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Controlled and Highly Effective Ring-opening Polymerization of α -chloro- ϵ -caprolactone using Zn- and Al-based catalysts

Anaëlle Bolley,^a Samir Mameri,^{a,§} and Samuel Dagorne^{a,*}

^a Institut de Chimie de Strasbourg, CNRS-Université de Strasbourg, UMR 7177, 1 Rue Blaise Pascal, F-67000 Strasbourg, France.

For correspondence, email: dagorne@unistra.fr

Present Address

§ IUT Robert SCHUMAN, Université de Strasbourg, 72 Route du Rhin, CS 10315, 67411 Illkirch Cedex, France.

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The highly effective and controlled ring-opening polymerization (ROP) of α -chloro- ϵ -caprolactone (α -Cl ϵ -CL) using Zn- and Al-based catalysts is reported and affords narrow disperse and chain-length-controlled P α -Cl ϵ -CL materials. The sequential ROP of *L*-lactide (LLA) and α -Cl ϵ -CL allows the preparation of well-defined PLLA-*b*-P α -Cl ϵ -CL diblock copolymers.

Abstract. The present study details the highly effective and controlled ring-opening polymerization (ROP) of α -chloro- ϵ -caprolactone (**1**, $\alpha\text{Cl}\epsilon\text{CL}$), a cyclic ester that has been little explored thus far in ROP catalysis, using Zn- and Al-based catalysts $[\text{Zn}(\text{C}_6\text{F}_5)_2(\text{toluene})]$ (**4**), $[\text{N},\text{N}'\text{-bis}(3,5\text{-di-}i\text{tert-butylsalicylidene})1,3\text{-diaminopropanato}]\text{aluminium(III)benzyloxide}$ (**5**) and $[\text{N},\text{N}'\text{-bis}(3,5\text{-di-}i\text{tert-butylsalicylidene})1,3\text{-diamino-2,2'-dimethylpropanato}]\text{aluminium(III)benzyloxide}$ (**6**). Chain-length-controlled $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ material is produced under solution ROP conditions, as deduced from GPC, NMR, MALDI-TOF and kinetic data. In contrast, the ROP of **1** is ill-defined under bulk ROP conditions due to partial thermal degradation of the polymer chain (presumably through C–Cl cleavage), reflecting the limited stability of $\text{P}\alpha\text{Cl}\epsilon\text{CL}$. The Al catalysts **5** and **6** are highly active ROP catalysts of $\alpha\text{Cl}\epsilon\text{CL}$ at room temperature (TOF up to 2400 h^{-1}) to afford well-defined $\text{P}(\alpha\text{Cl}\epsilon\text{CL})$. In the case of catalyst **6**, carrying out the ROP of $\alpha\text{Cl}\epsilon\text{CL}$ under immortal conditions (with BnOH as chain transfer agent) is clearly beneficial to ROP activity and control, with no apparent side-reaction of chloro-functionalized PCL chains as the ROP proceeds. The controlled character of these ROPs was further exploited for the production of chain-length-controlled $\text{PLLA-}b\text{-P}\alpha\text{Cl}\epsilon\text{CL}$ diblocks through sequential ROP of *L*-lactide and $\alpha\text{Cl}\epsilon\text{CL}$, affording copolymers with improved thermal and biodegradable properties.

Introduction

Aliphatic polyesters constitute an important class of biodegradable materials of current interest because of their wide range of applications.¹ Most notably, landmark polyesters such as polylactide acid (PLA) and poly(ϵ -caprolactone) (PCL), which are produced by ring-opening polymerization (ROP) of cyclic esters lactide (LA) and ϵ -caprolactone (CL), respectively, have found applications in the biomedical area and as packaging commodities.² Access to functionalized aliphatic polyesters is current attracting attention to extend the range of aliphatic polyesters and tailor important properties (including biodegradation rate, crystallinity, hydro-philicity/-phobicity, and mechanical properties).³ In the area, functionalization of materials such as PLA and PCL constitutes a direct approach but is complicated by the lack of reactive functions on the polymer chains. For instance, in early studies, Vert and co-workers showed that the functionalization of PCL occurs with chain degradation and only partial functionalization.⁴

Alternatively, the ROP of pre-functionalized cyclic esters monomers appears promising since it may directly lead to well-defined functionalized polyesters provided the ROP process proceeds in a controlled manner. In that regard, a number of lactones bearing halogen, alkene and alkyne moieties have been polymerized to produce the corresponding functional polymers.⁵ In particular, alkyne-functionalized PCLs have been successfully used for subsequent introduction of various chemical functions (including PEG, chemotherapy drugs and peptides) through click chemistry, to afford various functional biomaterials for biomedical applications.⁶

Figure 1. Halogen-bearing caprolactones **1-3**

The ROP of halogen-bearing caprolactones **1-3** (Figure 1) has been little explored though the resulting halogen-bearing PCLs may afford materials of potential interest on their own or subsequently functionalized thanks to the reactivity of the carbon-halogen bond. For instance, the production of poly(α -iodo- ϵ -caprolactone), a X-ray opaque material, was achieved through ROP of monomer **3** using a Sn-based catalyst.⁷ Poly(α -chloro- ϵ -caprolactone) (P α Cl ϵ CL), arising from the ROP of α Cl ϵ CL (**1**), may be readily converted to an azido-bearing PCL that was further functionalized through click chemistry.⁸ The ROP of α Br ϵ CL (**2**) was also shown to afford P(α Br ϵ CL), whose subsequent derivatisation may lead to functionalized polyesters of interest.⁹

