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ALUMINIUM ALKOXIDES: A FAMILY OF VERSATILE INITIATORS FOR THE RING-OPENING POLYMERIZATION OF LACTONES AND LACTIDES

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Abstract : Aluminium alkoxides, such as $Al(O^iPr)_3$ or $Et_{3-p}Al(O(CH_2)_2X)_p$ with $1 \leq p \leq 3$, are very effective in initiating the polymerization of lactones, e.g. ε -caprolactone and δ -valerolactone, and lactides (D,L- or L,L- isomers). The ring-opening polymerization proceeds through a "coordination-insertion" mechanism that involves the selective rupture of the acyl-oxygen bond of the monomer and its insertion into an Al-O bond of the initiator. Polymerization is typically "living" and allows block copolyesters with perfectly controlled molecular weight and composition to be prepared. Aluminium alkoxides carrying functional alkoxy groups (X = -Br, $-CH_2-NEt_2$, $-CH_2-CH=CH_2$, $-CH_2-OC(O)-C(Me)=CH_2$...) provide asymmetric telechelic polyesters (end-groups being -X and -OH, respectively) and very interesting polyester macromonomers. Coupling the asymmetric telechelic chains via the hydroxyl end-group - or better its Al alkoxide precursor - is a straightforward way to the symmetric telechelic polymer bearing the X functional group.

INTRODUCTION

Over the past 20 years, increasing attention has been paid to some synthetic aliphatic polyesters for applications in medicine and surgery. This interest is due to a valuable set of properties, i.e. non toxicity for living organisms, resorption after an appropriate period of implantation time and good ultimate mechanical properties (Ref. 1). Poly-ε-caprolactone (PCL), polylactides (PLA) and polyglycolide (PGA) are well-known for their hydrolytic degradation in vitro as well as in vivo with release of non-toxic by-products (Ref. 2). These aliphatic polyesters display a large range of biodegradability : their half-life time can vary from several days to several years and the copolymerization of the related monomers is an easy way to adjust more precisely the rate of biodegradation (Ref. 1). Because of a unique combination of biocompatibility, permeability and biodegradability, polymers and copolymers of ε-caprolactone, lactides and glycolide now have widespread applications in medicine, as biodegradable sutures, artificial skin, resorbable protheses, container for sustained drug release, and have potential applications in chemotherapy (Refs 1-5). Let us also recall the unique ability of PCL to be blended with a variety of other polymers and to improve some of their deficient properties, e.g. poor stress-crack resistance and lack of dyeability, gloss and adhesion (Ref. 6).

The ring-opening polymerization of lactones, lactides and glycolide provides a direct access to the related polyesters, in contrast to the traditional polycondensation method. Indeed, polycondensation of ω-hydroxy acids is characterized by the formation of side

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reaction products, long reaction times and high temperature, and it requires the addition of terminating (monofunctional) agents under a strict stoichiometry in order to control the molecular weight (particularly below 10 000) (Ref. 7).

The discovery that some organometallic compounds are very effective in the synthesis of high molecular weight PCL (Ref. 8) has promoted an extensive investigation of the ring-opening polymerization of ϵ-CL using alkylmetals and alkoxides as initiators (Refs 9,10). Living polymerization is rather an exception than a general rule. Most often, the anionic polymerization is perturbed by side intra- and intermolecular transesterification reactions leading to a mixture of linear and cyclic molecules (Ref. 11). As a rule, a decrease in the reactivity of the initiator, e.g. by an appropriate modification of the counterion, is favorable for the propagation of linear chains as compared to the macrocyclization process (Refs 12, 13).

