

Catalytic Activity of a Titanium(IV)/Iron(II) Heterometallic Alkoxide in the Ring-Opening Polymerization of ϵ -Caprolactone and *rac*-Lactide

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The activity of the heterometallic alkoxide $[\text{FeCl}\{\text{Ti}_2(\text{O}^i\text{Pr})_9\}]$ (**1**) towards polymerization of *rac*-lactide (*rac*-LA) and ϵ -caprolactone (ϵ -CL) was investigated in toluene solution and in bulk at various temperatures, monomer/heterometallic alkoxide molar ratio and reaction times. The alkoxide **1** was active in solution for ϵ -CL and in bulk for both monomers. Polymers were obtained in good yields with molecular weights ranging from 3890 to 15000 g mol⁻¹ and polydispersity indexes (PDI) values varying from 1.3 to 2.5. Based on the ¹H nuclear magnetic resonance (NMR) end-group analysis of polymers, a coordination-insertion mechanism was suggested for both monomers. The average number of growing chains *per* molecule of initiator (4 to 5 for *rac*-LA and 7 to 8 for ϵ -CL) indicates that both bridging and terminal isopropoxides are active initiating groups. Kinetic studies with ϵ -CL indicated that the polymerization rate is first order with respect to monomer concentration. The catalytic properties of **1** were compared to those found for other titanium(IV) and iron(II) complexes using ϵ -CL as a model monomer.

Keywords: heterometal alkoxide, ring opening polymerization, ϵ -caprolactone, *rac*-lactide, iron(II), titanium(IV)

Introduction

Biodegradable and biocompatible polyesters such as poly(ϵ -caprolactone) (PCL), poly(*rac*-lactide) (PLA) and their copolymers have been extensively employed in the biomedical field.^{1,2} The synthesis of these polymers requires the use of an initiator, usually a metal alkoxide or carboxylate, based on a choice of different metals.³ The most commonly used initiator has undoubtedly been stannous(II) octanoate, due to its easy handling and solubility in several organic solvents. Main inconveniences, on the other hand, lie on its relatively low polymerization activity and the occurrence of a large degree of intermolecular and intramolecular transesterification reactions when this initiator is employed.^{4,5}

As an alternative, the use of initiators based on biocompatible metals, such as zinc, calcium, magnesium,⁶ iron and titanium has been studied.⁷ The complex $[\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})_2]$, for example, requires an *in situ* formation of isopropoxide groups to show good control over polymerization.^{8,9} On the other hand, $[\text{Zn}_2\text{Cl}_2(\text{OEt})\text{L}]$

(L = 2,6-bis{*N*-(2-dimethylaminoethyl)-*N*-methyl}-4-methylphenol) produces poly-(*rac*-lactide) with low polydispersity index (PDI) values (ca. 1.1) and high molar mass.¹⁰ Simple titanium(IV) alkoxides or aryloxides such as $[\text{Ti}(\text{OPr}^n)_4]$, $[\text{Ti}(\text{O}^n\text{Bu})_4]$ and $[\text{Ti}(\text{OPh})_4]$ have also been tested and have shown good activity towards ring-opening polymerization (ROP) of cyclic esters.¹¹ Despite these promising results, lack of control upon the reaction pathway has been observed in most cases, evidencing the need to develop new initiators with ancillary bulky ligands in order to restrict chain growth to few catalytic sites.¹²

More complex, polynuclear titanium(IV) alkoxides have also been employed in bulk polymerization of cyclic esters in a reasonably well-controlled processes.^{13,14} In this context, our group has successfully employed the ionic $[\text{Ti}_3(\mu_3\text{-O}^i\text{Pr})_2(\mu\text{-O}^i\text{Pr})_3(\text{O}^i\text{Pr})_6][\text{FeCl}_4]^{15}$ halo-alkoxide in the bulk polymerization of lactides and ϵ -caprolactone, producing polyesters with M_n values ranging from 6350 to 13750 g mol⁻¹ and PDI varying from 1.2 to 1.5.¹⁶ Despite the heterometallic nature of the initiator, our work revealed that its activity could be assigned mainly to the trinuclear cation $[\text{Ti}_3(\text{O}^i\text{Pr})_{11}]^+$.

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A catalytic alternative towards the ROP of cyclic esters that has shown promising results is the use of bimetallic initiators containing the transition metal together with Zn, Mg or Al. These compounds apparently owe their activities to the cooperative effect of the different metal ions, which leads to higher catalytic activities than those from the corresponding mononuclear complexes.^{7,10,17-19} In this context, heterometallic alkoxides of titanium(IV) with alkali metals, magnesium or zinc improved the catalytic activity for ϵ -caprolactone (ϵ -CL) and *L*-lactide polymerization, probably due to the withdrawal of electron density from titanium by the second metal through the bridging alkoxide ligands.²⁰ Bimetallic alkoxides based on titanium(IV) and lanthanide(III) centers have also shown cooperative activity of the two metal centers in this type of polymerization.²¹

In spite of the growing interest in the application of heterometallic alkoxide complexes as catalytic tools in polymer chemistry,^{22,23} this line of research has not yet been completely established. Environmental and biomedical challenges, for example, point to the application of low toxicity metal ions such as iron(II) and iron(III) in the catalysts. Despite this, iron alkoxides are still barely reported and only few of them have been assessed for their activity towards ROP.²⁴⁻²⁶ Promising examples come from bimetallic iron(II) and sodium complexes with alkoxide and aryloxy ligands that were able to promote ring-opening polymerization of *rac*-lactide efficiently at room temperature and afforded good control of the molecular weight.²⁷

In the present work, the activity of the neutral, iron(II)/titanium(IV) alkoxide $[\text{FeCl}\{\text{Ti}_2(\text{O}^i\text{Pr})_9\}]$ ²⁸ (**1**, Figure 1) as initiator of ring-opening polymerization was investigated both in bulk (for *rac*-lactide and ϵ -CL) and in solution (for ϵ -CL). This complex is one of the few examples of heterometallic alkoxides that contain biocompatible metals (iron and titanium) in the same molecular framework. Its synthesis and characterization, both structural and spectroscopic, have been described earlier by our research group.²³ In the attempt to elucidate the role of the different metal ions present in **1** in the polymerization reaction, results obtained with this complex were compared with those given by $[\text{Ti}(\text{O}^i\text{Pr})_4]$ (**2**), $[\text{Fe}_4\text{Cl}_8(\text{thf})_6]$ ²⁹ (**3**)

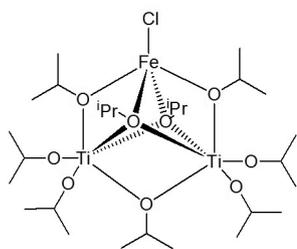


Figure 1. Schematic view of the molecular structure of $[\text{FeCl}\{\text{Ti}_2(\text{O}^i\text{Pr})_9\}]$ (**1**).²⁸

and $[\text{FeCl}_2(\text{Pr}^i\text{OH})_4]$ ³⁰ (**4**) as ROP initiators in the same experimental conditions.

