Synthesis and characterization of some block copolymers of lactides with cyclic monomers using yttrium alkoxide as initiator

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SUMMARY : Block copolymers were prepared by sequential addition of L- or D-lactide to a living ε-caprolactone prepared with $Y(OC_2H_4OiPr)_3$ initiator. In contrast, ε-caprolactone (CL) was not polymerized when added to a living polyL-lactide (LA) prepared with the same initiator in the same conditions. The polymerization of an equimolecular mixture of LA and CL using the yttrium alkoxide initiator produces only the pure lactide homopolymer. The copolymerization of LA with trimethylene carbonate (TMC) exhibits a different type of behaviour. The synthesis of pure block copolymers by sequential addition of monomers is obtained if starting from a living polylactide sequence. When starting with TMC sequence, mixture of products leading to a bimodal MWD is obtained. The polymerization of an equimolecular mixture of LA and TMC leads to a copolymer with a block structure. The PLA sequence is formed first, followed by the subsequent addition of TMC monomer up to complete conversion. All the prepared copolymers were characterized by SEC, ^1H and ^{13}C NMR techniques. No transesterification reactions were detected.

Introduction

Aliphatic polyesters derived from lactides and lactones are materials of great interest for biomedical and pharmacological applications [1-4]. There is also a growing interest in polyesters for packaging applications [5].

These materials are usually obtained from the corresponding monomers by ring-opening polymerization [6]. Block or random copolymers of lactides (LA) with ε-caprolactone (CL), for example, lead also to a wide range of polyesters presenting various interesting properties.

It is of great interest for macromolecular engineering to be able to synthesize polymers with well defined characteristics, i.e., with control of molecular weight (MW), molecular weight distribution (MWD) and end groups.

Controlled polymerizations of lactides and lactones has been achieved with aluminium alkoxides [7-9] and the selectivity of processes has been discussed [10,11]. These initiators exhibit however a somewhat low activity as compared to lanthanide compounds. The use of the latter was first

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reported by a Du Pont de Nemours group [12,13] and have since been the subject of increasing number of papers. The earlier works were summarized in a review by Stevels et al [14]. Various derivatives of lanthanides such as halogenides[15], cyclopentadienyl [16] and bimetallic [17] complexes are also used in the polymerization and copolymerization of cyclic esters and cyclic monomers.

The most detailed studies on controlled synthesis were devoted to lanthanide alkoxides, mainly to oxoalkoxide clusters of $Ln_5(\mu\text{-}O)(OiPr)_{13}$ type [18-20]. It is known that these clusters have a pentanuclearoxoaggregate structure [21,22]. In our group we have in addition used tris-alkoxyethoxide initiators $[Y(OC_2H_4OR)_3]_n$ for polymerization of lactide [23,24]. These initiators are prepared by reaction of yttrium with the corresponding alcohol according to the procedure described by Poncelet et al.[25] Kinetic data on polymerization of lactides with these initiators were recently reported[26]. The polymerization is faster than with the corresponding yttrium cluster compound and a living type behaviour is observed. Very recently we have shown that these initiators are also very active for the polymerization of other cyclic esters such as ε-caprolactone, δ-valerolactone (VL) and another cyclic monomer, trimethylene carbonate (TMC)[27]. Although a detailed study was not performed, it appears that a controlled type is observed which makes possible the synthesis of block copolymers.

In the present paper we want to report our results on the synthesis of lactide block copolymers with ε-caprolactone and trimethylene carbonate. We report also some features observed when mixtures of these monomers are copolymerized in the presence of yttrium alkoxide initiators.

Results and Discussion

In our previous study on the homopolymerization of (D,L)-lactide[26] with yttrium tris-alkoxyethoxide initiators $[Y(OCH_2CH_2OR)_3]_n$ we have not observed any important difference in behaviour between R=Me and R=iPr initiators and therefore both of these compounds were used indifferently in copolymerization reactions.

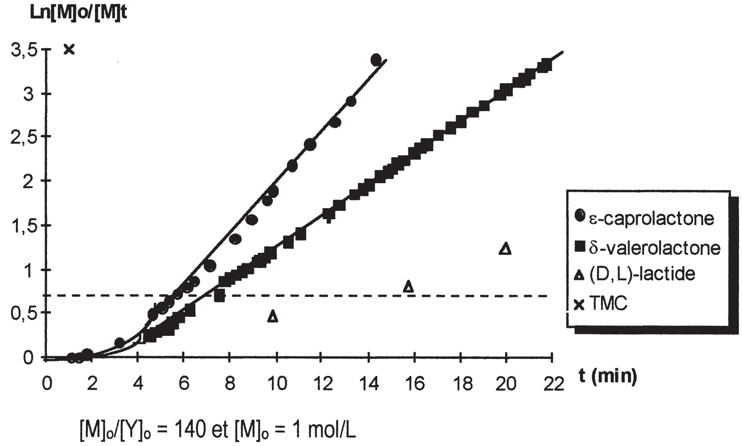
Homopolymerization of different cyclic monomers

