Research article

Copolymerization of L-Lactide and ε-Caprolactone promoted by zinc complexes with phosphorus based ligands

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ABSTRACT

The zinc complexes **1** and **2** bearing chelating phosphorous based pincer ligands were found to catalyze the ring-opening copolymerization of L-lactide and ε-caprolactone in the melt at 110 °C to obtain a series of random copolymers in which the monomer distributions were coherent with the monomer ratio in the feed. All the obtained copolymers showed high molecular masses with monomodal and moderately narrow distributions. The thermal properties of the achieved copolymers (T_g, glass transition temperature, and T_m, melting temperature) were strongly dependent on their composition. A linear dependence of T_g with molar percentage of lactide in the copolymers was observed over a temperature range from -59 °C (pure polycaprolactone) to 55 °C (pure polylactide).

1. Introduction

Poly (ε-caprolactone) (PCL) and poly (L-lactide) (PLLA) are biocompatible and bioresorbable polymers and, thanks to these properties, they are among the most valuable synthetic materials used in biomedical and pharmaceutical applications (Graulus et al., 2016). Biodegradable sutures, artificial skin, resorbable prostheses, and controlled drug release systems are some examples of the most common applications of these materials.

However, the functional parameters of such polymers, such as mechanical and thermal properties, permeability, and their degradation profiles (biologic or hydrolytic), differ considerably (L. S. Nair and Laurencin 2007). PCL has good thermal properties and shows high elasticity but poor mechanical strength, its efficient drug permeability and slow degradation rate make it suitable for durable applications (Cama et al., 2017). Differently, PLA displays good mechanical properties and shorter degradation times but it lacks elasticity because of its high glass transition temperature (above body temperature) (Hamad et al., 2015).

Therefore, the synthesis of copolymers of these monomers with different compositions and microstructures (block, gradient, or random) represents a good strategy to modulate their thermal properties, biodegradation behavior, and drug permeability (Huang et al., 2006) (Dalmoro et al., 2014; Deokar et al., 2016; Zhang et al., 2018) and thus to extend the use of these materials.

For medical applications where elasticity and degradability are required at the same time, CL/LA random copolymers, displaying an elastomeric character, are materials useful for the regeneration of soft tissues such as cardiac tissue. For example, for this application a good flexibility of the material is required to transfer, effectively and synchronically, the myocardium contraction and the mechanical stimulus from the myocardial microenvironment to the incorporated cells (Park et al., 2005; Jin et al., 2009).

The most efficient synthetic method for producing homo- and copolymers of CL and LA is the ring-opening polymerization (ROP) (Sutar et al., 2015; Fuoco and Pappalardo 2017; Santoro et al., 2020) (Gallegos et al., 2015; Strianese et al., 2020) of the corresponding cyclic esters and of their mixture (Li et al., 2014; Wang et al., 2014) by using coordination complexes of several metals as initiators.

Generally, although the homopolymerization rate of CL is significantly higher than that of LA (Phomphrai et al., 2010; Chumsaeng et al., 2019), in the copolymerization reactions the net reactivities of these comonomers are inverted (Chandanabodhi and Nanok 2017) therefore block or gradient copolymers are generally produced within a polylactide block is firstly formed. Nevertheless, random copolymers may be obtained as a result of side transesterification reactions which partially randomize the original copolymer composition (Kasperczyk and Bero 1993; Dakshinamoorthy and Peruch 2012; Webster et al., 2013).

In the literature, some well-characterized metal initiators are reported to directly promote the random copolymerization of LA and CL. The most important examples are metal complexes of aluminum (Florczak and Duda 2008; Pappalardo et al., 2009; Nomura et al., 2010; Li et al., 2012; Pilone et al., 2015; Zhang et al., 2017; Shi et al., 2018; Chumsaeng et al., 2019; Garcia-Valle et al., 2020), yttrium (Hu, Wang et al.; Shen et al., 1996; Florczak and Duda 2008; Fadlallah et al., 2017), titanium (Wei et al., 2009; Dakshinamoorthy and Peruch 2012; Lapenta et al., 2015; Santoro and Redshaw 2020; Sun et al., 2020) or zinc (Darensbourg and Karroonnirun 2010) often bearing phenoxy-based ligands.