Experimental

General considerations

The synthesis and manipulation of the initiators and the polymerization essays were carried out under nitrogen or under vacuum using either standard Schlenk techniques or a VAC/NEXUS 2000 glove-box. The complexes $[\text{FeCl}\{\text{Ti}_2(\text{O}^i\text{Pr})_9\}]$,²⁸ $[\text{Fe}_4\text{Cl}_8(\text{thf})_6]$ ^{29,30} and $[\text{FeCl}_2(\text{Pr}^i\text{OH})_4]$ ³¹ were prepared according to earlier literature reports. Toluene was refluxed over sodium benzophenone and freshly distilled prior to use. The compound ϵ -caprolactone (ϵ -CL, Aldrich, 97%) was distilled under vacuum over calcium hydride. The compound *rac*-lactide (*rac*-LA, Alfa Aesar, 99%) was dried under vacuum in the presence of phosphorus pentoxide. Both monomers were stored under N_2 . Polymeric products were precipitated in air using dichloromethane (Vetec, 99.5%) and methanol (Vetec, 99.9%).

Instruments

Molecular weights (M_n and M_w) and polydispersity indexes (PDI) of the polymers were determined by gel permeation chromatography (GPC) using a HPLC Waters 1515 equipment with a isocratic pump, two columns (Progel g 1000 HXL and Progel g 2000 HXL of 30 cm \times 7.8 mm) and two detectors, namely a refraction index Waters 2414 (40 °C) and an ultraviolet ($\lambda = 210$ nm e 254 nm) Waters 2487 cell. Tetrahydrofuran (thf) (Baker) was used as mobile phase at 40 °C. Calibration curves were obtained with polystyrene (PS) standards and correction values of 0.56 and 0.58 were used to calculate the PCL and PLA molecular weights, respectively.³² Electron paramagnetic resonance (EPR) data (X-band, 9.5 GHz) were recorded on an X-band Bruker EMX-MICRO spectrometer from solid samples at 77 K. Melting temperatures (T_m) of the polymers were determined by differential scanning calorimetry (DSC) using a Netzsch DSC 204 F1 MAIA calorimeter under continuous nitrogen purge and heating and cooling rates of 10 °C min^{-1} . Poly(ϵ -caprolactone) samples were analyzed sequentially from ambient temperature to 150 °C, with 5 min in isotherm, cooling to 120 °C, 5 min in isotherm and up to 150 °C, while poly(*rac*-lactide) samples were analyzed from 20 to 200 °C, 5 min in isotherm, cooling to -20 °C, 5 min in isotherm and up to 200 °C. Sample amounts ranged between 4 and 8 mg and indium was used to perform instrument calibration. Powder X-ray diffractograms were recorded with a Shimadzu XRD-600

equipment at 40 kV and 40 mA, using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) and scanning rates between $0.02^\circ \text{ s}^{-1}$ and 6° s^{-1} in 2θ . Samples were spread on a conventional glass sample holder. Powder silicon reflections were used for 2θ calibrations. The products of the *rac*-lactide and ϵ -caprolactone polymerization reactions were analyzed by ^1H nuclear magnetic resonance (RMN) spectroscopy on a Bruker AVANCE 400 spectrometer. Polymers (10 mg) were dissolved in CDCl_3 (0.1% tetramethylsilane, tms) and the percentage of conversion (α_c) was calculated from the integration of the polymer and monomer signals. Homodecoupled ^1H NMR spectra were acquired for poly(*rac*-lactide) by selective irradiation of the signal at 1.56 ppm employing the Bruker zgpd pulse sequence. The probability of racemic linkages between monomeric units (P_r) was determined as described by Ovitt and Coates³³ from the equation $P_r = 2I_1/(I_1 + I_2)$, in which I_1 = intensity of the tetrad signals at δ 5.20-5.25 ppm (*sis, sii/iis*) and I_2 = intensity of the signals at δ 5.13-5.20 ppm (*iii/sii, iii, isi*).³³ ^1H NMR spectroscopy was also employed to determine molecular weights of PCL for comparison with size exclusion chromatography data. Experiments were carried out according to previous literature reports.³⁴

Polymerization procedure and kinetic studies

Polymerization reactions of ϵ -caprolactone and *rac*-lactide were carried out varying temperature, reaction time and catalyst/monomer rate. Yields were calculated from the expected mass of products considering 100% of conversion. All experiments were performed at least in duplicate.

Polymerization of ϵ -caprolactone in solution

In a 10 mL Schlenk flask containing a magnetic stirring bar, 1.0 mL of toluene and the desired amount of the initiators were introduced. The resulting solution received the addition of ϵ -caprolactone (1.00 g, 8.76 mmol) and the system was heated to the appropriate temperature for the desired time, after which the solvent was removed under vacuum. The reaction media was then allowed to cool down to room temperature and the product was redissolved in dichloromethane (1 mL) and precipitated with cold methanol (10:1 v/v). The polymeric material was then filtered and dried under vacuum to constant weight.

