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ARTICLE

Living Ring-Opening Homo- and Copolymerization of ε-Caprolactone and L- and D,L-Lactides by Dimethyl(salicylaldiminato)aluminum Compounds

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ABSTRACT: The dimethylaluminum compounds {3-tBu-2-(O)C_6H_3CH=N−R}$AlMe_2$ [R = C_6H_5 (**1**); 2,6-$iPr_2C_6H_3$ (**2**); C_6F_5 (**3**)] were used as initiators in the ring-opening polymerization (ROP) of ε-caprolactone, L-lactide, and D,L-lactide. Compound **3**, in combination with 1 equiv of methanol, exhibited a *living* behavior in the ROP of the cyclic esters. Such a feature allowed the preparation of poly(D,L-lactide-*block*-ε-caprolactone) and poly(L-lactide-*block*-ε-caprolactone) copolymers. Random copolymers of ε-caprolactone and L-lactide and of ε-caprolactone and D,L-lactide were also synthesized by compound **3**. NMR and DSC characterization confirmed a highly random structure of these copolymers, even in the absence of transesterification reactions. All the materials, characterized by GPC, showed high molecular weight and narrow molecular weight distributions.

Introduction

Aliphatic polyesters are currently receiving a growing scientific interest as biodegradable and biocompatible materials.[1] Among them, polycaprolactone (PCL) is one of the most promising synthetic polymers prone to degradation in aqueous medium or by micro-organisms, having therefore large applications in various areas such as agriculture and medicine; polylactide (PLA) represents the potential candidate to replace traditional olefin-based polymers as ecological thermoplastic resin from renewable resources. PLA and PCL have attracted increasing attention in the pharmaceutical and medical fields such as sutures, artificial skins, bone fracture internal fixation devices, tissue engineering scaffolds, and drug delivery systems, since they are degradable in humid environments and the nontoxic products can be resorbed or excreted by the human body.[2]

Copolymerization or blending of PLA with PCL could allow the fabrication of a variety of biodegradable materials with improved properties in comparison to those of the parent homopolyesters. For example, PLA presents good mechanical properties but poor elasticity; PCL exhibits remarkable drug permeability, elasticity, and thermal properties but poor mechanical strength. Because the glass transition temperature of poly(D,L-lactide) and poly(L-lactide) is above body temperature, these materials are stiff with poor elasticity in the human body. On the contrary, PCL is in the rubbery state at room temperature, exhibiting a glass transition temperature of −60 °C. Moreover, PCL degrades much slower than PLA. The *in vitro* degradation of poly(L-lactide) is, in turn, much slower than that of poly(D,L-lactide).[3] Therefore, copolymers of poly(L-lactide) and PCL and/or poly(D,L-lactide) and PCL could be suitable for applications where elasticity and degradability are required in the same product.[4] Moreover, the PCL drug permeability and the rapid degradation rate of PLA may be combined in their copolymers, making drug delivery systems with adjustable properties depending on the composition.[3,5] By varying the copolymer composition, monomer sequencing, and molecular weight, the copolymer properties can be tailored to meet the requirements of various applications. Therefore, the synthesis of ε-CL/LA copolymers has been widely studied in recent years, focusing on either block[6] or random[7] copolymers.

As far as the synthesis of aliphatic polyesters is concerned, the ring-opening polymerization (ROP) of cyclic esters is the elected method. Various species, including alkoxy and alkyl complexes of aluminum, tin, lanthanides, and transition metals, have been used as initiators, some having the ability to initiate a *living* polymerization.[8] Since the discovery of the stereoselective polymerization of racemic lactides by chiral binaphthyl Schiff base aluminum complex,[9] both achiral and chiral five-coordinate salen aluminum complexes have been largely studied in order to elucidate the relationship between catalytic complexes and stereoselectivity of the polymerization.[8] On the contrary, just a few reports concerned the ROP of cyclic esters promoted by the closely related, lower coordinated (salicylaldiminato)aluminum compounds.[10] Recently, we reported the synthesis of dimethyl(salicylaldiminato)aluminum compounds and their reactivity toward ionizing agents and ethylene (Chart 1).[11] In the framework of our recent interest in the ROP of cyclic esters,[12] we tested these complexes as initiators for the ROP of ε-caprolactone (ε-CL), D,L-lactides (D,L-LA), and L-lactides (L-LA). The feasibility of the block and random copolymerization of LA and ε-CL has been explored. High molecular weight block and random copolymers in the absence of transesterification reactions have been obtained. Some of our results have been previously communicated.[13] During the course of our studies, Nomura et al. also reported the efficient ε-caprolactone ring-opening polymerization of analogous Al complexes containing phenoxyimine ligands.[14]

Results and Discussion

Polymerization of ε-Caprolactone. The reactivity of compounds **1**, **2**, and **3** in the ring-opening polymerization of

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ε-CL was studied. Polymerization screenings were performed under a nitrogen atmosphere by adding 1 equiv of MeOH in a toluene solution of ε-CL and of the proper aluminum compound. The polymers, precipitated from the reaction solution by addition of hexane, were analyzed by NMR and gel permeation chromatography (GPC). The main results of the polymerization studies are summarized in Table 1.