For biomedical applications, the use of catalysts based on biocompatible metals is a crucial aspect since residues of the initiator can contaminate the obtained material (Wang et al., 2012; Gallegos et al., 2013; Xie et al., 2014; Garcia-Valle et al., 2015; D'Auria et al., 2017; Liu et al., 2018; Liu et al., 2021).

We have reported the synthesis and the use of several metal complexes bearing uncommon phosphido pincer ligands as efficient initiators for the ring-opening polymerization of ε-caprolactone, L- and *rac*-lactide producing polymers with controlled macromolecular parameters (M_n, end groups) and low dispersities(Mazzeo et al., 2010; D'Auria et al., 2011; D'Auria et al., 2012; D'Auria et al., 2014). Preliminary investigations regarding zinc complexes showed that these represent promising candidates for the production of random copolymers of L-lactide and ε-caprolactone (D'Auria et al., 2012). In this paper we report the synthesis of copolymers of lactide and ε-caprolactone with different compositions. The obtained copolymers have been characterized by ^{1}H and ^{13}C NMR spectroscopy, by Differential Scanning Calorimetry (DSC) measurements, and by X-ray diffraction.

2. Results and discussion

2.1. Synthesis and characterization of the zinc metal complexes

The pro-ligands **L₁-H** and **L₂-H** have been synthesized following previously published synthetic procedures (Mankad et al., 2005; Whited et al., 2006). Complex **2** was synthesized with the same method used for complex **1**, by direct reaction of the zinc amide precursor with one equivalent of the neutral pro-ligand (Figure 1) in toluene solution at high temperature (D'Auria et al., 2012). The analytically pure complex **2** was obtained, in almost quantitative yield, after removal of the solvent and of the produced amine under reduced pressure. Homopolymerization Studies. Ring-Opening of ε-caprolactone and L-lactide.

The ^{1}H NMR spectrum of complex **2**, performed at room temperature, showed very large resonances for the signals of the aliphatic region (Figure S1 of the SI). In the spectrum registered at 50 °C (Figure S2 of the SI), sharper signals were detected that indicated the formation of a symmetric complex in which the pincer ligand and one amido group were coordinated at the metal centre with a mirror plane that includes the anionic phosphide donor, the zinc, and the silylamido group.
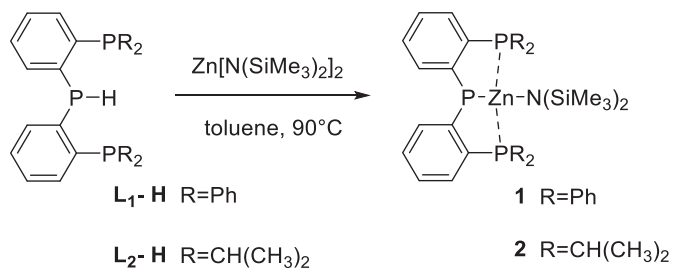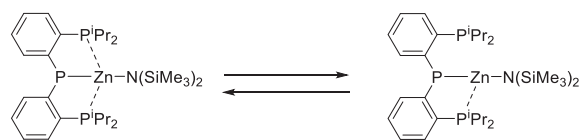

Figure 2. Fluxional behavior of the zinc complex **2**.

In the aliphatic region of the spectrum, a single sharp signal at 0.48 ppm was observed for the protons of the amide group, that was shifted downfield with respect to that of the Zn(N(SiMe₃)₂)₂ precursor (0.21 ppm). One resonance for the methine protons (at 2.02 ppm) and two doublets for the diasterotopic methyl protons of the isopropyl groups (at 1.01) ppm were also present. The ^{31}P{^{1}H} NMR spectrum displayed two signals: a doublet at δ = 0.92 ppm, corresponding to the neutral phosphorous donors and a triplet, at δ = -61.24 ppm, for the anionic phosphorous that resulted relatively upfield as compared to that of the corresponding proligand.

In the ^{13}C NMR spectrum (Figure S3 of the SI), two broad signals for the methine *C*H carbons, and two resonances for the methyl carbons *C*H₃ of the isopropyl groups were evident.

All the NMR data for complex **2** suggest the same picture already described for complex **1** in which the central metal is coordinated to the tridentate monoanionic phosphido pincer ligand for which both neutral phosphine atoms are coordinated to the zinc. The fluxional behavior observed on the NMR time scale could be a consequence of a fast equilibrium between the symmetric tetracoordinate species and the tricoordinate one derived by a reversible dechelation of one of the two phosphine arms of the chelanting ligand (Figure 2).