Polymerization of ϵ -caprolactone and *rac*-lactide in bulk

In an ampoule-type vial, *rac*-LA (1.0 g, 6.94 mmol) and the desired amount of **1** were mixed under N_2 in a small

volume of toluene (3 mL). After the complete evaporation of the solvent, the ampoule was sealed under vacuum and immersed in an oil bath at the required temperatures. For ϵ -CL, 1.0 g (8.76 mmol) of monomer was introduced in a similar tube with the required amount of each initiator (**1** to **4**); the reaction mixture was then heated to the appropriate temperature for the required time. After reaction, the polymers were cooled to room temperature and exposed to the air. The solids were dissolved in dichloromethane, precipitated with methanol (1:10 v/v) and dried under vacuum to constant weight.

Kinetic studies of ϵ -caprolactone in bulk polymerization

Kinetic studies of the bulk polymerization of ϵ -CL were performed by ^1H NMR spectroscopy by quantifying the conversion of monomer to polymers at different reaction times. Reactions were conducted as described above, with 1.0 g (8.76 mmol) of ϵ -CL mixed with $[\text{FeCl}\{\text{Ti}_2(\text{O}^i\text{Pr})_9\}]$ (**1**) in ϵ -CL/**1** ratios ranging from 500 to 1000. After the pre-established time under the desired temperature, an aliquot of the reaction mixture was taken, cooled to 0°C and dissolved in CDCl_3 to be analyzed. The monitored signals of PCL and ϵ -CL were those at 2.31 ppm and 2.64 ppm, respectively, assigned to $-\text{CH}_2$ groups. For comparison, kinetic studies with titanium(IV) isopropoxide ($[\text{Ti}(\text{O}^i\text{Pr})_4]$) (**2**) in ϵ -CL/**2** ratios of 250 and 500 were also conducted. These amounts were chosen because they correspond to the same amount of titanium(IV) present in an ϵ -CL/**1** ratio of 500.

Results and Discussion

Solution polymerization

The initiator $[\text{FeCl}\{\text{Ti}_2(\text{O}^i\text{Pr})_9\}]$ (**1**, Figure 1) was initially investigated for its activity in the solution polymerization of *rac*-LA and ϵ -CL in toluene, with good yields for ϵ -CL even at 30°C . On the other hand, all attempts to run the polymerization of *rac*-LA in similar conditions were unfruitful. The ϵ -CL polymerization reactions were performed with a fixed ϵ -CL/**1** molar ratio of 500, according to a previous report by our research group¹⁶ and varying temperature (from 30 to 90°C) and time (8 to 16 h). Selected reaction results are presented in Table 1 (entries 1 to 9). In the majority of the essays, narrow ranges of molecular weight (M_n) and PDI values were observed; also, M_n values are in good agreement with those calculated by ^1H NMR. Optimum reaction conditions for ϵ -CL polymerizations were found to be 90°C for 8 h. Reactions carried out for 16 h produced polymers similar to those presented in Table 1 (data not shown).

Table 1. Polymerization of ϵ -caprolactone in toluene solution (entries 1 to 9) and in bulk (entries 10 to 17)

entry	ϵ -CL/ 1 ^a	T / °C	time / h	α_c / %	Yield ^b / %	M_n (theoretical) ^c / (g mol ⁻¹)	M_n (¹ H NMR) ^d / (g mol ⁻¹)	M_n (GPC) ^e / (g mol ⁻¹)	PDI ^f	N_n ^g
Blank	–	120	48	3	–	–	–	–	–	–
1	500	30	8	86	77	55928	6280	6900	1.61	8.0
2	500	60	8	99	93	63948	7760	8030	1.61	8.0
3	500	90	8	99	98	63948	9470	9080	1.60	7.0
4	500	30	12	89	66	57640	4570	7740	1.59	8.3
5	500	60	12	99	96	63948	6280	8160	1.60	7.8
6	500	90	12	99	81	63948	7070	8760	1.56	7.3
7	250	90	8	99	89	35098	4100	7000	1.62	5.0
8	1000	90	8	99	89	119846	10670	9600	1.58	12.5
9	1500	90	8	99	99	176365	12600	14390	1.99	12.3
10	500	30	24	90	85	58208	3100	3900	1.77	14.9
11	500	60	1	97	75	62202	7880	7490	1.59	8.3
12	500	90	0.5	98	83	63948	7730	9090	1.53	7.0
13	500	90	1	98	98	62773	8790	8630	1.51	7.3
14	500	120	0.08	99	95	63948	6730	7780	1.55	8.2
15	250	90	0.5	99	80	35098	4400	6800	1.65	5.2
16	1000	90	0.5	99	90	119846	11240	9880	1.65	12.2
17	1500	90	0.5	99	95	176365	18310	6100	2.46	28.9

^aMonomer to initiator molar ratio. The monomer concentration used for solution polymerization was 8.76 mol L⁻¹. Also, initiator concentrations in mmol L⁻¹ were as follows: for ϵ -CL/**1** = 250: 35 mmol L⁻¹; ϵ -CL/**1** = 500: 17.5 mmol L⁻¹; ϵ -CL/**1** = 1000: 8.8 mmol L⁻¹ and ϵ -CL/**1** = 1500: 5.8 mmol L⁻¹; ^byield based on the isolated amount of solid; ^ctheoretical molecular weight calculated from the formula: $[M_{w(\text{CL})} \times (\text{CL}/\mathbf{1}) \times \alpha_c] + 60$ (for the terminal groups); ^daverage molecular weight determined by ¹H NMR; ^eaverage molecular weight determined by gel permeation chromatography (GPC) and multiplied by the correction value of 0.56;³² ^fpolydispersity index determined by GPC; ^gcalculated from $M_n(\text{theoretical})/M_n(\text{GPC})$. It refers to the average number of growing chains *per* molecule of the initiator. Blank = experiment carried out in the absence of **1**.