The ROP of cyclic esters mediated by metal-based species has been intensively studied over the past twenty years as it constitutes a method of choice for a controlled polymerization process allowing access to well-defined and chain-length-controlled polyesters.¹⁰ Depending on the metal catalyst (*i.e.* metal center and supporting ligands), the ROP may proceed under mild conditions,¹⁰ which is of particular importance for the polymerization of more reactive functionalized lactones. Thus far, studies on the ROP of α -halogen-functionalized CL monomers **1-3** have only been performed with Sn-based catalysts, whose toxicity may be problematic for application of the derived materials in the biomedical area.^{7b,8,11} Besides, the ROP of such monomers is frequently carried under high temperature reaction conditions, which may be detrimental to the well-defined nature and properties (such as chain length control and polydispersity) of the resulting materials.^{7b,8} For instance, thermal degradation occurs during the ROP of monomer **3** (Sn-based catalyst, 100 °C, toluene), which was attributed to cleavage of the carbon-halogen bonds of the polymer chains.^{7b}

Within the above context and as part of our studies on ROP of cyclic esters mediated by discrete metal complexes, we investigated selected ROP initiators incorporating non-toxic

and earth-abundant Zn(II) and Al(III) metal species for the controlled ROP of α Cl ϵ CL (**1**) under mild conditions, preferably at room temperature. We here report on the use of Zn- and Al-based species for the production of well-defined P α Cl ϵ CL *via* controlled ROP of α Cl ϵ CL. The living character of the ROP processes under the reaction conditions allowed the synthesis of chain-length controlled PLLA-*b*-P α Cl ϵ CL block co-polymers for properties tuning. Such materials also characterized herein and compared to the corresponding homopolymers.

Results – Discussion.

Synthesis and molecular structure of α -chloro- ϵ -caprolactone (α Cl ϵ CL, **1**).

Monomer **1** was prepared according to a literature procedure through a Baeyer-Villiger oxidation reaction of 2-chlorocyclohexanone with *m*CPBA (room temperature, dichloromethane).¹¹ Monomer **1** was isolated in a pure form as colorless oil in 63 % yield (Figure S1, SI). Upon storage at low temperature (-35 °C), species **1** crystallized and X-ray diffraction studies on collected single crystals allowing further confirmed compound **1** as a racemic seven-membered ring cyclic ester α -functionalized by a chlorine atom. Species **1** crystallizes as a racemate in centro-symmetric space group *P*_{-bca}. Figure 2 depicts the molecular structure of the chiral carbon center in *R* configuration. All geometrical and bonding parameters are as expected and a summary of crystallographic data for **1** is provided in the SI (Table S1).

Figure 2. ORTEP view of the molecular structure of cyclic ester **1** (chiral carbon center in *R* configuration). Hydrogen atoms are omitted for clarity and the ellipsoids enclose 50% of electron density probability.

ROP of α Cl ϵ CL (1**) with metal catalyst $\text{Zn}(\text{C}_6\text{F}_5)_2(\text{toluene})$ (**4**).** Since Zn is a cheap, benign and earth-abundant metal source, Zn-based ROP initiators of cyclic esters are of particular interest and are currently attracting attention.¹⁰ In earlier studies, we showed that a 1/1 **4**/BnOH mixture effectively catalyzes the controlled ROP of cyclic esters/carbonates, such as lactide and trimethylene carbonate, presumably *via* a monomer-activated mechanism.¹² The ROP of **1** was thus first investigated with the Lewis acid $\text{Zn}(\text{C}_6\text{F}_5)_2(\text{toluene})$ (**4**) in the presence of an alcohol source such as BnOH. The ROP results are compiled in Table 1.

Table 1. ROP of α Cl ϵ CL mediated by $\text{Zn}(\text{C}_6\text{F}_5)_2/\text{BnOH}$

entry ^a	Cat.	BnOH (eq.)	Time ^b (h)	Conv. ^c (%)	$M_{n, \text{theo}}$ ^d (g/mol)	$M_{n, \text{GPC}}$ ^e (g/mol)	$M_{n, \text{corr}}$ ^f (g/mol)	$\bar{D}$	TOF (h ⁻¹)
1	4	1	3	23	3400	3150	2700	1.15	7.7
2	4	1	5	40	5920	5550	4800	1.10	8
3	4	1	22	100	14800	14050	12100	1.44	4.54

^a Conditions: $[\alpha\text{Cl}\epsilon\text{CL}]_0 = 1 \text{ M}$, 1 equiv. $\text{Zn}(\text{C}_6\text{F}_5)_2/\text{BnOH}$, 100 equiv monomer, toluene, 90 °C.

^b Reaction time. ^c Monomer conversion, ^d Calculated using $M_{n, \text{theo}} = [M_{\alpha\text{Cl}\epsilon\text{CL}} \times \text{conversion} \times 100] + M_{\text{BnOH}}$. ^e Measured by GPC in THF (30 °C) using PS standards. ^f Calculated using a correcting factor of 0.88 for P α Cl ϵ CL: $M_{n, \text{corr}} = 0.88 \times M_{n, \text{GPC}}$ (for its estimation, see experimental section).