Mc Lain et al. [12] have reported on the polymerization of ε-caprolactone using $Y(OC_2H_4OEt)_3$ as initiator in toluene solution at room temperature. The polymerization is fast (91% conversion in

5 min) giving a polymer with a narrow MWD, but after 30 min of reaction an important broadening of MWD (1.96) occurs.

We have run the polymerization of LA, CL, TMC and VL in dichloromethane (DCM) solution at room temperature using $Y(OC_2H_4OiPr)_3$ as initiator. The polymerization is fast (90% conversion in 10 min in the case of CL) but the broadening after the completion of reaction (60 min) is much less important (1.33) than in the previous case. Similar results are observed for LA and VL. The polymerization of TMC is extremely fast, a quantitative yield being obtained in less than 1 min with a broad MWD (2.26). The kinetic data for these monomers, semi-logarithmic plots log $[M]_o/[M]_t$ versus time, are shown in Fig. 1. After a short period of induction a linear relationship is observed . The MW's found are consistent with initiation by every alkoxide group, i.e., 3 alkoxide groups per Y atom, for VL and LA polymerization, while for CL only two alkoxide groups are active and an average of 1.4 group in the case of TMC polymerization.

Figure 1 : Variation of $Ln[M]_o/[M]_t$ with time, for different cyclic monomers polymerized with $[Y(OCH_2CH_2OiPr)_3]_2$ in dichloromethane solution at room temperature.



Synthesis of diblock copolymers

The controlled character of the polymerization of cyclic monomers discussed in the previous chapter make it possible the synthesis of block copolymers. In this paper block copolymers containing an initial or terminal polylactide sequence will be discussed. The second block is either poly CL or poly TMC.

Diblock copolymers based on CL and LA

Diblock CL-b-LA copolymers were already prepared by sequential addition of the corresponding monomer using different types of initiators, e.g., Zn-Al-μ-oxoalkoxide 28), aluminium isopropoxide 29). It was found that CL must be the monomer first polymerized, since CL is not at all polymerized when added to living polylactide. Very recently, however, Duda et al 30) reported that the initiation of CL on living LA is possible, but the reaction is extremely slow and leads at completion to copolymers with a random type structure.

Preparation of CL-b-LA diblock copolymers was reported by Mc Lain et al. 13), using $Y(OC_2H_4NMe_2)_3$ initiator system, and by the group of Feijen using commercial $Y_5(O)(OiPr)_{13}$ initiator 31) or the in situ prepared yttrium isopropoxide initiator 19). In contrast to aluminium initiators which necessitate to work at elevated temperatures, lanthanide initiators allow the synthesis of block copolymers at room temperature in dichloromethane. The most reactive system found up to now was the in situ prepared yttrium isopropoxide system 19).

We have used $Y(OC_2H_4OMe)_3$ initiator system for the preparation of β-butyrolactone-b-L-lactide block copolymers 32). In that case β-butyrolactone block was prepared first at room temperature in toluene solution, then the sequential addition of L-lactide was performed at 70°C, temperature necessary for solubilization of L-lactide in toluene.

The synthesis of CL-b-L-LA block copolymers in the present work was performed in dichloromethane solution at room temperature using $Y(OC_2H_4OiPr)_3$ as initiator system. The CL sequence was prepared first and L-LA was added immediately after achievement of CL polymerization in order to avoid any possible transesterification. Blocks with different contents of CL/LLA were prepared. Examples of blocks with 50/50 and 70/30 contents are given in Table 1.

The authenticity of block copolymers was substantiated by GPC analysis : increase of MW, which confirms the living type process, absence of homopolylactide. The presence of homopolylactide could be eventually expected, since during polymerization of CL only two of the three active alkoxide groups of initiator are used. ^1H and ^{13}C NMR confirm also the block copolymer structure. It was also controlled by ^{13}C NMR that the block copolymers remain unchanged even after 15 days of reaction (Fig. 2).