The increase in the ϵ -CL/**1** ratio from 250 to 3000 showed that this monomer could be quantitatively polymerized even at the lowest concentrations of **1**. As expected, the obtained PCL samples present increasing molecular weights as the ϵ -CL/**1** ratio increases from 250 to 1500; this is due to the larger amount of monomer present in the reaction medium, which leads to longer macromolecules (entries 7 to 9). Even for ϵ -CL/**1** ratios of 2000 and 3000, PCL was obtained quantitatively within the same M_n range; however, the obtained PDI values were higher than 2 and evidenced poor control over the polymerization process in these conditions (data not shown). At low initiator concentrations, the structure of **1** probably breaks down, generating metal alkoxides of different nuclearities that compete for the monomer molecules. Aggregation equilibria are common in alkoxide chemistry, being highly dependent on the chemical nature of the metal center and on the bulk of the alkoxide group. The composition of the equilibrium mixture may vary with alkoxide concentration, temperature and storage time.³⁵⁻³⁷

Once the optimized reaction conditions for ϵ -CL polymerization in solution were established, three more

consecutive additions of the monomer to the initial polymerization reaction mixture were made in 8 h intervals (Table S1 of the Supplementary Information). After the first addition, quantitative conversion of the monomer was again observed and, after purification of the product, its average molecular weight (M_n) increased from 9080 to 15400 g mol⁻¹ without increasing the PDI value (1.60). After the second and third additions, polymers with similar molecular weights (13,000-15,000) and PDI values (ca. 1.5) were isolated, but in lower yields. In fact, the chromatograms of the raw reaction mixtures obtained after the second and third additions of ϵ -CL both contain broad peaks assigned to the monomer. These results suggest that **1** achieves its best performance for the production of PCL after the first addition of monomer and that this is a more efficient procedure than the use of diluted conditions.

ϵ -Caprolactone and *rac*-lactide polymerization in bulk

Polymerizations of ϵ -CL and *rac*-LA employing **1** as initiator were successfully performed in bulk without addition of co-initiators. The experiments were performed

Table 2. Bulk polymerization of *rac*-lactide with complex **1** as initiator

entry	<i>rac</i> -LA/ 1 ^a	Temperature / °C	time / h	α_c / %	Yield ^b / %	M_n (theoretical) ^c / (g mol ⁻¹)	M_n (GPC) ^d / (g mol ⁻¹)	PDI ^e	N_n ^f
Blank	–	130	24	0	0	–	–	–	–
18	250	130	1	96	90	34650	7980	1.49	4.3
19	500	130	0.08	87	76	62760	12180	1.37	5.1
20	500	130	1	95	85	68520	12970	1.37	5.3
21	500	130	2	100	98	72125	14030	1.37	5.1
22	500	160	1	96	85	69240	13090	1.37	5.3
23	750	130	1	93	82	100590	14350	1.32	7.0
24	1000	130	1	75	68	108160	14270	1.30	7.6
25	1000	130	2	84	78	121130	14980	1.31	8.1

^aMonomer to initiator molar ratio. Initiator concentrations in mmol L⁻¹ were as follows: *rac*-LA/**1** = 250 (27.7 mmol L⁻¹), *rac*-LA/**1** = 500 (13.9 mmol L⁻¹), *rac*-LA/**1** = 750 (9.3 mmol L⁻¹), *rac*-LA/**1** = 1000 (6.9 mmol L⁻¹); ^byield based on the weight of isolated solid; ^ctheoretical molecular weight calculated from the formula: $[M_{w(LA)} \times (LA/I) \times \alpha_c] + 60$ (for the terminal groups); ^daverage molecular weights determined by GPC, considering the correction value of 0.58; ^epolydispersity index calculated from GPC data; ^fcalculated from $M_n(\text{theoretical})/M_n(\text{GPC})$. It refers to the average number of growing chains per molecule of the initiator. Blank = experiment carried out in the absence of **1**.

from 30 to 120 °C for ϵ -CL and 130 to 160 °C for *rac*-LA, by varying time (5 to 60 min) and monomer/initiator molar ratio (Table 1, entries 10 to 17, for ϵ -CL, and Table 2 for *rac*-LA). The temperature ranges were established as a function of the melting point of the monomers (–1 °C for ϵ -CL and 125–127 °C for *rac*-LA).

Polymerization essays with ϵ -CL in bulk have demonstrated a more expressive dependence on temperature than in solution. As an example, at 30 °C with an ϵ -CL/**1** ratio of 500, an oligomer was the only product obtained, even after 24 h of reaction (Table 1, entry 10). This low activity observed at room temperature could be related to the energy required to the first monomer insertion. Quantitative yields and higher molecular weight polymers were obtained when the reaction was conducted at 90 °C for 30 min (entry 12), suggesting that the higher activity of **1** could be related to its melting point of 68.4 °C as determined by DSC analysis, which favors a homogeneous reaction medium or even some thermal activation of the initiator. Similarly to the observed in solution, the control over the polymerization process in bulk showed to be highly dependent on the concentration of **1**, being poor at an ϵ -CL/**1** ratio of 1500 (entry 17). In this case, a broad molecular weight distribution indicated that undesired transesterification reactions took place. In contrast to the results obtained in solution, the reactions carried out in bulk showed decreased M_n values for an ϵ -CL/**1** ratio of 2000 and no activity was observed at an ϵ -CL/**1** ratio equal to 3000 (data not shown).

Reactions of *rac*-LA conducted with a monomer/initiator ratio of 500 at 130 °C showed that **1** is able to produce PLA with an M_n of ca. 14000 g mol⁻¹ and a PDI

value of 1.37; this reaction gives quantitative yield in 2 h. For *rac*-LA/**1** ratios of 500 and 1000, the reaction time has a stronger influence in reaction yield than in the final molecular weight or PDI values, evidencing a better controlled polymerization process than the observed with ϵ -CL. The *rac*-LA/**1** ratio of 750 was found to be the best proportion considering reaction time, temperature and final molecular weight. As far as reaction temperature is concerned, essays performed at a higher temperature, for instance 160 °C, produced polymers with similar GPC data as compared with 130 °C. This result is equivalent to those reported for the trinuclear $[\text{Ti}_3(\text{O}^i\text{Pr})_{11}]^+$ cation in similar reaction conditions,¹⁶ in which the advantage of the trinuclear species over other polynuclear titanium(IV) alkoxides such as $[\text{Ti}_4(\text{toeed})(\text{O}^i\text{Pr})_{12}]$ (toeed = tetrapodal *N,N,N',N'*-tetrakis(2-hydroxy-ethyl)ethylenediamine) and $[(\text{MeC}(\text{CH}_2-\mu_3\text{-O})(\text{CH}_2-\mu\text{-O})_2)_2\text{Ti}_4(\text{O}^i\text{Pr})_{10}]$ consists in a lower molecular weight distribution of the PLA product.^{14,38}