While catalyst **4**/BnOH is inactive in the ROP of **1** at room temperature (no conversion after 24 h), it was found to polymerize monomer **1** (100 equiv) upon heating (90 °C, toluene, 22 h) to quantitatively afford chain-length controlled P α Cl ϵ CL ($M_{n,corr}$ = 12100 g.mol⁻¹, $\bar{D}$ = 1.44), as deduced from gel permeation chromatography (GPC) and NMR data on isolated polymer (Figures S2-S7, SI). The ¹H NMR spectrum of P α Cl ϵ CL contains characteristic resonances for BnO-ester (δ 7.37, 5.21) and CH₂OH (δ 3.66) chain end groups, in line with BnOH acting as an effective initiator for polymer chain growth. For all runs, the NMR-estimated M_n values for P α Cl ϵ CL are also in agreement with GPC data. The ¹³C NMR spectra also agree with the formation of a P α Cl ϵ CL chain. All experimental data are consistent with a controlled ROP process, which is best indicated by a linear correlation between the M_n values of P α Cl ϵ CL and monomer conversion (Figure 3). The moderately narrow polydispersity of the produced P α Cl ϵ CL likely results from transesterification reactions of the growing polymer chains as the ROP proceeds. Based on earlier results in lactide ROP catalysis,¹² the ROP of **1** by **4**/BnOH likely occurs *via* a monomer-activated mechanism with an initial monomer coordination/activation to the Zn center followed by a nucleophilic attack by BnOH to afford the ring-opened product for subsequent chain growth.^{13,14} The lower ROP activity of Zn(II) species **4** compared to Al(III) and Ga(III) catalysts **5** and **6** discussed below (*vide infra*), the latter mediating the ROP of **1** through a coordination–insertion mechanism, may arise from the different operating ROP mechanism and the moderate Lewis acidity of Zn(II).

Figure 3. Plot of $P\alpha\text{Cl}\varepsilon\text{CL}$ M_n values as a function of $\alpha\text{Cl}\varepsilon\text{CL}$ conversion in the ROP of $\alpha\text{Cl}\varepsilon\text{CL}$ using a 1/1 **4**/BnOH mixture as catalyst. Conditions: $[\alpha\text{Cl}\varepsilon\text{CL}]_0 = 1$ M, 1 equiv. BnOH, 100 equiv. in monomer, toluene, 90 °C.

ROP of monomer 1 by salen-Al complexes 5 and 6. Though the $\text{Zn}(\text{C}_6\text{F}_5)_2/\text{BnOH}$ mixture allows a controlled ROP catalysis, its activity is rather moderate despite prolonged heating, as discussed above. In search for more active ROP catalysts, salen-Al benzyloxide complexes **5** and **6** (Figure 4), synthesized according to literature procedures,^{27,28} were selected for the ROP of **1** since known to be effective initiators for the controlled ROP of cyclic esters such as LA.^{27,28}

Figure 4. Molecular structure of the salen-Al benzyloxide complexes **5** and **6**

Table 2. ROP of $\alpha\text{Cl}\varepsilon\text{CL}$ mediated by the Al(III) catalysts **4** and **5**.

Entry ^a	Cat.	Monomer (equiv)	Time ^b (min)	Conv. ^c (%)	$M_{n, \text{theo}}^d$	$M_{n, \text{GPC}}^e$	$M_{n, \text{corr}}^f$	$\bar{D}$	TOF (h ⁻¹)
1	5	100	11	100	14800	16400	14500	1.28	545
2	6	100	1	40	6200	6900	6100	1.32	2400
3	6	100	2.7	82	12900	14500	12700	1.44	1820
4	6	100	4.3	93	13800	16500	14500	1.05	1300
5	6	100	6.9	100	14900	17700	15600	1.17	860
6	6	250	10	33	12300	29000	25500	1.28	500
7	6	250	15	42	18600	34200	30200	1.16	420

8	6	250	35	64	26000	56900	50100	1.58	275
9	6	250	130	100	37200	90500	79600	1.25	115
10	6	500	480	100	74300	61400	54000	1.56 ^g	63
11	6^h	100	15	100	14900	34300	30200	1.54	400

^a Conditions: $[\alpha\text{Cl}\epsilon\text{CL}]_0 = 1\text{ M}$, 1 equiv of catalyst, CH_2Cl_2 , room temperature. ^b Reaction time. ^c Monomer conversion, ^d Calculated using $M_{n, \text{theo}} = [M_{\alpha\text{Cl}\epsilon\text{CL}} \times \text{conversion} \times 100] + M_{\text{BnOH}}$. ^e Measured by GPC in THF (30 °C) using PS standards. ^f Calculated using a correcting factor of 0.88 for $\text{P}\alpha\text{Cl}\epsilon\text{CL}$: $M_{n, \text{corr}} = 0.88 \times M_{n, \text{GPC}}$ (for its estimation, see experimental section). ^g A bimodal distribution is observed. ^h Solvent-free conditions, 55 °C.