Compounds **1**, **2**, and **3** appeared poorly active at room temperature, but the activity increases upon temperature increase. The catalytic activity depends on the aryl group present on the imine nitrogen and follows the order: C_6F_5 > iPr$_2$C$_6$H$_3$ > C_6H_5. The same order of activity was observed by Nomura.[14] Compound **3**, bearing the perfluorinated *N*-aryl ring, afforded almost complete monomer conversion in about 2 h at 70 °C (Al:ε-CL molar ratio = 1:360). The obtained PCL showed monomodal GPC curves, with quite narrow molecular weight distribution.

Compound **3** behaves in a well-controlled manner in the presence of alcohol. Polymerization tests performed at 70 °C displayed a linear correlation between the polymer molecular weight and the conversion, evidencing the "*living*" character of the polymerization (Figure 1). In this case molecular weight distribution is kept narrow until nearly complete monomer conversion, and only broadens for longer reaction times, when transesterifications become significant. Such a behavior is compatible with the presence of a highly selective active species.

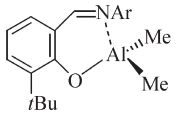
In the absence of MeOH, the ring-opening of ε-CL did not take place (Table 1, run 4). It is reasonable to assume that the dimethylaluminum compound reacts with the MeOH, giving rise to methane and an Al−OMe bond, on which the ring-opening polymerization should starts. As a matter of fact, ^{1}H NMR analysis of PCL sample (Figure 2) disclosed the presence of methyl ester end groups (−COOCH_3; 3.65 ppm), generated via insertion of the monomer unit into the Al−OCH$_3$ bond, with cleavage of the acyl−oxygen bond of the monomer and hydroxyl end groups (CH$_2$CH_2OH; 3.62 ppm), generated by hydrolysis of the growing chain. Therefore, a *coordination−insertion* mechanism proceeding through acyl−oxygen cleavage of the monomer should be operative in these systems.[15]

A polymerization run (Table 1, run 5) was performed without any alcohol but in the presence of the Lewis acid B(C$_6$F$_5$)$_3$, which, according to previous results, can abstract a methyl group from the neutral dimethyl(salicylaldiminato) aluminum compounds, generating a cationic aluminum species.[11] In this case a lower activity and a broader molecular weight distribution were observed: this feature is ostensibly due to ε-CL ROP through a cationic mechanism. The lower activity observed for the cationic species, which are expected to be highly electrophilic, and therefore more reactive toward electron donor monomers such as cyclic esters may be related to the strong Lewis acidity of such cations, which favors the stability of four-coordinate cationic species (i.e., by monomer coordination) and limits further reactivity.[16]

Polymerization of Lactides. Polymerizations of L- and D,L-lactide were performed in toluene solution at 70 °C, in the presence of 1 equiv of MeOH. Polymers were characterized by NMR and GPC. The main results of the polymerization studies are summarized in Tables 2 and 3. Compounds **1**, **2**, and **3** behave as single-site initiators, giving rise to controlled polymerization; GPC analysis disclosed monomodal curves and narrow molecular weight distributions. For compound **3** the *living* behavior in the polymerization of L-LA and D,L-LA was also assessed (Figure 3).

Figure 4 shows the homonuclear decoupled ^{1}H NMR spectrum in the methine range of poly(D,L-LA). The peaks were assigned to the appropriate tetrads in accordance with the shifts reported in the literature.[18] A small dependence of the microstructure on the structure of the salicylaldiminato ligand can be observed: slightly prevailingly isotactic polylactides were obtained with compounds **1** and **3**, while an atactic polymer was obtained with **2**. Epimerization of the chiral centers in poly(L-LA) does not occur.

Chart 1



1 Ar = C_6H_5
2 Ar = 2,6-iPr$_2$C$_6$H$_3$
3 Ar = C_6F_5

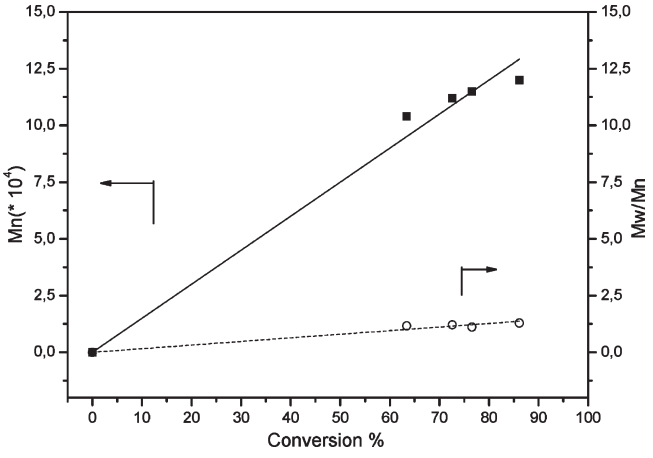


Figure 1. Polymerization of ε-CL initiated by **3** at 70 °C: relationship between molecular weight (■) and molecular weight distribution (○) and conversion.