Several years ago, some of us reported that the living polymerization of ϵ-CL could be promoted by aluminium alkoxide functions such as bimetallic (Zn, Al) μ-oxo alkoxides (Refs 14, 15) and trialkoxy-aluminium(Ref. 16). The living polymerization of ϵ-CL has also been reported by Inoue (Ref. 17) and Penczek (Ref. 18) using α, β, γ, δ-tetraphenylporphinato aluminium ([TPP]AlX) derivatives and diethylaluminium methoxide, respectively, as initiators. Furthermore, Hamitou et al took advantage of the bimetallic μ-oxo alkoxides in order to synthesize block copolymers of ϵ-CL and β-propiolactone (β-PL) (Ref. 19). It is worth noting that judicious modification of these initiators by exchanging alkoxide functions by a hydroxylated prepolymer, such as ω-hydroxyl polystyrene or polybutadiene, provides a direct access to the related PS (or PBD)-b-PCL diblock copolymers (Ref. 20).

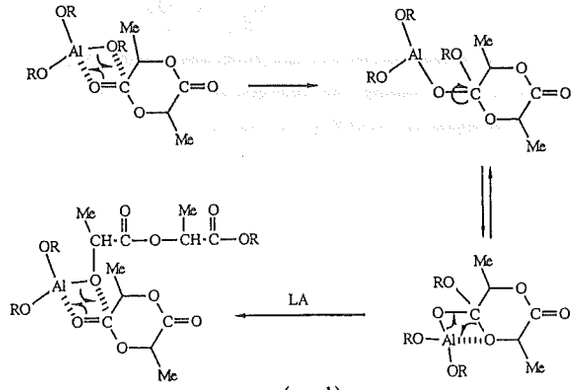
This paper aims at reporting additional potential uses afforded by the extension of the living polymerization of ϵ-CL, first to other monomers and secondly to aluminium alkoxides bearing functional groups. The controlled synthesis of high-molecular-weight polylactides (PLA) initiated by the commercially available aluminium isopropoxide $Al(O^iPr_3)$ will be first discussed. On the basis of this data, conditions will be defined for the tailoring of PCL-b-P(L,L or D,L)LA copolyesters. Finally, the discussion will focus on the synthesis of telechelic poly-ϵ-caprolactone with predictable molecular weight, rather narrow polydispersity and quantitative control of the end-groups, including the controlled synthesis of macromonomers.

HOMOPOLYMERIZATION OF LACTIDES INITIATED BY $Al(O^iPr)_3$

The best method for the synthesis of high molecular weight PLA is the ring-opening polymerization of a cyclic diester (or lactide) using tin catalysts, e.g. tin octoate and tetraphenyl tin (Refs 2, 5, 21) or various metal alkoxides (Ref. 10). Polymerization is generally carried out in bulk at a high temperature (more than 130°C). The molecular weight

distribution is broad ($\bar{M}_w/\bar{M}_n \geq 2$) and the number-average molecular weight does not match the theoretical value predicted by the monomer/initiator mole ratio. More recently, Inoue et al. (Ref. 22) reported the living polymerization of lactide using [TPP]AlOMe as an initiator. Feng and Song (Ref. 23) also exploited the living polymerization of (D,L)LA as promoted by a bimetallic (Zn, Al) μ-oxo alkoxide the block polymerization with ϵ-CL. In each case, the reported number-average molecular weight never exceeded 30,000.

It has been previously reported from our laboratory that aluminium isopropoxide is very effective in promoting the living polymerization of ϵ-CL in toluene at 0°C (Ref. 16). These polymerization conditions have been extended successfully to lactide polymerization. Indeed, (D,L or L,L) lactides can be polymerized by $Al(O^iPr_3)$ in toluene at 70°C according to a "coordination-insertion" mechanism which involves the insertion of the lactide into the "Al-O" bond of the initiator and the selective acyl-oxygen cleavage of the monomer (eq. 1) (Ref. 24).