Polymerization mechanism

¹H NMR analysis of PCL and PLA samples obtained in this work confirmed that the ROP reaction proceeded through the coordination/insertion mechanism for both monomers. The comparison between the ¹H NMR spectra of ϵ -CL and PCL revealed a shift of the resonance peaks assigned to the methylene groups directly bound to the ester carbonyl groups (Figure S2 of the Supplementary Information), which were found at 2.6 and 4.3 ppm for the monomer and 2.3 and 4.1 ppm for the polymers. Low intensity signals at 1.2, 5.0 and 3.7 ppm were assigned to the hydrogen atoms of terminal isopropyl groups, $(\text{CH}_3)_2\text{CH}$,

(CH₃)₂CH and HOCH₂, respectively, whose presence is largely accepted as an evidence for the ring opening polymerization mechanism.³⁹ In turn, the ¹H NMR spectra of PLA showed signals at 1.56 and 5.17 ppm assigned to the methylic and methinic hydrogens of the polymer (Figure S3 of the Supplementary Information). As observed for PCL, the obtained PLA molecules contain isopropyl ester as end groups, as shown by low intensity signals at 1.25 and 4.36 ppm, attributed to the (CH₃)CH- and (CH₃)₂(CH)O hydrogens.

On the polynuclearity of **1** and the nature of the active species

The molecular weights of PCL and PLA shown in Tables 1 and 2 are not in agreement with the expected theoretical values, M_n (theoretical), calculated for an intact molecule of **1** acting as initiator. This suggests the occurrence of transesterification during the polymerization reaction and indicates that the nine alkoxide groups and the terminal chloride present in **1** were not equally able to initiate polymer chains. The literature has demonstrated that terminal and bridging alkoxide have different activities⁴⁰ for polymerization of ϵ -CL and *rac*-LA, while the activity of halide ligands (chloride, in this case) is not well established. One of the few studies developed applying titanium(IV) complexes with adamantoxo and borneoxo ligands suggest that the reactivity of the ligand groups follow the order alkoxide > alkyl > halide.⁴¹

The identity of the active species in the reaction mixture was tentatively investigated by the estimation of the $M_n(\text{theoretical})/M_n(\text{GPC})$ ratio (N_n), which accounts for the number of isopropoxide groups available to initiate new chains in the ROP of each monomer. At the most controlled ϵ -CL polymerization conditions, both in solution and bulk (entries 3 and 12, Table 1), the calculated N_n values are close to seven growing chains of PCL *per* molecule of **1**, which could correspond, in the structure of **1**, to four terminal ($-\text{O}^i\text{Pr}$) and three bridging ($\mu_2-\text{O}^i\text{Pr}$) active groups (see Figure 1). These results agree with early reports pointing to the following relative order of alkoxide activities in ROP processes: $-\text{O}^i\text{Pr} > \mu_2-\text{O}^i\text{Pr} > \mu_3-\text{O}^i\text{Pr}$.^{40,42} In fact, if seven active isopropoxide groups *per* molecule of **1** are considered together with the results shown in Table 1 for PCL, the resulting range of calculated $M_n(\text{theoretical})$ values, 7890 to 9130 g mol⁻¹, is close to the experimental M_n range obtained in this work from both GPC and ¹H NMR analyses. As far as the concentration of **1** is concerned, in more diluted media N_n values become higher than nine, the total number of alkoxide groups in **1** (entries 8, 9, 16 and 17, Table 1), reflecting a higher number of back-biting

reactions for both bulk and solution polymerization of ϵ -CL. This outcome reinforces the hypothesis that diluted media favors the establishment of an equilibrium between different nuclearity alkoxide species in solution, which are all capable to initiate ϵ -CL polymerization and give rise to an unknown number of coordinating sites.

This kind of aggregation/disaggregation equilibrium was observed earlier in the polymerization of ϵ -CL and lactides initiated by Al(O^{*i*}Pr)₃,⁴² La(O^{*i*}Pr)₃,³² and, more recently, by the [Ti₃(O^{*i*}Pr)₁₁]⁺ cation.²⁸ For all initiators, the number of active alkoxides capable to initiate ROP process varied with monomer nature and initiator concentration.⁴³ The dependence on the concentration of **1** was clearly observed in Table 2 and Figure 2, for example, when the *rac*-LA/**1** ratio was gradually increased from 250 to 1000 and supposedly a higher number of catalytic sites was made available to produce growing chains. At a first glance, this monomer shows an opposite tendency to that observed for ϵ -CL in both bulk and solution polymerizations, that is, N_n varying from 4.3 to 8.1. Despite this, better PLA (higher molecular weight and lower PDI) was obtained exactly in the same N_n range (7 to 8) in which better PCL was also produced in both bulk and solution reactions. As this N_n range can be tentatively associated with the intact molecule of **1** performing as the active polymerization species, this result indicates that the trinuclear structure of **1** resists better to disaggregation in *rac*-LA than in ϵ -CL media and suggests that this trinuclear species is indeed the responsible for the best polymerization results obtained in this work.

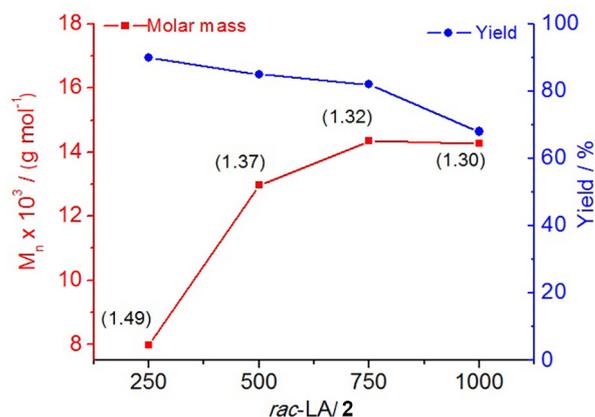


Figure 2. Variation of M_n and reaction yields for the production of PLA as a function of monomer/**1** molar ratio at 130 °C. PDI values are presented in brackets.