Table 1. Polymerization of ε-Caprolactone[a]

run	catalyst	cocatalyst	temp (° C)	time (h)	conv (%)	$M_{n,GPC}$[d] (10^3)	M_n[e] (10^3)	M_w/M_n[d]
1[b]	**1**	MeOH	70	1.5	17	16.6	93.1	1.14
2[b]	**2**	MeOH	70	1.5	58	44.5	24.9	1.18
3[b]	**3**	MeOH	70	1.5	77	206.0	115.4	1.12
4	**3**	−	70	5				
5[c]	**3**	B(C$_6$F$_5$)$_3$	70	7	13	38.6	21.6	1.66
6[b]	**3**	MeOH	70	2	82	215.0	120.4	1.29
7[b]	**3**	MeOH	70	1	73	200.7	112.4	1.21
8[b]	**3**	MeOH	70	0.5	63	187.3	104.9	1.17
9[b]	**1**	MeOH	25	21	14	4.5	2.5	1.05
10[b]	**2**	MeOH	25	21	82	126.0	70.6	1.39
11[b]	**3**	MeOH	25	21	83	107.2	60.0	1.34

[a] Polymerization conditions: toluene = 4 mL; ε-caprolactone = 1 mL; catalyst = 25 μmol. [b] MeOH = 25 μmol. [c] B(C$_6$F$_5$)$_3$ = 25 μmol. [d] Determined by GPC in THF vs polystyrene standards. [e] M_n values corrected by the equation: $M_n = 0.56M_{n,GPC}$.[17]

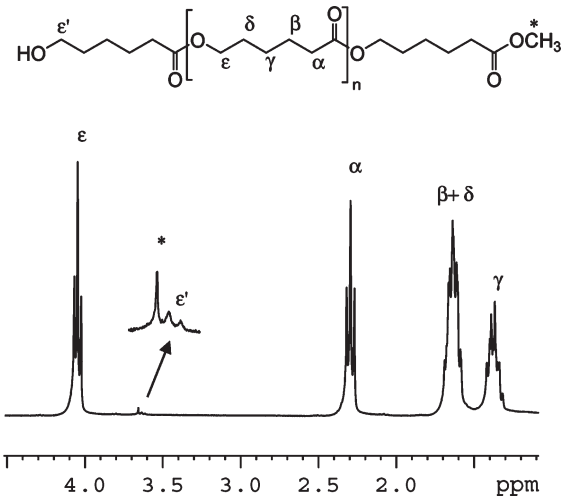


Figure 2. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of the polycaprolactone sample obtained using compound **1** (run 8, Table 1).

Table 2. Polymerization of L-Lactide[a]

run	catalyst	*t* (days)	conv (%)	$M_{n,GPC}$[b] (10^3)	M_n[c] (10^3)	M_w/M_n[b]
1	**1**	4	90.4	29.6	17.2	1.0
2	**2**	4	95.8	31.3	18.1	1.1
3	**3**	1	20.8	15.3	8.9	1.0
4	**3**	2	51.3	26.4	15.3	1.1
5	**3**	3	98.4	37.0	21.5	1.1
6	**3**	4	>99	41.8	24.2	1.2

[a] Polymerization conditions: toluene = 4 mL; L-lactide = 2.4 mmol; catalyst = 25 μmol; MeOH = 25 μmol; temperature = 70 °C. [b] Determined by GPC in THF vs polystyrene standards. [c] M_n values corrected by the equation: $M_n = 0.58M_{n,GPC}$.[19]

Table 3. Polymerization of D,L-Lactide[a]

run	catalyst	*t* (days)	conv (%)	$M_{n,GPC}$[b] (10^3)	M_n[c] (10^3)	M_w/M_n[b]
1	**1**	5	86.2	13.6	7.4	1.1
2	**2**	4	>99	20.7	12.0	1.3
3	**3**	1	36.9	15.5	8.9	1.1
4	**3**	2	68.5	22.8	13.2	1.1
5	**3**	3	97.4	26.2	15.2	1.1
6	**3**	4	>99	31.3	18.1	1.2

[a] Polymerization conditions: toluene = 4 mL; D,L-lactide = 2.4 mmol; catalyst = 25 μmol; MeOH = 25 μmol; temperature = 70 °C. [b] Determined by GPC in THF vs polystyrene standards. [c] M_n values corrected by the equation $M_n = 0.58M_{n,GPC}$.[19]