(eq. 1)

A kinetic study has shown that the polymerization starts after an induction period and is first order in both monomer and initiator. This lactide polymerization is a perfectly "living" process as supported by a linear dependence of the experimental number-average molecular weight ($\bar{M}_n$ exp.) and the monomer/initiator mole ratio calculated for the actual monomer conversion ($[LA]_0/[Al].x/100$, where x is the monomer conversion) (Fig. 1). In toluene at 70°C, each alkoxide group of the initiator (aluminium isopropoxide) participates to the polymerization; there are thus three active polymerization sites per aluminium molecule (n = 3). This is in sharp contrast to the polymerization of ϵ-CL in toluene at 0°C when n = 0.9. The most important conclusion is that molecular weight is predictable on the basis of the monomer/initiator ratio (at least up to ca. 1800), the monomer conversion and the average number of active sites per aluminium molecule. The polydispersity is rather narrow (1.1 - 1.4).

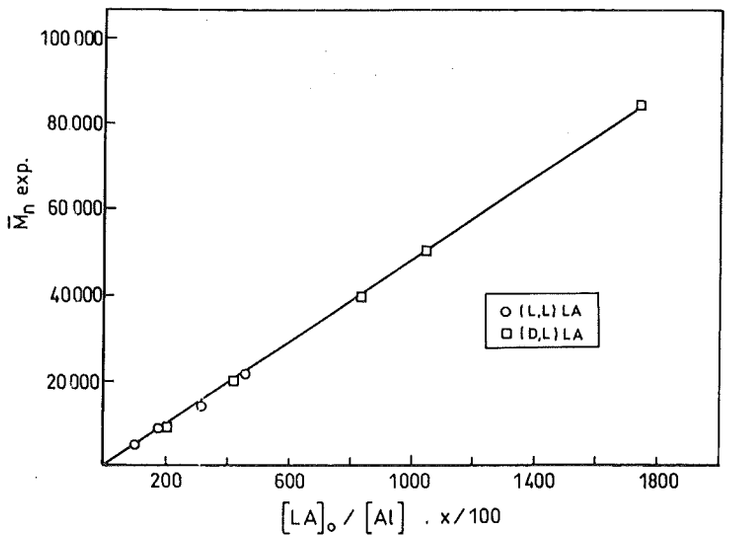


Fig. 1 . Dependence of the number-average molecular weight ($\bar{M}_n$ exp.) on the monomer/initiator mole ratio taking the conversion of (L,L or D,L)LA into account. Polymerization is initiated by $Al(O^iPr_3)$ in toluene ($[LA]_o = 6.0\ 10^{-1}$ mol·l^{-1}), at 70°C

The analysis of the first polyaddition products has shown that the polymerization mechanism of lactides is identical to that reported for ϵ-CL in the presence of $Al(O^iPr_3)$; it is thus attractive to investigate the copolymerization of ϵ-CL and lactides using that initiator. Random copolyesters P(ϵ-CL-co-(L,L)LA) have been prepared, the reactivity ratios determined (Table I) and the main physical properties characterized (Ref. 25). Compared to random copolymers, block copolymers P(ϵ-CL-b-LA) are of great interest since they can combine interestingly the excellent permeability of PCL and the remarkable biodegradability of PLA segments (Ref. 26).

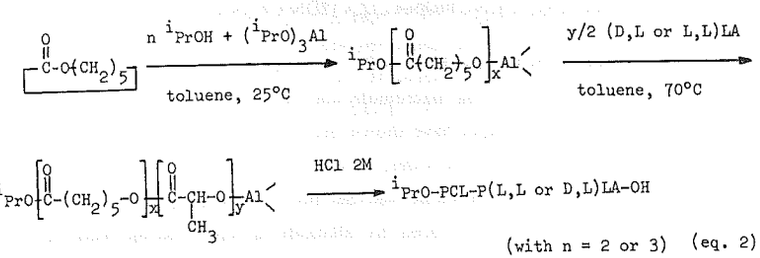
Table I . Kinetic constants characteristic of the polymerization of ϵ-CL (i) and (L,L)LA (j) in toluene at 70°C. The reactivity ratios of ϵ-CL and (L,L)LA are 0.58 and 17.9, respectively ($[\epsilon\text{-CL}]_o = [(L,L)LA] = 1$ mol·l^{-1})