Table 1 : Synthesis of block copolymers polyCL-b-L-LA using $[Y(OC_2H_4OiPr)_3]_2$ as initiator in dichloromethane at room temperature

Sample	n8	$[M]_o/[Y]_o$		Time	Conv(%) [(a)]		$\overline{Mn}$			MWD [(d)]
		CL	LA	(min)	CL	LA	calc [(b)]	NMR [(c)]	GPC [(d)] (corr)	
P(CL)	1	140	0	15	100	0	7900	7700	14500 (7600)	1.15
P[CL(70)-LLA(30)]	2	140	42	195	100	100	9900	/	16700	1.17
P(CL)	1	110	0	30	100	0	6300	8450	14800 (7700)	1.45
P[CL(50)-LLA(50)]	2	110	110	135	100	100	13700	/	27500	1.4

[(a)] determined from ^1H NMR
[(b)] on the basis of 2 initiating OCH_2CH_2OiPr groups per yttrium atom
[(c)] deternined from CO($C\mathbf{H_2}$)-CH_2-OiPr end group located at 4,1 ppm
[(d)] GPC in THF polystyrene standards ; in brackets corrected values for PCL

Identical block copolymers were also prepared with D-lactide sequences. It was also confirmed that no block copolymers were formed when starting the synthesis with a living polylactide sequence : CL is not added at all.

The same result was recently observed by Shen et al. [33)] in block copolymerization of CL with (D,L)-LA using isopropoxy lanthanide diethyl acetoacetate $(EA)_2LnOiPr$ (Ln = Nd,Y) as initiator. The polymerization of CL with this monoalkoxide initiator carried out in THF at room temperature exhibited a living type behaviour and block copolymers between CL and (D,L)-LA or TMC with CL were prepared. However living poly(D,L)-LA failed to initiate the polymerization of CL.

Figure 2 : ^{13}C NMR spectrum of block copolymer [CL(50)-*b*-L-LA(50)] in CDCl$_3$
Figure A : Carbonyl region after 3h of copolymerization
Figure B : Carbonyl region after 15 days of copolymerization

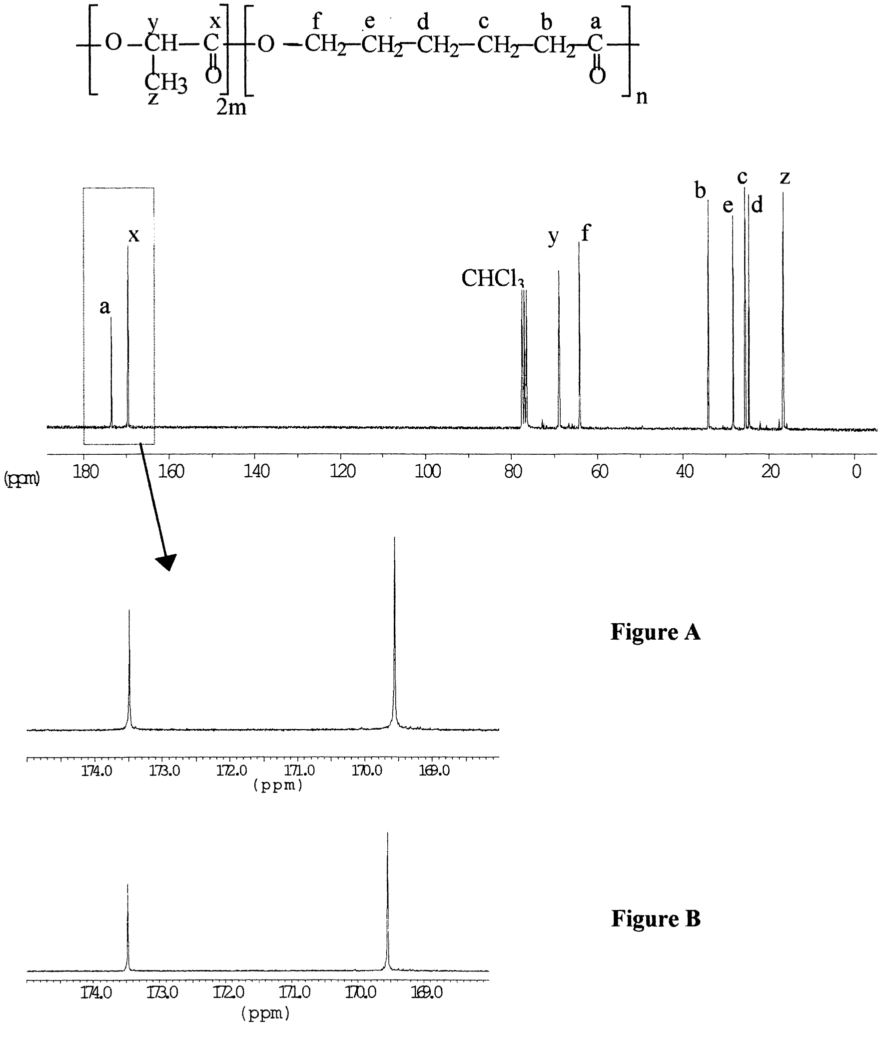


Figure A

Figure B

In an other recent publication by the group of Feijen, [34)] a melt block copolymerization of CL with L-LA was described using stannous octoate and a hydroxyl compound as a catalyst-initiator system. It was again concluded that block copolymers of CL and L-LA can be only prepared if CL is polymerized first.