Block Copolymerization. The *living* character of both LA and ε-CL polymerizations initiated by **3**, allowed the preparation of poly(D,L-lactide-*block*-ε-caprolactone) and poly(L-lactide-*block*-ε-caprolactone). The block copolymers were prepared by polymerizing first the L-LA (or the D,L-LA), to almost complete conversion. In the ROP of L-LA, as well as in that of D,L-LA, the molar mass of the polymer increases with the conversion, while the molecular weight distribution remains narrow until almost complete conversion. A sample was analyzed by GPC, showing monomodal distribution. The addition of the ε-caprolactone monomer to the reaction mixture gave the block copolymer PLA−PCL. The formation of block copolymer was confirmed by the increased molecular weight and by the monomodal nature of the GPC curve (see Experimental Section). The carbonyl region of the ^{13}C NMR spectrum revealed the exclusive presence of carbonyl due to the homosequences CL−CL and LA−LA, while random heterosequences where not detected (*vide ultra*).[7a] This observation on one hand is a further support to the diblock structure and on the other hand demonstrated

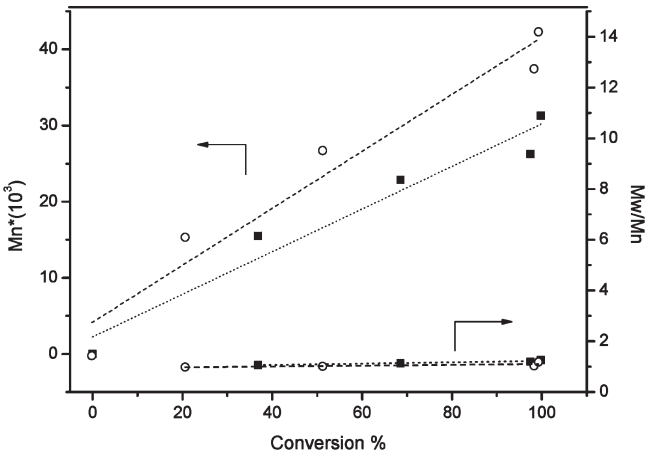


Figure 3. Polymerization of *rac*-lactide (■) and L-lactide (○) initiated by **3** at 70 °C: relationship between molecular weight (■) and molecular weight distribution (○) and conversion.

that the polymer chain remains attached to the metal center even at high conversion, while transesterification reactions do not occur.

Random Copolymerization. To gain further insight into the ROP of cyclic esters by the dimethyl(salicylaldiminato)-aluminum compounds, the behavior of complex **3** in the random ε-CL/L-LA and ε-CL/D,L-LA copolymerization was investigated. The copolymers were prepared by mixing in appropriate proportion the two monomers, in conditions analogous to those used for the preparation of the parent homopolymers (i.e., toluene solution, 70 °C, 1 equiv of MeOH). The products were characterized by ^{13}C and ^{1}H NMR, GPC, and DSC. The results of these copolymerizations are reported in Table 4.

The chemical compositions of the copolymers were determined by ^{1}H NMR spectroscopy, through the ratio of the integrated values of the methylene signal of the CL segment (−COO−CH_2−) around 4.00 ppm, and the methine signal of LA (−COO−C*H*CH_3−) around 5.20 ppm. The percentage of the opened CL in the copolymer was always reduced in comparison to the percentage in the feed. Apparently, this is in contrast to the results of the homopolymerization of CL and LA, in which the CL ROP is much faster than that of LA. Nevertheless, such a behavior seems to be a common feature for the random ε-CL/LA copolymerization.[7]

The percentage of CL−LA heterodiads were calculated by comparing, in the ^{1}H NMR spectrum, the intensity of the signals of the methylene protons close to the carbonyl (−CH_2−C═O and −COOCH_2−) of the CL−LA heterosequences with the same methylene protons for the CL−CL homosequences, which appear at higher field. As expected, the amount of CL−CL homosequences increases upon increasing the amount of ε-CL/LA molar ratio in the feed (Figure 5). Nevertheless, a high propensity to the random copolymerization behavior can be observed; all the obtained copolymers had random sequences, with percentage of heterodiads higher than 50%.

The chain microstructure of the copolymers was studied by analysis of the carbonyl region of the ^{13}C NMR spectra (between 165 and 175 ppm). Spectra of the carbonyl regions of the random ε-CL/D,L-LA copolymers are shown in Figure 6. According to the general case of a binary copolymerization, eight different triads are observed; the peaks were assigned according to the literature.[7a] The average length of the blocks (L_{CL} and L_{LA}) can been calculated from the integrals of the triads sequences signals, as previously