Type of polymerization	k(l·mol^{-1}·min^{-1})
PCL-O-Al≺ + ϵ-CL	$k_{ii} = 3600$
PCL-O-Al≺ + (L,L)LA	$k_{ij} = 6300$
P(L,L)LA-O-Al≺ + ϵ-CL	kji = 0,03
P(L,L)LA-O-Al≺ + (L,L)LA	$k_{jj} = 0,60$

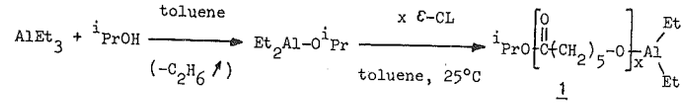
BLOCK COPOLYMERIZATION OF ϵ-CL AND (L,L OR D,L)LA

Aluminium isopropoxide has been tested as a possible initiator for the sequential polymerization of lactides (D,L or L,L)LA and ϵ-CL. According to the cross-propagation rates reported in Table I, ϵ-CL must be first polymerized in toluene at 0°C followed by LA at 70°C (Ref. 26). As expected, the mean number of active sites per aluminium which is 0,9 in the presence of ϵ-CL increases up to 3 when LA is added to the living PCL chains. The extra polymerization sites made available are responsible for the homopolymerization of LA that competes with the block copolymerization. There are two possible ways to avoid that drawback. Either the initiator should be unassociated ($n \geq 3$) during the whole block copolymerization process, or the initiator should be modified so that there exists only one active sites per Al molecule (n = 1).

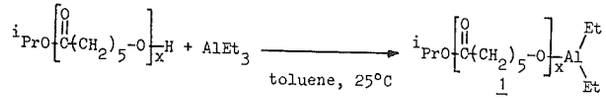
The first approach has been investigated by adding 2 or 3 equivalents of 2-propanol to aluminium isopropoxide. Under such conditions, $Al(O^iPr_3)$ is prevented from any coordinative associations. However, the mean number of active sites per Al is not 3, as expected, but larger. Its value has a strong dependence on the relative molar amount of 2-propanol compared to $Al(O^iPr_3)$ (eq. 2). Quite clearly, the experimental molecular weight values show that each 2-propanol molecule contributes to the ring-opening polymerization. This can be explained by an alkoxide-alcohol exchange that is much faster than the propagation event.



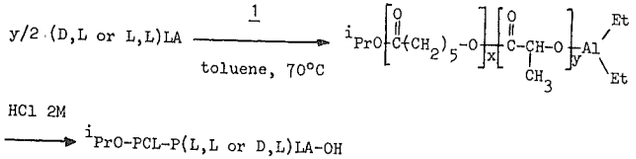
In the second approach, the mean number of growing chains per Al has been limited to one (n = 1) by substituing two of the three isopropoxide functions by an alkyl group which is totally inactive in the lactone and lactide polymerization (eq. 3). This type of initiator is easily prepared from triethylaluminium and an equimolar amount of 2-propanol, the formation of ethane as a volatile byproduct completely displacing the reaction equilibrium towards the expected diethylaluminium isopropoxide (eq. 3). Although indirect, a third strategy should be mentioned for the synthesis of the P(ϵ-CL-b-LA) copolymers. It consists of the equimolar reaction of $AlEt_3$ and a preformed hydroxy terminated PCL. The polymeric alkoxide is then used as an initiator for LA polymerization (eqs 4 and 5).



(eq. 3)



(eq. 4)



(eq. 5)

In all cases, the molecular weight of each block is in good agreement with the value expected from the monomer/initiator mole ratio and the number of active sites per Al. Furthermore, no detectable transesterification reactions occur under the experimental conditions used for the polymerization of each comonomer (25°C for ϵ-CL and 70°C for lactide).