Diblock copolymers based on TMC and LA

Aliphatic polycarbonates and (carbonate-cyclic ester) copolymers are attractive biodegradable and resorbable materials. The polymerization of TMC was substantially studied by cationic and coordination-insertion initiators [35-43)]. Rare-earth initiators were tried only recently on the example of $La(OiPr)_3$ [44)] and rare earth halides.[45)]

Copolymers with different cyclic monomers were also extensively studied as reported later in this paper. However according to our knowledge block polymers with lactides were never prepared. We have therefore attempted to prepare these block copolymers using $Y(OC_2H_4OiPr)_3$ initiator. The polymerization of TMC with this initiator is the fastest of the series of cyclic monomers and the reaction in our conditions is completed in less than 1 min.

In a first series of experiments we have started with poly TMC as first block and further added L-LA. The monitoring of the reaction was achieved by withdrawing samples from the polymerization medium and analyzing them by ^1H NMR and GPC in THF. The experimental conditions are similar to those found in Table 1 but with $[M]_o/[Y]_o = 100$.

It appears from GPC that the copolymers prepared exhibit a large bimodal MWD (around 2.0) and are accompanied by some oligomers . The molecular weights are lower than those expected (referring to polystyrene standard) for a pure block copolymer at complete conversion.

^1H and ^{13}C NMR spectra of prepared products correspond to the superimposition of poly TMC and poly L-LA spectra. No supplementary peaks due to transesterification reactions, were detected. We were however not able to find a selective way (solubilisation, precipitation) showing the presence of different species in prepared copolymers.

It is worthy to notice that the rate of polymerization of lactide on living poly TMC species (92% of conversion in 15 hr) is much slower than that of direct polymerization of lactide by $Y(OC_2H_4OiPr)_3$ initiator (98% of conversion in 1.5 hr).

In a second series of experiments the starting active precursor was PL-LA and TMC was added after completion of L-LA polymerization. The initiator used was $Y(OCH_2CH_2OMe)_3$. GPC curves show an unimodal distribution with increase of MW with conversion. MWD remains narrow (<1.4) and corresponds to that expected for a block copolymer. The ^{13}C NMR spectrum is again a clean superimposition of PLA and PTMC signals . No heterodiad signals in the carbonyl region were detected. Thus, no transesterification reactions occurred. These findings substantiate the synthesis of a diblock P(LA-b-TMC) copolymer. The polymerization of the second monomer TMC takes a very long time for completion (20 hr) as compared with its homopolymerization (100% in less than 1 min) in the same experimental conditions.

Copolymerization of mixtures of cyclic monomers.

The results previously obtained in sequential polymerization of LA with CL and TMC prompted us to investigate the copolymerization of mixtures of these monomers in the presence of $Y(OC_2H_4OR)_3$ initiators. Such works were already reported in the literature with other types of initiators.

Copolymerization of L-LA and CL mixtures

Random copolymerization of LA with CL has been performed using zinc or aluminium initiator [46-50] in toluene or chlorobenzene solution at elevated temperatures (50-150°C) and during a long time of reaction (more than 50 hours).

It was concluded that despite of its lower reactivity in homopolymerization, the reactivity ratio in copolymerization of lactide is much higher than that of CL and lactide is favorably introduced in copolymer chain leading to blocky structures. By increasing temperature more random copolymers are obtained but the transesterification reactions are highly increased. Copolymerization in bulk was also attempted using tin octoate as initiator. [51-53] Again blocky structures were obtained with composition depending on the temperature of the reaction.

The only report on the random copolymerization of CL and LA using rare-earth initiator is due to Shen et al.[15]. The best initiator was derived from a prepolymer of propylene oxide initiated with $NdCl_3$ ($NdCl_3$-5 PO). The copolymerization was carried out in bulk at 90°C. Random copolymers were obtained.

There were no reports on the possible copolymerization of CL and LA with current lanthanide alkoxides successfully used for homopolymerization of cyclic esters.