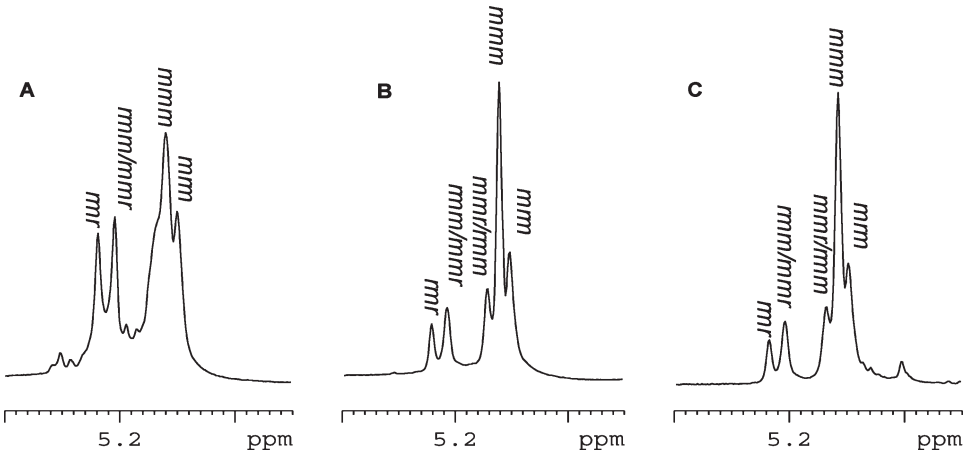


Figure 4. Homonuclear decoupled ^{1}H NMR spectra ($CDCl_3$, 25 °C) of the methine range of PLA obtained from D,L−LA using complex **2** (A), complex **1** (B), and complex **3** (C).

Table 4. Copolymerization of ε-Caprolactone and Lactide with Compound 3[a]

run	lactide in the feed (mmol)	ε-CL in the feed (mmol)	CL in the copolymer (mol %)	L_{CL}	$L_{lactide}$	T_g (°C)	T_g[c] (°C)	T_m (°C)	M_n[b] (10^3)	M_w/M_n[b]	yield (g)
1	D,L 4,8	1,2	7	1	15.9	11.0; 45.0	36.0		42.6	1.06	0.196
2	D,L 2,4	1,2	18	1	9	2.8	24.0		86.3	1.11	0.212
3	D,L 2,4	2,4	38	1.5	3.7	−18.0; 10.0	0.1		37.2	1.20	0.320
4	L 4,8	1,2	6	1	20	51.0	48.1	157.3	37.1	1.09	0.200
5	L 2,4	2,4	40	1.5	6.5	10.0	5.3		43.1	1.24	0.350

[a] Polymerization conditions: toluene = 5 mL; compound **3** = 25 μmol; MeOH = 25 μmol; temperature = 70 °C; time = 96 h. [b] Determined by GPC in THF vs polystyrene standards. [c] Theoretical values, as calculated by Fox equation, by using for the T_g of the homopolymers the following literature values: PCL = −60 °C; poly (D, L-LA) = 45 °C; poly (L-LA) = 57 °C.[7a]

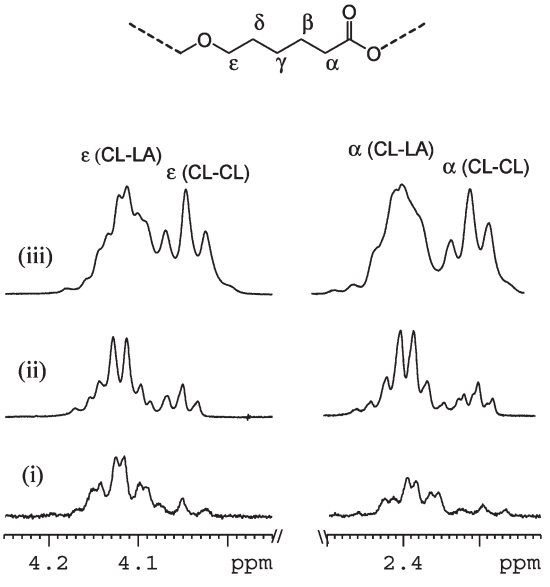


Figure 5. ^{1}H NMR spectra ($CDCl_3$, 25 °C) of the ε- and α-methylene ranges for copolymers of runs 1 (i), run 2 (ii), and run 3 (iii) in Table 4.

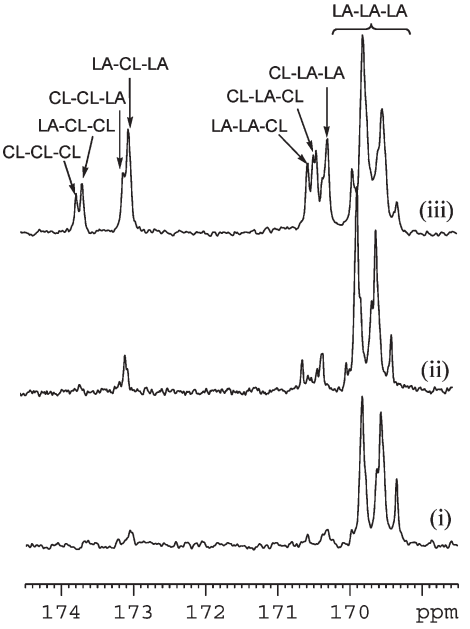


Figure 6. Carbonyl range of ^{13}C NMR spectra ($CDCl_3$, 25 °C) of copolymers of run 1 (i), run 2 (ii), and run 3 (iii) in Table 4.

reported in the literature. As expected, by increasing the CL/LA molar ratio in the feed, the amount of the homosequences CL−CL increases. A similar behavior was observed for the random ε-CL/L-LA copolymers.

It is worth noting that in the ^{13}C NMR spectra the carbonyl signal relative to the triad CL−CL−CL homosequence was detected only when the ε-CL/LA molar ratio in the feed was as high as 1:1 (see Table 4, runs 3 and 5). Below this value, instead, only isolated CL units were observed.