The ROP results are compiled in Table 2. Satisfyingly, catalysts **5** and **6** were found to be highly active in the ROP of **1** (100 equiv) at room temperature leading to the production of chain-length-controlled and narrowly disperse $\text{P}\alpha\text{Cl}\epsilon\text{CL}$, as deduced from **GPC** and NMR data (entries 1-5, Table 2; Figure S8-S15, SI).¹⁵ At best, catalyst **6** quantitatively polymerized 100 equiv of $\alpha\text{Cl}\epsilon\text{CL}$ within 7 min at room temperature to afford well-defined $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ with $M_{n, \text{corr}}$ and $M_{n, \text{theo}}$ values in good agreement ($\text{TOF} = 860\text{ h}^{-1}$, entry 5, Table 2). Similarly, catalyst **5**, which incorporates a non-substituted propylene bridge salen ligand, also led to a controlled ROP process, albeit with a lower activity than species **6** ($k_{\text{obs } 6}/k_{\text{obs } 5} = 1.58$, Figure 5). All ROP data mediated by **5** and **6** agree with a controlled polymerization, including: 1) a reaction rate found to be pseudo-first-order relative to monomer (Figure 5) and 2) a linear correlation between the M_n values of the growing polymer chains and monomer conversion (Figure 6). Also, **Matrix Assisted Laser Desorption Ionization - Time of Flight** (MALDI-TOF) data of a polymer sample arising from the ROP of $\alpha\text{Cl}\epsilon\text{CL}$ (15 equiv) with catalyst **6** agree with the sole formation of linear $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ chains bearing a BnO-ester at one end (Figure S16, SI).¹⁶ All mass peaks are equally spaced by 148 a.u., the monomer mass, as expected. The ^1H NMR data are also in line with a linear $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ materials with a BnO-ester and CH_2OH ends (Figure S11, SI). Altogether, the polymer structure is consistent with a ROP occurring through coordination-insertion mechanism, as typically observed with the ROP of cyclic esters by metal alkoxides.

Figure 5. Plot of $\ln(M_0/M)$ (M = monomer) as a function of time in the ROP of $\alpha\text{Cl}\epsilon\text{CL}$ using the Al(III) catalysts **5** and **6**. Conditions: $[\alpha\text{Cl}\epsilon\text{CL}]_0 = 1 \text{ mol. L}^{-1}$, 100 equiv of $\alpha\text{Cl}\epsilon\text{CL}$, CH_2Cl_2 , room temperature.

Figure 6. Plot of $P\alpha\text{Cl}\epsilon\text{CL}$ M_n values as a function of $\alpha\text{Cl}\epsilon\text{CL}$ conversion in the ROP of $\alpha\text{Cl}\epsilon\text{CL}$ using catalyst **6**. Conditions: $[\alpha\text{Cl}\epsilon\text{CL}]_0 = 1 \text{ M}$, 100 equiv of monomer **1**, CH_2Cl_2 , room temperature.

To further investigate and probe the potential and limits of Al(III) catalyst **6**, it was also tested at higher monomer loading (250 and 500 equiv vs. catalyst) for the production of higher molecular weight $P\alpha\text{Cl}\epsilon\text{CL}$ (entries 6-10, Table 2). Thus, species **6** also efficiently polymerizes 250 equiv of $\alpha\text{Cl}\epsilon\text{CL}$ with the quantitative formation of narrow disperse $P\alpha\text{Cl}\epsilon\text{CL}$ within 130 min (entry 9, Table 2) as deduced from GPC data (Figures S17-S19, SI). Kinetic data agree with a controlled ROP process with, in particular, a linear correlation of M_n values of the growing polymer and monomer conversion. (Figures S20-S21, SI). The ^1H NMR data agree with the formation of a linear $P\alpha\text{Cl}\epsilon\text{CL}$ with a BnO-ester end (Figure S22, SI). However, the M_n values of the produced polymers are all higher than the expected ones,

along with only moderately narrow polydispersities ($1.16 < \bar{D} < 1.58$). Also, when compared to the ROPs performed using 100 equiv of monomer, species **6** is much less active, as reflected by the TOF values (see, for instance, entry 5 vs. 10 in Table 2 with TOF = 860 vs. 115 h⁻¹). Both the higher M_n values and the lower TOFs may arise from partial catalyst decomposition due to impurities in the monomer source, resulting into a lower amount of effective ROP catalyst. A further increase in monomer feed (500 equiv vs. catalyst **6**) led to the production of ill-defined P α Cl ϵ CL material, as reflected by the bi-modal GPC trace (Figure S23, SI).

The ROP of α Cl ϵ CL mediated by species **6** may also proceed under bulk conditions (neat α Cl ϵ CL, 55 °C, 15min; entry 11, Table 2), yet to afford broadly disperse P α Cl ϵ CL ($\bar{D}$ = 1.54) with no chain length control (Figures S24-S26, SI). NMR and MALDI-TOF data of the isolated material both show the presence of olefinic moieties on the polymer chains, which is in line with partial thermal decomposition of P α Cl ϵ CL chains (presumably through halide elimination) under the reaction conditions.¹⁷

Immortal ROP of α Cl ϵ CL catalyzed by Al(III) catalyst **6.** To improve ROP control at higher monomer loading, the ROP of α Cl ϵ CL catalyzed species **6** was carried out in the presence of an alcohol source expected to act as a chain transfer, which may limit side reactions (such as chain backbiting) as the ROP proceeds.¹⁸ As summarized in Table 3, the addition of BnOH is clearly beneficial regarding to the ROP process, regarding both catalytic activity (TOF up to 1720 h⁻¹) and control ($1.02 < \bar{D} < 1.10$), with the production and very narrow disperse P α Cl ϵ CL materials. Thus, up to 1000 equiv of α Cl ϵ CL may be quantitatively polymerized within 110 min at room temperature in the presence of species **6** and 5 equiv of BnOH to afford a well-defined material with M_n values in the expected range. All characterization and kinetic data agree with a controlled ROP and the formation of a linear BnO-ester ended P α Cl ϵ CL material, indicating that BnOH behaves as a fast and effective chain transfer agent during ROP catalysis (Figure S27-S32, SI).