We have run our copolymerization reactions in the same conditions as the corresponding homopolymerizations, i.e., concentration, DCM solution, room temperature). We have always observed the same results : formation of PL-LA corresponding to the conditions used and no further polymerization of CL. These results are in agreement with the previously reported findings18). A rapid initiation of LA generate PLA active centers, the latter for reactivity ratio reasons are not initiating the polymerization of CL.

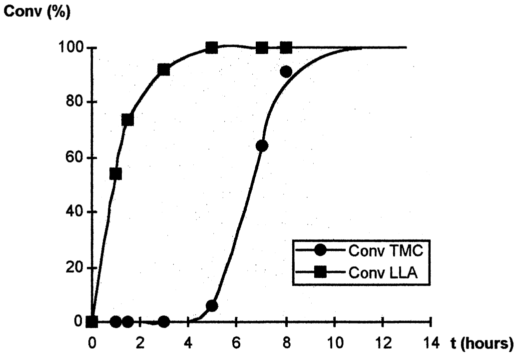
Copolymerization of L-LA and TMC mixtures

The copolymerization of mixtures of TMC with other cyclic compounds has been investigated in the group of Albertsson on the examples of CL, adipic anhydride (AA) using usual anionic, cationic and Al or Sn coordination-insertion initiators54-56). Cationic copolymerization of TMC with oxetane led to the formation of a block copolymer 57). CL was copolymerized with TMC using a rare earth monoalkoxide initiator $(EA)_2LnOiPr$ 33). Mixtures of TMC with glycolide (GA) were polymerized using stannous octoate as initiator 58). This initiator was also used in the case of copolymerization of TMC with LA 53,59,60). It was found 53) that TMC polymerizes more slowly than L-LA, transesterification reactions occur and copolymers with blocky structures are obtained.

We have polymerized mixtures of L-LA and TMC in DCM solution at room temperature using $Y(OC_2H_4OMe)_3$ as initiator system. The time-conversion course was followed by ^1H NMR and the increase of MW by GPC in THF. The structure of obtained copolymers was established from ^{13}C NMR.

From conversion curves (Fig.3) it appears very clearly that L-LA is polymerized first and TMC remains untouched till the completion of L-LA polymerization which is obtained after 4 hours of reaction. The MW of prepared PL-LA is in agreement with MW calculated on the basis of 3 active alkoxide groups per yttrium atom. The MWD is narrow : 1.21 at 92% of conversion. Then TMC begins to polymerize. The GPC curves showed an increase of MW which is a good indication for the formation of a copolymer. The MWD broadens but not excessively (1.45 after 91% of conversion in TMC).

Figure 3 : Conversion versus time curves during copolymerization of L-LA and TMC mixtures initiated by $[Y(OCH_2CH_2OMe)_3]_{10}$ in dichloromethane solution at room temperature.



$[M_{LA}+M_{TMC}]_0/[Y]_0 = 140,\ [M_{LA}+M_{TMC}]_0 = 1\ mol/L$

Once more the completion of reaction takes much more time as compared to homopolymerization (91% conversion of TMC in 4 hours versus 100% in less than 1 min in homopolymerization). A comparable behaviour was observed by Schmidt et al. [61)] in bulk copolymerization of L-LA with 2,2-dimethyltrimethylene carbonate (DMTC) using zinc and tin initiators. PL-LA active centers are much more stable than those of polyDMTC, which can be due to the formation of a five-membered cycle by intramolecular complexation of the carbonyl group of lactide. After formation of PL-LA, DMTC is progressively incorporated. However DMTC species attack PL-LA chains and as result, according to ^{13}C NMR spectra, almost random copolymers are obtained at the end of the copolymerization. Our results are quite different, since the ^{13}C NMR spectrum of final copolymer is again a superimposition of PL-LA and PTMC signals, i.e., a block LA-b-TMC structure can be assumed with absence of signals due to random distribution and transesterification reactions. The differences between the results may be due to the difference in experimental conditions since the polymerizations were performed at elevated temperatures (100-130°C) in the work by Schmidt et al.

Conclusions

Block copolymers between LA and CL or TMC were prepared by sequential polymerization using $Y(OC_2H_4OR)_3$ type initiators at room temperature in DCM solution. For P(CL-b-LA) diblock copolymer, PCL sequence must be prepared first. Otherwise PL-LA active chains are not initiating the CL polymerization.

For P(LA-b-TMC) it is preferable to start from LA sequence in order obtain clean diblock copolymers. The opposite operation produces not yet well identified products which can be mixtures of block copolymers and homopolymers.

In the polymerization of LA/CL equimolar mixture only PL-LA homopolymer is obtained, CL being not polymerized. On the other hand, the polymerization of LA/TMC equimolar mixture produces a diblock P(LA-b-TMC) copolymer.

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