ROP activity of **1** compared to other titanium(IV) and iron(II) complexes, with ϵ -CL as a model monomer

In an attempt to explain the role of the two metal ions and of the ligands present in **1** in the ROP of ϵ -CL, three soluble

complexes of titanium(IV) or iron(II) were employed as possible initiators in reaction conditions similar to those applied to **1**: (i) the mononuclear $[\text{Ti}(\text{O}^i\text{Pr})_4]$ (**2**), chosen due to its well-known activity towards polymerization of ϵ -CL and lactides;¹² (ii) the tetranuclear complex $[\text{Fe}_4\text{Cl}_8(\text{thf})_6]$ ³⁰ (**3**), which contains tetrahydrofuran (thf) as neutral ligand, together with terminal and bridging chlorides; and (iii) the mononuclear iron(II) complex *trans*- $[\text{FeCl}_2(\text{Pr}^i\text{OH})_4]$ ³¹ (**4**), which possesses two chlorides and four isopropanol ligands (Figure S1 of the Supplementary Information). Besides them, anhydrous FeCl_2 was also tested for its activity towards the same reaction. Isopropanol is largely applied as co-initiator of ROP because it potentially produces alkoxide groups *in situ* to activate the metal site, whereas thf is considered a non-reactive ligand.

Experiments with $[\text{Ti}(\text{O}^i\text{Pr})_4]$ (**2**) were carried out in bulk, for 30 min to 24 h, in the temperature range of 30–120 °C. The ϵ -CL/**2** ratio was fixed at 250 because it corresponds to the same amount of titanium(IV) centers present in the ϵ -CL/**1** ratio of 500 (Table S2 of the Supplementary Information). PCL molecules produced with **2** as initiator had molecular weights ranging from 7210 to 7900 g mol^{-1} with PDI values from 1.49 to 1.68. The obtained N_n values, close to 4, were compatible with the mononuclear nature of **2** in the reaction conditions employed in this work. Based on GPC data, alkoxides **1** and **2** showed a similar behavior towards the ROP of ϵ -CL, as the isolated polyesters were comparable in M_n and PDI values, with a small advantage in favor of **1** when the reaction was conducted at 90 °C for 30 min (higher molecular weight and lower PDI). In many systems, polymers obtained with heterometallic initiators usually show a broader molecular weight distribution compared to those produced with homometallic complexes, probably due to the different activities of the distinct metal centers. In this context, our results suggest that both titanium(IV) and iron(II) centers show similar ROP activities towards ϵ -CL, or alternatively that only one of the metal ions actually contribute to the growth of the polymer chains.

In order to probe the reactivity of iron(II) towards the polymerization of ϵ -CL and compare the results with those given by **1** in similar reactions conditions, complexes **3** and **4** were tested both in bulk and in toluene solution. They revealed poor activities to promote the ROP reaction in the same ϵ -CL/initiator ratio employed for **1**. Small activity was observed only for complex **4** in toluene solution with an ϵ -CL/**4** ratio of 500 at 90 °C for 20 h, producing an oligomer ($M_n = 1690 \text{ g mol}^{-1}$) in low yield (20%). Anhydrous FeCl_2 was tested in bulk at 120 °C *per* 1 h, with an ϵ -CL/ FeCl_2 ratio of 500. However, this reaction did not lead to any monomer consumption. On the other hand, the literature

reports the use of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as ROP initiator with ϵ -CL,⁴⁴ in which case an addition of alcohol (co-initiator) is made to allow the *in situ* formation of an Fe–OH bond that attacks the carbonyl group of ϵ -CL. This opens the ring and then forms an alkoxide that initiates the polymerization process. Even so, products obtained with this initiator presented low molecular weights and broad PDI ranges from 1.41 to 2.15. In the present work, the addition of isopropanol to **4** (ϵ -CL/**4** ratios of 250 to 2000) produced solids in the low molecular weight range of ca. 1000 g mol^{-1} (Table S3 of the Supplementary Information). The improvement in yield (85%) and PDI values close to 1.0 obtained with this initiator, as compared to the results given by $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, is possibly related to the existence of only one active species in the solutions of **4**, while a mixture of active $\text{Fe}(\text{H}_2\text{O})_m(\text{OH})_x$ species is probably present in hydrated iron(II) chloride solutions.⁴⁴

It has been reported recently that the complex $[\text{Fe}(\text{bppyH}_2)\text{Cl}_2]$ ($\text{bppyH}_2 = 2,6\text{-di}(1H\text{-pyrazol-3-yl})\text{pyridine}$) showed to be completely inactive towards the ROP of ϵ -CL, even after addition of alcohol, while the correspondent iron(III) complex was a suitable pre-catalyst in the same reaction conditions.⁴⁵ All these reports reinforce the possible low activity of the terminal iron(II)–Cl bond in **1** and suggest that any activity of the iron(II) center in this initiator would only come from the bridging alkoxides.

While the chemistry of iron(III) alkoxides has been more frequently investigated, and the existence of well documented examples of controlled polymerization of cyclic esters by these complexes to produce high molecular weight polymers is long known,^{25,46} investigations with iron(II) compounds are rare and only few of them have been successfully tested in their ability to promote ROP.^{24,27} High activity of iron(II) homometallic alkoxides for ROP of lactides has been reported only for iron in low coordination environments provided by bulky ligands.²⁵ In the case of the five coordinated iron(II) center in **1**, which would present one vacant coordination site for binding the monomer, there is no clear evidence of reactivity or even of the maintenance of this coordination environment in solution. In this context, our polymerization results agree with earlier reports and point to the idea that the iron(II) reactivity in **1** could be due to the presence of the bridging alkoxides.

Kinetic studies of ϵ -CL bulk polymerization

Lactides and lactones undergo similar ROP processes via coordination-insertion mechanism. Our interest in examining the kinetics of the reaction of **1** with ϵ -CL comes from the need for additional evidences on the real composition of the reaction mixtures during

polymerization. These studies were not carried out with *rac*-lactide because of the difficulties created by the high reaction temperature and high viscosity of the reaction medium, as reported earlier by our research group.¹⁶ Also, our kinetic studies with ϵ -CL were performed only in bulk, to avoid misinterpretation of the results caused by the presence of toluene signals in the ^1H NMR spectra. The reaction conditions employed were an ϵ -CL/**1** ratio equal to 500 and a temperature range of 90–130 °C, which provided polymers with M_n values similar to those presented in Table 1.