SELECTIVE END-FUNCTIONALIZATION OF PCL

Synthesis of end-reactive PCL (telechelic PCL) with precisely controlled molecular weights is of particular interest in the macromolecular engineering of polyesters. Some of the results discussed in this paper have shown that isopropoxide groups of $Al(O^iPr_3)$ can be subsituted by polymeric alkoxides, which are active in the ring-opening polymerization and lead to the formation of well-defined block copolymers. In the same way, isopropoxide groups can be replaced by alkoxide groups bearing well-defined functional groups. As schematized below, potential initiators can be comprised of one to three functional alkoxide groups, associated with 2 to 0 alkyl groups, respectively :

$$(C_2H_5)_{3-p}\ Al(O\text{-}CH_2\text{-}X)_p$$

1 : p = 1

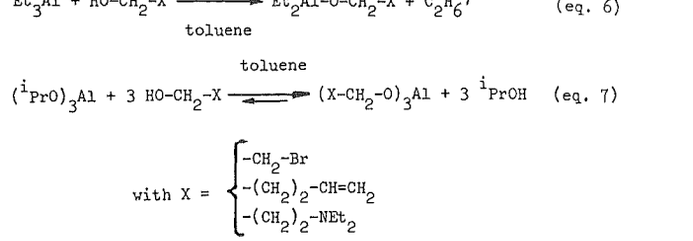
2 : p = 3 with

a : $-CH_2-Br$

b : $-(CH_2)_2-CH=CH_2$

c : $-(CH_2)_2-NEt_2$

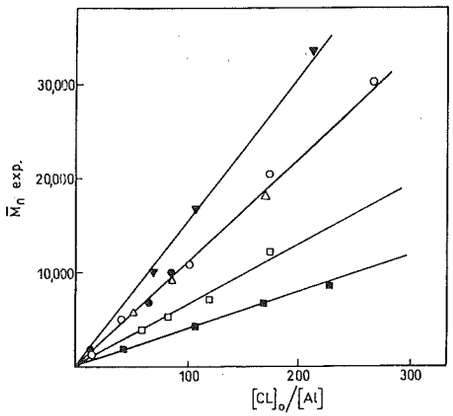
Diethylaluminium alkoxides 1 have been prepared by reaction of $AlEt_3$ with an equimolar amount of the corresponding alcohol; the reaction equilibrium is favorably displaced by the formation and elimination of ethane (eq. 6). Aluminium trialkoxides 2 have been synthesized by displacing the three alkoxy groups of aluminium isopropoxide by the equimolar amount of the appropriate alcohol. The toluene/ 2-propanol azeotrope has been distilled off continuously allowing the substitution reaction to be complete (eq. 7) (Ref. 27).



A perfectly "living" mechanism is observed when the polymerization of ϵ-CL is initiated by any of the functional aluminium alkoxides of the 1 a,b,c, and 2 a,b,c series, in toluene at 25°C. This is supported by the close agreement between the number–average molecular weight ($\overline{M}_n$ exp.) at total conversion and the monomer/initiator mole ratio (Fig. 2). These relationships hold even for the preparation of molecular weights as high as 100 000. From the slope of the $\overline{M}_{n\ exp.}$ vs. $[\epsilon\text{-CL}]_o/[Al]$ (Fig. 2), it appears that the mean number of active alkoxide groups per aluminium molecule (n) is equal to 1 at 25°C when the initiator is a diethylaluminium alkoxide of the 1 a,b,c series. In constrast, the value of n depends on the functional radical ($-O-CH_2-X$) of the aluminium trialkoxides of the 2 a,b,c, series.

Kinetic studies have shown that the polymerization of ϵ-CL initiated by the previously discussed functional aluminium alkoxides, in toluene at 25°C, is again first order in both monomer and initiator. Kinetic results will be discussed extensively in a forthcoming paper, particularly in relation to the nature of the functional groups.