2.2. Homopolymerization Studies. Ring-Opening of ε-caprolactone and L-lactide

We previously reported the phosphido pincer complex **1** (Figure 1) as active initiator in the ring-opening polymerization (ROP) of ε–caprolactone, L- and *rac*-lactide providing polymers with the expected molecular weights and with low dispersities (D'Auria et al., 2012).

As previously described, in the presence of added alcohol (^{i}PrOH) as cocatalyst, complex **1** showed a moderate activity in the ROP of ε–caprolactone (Figure 3) that increased significantly with the reaction temperature (cf run 1 and run 2 in Table 1) (D'Auria et al., 2012). In the ROP of lactide, under the same polymerization conditions, a higher activity was achieved (cf. run 1 vs run 4 in Table 1).

In this paper we extend our studies to an analogous phosphido zinc complex bearing isopropyl groups on the ligand skeleton (complex **2**, see Figure 1).

The zinc complex **2** showed catalytic activities towards the two monomers comparable to those achieved with complex **1** (compare runs 2 and 4 respectively with runs 3 and 5 of Table 1) thus, the structure of the substituents does not seem to have any influence on the productivity.
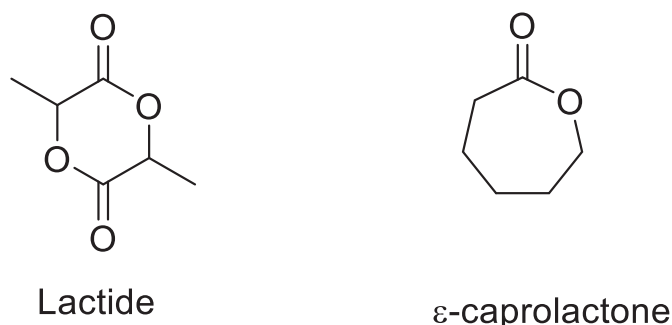

Figure 1. Structures of PPP-H proligands and synthesis of the zinc complexes **1** and **2**.

Figure 3. Cyclic esters investigated in this paper.

Table 1. Ring Opening Polymerization of ε-CL and L-LA by **1** and **2**.

Run[a]	cat	Monomer	T (°C)	Time[b] (min)	Yield (%)	M_n^c GPC (KDa)	Đ[c]	M_n^d th (KDa)
1	1	ε-CL	25	480	100	9.1	1.11	11.4
2	1	ε-CL	50	100	98	13.8	1.19	11.4
3	2	ε-CL	50	100	97	38.5	1.13	11.4
4	1	L-LA	25	20	91	8.8	1.05	13.1
5	2	L-LA	25	20	97	30.0	1.10	13.9

[a] All reactions were carried out with $[Zn]_0 = 5$ mM, $[^iPrOH] = 10$ mM and $[\varepsilon$ -CL or LA$] = 1$ M in toluene (2 mL).
[b] Reaction time was not necessarily optimized.
[c] Experimental M_n (corrected using the factor of 0.56 for PCL and 0.58 for PLA) and Đ values were determined by GPC analysis in THF using polystyrene standards.
[d] Calculated M_n of PCL (in gmol^{-1}) = 114,13 x ([ε-CL]/[^iPrOH]) x conversion ε-CL; M_n of PLA (in gmol^{-1}) = 144,14 x ([L-LA]/[^iPrOH]) x conversion L-LA.

On the other hand, a significant difference emerged about the experimental molecular weights of the obtained polymers, since, when **2**/^iPrOH was used as the catalytic system, they were significantly higher than the theoretical values. However, in all cases, the obtained polymers show narrow dispersities, Đ ≤ 1.19. In MALDI-ToF analysis (Figure 4) of a low molecular PLA sample the expected chain end groups were evident.

The discordance between the experimental Mn values and the theoretical ones may suggest a scarce efficiency in the initiation step of complex **2** or the formation in the reaction mixture of inactive homoleptic species, reasonably produced by ligand-exchange reactions, in analogy with that observed for complex **1**. The formation of homoleptic species was much faster for complex **2** (after 2 h at RT) than for complex **1** This may be favored by the different structure of the ancillary ligand.