The polymerization process was very fast, reaching conversions up to 90% in 7 minutes at 110 °C and in only 2 min at higher temperatures (Figure 3a). To bring light into the kinetic behavior of **1** in these reaction conditions, a comparative experiment was carried out with $[\text{Ti}(\text{O}^i\text{Pr})_4]$ (**2**), employing an ϵ -CL/**2** ratio of 250 (Figure S4 of the Supplementary Information). Plots of $\ln(1-\alpha_c)$ for **1** and **2** as a function of time are shown in Figure 3b and Figure S4b of the Supplementary Information, respectively. In both cases, the polymerization processes were shown to be

first-order in monomer concentration, affording the apparent propagation rate constants (k_p) summarized in Table 3. There is an induction time of about 1 min, probably determined by the time required for coordination of the monomer to the active sites. Comparison of the rate constants obtained for **1** at 90, 120 and 130 °C reveals that the reaction is 17 and 26 times faster, respectively, at the highest two temperatures, while the same comparison involving 90, 100 and 110 °C shows reaction rates that are only 1.8 and 3.1 times higher, respectively (Table 3). Reactions with initiator **2**, in turn, gave less abrupt variation of k_p with temperature, being only 10 times faster at 130 °C than at 90 °C. Additionally, the k_{p2}/k_{p1} ratio changes remarkably above 110 °C. These facts reveal a significant kinetic change in the reaction promoted by **1** above 110 °C, which could be associated to the breakage of the trinuclear structure of **1** to give lower nuclearity species in ϵ -CL medium.

Table 3. Apparent propagation rate constants (k_p) for the ROP of ϵ -CL with $[\text{FeCl}(\text{Ti}_2(\text{O}^i\text{Pr})_9)]$ (**1**) or $[\text{Ti}(\text{O}^i\text{Pr})_4]$ (**2**) as initiators

Temperature / °C	k_p / min^{-1} (ϵ -CL/ 1 = 500)	k_p / min^{-1} (ϵ -CL/ 2 = 250)	k_{p1}/k_{p2}
90	0.168	0.605	3.6
100	0.304	1.483	4.9
110	0.525	2.177	4.1
120	2.903	3.993	1.4
130	4.463	6.053	1.4

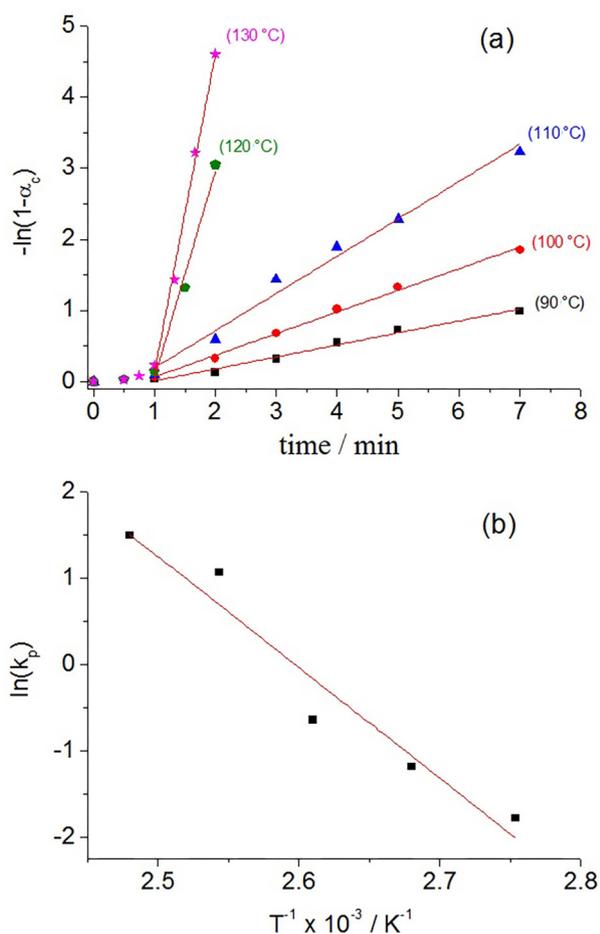


Figure 3. First order plot for ϵ -CL consumption initiated by **1** at different temperatures (ϵ -CL/**1** molar ratio of 500) in (a). In (b) $\ln(k_p)$ versus $1/T$ plot obtained from kinetic data gathered for **1**.

The activation energy (E_a) required for ϵ -CL polymerization with initiator **2** (65.7 kJ mol⁻¹), obtained from a plot of $\ln(k)$ as a function of T^{-1} (Figure S4 of the Supplementary Information), is close to values reported for $[\text{Ti}(\text{OPr}^n)_4]$ (42.0 kJ mol⁻¹),⁴⁷ $[\text{Ti}(\text{OCH}_2\text{CCl}_3)_4]$ (70.0 kJ mol⁻¹),³⁴ and the trinuclear $[\text{Ti}_3(\mu_3\text{O}^i\text{Pr})_2(\mu\text{O}^i\text{Pr})_3(\text{O}^i\text{Pr})_6][\text{FeCl}_4]$ ¹⁶ (35 kJ mol⁻¹), respectively. Unfortunately, in the case of **1**, the kinetic complexity of the system has prevented the determination of a reliable value of E_a for data in the whole temperature range employed in this work, from 90 to 130 °C. For temperatures below 120 °C, an E_a value of approximately 100 kJ mol⁻¹ was obtained, which lies in the range reported for other titanium(IV) alkoxides in similar reaction conditions.