When the previously mentioned functional alkoxides are used to initiate the ϵ-CL polymerization in toluene, samples of rather narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n$ = 1,05 to 1,30) are obtained. Quite clearly, that distribution is substantially broadened when the living polymer is left in the reactor beyond the reaction time required for complete monomer conversion. This is likely due to the occurrence of intra- and intermolecular transesterification reactions.



-X	$Al(O-CH_2-X)_3$	$([CL]_o/[Al])$	$Et_2-Al-O-CH_2-X$	$([CL]_o/[Al])$
$-CH_2-Br$	■	(167)	○	(88)
$(CH_2)_2-CH=CH_2$	▼	(200) 1)	△	(44)
$(CH_2)_2-NEt_2$	□	(174)	●	(87) 2)

1) Polymerization at 0°C.
2) Polymerization at 35°C.

Fig. 2 . Dependence of number average molecular weight ($\bar{M}_{n\ exp.}$) on the ϵ-CL/initiator mole ratio. The ϵ-CL polymerization has been initiated by each of the 1 a,b,c ($[\epsilon\text{-CL}]_o = 10{,}6\cdot10^{-1}$ mol·l^{-1}) and 3 a,b,c ($[\epsilon\text{-CL}]_o = 8{,}6\cdot10^{-1}$ mol·l^{-1}) alkoxides in toluene at 25°C

More interestingly, GPC, IR and ^1H NMR studies unambiguously show that the function X associated with the alkoxy groups of the initiator is selectively and quantitatively attached to one chain-end, and that the second end-group is systematically a hydroxyl function resulting from the hydrolysis of the living growing site. As an example, the polyester prepared using $Br-(CH_2)_2-O-AlEt_2$ 1a as an initiator has been characterized by ^1H NMR spectroscopy (Fig. 3). The signals observed at δ = 3,52 ppm and 4,39 ppm are quite consistent with the quantitative presence of the bromoalkyl group of the initiator.

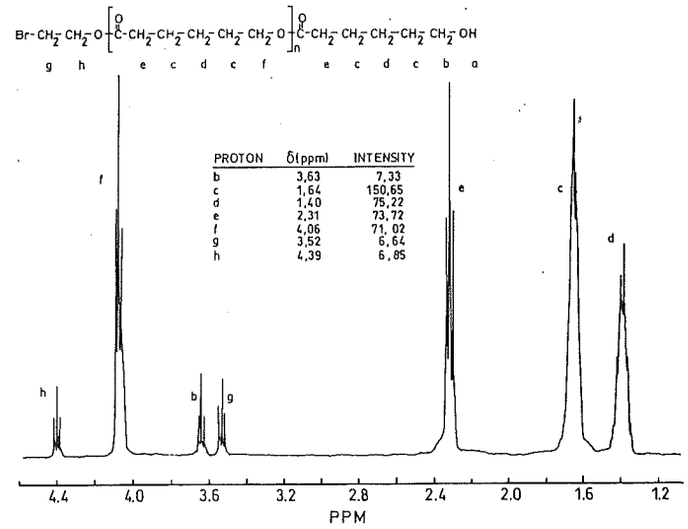
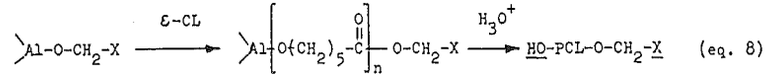


Fig. 3 . ^1H NMR spectrum of PCL as recovered after hydrolysis of the living polymer initiated by $Br-(CH_2)_2-O-AlEt_2$ 1 a

Kinetic and structural data support a typical coordination-insertion type of mechanism that proceeds through the insertion of the lactone in the metal-alkoxide bond (eq. 8). The presence of a halide, tertiary amine or unsaturated group attached to the alkoxide moieties has no disturbing effect on the general course of the ϵ-CL polymerization.