Table 3. Immortal ROP of α Cl ϵ CL catalyzed by Al(III) catalyst **6 in the presence of BnOH**

Entry ^a	Monomer (equiv)	BnOH (equiv)	Time ^b (min)	Conv. ^c (%)	$M_{n, theo}$ ^d	$M_{n, GPC}$ ^e	$M_{n, corr}$ ^f	$\bar{D}$	TOF (h ⁻¹)
1	1000	5	23	66	17400	16400	14400	1.02	1720

2	1000	5	40	83	21500	21050	18500	1.05	1250
3	1000	5	110	100	25600	25300	22250	1.10	545

^a Conditions: $[\alpha\text{Cl}\epsilon\text{CL}]_0 = 1$ M, 1 equiv of catalyst, CH_2Cl_2 , room temperature. ^b Reaction time. ^c Monomer conversion, ^d Calculated using $M_{n, \text{theo}} = [\text{M}_{\alpha\text{Cl}\epsilon\text{CL}} \times \text{conversion} \times [\text{monomer}]_0 / ([\text{BnOH}]_0 + [\mathbf{6}]_0)] + \text{M}_{\text{BnOH}}$. ^e Measured by GPC in THF (30 °C) using PS standards. ^f Calculated using a correcting factor of 0.88 for $\text{P}\alpha\text{Cl}\epsilon\text{CL}$: $M_{n, \text{corr}} = 0.88 \times M_{n, \text{GPC}}$ (for its estimation, see experimental section).

Synthesis of PLA-*b*- $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ block co-polymers. Taking advantage of the living and controlled ROP of $\alpha\text{Cl}\epsilon\text{CL}$ by initiator **6**, PLA-*b*- $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ block co-polymers were produced through sequential ROP of *L*-LA and then $\alpha\text{Cl}\epsilon\text{CL}$. The introduction of a crystalline PLLA segment to a $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ chain is expected to improve thermal/mechanical properties of the resulting materials (*vide infra*). For all runs, the ROP of *L*-LA initiated by species **6** was first performed and was quantitative after 9 h at 80 °C in toluene (from 100 to 200 equivalents). The reaction was then allowed to cool to room temperature over 1h and $\alpha\text{Cl}\epsilon\text{CL}$ (30 to 150 equivalents) was then added and polymerized within 14-19 h. As summarized in Table 4, the production of well-defined $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ -*b*-PLA with variously tailored chain lengths may be achieved, as deduced from NMR data and monomodal GPC traces (Figures S33-S36, SI). The ¹H NMR data for all samples feature a characteristic $\text{CH}_2\text{-Ph}$ benzyloxy initiator signal¹⁹ and a multiplet resonance for the α -chloro-caprolactyl $\text{CH}_2\text{-OH}$ chain end, in line with the expected linear structure of such diblock copolymers. The formation of diblocks was further confirmed by DOSY NMR analysis of a 100/100 $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ -*b*-PLA copolymer and the corresponding $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ homopolymer for comparison (Figures S38 and S39, SI). These diffusion data, with only one diffusion coefficient for each sample, agree with the formation of well-defined and chain-length controlled materials. A larger hydrodynamic radius is estimated for the copolymer ($R_h = 64.2$ vs. 47.6 Å for $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ -*b*-PLA vs. $\text{P}\alpha\text{Cl}\epsilon\text{CL}$), consistent with longer polymer chains in the diblock structure.

Table 4. Synthesis of PLA-*b*- $\text{P}\alpha\text{Cl}\epsilon\text{CL}$ block co-polymers mediated by catalyst **6**

Entry ^a	Monomer	LA (equiv)/ ($\alpha\text{Cl}\epsilon\text{CL}$) (equiv)	$M_{n, \text{theo}}$ ^b (g/mol)	$M_{n, \text{GPC}}$ ^c (g/mol)	$\bar{D}$
1	<i>L</i> -LA	100/100	29250	33100	1.50
2	<i>D</i> -LA	100/100	29250	33750	1.45
3	<i>L</i> -LA	150/150	43950	62200	1.08
4	<i>L</i> -LA	200/100	43700	53300	1.09

5	<i>L</i> -LA	100/30	18900	22300	1.48
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^a Conditions: 1) LA as monomer [LA] = 1 M, 80 °C, toluene; 2) α Cl ϵ CL as co-monomer, [α Cl ϵ CL]₀ = 1 M, CH₂Cl₂, room temperature; complete conversion of both monomers was achieved in all cases prior to GPC analysis. ^b Calculated using lactide equiv. $\times M_{LA} + \alpha$ Cl ϵ CL equiv. $\times M_{\alpha$ Cl ϵ CL. ^c Measured by GPC in THF (30 °C) using PS standards.