Characterization of the polymers

Powder X-ray diffractograms of the PCL samples produced in this work showed high intensity peaks, typical of the crystalline portion of the polymer chains,⁴⁸ at 2θ values equal to 21.6 and 23.9°, and smaller peaks at 15.8° and in the region ranging from 30 to 50° (Figure S5

of the Supplementary Information). On the other hand, diffractograms of PLA were predominantly amorphous (Figure S6 of the Supplementary Information). All these results are in accordance with data obtained by homonuclear decoupled ^1H RMN analysis (Figure S7 of the Supplementary Information). The spectra displayed five methyne resonances in the range of 5.10-5.25 ppm, typical of the stereosequences *isi*, *sis*, *iii*, *iis* and *sii*, which are known to hamper the orientation of polymer chains in crystalline domains.⁴⁹ The probability of occurrence of racemic linkages between *rac*-LA monomers (P_r) was 0.55, which is slightly higher than the commonly accepted value for atactic polymers.⁴⁹ It is, however, in the range (0.50 to 0.56) reported for other titanium(IV) alkoxides, including $[\text{Ti}(\text{O}^i\text{Pr})_4]$ and polynuclear complexes containing piperazine and four or more isopropoxide ligands.⁵⁰ Stereospecific polymerization of *rac*-lactide was not observed in this work, reflecting that not only transesterification, but also cyclization and back biting probably occur during polymerization.

Results of DSC analyses were compatible with the expected for PCL polymers (Figure S8 of the Supplementary Information). In DSC curves, all ϵ -PCL samples showed to be semicrystalline (49 to 58%), presenting a single fusion peak. The melting temperature (T_m) in the range of 55.9 to 57.5 °C and a glass transition temperature (T_g) of -64.1 °C are in accordance with data reported for polymers of similar molecular weights described in the literature.⁵¹ In turn, DSC analysis performed for products obtained from *rac*-LA showed similar thermal behavior for all samples. DSC curves confirmed the amorphous nature of PLA by the absence of T_m and T_c . The value of T_g increases from 43.3 to 48.2 °C following the increase in M_n values from 7900 to approximately 14000 g mol⁻¹; this is in accordance with values reported in the literature.⁵²

The molecule of initiator **1** contains metal centers, iron(II) and titanium(IV), that are EPR silent when analysed in the X-band. However, EPR studies of the polymeric products performed at 77 K revealed the presence of residual iron(III) in both polymers, probably formed during the precipitation of the products under air. EPR spectra of PLA and PCL are typical of high spin iron(III) ($S = 5/2$) in rhombic ($g = 4.3$) and axial ($g = 2.0$) environments (Figure 4).⁵³ This spectral pattern is compatible with those reported for oxides and oxo-hydroxides of iron(III) and can be assigned as follows: the signals at $g = 4.3$ are due to isolated iron(III) species and the peak at $g = 2.0$ arises from oxide-bound or oxo-hydroxo iron(III) in which ions interact magnetically with each other.⁵⁴ After one step of purification, the signal at $g = 2$ disappeared from the EPR spectra of PLA, but a weak signal at $g = 4.3$ remained even after two consecutive reprecipitation steps, suggesting that

the rhombic iron(III) centres are trapped in the polymeric matrix. From the bulk polymerization of ϵ -caprolactone, pure PCL, that is, without contamination with iron(III), was obtained after the first purification step, due to an easy leaching of this metal ion from the polymeric matrix (Figure S9 of the Supplementary Information).

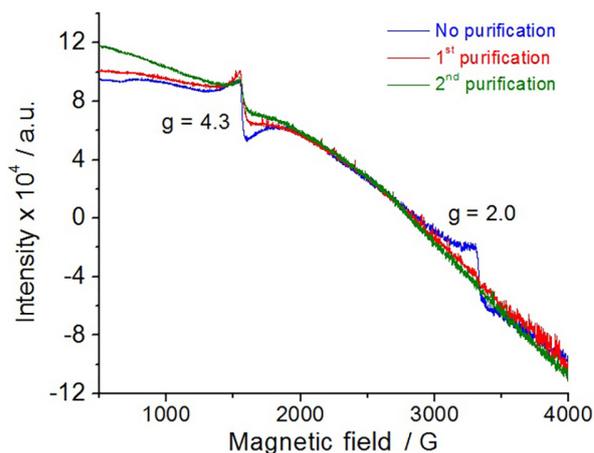


Figure 4. X-Band EPR spectra of PLA at 77 K prepared with **1** as initiator.

Conclusions

In the present work, the heterometallic titanium(IV)/iron(II) alkoxide **1** was employed as an initiator in the ROP of ϵ -CL and *rac*-lactide, producing polymers within a molecular weight range expected for titanium(IV) alkoxides. In spite of the complexity of titanium(IV) alkoxide chemistry in solution, which often contributes to a substantial degree of uncertainty in identifying the catalytically active species, our results suggest that initiator **1** is the main responsible for the ROP of both monomers at the optimized conditions described in this work.

With ϵ -CL polymerization as a model, it was possible to identify a small, but systematic, improvement in polymer characterization parameters for **1** in relation to mononuclear $[\text{Ti}(\text{O}^i\text{Pr})_4]$ as initiator, probably due to a small electron-withdrawing effect of the iron(II) ion towards titanium(IV) through the bridging alkoxide ligands. These results are in accordance with the intermediary Pearson hardness of iron(II) centers and suggest that other first-row transition metals harder than iron(II), or even lanthanides, could improve the activity of the $[\text{MX}_n\{\text{Ti}_2(\text{O}^i\text{Pr})_9\}]$ trinuclear framework. The poor reactivity of the terminal chloride ligand present in **1** has probably helped in avoiding competition between the two different metal ions for the monomer and also probably improved the activity of the initiator by a cooperative effect of the two metals through the alkoxide bridges.

As for the alkoxide ligands, the estimate of the average number of growing chains *per* molecule of initiator points

to systematic higher values of N_n for ϵ -CL (7 to 8) than for *rac*-LA (4 to 5). Such N_n values are in agreement with the better control over polymerization observed for *rac*-LA, probably due to a reduced number of active alkoxide sites. On the other hand, for ϵ -CL, both bridging and terminal alkoxides were active initiating groups, giving a higher number of sites able to grow polymer chains.

Even though **1** did not promote a living polymerization process, it was possible to increase the M_n of PCL in solution polymerization without increasing PDI values. Also, complex **1** could be explored as an initiator of block co-polymerization, especially with lactide as comonomer.

Supplementary Information

Supplementary data associated with this article can be found online at <http://jbcbs.sbq.org.br>.

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