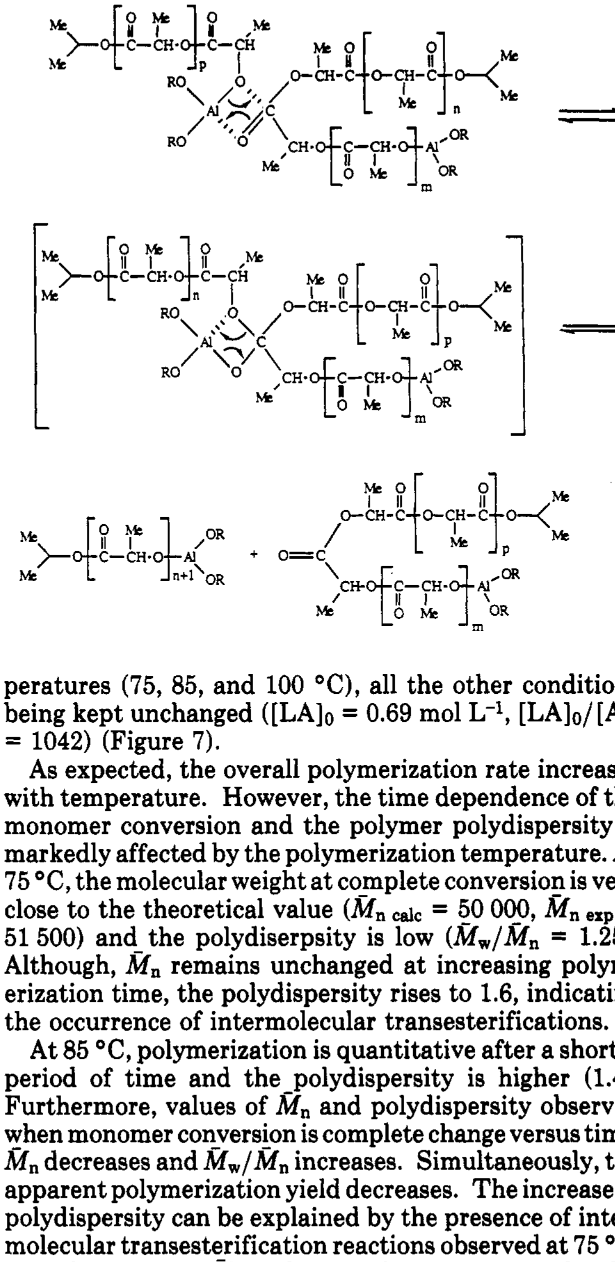
Figure 6. Dependence of the average-number molecular weight and the polydispersity on the polymerization time of (D,L)LA at 70 °C promoted by $Al(O^iPr)_3$ in toluene ($[LA]_0 = 6.0 \times 10^{-1}$ mol L^{-1}; $[LA]_0/[Al] = 417, 833, 1875,$ and 3125). The polydispersity is noted in parentheses.

All these observations agree with the occurrence of transesterification reactions. Indeed, the apparently limited monomer conversion could be due to an *intra*molecular transesterification process, known as "back-biting" (eq 4). Since the polyester is not recovered quantitatively by precipitation and the monomer conversion appears to be partial. Nevertheless, intramolecular transesterification reactions can also produce higher molecular weight cyclic PLA, insoluble in methanol, which are responsible for the broadening of the molecular weight distribution and for a decrease in the average-number molecular weight. Moreover, *inter*molecular transesterification (eq 5) could also be responsible for the polydispersity increase with the polymerization time. Similar observations have already been reported by Kricheldorf et al.[32,33] for the synthesis of various polyesters. Finally, when the theoretical molecular weight is high, the initiator amount is small and the polymerization is much more sensitive to impurities inherent to the conditions reported in the Experimental Section.



(4)

In order to investigate the possible effect of temperature on the extent of the transesterification reactions, the (D,L)LA polymerization was carried out at different temperatures (75, 85, and 100 °C), all the other conditions being kept unchanged ($[LA]_0 = 0.69$ mol L^{-1}, $[LA]_0/[Al] = 1042$) (Figure 7).



(5)

As expected, the overall polymerization rate increases with temperature. However, the time dependence of the monomer conversion and the polymer polydispersity is markedly affected by the polymerization temperature. At 75 °C, the molecular weight at complete conversion is very close to the theoretical value ($\bar{M}_{n\,calc} = 50\,000$, $\bar{M}_{n\,exp} = 51\,500$) and the polydiserpsity is low ($\bar{M}_w/\bar{M}_n = 1.25$). Although, $\bar{M}_n$ remains unchanged at increasing polymerization time, the polydispersity rises to 1.6, indicating the occurrence of intermolecular transesterifications.

At 85 °C, polymerization is quantitative after a shorter period of time and the polydispersity is higher (1.4). Furthermore, values of $\bar{M}_n$ and polydispersity observed when monomer conversion is complete change versus time; $\bar{M}_n$ decreases and $\bar{M}_w/\bar{M}_n$ increases. Simultaneously, the apparent polymerization yield decreases. The increase in polydispersity can be explained by the presence of intermolecular transesterification reactions observed at 75 °C. The decrease in $\bar{M}_n$ indicates that an intramolecular process also occurs, leading to lower molecular weight cyclic compounds still insoluble in methanol.