Polymers characterization. All PLA-*b*-P α Cl ϵ CL block copolymers as well as some P(α Cl ϵ CL) and PLLA homopolymers were analyzed by DSC and TGA to evaluate the thermal properties of such materials as well as the influence of the PLA chain on materials properties. The DSC results are compiled in Table 5 while TGA data are depicted in Figure 7 and Figure S40.

P α Cl ϵ CL (entry 1, Table 5) is an amorphous material since only exhibiting a glass transition at -33 °C (Figure S40, SI), contrasting with the well-known semi-crystallinity of structurally related PCL.²⁰ The DSC data for semi-crystalline PLLA (entry 2, Table 5) are in line with literature data.²¹ In contrast to P α Cl ϵ CL, all PLA-*b*-P α Cl ϵ CL diblock polymers (entries 3, 4, 5, and 6, Table 5) are semi-crystalline, feature one melting transition at T_m and two different T_g values. The latter is consistent with the presence of separate P(α Cl ϵ CL) and PLLA phases as frequently observed in diblock polymer structures. The presence of crystallization temperature upon cooling (T_C) further indicates the crystallinity of all diblocks. From DSC data, the following trends may be established: 1) the crystallinity of the copolymers increases with the length of the PLA segment relative to that of P α Cl ϵ CL; 2) For a given P α Cl ϵ CL/PLLA ratio in the block material, chain length seems to little influence the resulting properties as deduced from the similar properties of PLLA-*b*-P α Cl ϵ CL (100/100) and PLLA-*b*-P α Cl ϵ CL (150/150) (entries 3 vs. 5, Table 5). Overall, these data show that the thermal and crystalline properties of functional polyester P α Cl ϵ CL may be readily improved and tuned in a controllable manner by incorporation of a PLLA segment.

Figure 7. Superimposition of TGA data for PLA-*b*-P α Cl ϵ CL diblocks. Conditions: all samples were heated at 10 °C/min under a nitrogen flow (100 mL/min) then under air flow from 700 °C.

TGA analysis of P(α Cl ϵ CL) homopolymer shows a decomposition occurring in two steps (from 220 °C and after 340 °C), thus at a much lower temperature than PCL for which decomposition occurs from 430 °C.²⁰ The lower thermal stability of P(α Cl ϵ CL) may be attributed to the cleavage of carbon-chloride bonds early on upon rising temperature. As shown in Figure 7, all diblock copolymers decompose within a higher temperature range (from 220 to 290 °C under nitrogen) with a residue (at 700 °C) ranging from 3.6 to 13 % of the initial mass. For instance, PLLA-*b*-P α Cl ϵ CL (100/100 and 150/150) samples decompose after 280 and 290 °C, respectively, thus at substantially higher temperatures than P(α Cl ϵ CL).

Table 5. DSC measurements for PLLA-*b*-P α Cl ϵ CL materials and corresponding homopolymers

Entry	sample	α Cl ϵ CL (equiv)/LA (equiv)	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	ΔH_m^a (J/g)	T_c (°C)	ΔH_c^b (J/g)	Cryst. rate ^c (%)
1	P α Cl ϵ CL ($M_n = 15600 \text{ g.mol}^{-1}$, $\bar{D} = 1.17$)	100/0	-33	-	-	-	-	-	-
2	PLLA ($M_n = 14500 \text{ g.mol}^{-1}$, $\bar{D} = 1.10$)	0/100	-	56	165	63	111	52	60
3	PLLA- <i>b</i> -P α Cl ϵ CL ($M_n = 33100 \text{ g.mol}^{-1}$, $\bar{D} = 1.50$)	100/100	-32	55	158	29	106	22	13
4	PLLA- <i>b</i> -P α Cl ϵ CL ($M_n = 22300 \text{ g.mol}^{-1}$, $\bar{D} = 1.48$)	30/100	-29	n. d.	155 to 168	41	108	33	29
5	PLLA- <i>b</i> -P α Cl ϵ CL ($M_n = 62200 \text{ g.mol}^{-1}$, $\bar{D} = 1.08$)	150/150	-28	n. d.	157	28	93	18	13
6	PLLA- <i>b</i> -P α Cl ϵ CL ($M_n = 53300 \text{ g.mol}^{-1}$, $\bar{D} = 1.09$)	100/200	n. d.	n. d.	157	32	91	15	20

^a ΔH_m : melting enthalpy; ^b ΔH_c : recrystallization enthalpy. ^c Crystalline rate calculation: $\Delta H_{m1} \times \text{PLA \%} \times 0.93$.²²

Conclusion

The present study shows that the ROP of α Cl ϵ CL is efficiently performed under mild conditions using rather simple Zn- and Al-based catalysts for the production of chain-length-controlled and narrowly disperse P(α Cl ϵ CL), with a ROP that may proceed through a monomer-activated mechanism (with Zn(C₆F₅)₂ as catalyst) or coordination-insertion (with salen-Al-OR catalysts **5** and **6**). The Al catalysts **5** and **6** are highly active ROP catalysts of α Cl ϵ CL at room temperature (TOF up to 2400 h⁻¹) to afford a well-defined P(α Cl ϵ CL) materials. Yet, thermal degradation of P(α Cl ϵ CL) was observed under bulk ROP conditions using ROP catalyst **6**, presumably resulting from C–Cl cleavage reactions during chain growth under such reactions conditions. In the case of Al catalyst **6**, carrying out the ROP of α Cl ϵ CL under immortal conditions (with an excess of an alcohol source) is clearly beneficial both to ROP activity and control with no detrimental reaction involving of chloro-functionalized PCL chain as the ROP proceeds. The controlled character of these ROPs allowed the ready introduction of chain-length-controlled PLA segments for the production of various tailored PLA-*b*-P α Cl ϵ CL diblocks providing improved thermal and biodegradable properties to the functionalized materials.