(eq. 8)

This new pathway to end-functional PCL has been extended first to other functional alkoxides mainly prepared from the appropriate functional alcohol and trialkylaluminium (Table II)

It is worth noting that the use of 2-hydroxyethyl methacrylate (HEMA) (Code 6) is a straightforward route to PCL macromonomers and, in a further step, to graft copolymers containing well-defined PCL branches (Ref. 28). One mole of a diol can also be reacted with 2 mole of $AlEt_3$ and an initiator is made available [$Et_2Al-O-CH_2-X-CH_2-O-AlEt_2$] for the controlled synthesis of α,ω-hydroxy-PCL. Similarly, 2,2'-methyliminodiethanol (Code 5) is another particular diol that offers the opportunity to insert a tertiary amine in a central position of hydroxy-telechelic PCL. This "living" polymerization and

Table II . Polymerization of ε-caprolactone (ε-CL), δ-valerolactone (δ-VL) and lactide [(D,L)LA] initiated by the reaction product of $AlEt_3$ and a functional alcohol ([Al]/[OH] = 1) in toluene

Code	Monomer	Functional alcohol	T° (C)	Time (h)	$[CL]_o/[Al]$	Conversion (%)	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$
1	ε-CL	$HO\{CH_2\}_2Br$	25	3	26	100	1.2	3,100
2	ε-CL	$HO\{CH_2\}_3CH=CH_2$	25	2	13	100	1.1	1,500
3	ε-CL	$HO\{CH_2\}_3NEt_2$	35	8	88	90	1.2	9,000
4	ε-CL	$HO\{CH_2\}_4OH$ 1,2)	25	19	66	96	-	3,500
5	ε-CL	$HO\{CH_2\}_2N(Me)\{CH_2\}_2OH$ 2)	40	4	53	100	-	3,500
6	ε-CL	$HO\{CH_2\}_2O_2C-C(Me)=CH_2$	25	2	13	100	1.2	1,500
7	δ-VL	$HO\{CH_2\}_2O_2C-C(Me)=CH_2$	40	26	13	88	1.25	2,650
8	(D,L)LA	$HO\{CH_2\}_2Br$	70	72	35	81	1.2	4,200

1) Solvent = tetrahydrofuran (THF).

2) The initiator was prepared by reaction of 2 mole of $AlEt_3$ and 1 mole of the diol.

selective end-functionalization procedure can be safely extended to other lactones, e.g. δ-valerolactone (Code 7) and lactides (Code 8).

Furthermore, the asymmetric α-hydroxy-ω-X functional PCL can be coupled within very high yields (>95%) by a difunctional agent, such as an aromatic diisocyanate or an aromatic diacid chloride. Asymmetric α,ω-X functional PCL of a twofold increased molecular weight is accordingly obtained as described by eq. 9 for α-bromo-ω-hydroxy-PCL. The same coupling reactions can be carried out successfully using the precursor living polymer rather than the PCL recovered after hydrolysis of the living growing sites (eq. 10 where X = $Br-CH_2-$).

(eq. 9)

(eq. 10)

It is worth noting that the addition of methacryloyl chloride to α-X-ω-Al alkoxide PCL is a termination reaction that provides PCL macromonomers bearing the X function as the second end-group.

HOMOPOLYMERIZATION OF ε-CL BY $H_2N\{CH_2\}_3OAlEt_2$

According to Table II, the use of 3-dimethylamino-1-propanol allows attachment of a tertiary amine at one end of PCL. It was of interest to learn whether the same strategy could be applied to a primary amine. When $AlEt_3$ is reacted with an equimolar amount of 3-amino-1-propanol, the volume of ethane formed as a byproduct indicates that only one ethyl group per Al has reacted. That the hydroxyl group of the amine alcohol has reacted with $AlEt_3$ has been assessed by NMR analysis of the structure of the final product which is actually $Et_2Al-O-(CH_2)_3-NH_2$. This initiator has proven to be active in the ε-CL polymerization, but surprisingly, no amino group can be detected at the end of the polyester chains. Rather, ^1H NMR spectroscopy shows the presence of an α-hydroxymethylene end-group, $\delta(-CH_2-OH)$ = 3,64 ppm, and that of an N-methylene-amide group, $\delta(-CH_2-NH-C(O)-)$ = 3,25 ppm, in the polyester chain. IR spectroscopy