When the reaction time is increased further, a decrease in the high polymer yield is observed due to extra "backbiting" intramolecular transesterification, producing small cyclic oligomers, soluble in methanol (Figure 7). This evolution can only be accounted for by inter- and intramolecular transesterification.

At 100 °C, all the phenomena observed at 85 °C are still much more pronounced. In addition, the long-chain formation is never quantitative and the average-number molecular weight does not exceed 40 500.

After the polymer precipitation in methanol and filtration, the soluble cyclic and linear oligomers are recovered (see Experimental Section) and analyzed by GPC and ^{1}H NMR. By GPC analysis, we observe a broad molecular weight distribution at high elution volume (corresponding to $\bar{M}_n \sim 500$), which could be attributed either to a bad resolution of the apparatus or more probably to a simultaneous presence of cyclic and linear oligomers.

This has been ascertained by ^{1}H NMR (Figure 8), which shows a singlet at 3.70 ppm assigned to terminal methyl ester protons, whereas no isopropyl ester protons are observed. Linear oligomers more likely result from the

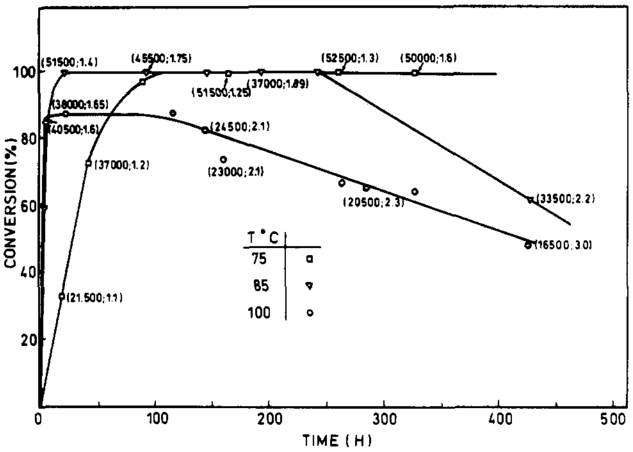


Figure 7. Effect of temperature and time on the polymerization of (D,L)LA initiated by $Al(O^iPr)_3$ in toluene ($[LA]_0 = 6.9 \times 10^{-1}$ mol L^{-1}; $[LA]_0/[Al] = 1042$; $T = 75, 85,$ and 100 °C). The number-average molecular weights and polydispersity are noted in parentheses.

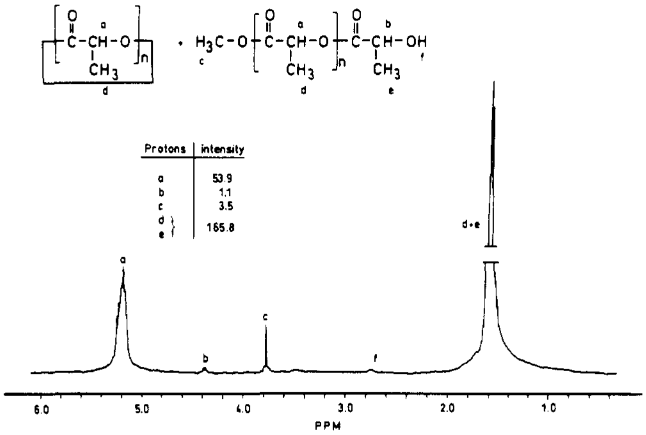


Figure 8. ^1H NMR spectrum of cyclic and linear P(D,L)LA in $CDCl_3$.

partial methanolysis of cyclic oligomers in the presence of HCl used to terminate the polymerization. Linear oligomers represent ca. 15% of the whole amount of oligomers as estimated by GPC and ^1H NMR.

Conclusions

This study has clearly shown that lactides can be polymerized by aluminum isopropoxide according to a "coordination–insertion" mechanism, which involves the selective rupture of the acyl oxygen bond of the monomer. Nevertheless, the living character of that polymerization in toluene at 70 °C seems to be limited to an average-number molecular weight of ca. 90 000. In that range, the molecular weight of PLA is predictable on the basis of the monomer/initiator molar ratio and the monomer conversion. Beyond a molecular weight of 90 000 secondary inter- and intramolecular reactions of the growing chains become significant and account for a nonliving process.

The polymerization mechanism of lactides is identical with that reported for ε-CL in the presence of the same initiator. Secondary reactions are not observed when CL is polymerized in toluene, probably because of a much lower polymerization temperature (0–20 °C).

In conclusion, the commercially available aluminum isopropoxide should allow block copolymers of ε-CL and LA to be synthesized in a controlled way. These copolymers could expectedly combine the excellent permeability of P-ε-CL and the higher biodegradability of PLA segments.[34] Let us note that random copolymers P(ε-CL-*co*-LA) have already been synthesized by using aluminum isopropoxide as an initiator.[35]

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