Experimental Section

General procedure: Air sensitive experiments were carried out under N₂ using standard Schlenk techniques or in a nitrogen-filled MBraun Unilab glovebox. Dichloromethane, pentane, and toluene were first dried through a solvent purification system (MBraun SPS) and stored for at least a couple of days over activated molecular sieves (4 Å) in a glovebox prior to use. Tetrahydrofuran was distilled over Na/benzophenone and stored over activated molecular sieves (4 Å) for a couple of days in a glovebox prior to use. Methanol, ethanol and DMF were distilled over KOH and stored over activated molecular sieves (4 Å) for a couple of days in a glovebox prior to use. *L*- and *D*- lactide were provided by Corbion and were sublimed prior to use. All other chemicals were purchased from Aldrich, T.C.I Europe Corporation and Strem Chemicals and were used as received unless otherwise indicated. Deuterated solvents were purchased from Eurisotope (CEA, Saclay, France), degassed under a N₂ flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. NMR spectra were recorded on BrukerAC 300 MHz, 400 MHz, 500 MHz or 600 MHz NMR spectrometers, in Teflon-valved J-Young NMR tubes at ambient temperature unless otherwise indicated. H, F and C chemical shifts are reported vs. SiMe₄ and were determined by reference to the residual H, F and C solvent peaks.²³ Chemical shifts (δ) are given in ppm. The number-average, weight-average molar masses (M_n and M_w , respectively) and molar mass distribution (M_w/M_n) of the polyesters (PLA, P(α Cl ϵ CL)) samples were determined by gel permeation chromatography (GPC) at 30 °C with Shimadzu LC20AD ultra-fast liquid chromatography equipped with a Shimadzu RID10A refractometer detector. Tetrahydrofuran (THF) was used as the eluent and the flow rate was set up at 1.0 mL/min. A Varian PLGel pre-column and a Varian PLGel 5 μ m were used. Calibrations were performed using polystyrene standards (400-100000 g/mol) and raw values of M_n values ($M_{n, \text{GPC}}$) were thus obtained. Mass spectra were acquired on a time-of-light mass spectrometer (MALDI-TOF-TOF-Autoflex II TOF-TOF, Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser ($\lambda = 337$ nm) at the « Service de Spectrométrie de Masse de l'Institut de Chimie de Strasbourg » and run in a positive mode. An external multi-point calibration was carried out before each measurement using the singly charged peaks of a standard peptide mixture (0.4 μ m in water acidified with FlewAnalysis 3.0 software). α -cyano-4-hydroxy-cinnamic acid (CHCA) was obtained from Sigma (St Louis, MO, USA) and 1,8, 9-anthracenetriol (dithranol) from Alfa Aesar (Karlsruhe, Germany). Matrix solutions were freshly prepared: CHCA was dissolved to saturation in H₂O, CH₃CN, HCOOH (50/50.1%) solution and

dithranol to saturation in THF. Typically, a 1/1 mixture of the sample solution in CH₂Cl₂ was mixed with the matrix solution and 0.5 µL of the resulting mixture was deposited on the stainless plate. Elemental analyses for all compounds were performed at the “Service de Microanalyse” of the Université de Strasbourg (Strasbourg, France). Single crystals of monomer **1** was mounted on glass fibers and data collected on a Nonius Kappa-CCD or Bruker Apex II DUO Kappa-CCD area detector diffractometer (MoK_α λ= 0.71073 Å). The complete conditions of data collection (Denzo software).²⁴ The structure was solved using direct methods (SHELXS97) and refined against F² and using the SHELXL97 software.²⁵ All non-hydrogen atoms were refined anisotropically.

The ROP catalysts [Zn(C₆F₅)₂(toluene)] (**4**),²⁶ [N,N'-bis(3,5-di-*tert*-butylsalicylidene)1,3-diaminopropanato]aluminium(III)benzyloxide (**5**)²⁷ and [N,N'-bis(3,5-di-*tert*-butylsalicylidene)1,3-diamino-2,2'-dimethylpropanato]aluminium(III)benzyloxide (**6**)²⁸ were synthesized according to literature procedures.