also shows an absorption band at $\lambda = 1530\ cm^{-1}$, which is characteristic of an amide function. As a whole, these data suggest that the amino group participates to the ϵ-CL polymerization in addition to the alkoxide function. This hypothesis is supported by the polymerization of ϵ-CL that occurs in toluene at 40°C when $AlEt_3$ - inactive in itself - is added with n-butylamine. The final product an α-butylamido-ω-hydroxy-PCL. The polymerization reaction initiated by $Et_2Al\text{-}O(CH_2)_3\text{-}NH_2$ is schematized below and its detailed mechanism is under current investigation.

$$Et_3Al + H_2N(CH_2)_3\text{-}OH \xrightarrow[\text{toluene, } 40°C]{(-\ 1\ mol\ C_2H_6\uparrow)} Et_2Al\text{-}O(CH_2)_3\text{-}NH_2$$

$$\xrightarrow[2)\ H_3O^+]{1)\ (n+m)\ \varepsilon\text{-CL, toluene, } 40°C} H\left[O(CH_2)_5\text{-}C(=O)\right]_n O(CH_2)_3\text{-}NH\left[C(=O)\text{-}(CH_2)_5\text{-}O\right]_m H \qquad \text{(eq. 11)}$$

CONCLUSIONS

Aluminium alkoxides are very powerful initiators for the ring-opening polymerization of lactones and lactides. The great versatility of their structure - polymeric or low molecular weight functional alkoxide groups - paves the way to the macromolecular engineering of these polyesters. Block copolymers, telechelic polymers, macromonomers and the related graft copolymers are now available in a very well-controlled manner.

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CATIONIC RING-OPENING POLYMERIZATION OF LACTONES IN THE PRESENCE OF ALCOHOL

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Abstract: Cationic ring-opening polymerization of ε-caprolactone using triethyloxonium hexafluorophosphate initiator in the presence of alcohol to produce low molecular weight polyester glycol was examined. The polymerization proceeded by an activated monomer mechanism; thus the polymer molecular weight increased directly with the monomer conversion. Polymerization of lactones other than ε-caprolactone were also examined, and the overall rate of polymerization was in the order δ-valerolactone> ε-caprolactone>> β-butyrolactone> diketene> γ-butyrolactone.

INTRODUCTION

Previously, cationic ring-opening polymerization of epichlorohydrin (ECH) in the presence of ethylene glycol (EG) to produce hydroxy-terminated low molecular weight poly(ECH) was studied, and a novel polymerization mechanism has been postulated [1]. According to this mechanism, the polymerization initiated at the hydroxy group in EG and the polymer chain propagates simultaneously at both ends through the addition of the monomer. An almost identical polymerization mechanism was also postulated for the cationic ring-opening polymerization of ethylene oxide, propylene oxide, and 1,3-dioxolane and a kinetic study of this novel mechanism has been conducted [2,3]. Applying this novel mechanism to prepare other polymers, several block copolymers and graft copolymers were also synthesized using the hydroxy-terminated prepolymers such as hydroxy-terminated poly(butadiene) and poly(tetramethylene oxide) [4-6].

Besides ECH, ethylene oxide, and 1,3-dioxolane monomers, the literature reveals that cationic ring-opening polymerization of ε-caprolactone (CL) in the presence of alcohols and poly(ethylene glycol) produces the corresponding hydroxy-terminated polyester and the polyether-polyester block

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