The controlled behavior of the ROP appears to be preserved also in the copolymerization. It is worth noting that in the carbonyl range of the ^{13}C NMR spectra the signal at 171 ppm, related to the triad having one single "lactic" ester unit between two CL units, was never detected. That triad is indicative of the occurrence of transesterification reactions because it cannot result from the insertion of the lactide monomer into the chain.[7a] The absence of transesterification reaction was further confirmed by the GPC analysis, disclosing in all cases narrow molecular weight distributions (M_w/M_n = 1.01−1.24). Transesterification reactions were

instead responsible of the randomized structure of copolymers prepared in the presence of Al(O*i*Pr)$_3$,[7a] rare earth catalysts,[7b] Al(acac)$_3$,[7c] and stannous octoate.[7f]

A rough estimate of the reactivity ratio r_1 (M_1 = LA) and r_2 (M_2 = CL) was achieved from the monomer composition in the feed and in the resulting copolymers.[20] Analogously to previous results for CL/LA copolymerizations initiated by Al(O*i*Pr)$_3$, r_1 is larger that r_2.[7a] The values for r_1 and r_2 are in the range of 5.7−9.8 and 0.96−1.6, respectively. The reactivity ratio products $r_1\ r_2 > 1$ indicated a nonideal, nonazeotropic copolymerization, also in agreement with the just above cited results.

Thermal analysis of the copolymers was carried out by means of differential scanning calorimetry (DSC), in the range −100 to 200 °C. The glass transition temperature, T_g, and the melting temperature, T_m, are given in Table 4. The copolymers were amorphous. The DSC thermograms recorded after the second scan for the samples of runs 4 and 5, prepared with L-lactide, displayed a unique glass transition temperature with value intermediate between those of the pure homopolymers and changing as a function of the compositions. That experimental T_g values are in good agreement with the theoretical one, calculated by the Fox equation, is a further support to the random structure. On the contrary, for the D,L-lactide-based samples (runs 1 and 3 of Table 4) two T_g were observed, having values intermediate between those of the pure homopolymers. An analogous behavior was previously observed for copolyesters of ε-CL and L- or D,L-lactide prepared in the presence of Al(O*i*Pr)$_3$.[7a] In this latter case, up to three T_g were observed for the D,L-lactide-based copolymers, while the L-lactide-based copolymers obeyed the Fox equation.

A melting peak (T_m = 157 °C) was observed only for the sample of run 4. This peak is clearly related to the presence of crystalline PLLA microdomains in this copolymer, for which the NMR analysis disclosed the longest average length ($L_{lactide}$ = 20) of the blocks of L-LA.

Conclusions

Compounds **1**, **2**, and **3** turned out to be very efficient initiators of the ε-caprolactone ROP in the presence of alcohol, giving rise to narrow molecular weight distributions. NMR analysis of a PCL sample suggested that the polymerization is achieved with a polyinsertion mechanism via acyl−oxygen bond cleavage of the monomer. By contrast, activation by the Lewis acid B(C$_6$F$_5$)$_3$ led to lower activity and broader molecular weight distribution, suggesting a cationic mechanism of polymerization.

In the case of compound **3**, bearing the perfluorinated *N*-aryl ring, a linear correlation between the polymer molecular weight and the conversion, evidenced the "*living*" character of the polymerization in the ε-CL, D,L-LA, and L-LA ring-opening polymerization. Such a feature allowed the preparation of high molecular weight diblock ε-CL/D,L-LA and diblock ε-CL/L-LA copolymers, without any transesterification reactions.

The random copolymers of L-LA (or D,L-LA) and ε-CL were easily prepared by mixing the two monomers in appropriate proportion. The amount of CL−CL homosequences in the copolymers increases by increasing the amount of ε-CL/LA molar ratio in the feed. A high trend to random copolymerization behavior was observed; all the obtained copolymers had percentage of heterodiads higher than 50%. The controlled behavior of the ROP seems to be preserved also in the copolymerization because transesterification reactions have never been observed.

In conclusion, (salicylaldiminato)aluminum compounds are well performing and very versatile initiators in the ROP of ε-CL and lactides, allowing a well-controlled chain growth, not only in the homopolymerization but also in the block and random copolymerizations. Moreover, the simple formulation, the straightforward synthesis, and the easy activation are advantageous features with respect to most ROP aluminum catalysts based on more complex polydentate ligand systems.

Experimental Section

General Procedure. Moisture and air-sensitive materials were manipulated under nitrogen using Schlenk or glovebox techniques. Toluene was refluxed over sodium/benzophenone and distilled under nitrogen prior to use. Anhydrous methanol was purchased from Aldrich and used as received. ε-Caprolactone was distilled in vacuum from CaH_2 and stored on 4 Å molecular sievies, *rac*-lactide was recrystallized twice from dry toluene, and L-lactide was dried *in vacuo* with phosphorus pentoxide for 72 h. The aluminum compounds **1**, **2**, and **3** were synthesized according to a previously reported procedure.[11] NMR spectra of the polymers were performed in $CDCl_3$ and recorded on Bruker Avance 400 MHz spectrometer. Molecular weight and molar mass distribution of polymers were measured by gel permeation chromatography (GPC) at 30 °C, using THF as solvent, a flow rate of eluant of 1 mL/min and narrow polystyrene standards as references. The measurements were performed on a water 1525 binary system equipped with a water 2414 RI detector using four styragel columns (range 1000−1 000 000 Å).