Thermogravimetric Analysis (TGA)

TGA measurements were performed at the Institut Charles Sadron (Strasbourg, France) and were taken using a TGA2 (Mettler-Toledo). Samples mass about 5 mg powder were heated from room temperature to 1000 °C from 0.02 to 150 °C/min. The TGA data were plotted as temperature versus weight percent, from which onset and final decomposition temperatures were obtained. The analytical method used for all these samples is 25 °C to 700 °C at 10 °C/min under a nitrogen flow of 1000 mL/min and 700 °C to 1000 °C at 10 °C/min under an air flow of 100 mL/min.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out using a DSC Q200 thermal analyser instrument. Powdered sample (about 5 mg) were loaded and sealed in a stainless steel high volume pan. Samples were heated from -80 °C to 550 °C using nitrogen as gas vector. The glass transition temperature, the melting temperature and crystallization temperature were measured after heating the samples up to 180 °C and cooling to -80 °C. Thermograms were recorded during the first cycle at 10 °C/min. Results and measurements were performed with the TA universal Analysis software.

Determination of the correcting factor for estimation of the real M_n values of $P\alpha\text{Cl}\epsilon\text{CL}$.

A set of ROP experiments using catalyst **5** and various $\alpha\text{Cl}\epsilon\text{CL}$ feeds (75, 100, 150 and 170 equiv) were carried out till quantitative consumption of the monomer. The ^1H NMR data were in line with the sole formation of BnO-chain end functionalized $P\alpha\text{Cl}\epsilon\text{CL}$ (Figures S41-S43, SI). Their real M_n values could thus be NMR estimated and are plotted in Figure 8 (vs. M_n values as estimated by GPC using a PS standard, Figures S44-S46, SI). The ratio of the two slopes, *i.e.* $M_{n,\text{NMR}}/M_{n,\text{GPC}} = 0.88$, was applied as a correcting factor. Thus, in all ROP runs of $\alpha\text{Cl}\epsilon\text{CL}$, $M_{n,\text{corr}} = 0.88 \times M_{n,\text{GPC}}$.

Figure 8. Plot of the M_n values of $P\alpha\text{Cl}\epsilon\text{CL}$ as estimated by ^1H NMR. Red: ROP using catalyst **5** and 75, 100, 150 and 170 equiv of Cl-CL after complete conversion; blue: the corresponding M_n values as determined by GPC (PS standard).

Typical procedure for $\alpha\text{Cl}\epsilon\text{CL}$ (1) polymerization. In a glovebox, the catalyst (1 eq.) was charged in a vial equipped with a TeflonTM-tight screw cap and a dichloromethane or toluene solution (1M, typically a 1 mL solution) of the appropriate amount of monomer was added *via* a syringe all at once. The resulting solution was vigorously stirred (at room temperature or heated) for the appropriate time. The vial was then removed from the glovebox and the reaction mixture was quenched with pentane provoking the precipitation of the polymer which was washed several times with pentane, dried *in vacuum* until constant weight. The sample was subsequently analyzed by ^1H NMR, GPC and by MALDI-TOF spectrometry.

Typical procedure for immortal α Cl ϵ CL polymerization: the same procedure as previously described was used for polymerization with the addition of a monomer solution (1M) containing some known amount of the desired alcohol (BnOH) onto the corresponding initiator.

General procedure for PLA-*b*-P α Cl ϵ CL diblock copolymers: *L*-lactide (30, 100 or 150 equiv) was dissolved in toluene and the Al(III) catalyst **6** (1 equiv) and the mixture was stirred for 9 hours at 80 °C. To the PLA mixture was added the appropriate α Cl ϵ CL amount (100, 150 or 200 equiv) and the mixture was stirred at room temperature until the total conversion in P(α Cl ϵ CL). The toluene was then removed under vacuum and the solid obtained was washed three times with pentane then was dried under vacuum. The polymers were washed several times with pentane, dried in vacuum until the obtention of a constant weight and subsequently analysed by ^1H NMR, GPC and MALDI-TOF spectrometry.

α -chloro- ϵ -caprolactone (α Cl ϵ CL, **1).** 20 g (81 mmol) of *m*CPBA (70%) was added to a solution of 10 g (75 mmol) of 2-chlorocyclohexanone in 100 mL of dichloromethane at room temperature. The reaction was stirred at room temperature for 96 hours, then the flask was cooled overnight at -20 °C in order to precipitate *m*-chlorobenzoic acid. The precipitate was removed by filtration and the solution was washed with a saturated aqueous solution of NaHSO₃ (three times), with an aqueous solution of NaHCO₃ (three times), and finally with water. After drying over MgSO₄, the organic phase was filtered, and the solvent was removed under reduced pressure to give a yellowish oil. The oil was purified by silica column chromatography using petroleum ether/ethyl acetate (82/18) as eluent separating α -chlorocyclohexanone and ϵ -chloro- ϵ -caprolactone and then increasing polarity petroleum ether/ethyl acetate (70:30) for collection of α -chloro- ϵ -caprolactone. The solvent was removed in vacuum, and the colourless oil was dried under vacuum for two days (5 g, 63%), R_f = 0.36 (UV). C₆H₉ClO₂ (148.03): Anal. Calcd. C, 48.50, H 6.11; Anal Found. C, 48.47, H 6.12. ^1H NMR (CDCl₃, 300 MHz): δ 1.76-2.22 (m, 6H, CH₂), 4.19-4.27 (m, 1H, COOCH₂), 4.56-4.67 (m, 1H, COOCH₂), 4.78-4.81 (dd, 1H, CHCl) ppm.

.Supporting Information: Characterization data for all polymers, including selected NMR, MALDI-TOF , GPC, DSC and TGA data. Kinetic data for ROP studies.

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