Glass transition temperatures (T_g) and melting points (T_m) of the copolymers were measured by differential scanning calorimetry (DSC) using a DSC 2920 TA Instruments in nitrogen flow with a heating and cooling rate of 10 °C min^{-1} in the range −100 to + 200 °C. Glass transition temperatures and melting temperatures were reported for the second heating cycle.

ε-Caprolactone Polymerizations. In a typical polymerization, a magnetically stirred reactor vessel (50 cm^3) was charged sequentially with a solution of precatalyst (25 μmol in 4 mL of dry toluene) and monomer (1 mL, 9.0 mmol). Subsequently, 0.25 mL of a solution 0.1 M of methanol in toluene (25 μmol) was added. The mixture was thermostatized at the required temperature and, after the required polymerization time, poured into hexane. The precipitated polymer was recovered by filtration and dried at 40 °C in a vacuum oven. The polymer was characterized by NMR spectroscopy and GPC analysis. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.34 (m, 2H, $-CH_2-$), 1.62 (m, 4H, $-CH_2-$), 2.29 (t, 2H, $-CH_2C(O)O-$), 4.04 (t, 2H, $-CH_2OC(O)-$), 3.62 (t, 2H, $-CH_2OH$), 3.65 (s, 3H, $-C(O)OCH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 24.7, 25.7, 28.5, 34.3, 64.3 ($-OCO(CH_2)_5-$), 51.7 ($-C(O)OCH_3$), 62.7 ($-CH_2OH$), 173.7 ($-COO-$).

Lactide Polymerizations. In a typical polymerization, a magnetically stirred reactor vessel (50 cm^3) was charged sequentially with the monomer (*rac*- or L-lactide, 350 mg, 2.4 mmol), the precatalyst (25 μmol), and 4 mL of dry toluene. Subsequently, 0.25 mL of a solution 0.1 M of methanol in toluene (25 μmol) was added. The mixture was thermostatized at the required temperature and, after the required polymerization time, poured into hexane. The precipitated polymer was recovered by filtration and dried at 40 °C in a vacuum oven. Conversions were determinated by integration of the monomer vs polymer methine resonances in the ^{1}H NMR spectrum of crude product (in $CDCl_3$). The polymer was purified by redissolving in CH_2Cl_2 and precipitating from rapidly stirring methanol. The polymer was characterized by NMR spectroscopy and GPC analysis. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.56 (m, 6H, $-CHCH_3-$), 3.79 (s, 3H, $-C(O)OCH_3$), 5.18 (m, 2H, $-CHCH_3-$). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 16.8 ($-C(O)OCHCH_3-$), 69.2 ($-C(O)OCHCH_3-$), 169.5, 169.8 ($-COO-$).

Synthesis of Poly(D,L-lactide-*block*-ε-caprolactone). The reactor vessel (50 cm^3) was charged sequentially with the monomer (*rac*-lactide, 350 mg, 2.4 mmol), compound **3** (25 μmol), and 4 mL of toluene. Subsequently, 0.25 mL of a solution 0.1 M of

methanol in toluene (25 μmol) was added. The mixture was thermostatized at 70 °C. After 4 days, an aliquot (0.5 mL) of the polymerization mixture was quenched in hexane, and the polymer was recovered by filtration, dried *in vacuo*, and analyzed by GPC (M_n = 31 292; M_w/M_n = 1.25). 1 mL of ε-caprolactone was added to the residual mixture. After 5 h the mixture was poured into hexane. The precipitated polymer was recovered by filtration and dried at 40 °C in a vacuum oven. The copolymer was purified by redissolving in CH_2Cl_2 and precipitating from rapidly stirring methanol. The copolymer was characterized by NMR spectroscopy and by GPC analysis. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.34 (m, 2H, $-CH_2-$), 1.56 (m, 6H, $-CHCH_3-$), 1.62 (m, 4H, $-CH_2-$), 2.29 (t, 2H, $-CH_2C(O)O-$), 4.04 (t, 2H, $-CH_2OC(O)-$), 3.73 (s, 3H, $-C(O)OCH_3$), 5.18 (m, 2H, $-CHCH_3-$). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 16.8 ($-C(O)OCHCH_3-$), 24.7, 25.7, 28.5, 34.3, 64.3 ($-OCO(CH_2)_5-$), 69.2 ($-C(O)OCHCH_3-$), 169.3−169.8 ($-COOCHCH_3-$), 173.7 ($-COO(CH_2)_5-$). GPC: M_n = 55 522; M_w/M_n = 1.58.

Synthesis of Poly(L-lactide-*block*-ε-caprolactone). The copolymer was prepared as above, but L-lactide was used instead of *rac*-D,L-lactide. After 4 days, an aliquot (0.5 mL) of the polymerization mixture was quenched in hexane, and the polymer was recovered by filtration, dried *in vacuo*, and analyzed by GPC (M_n = 25 961; M_w/M_n = 1.22). 1 mL of ε-caprolactone was added to the residual mixture, and the above procedure was followed. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.34 (m, 2H, $-CH_2-$), 1.56 (d, 6H, $-CHCH_3-$), 1.62 (m, 4H, $-CH_2-$), 2.29 (t, 2H, $-CH_2C(O)O-$), 4.04 (t, 2H, $-CH_2OC(O)-$), 3.73 (s, 3H, $-C(O)OCH_3$), 5.18 (q, 2H, $-CHCH_3-$). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 16.8 ($-C(O)OCHCH_3-$), 24.7, 25.7, 28.5, 34.3, 64.3 ($-OCO(CH_2)_5-$), 69.2 ($-C(O)OCHCH_3-$),169.8 ($-COOCHCH_3-$), 173.7 ($-COO(CH_2)_5-$). GPC: M_n = 27 209; M_w/M_n = 1.39.

Synthesis of Poly(D,L-lactide-*co*-ε-caprolactone). In a typical preparation, the reactor vessel was charged sequentially with *rac*-D,L-lactide, compound **3** (25 μmol), 4 mL of toluene, and ε-caprolactone. The mixture was thermostatized at 70 °C, and 0.25 mL of a solution 0.1 M of methanol in toluene (25 μmol) was added. After 4 days, the polymerization solution was quenched in hexane.

The copolymer was purified by redissolving in CH_2Cl_2 and precipitating from rapidly stirring methanol. The polymer was recovered by filtration, dried at 40 °C in a vacuum oven, and characterized by NMR spectroscopy and by GPC analysis. ^{1}H NMR ($CDCl_3$, 25 °C) (copolymer run 1, Table 4): δ = 1.36 (m, 2H, $-CH_2-$), 1.53 (m, 6H, $-CHCH_3-$), 1.63 (m, 4H, $-CH_2-$), 2.38 (m, 2H, $-CH_2C(O)O-$), 4.12 (m, 2H, $-CH_2OC(O)-$), 3.73 (s, 3H, $-C(O)OCH_3$), 5.15 (m, 2H, $-CHCH_3-$). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 16.8−16.9 ($-C(O)OCHCH_3-$), 24.4−24.7, 25.3−25.7, 28.3, 28.5, 33.8−34.3, 64.3, 65.5, 68.4 ($-OCO(CH_2)_5-$), 69.0−69.2 ($-C(O)OCHCH_3-$),169.3−169.8 ($-COOCHCH_3-$), 170.3 (*C*(O)O, CL−LA−LA), 170.5 (*C*(O)O, LA−LA−CL), 173.0 (*C*(O)O, LA−CL−LA).

Synthesis of Poly(L-lactide-*co*-ε-caprolactone). The copolymer was prepared as above, but L-lactide was used instead of *rac*-D,L-lactide. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.36 (m, 2H, $-CH_2-$), 1.53 (m, 6H, $-CHCH_3-$), 1.63 (m, 4H, $-CH_2-$), 2.38 (m, 2H, $-CH_2C(O)O-$), 4.12 (m, 2H, $-CH_2OC(O)-$), 3.73 (s, 3H, $-C(O)OCH_3$), 5.15 (m, 2H, $-CHCH_3-$). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 16.8−16.9 ($-C(O)OCHCH_3-$), 24.4−24.7, 25.3−25.7, 28.3, 28.5, 33.8−34.3, 64.3, 65.5, 68.4 ($-OCO(CH_2)_5-$), 69.0−69.2 ($-C(O)OCHCH_3-$),169.7−169.9 ($-COOCHCH_3-$), 170.3 (*C*(O)O, CL−LA−LA), 170.5 (*C*(O)O, LA−LA−CL), 173.0 (*C*(O)O, LA−CL−LA).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of the polymers and copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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$$r_1(1/f) = 2[\text{LA}-\text{LA}]/[\text{LA}-\text{CL}] \quad \text{(A)}$$

$$r_2 f = 2[\text{CL}-\text{CL}]/[\text{CL}-\text{LA}] \quad \text{(B)}$$

where f is the composition in the feed (f = [CL]/[LA]), and the mole fraction of the monomer diads CL−CL and LA−LA and of the heterodiads CL−LA in the copolymers have been evaluated by integration of the appropriate ^{1}H NMR signals (see above). Equations A and B have been previously reported for styrene−butadiene copolymerizations: (a) Zambelli, A.; Caprio, M.; Grassi, A.; Bowen, D. E. *Macromol. Chem. Phys.* **2000**, *201*, 393–400. (b) Cuomo, C.; Serra, M. C.; Maupoey, M. G.; Grassi, A. *Macromolecules* **2007**, *40*, 7089–7097.