Both catalysts showed an unusual behavior: a marked preference for lactide than caprolactone. Although for the most metal catalysts the polymerization of ε-CL is faster than that of lactide, some examples of zinc complexes for which an opposite reactivity is observed have been reported (Chai et al., 2005; Chen et al., 2005; Darensbourg Donald and Karroonnirun, 2010). Considering that LA is a more sterically encumbered monomer than CL, its higher reactivity might be attributed to a higher coordination ability because of the presence of two carboxyl groups. Another plausible explanation is the higher stability of the primary alkoxidic chain resulting after the insertion of a caprolactone unit which should bind to zinc more strongly than the secondary alkoxidic chain derived from ring-opening of lactide, thereby resulting in a slower polymerization process (Pang et al., 2005; Darensbourg and Karroonnirun 2010; D'Auria et al., 2017).

2.3. Copolymerization of L-Lactide and ε-Caprolactone

As described in the previous paragraph, the zinc complexes **1** and **2** were efficient catalysts for both the ROP of lactides and ε-caprolactone. In the investigated reaction conditions, complex **1** showed a better control of the molecular weights, thus it was selected to investigate the copolymerization of these monomers. Polymerizations were undertaken in the absence of solvent, at 110 °C, with different molar ratios of L-lactide and ε-caprolactone and by adding three equivalents of isopropanol. The presence of more than one equivalent of alcohol, in so called "immortal" conditions (Li et al., 2014), increases the productivity of the catalytic system making more than one polymer chain for metal centre. The copolymers obtained were characterized by ^1H and ^{13}C NMR, GPC, and DSC. The main results are reported in Table 2.

The monomer and isopropanol amounts were chosen to obtain polymers with molecular weights of about 60 kDa.

GPC analysis showed that all the achieved polymers have molecular weights coherent with the formation of copolymers showing monomodal distributions with moderately narrow dispersities (Đ = 1.41–2.25). Larger distributions were observed for the samples produced in the presence of high concentration of CL.

A detailed characterization of their composition was performed by ^1H NMR and ^{13}C NMR analysis at diads and triads level, respectively.

In the ^1H NMR spectra the ratio between the intensity of the signals of methylene protons of the CL units, observed at 4.00 ppm, and the values of the methine signals of polylactide units, observed at 5.20 ppm, reveals
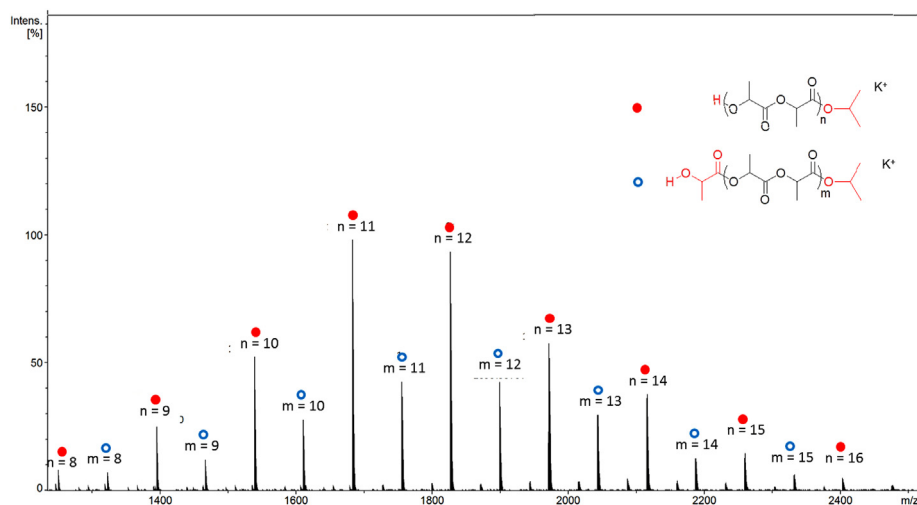

Figure 4. MALDI-ToF-MS spectrum of PLA synthesized by **2**/^iPrOH. ([LA]/[**2**] = 50; reaction conditions as run 5 of Table 1).

Table 2. Copolymerization of L-Lactide and ε-Caprolactone by **1**.

Run[a]	[LA]/[CL]	Conv. LA/CL (%)	LA (%)	ε(CL-LA) (%)	M_{nGPC}[b] (KDa)	Đ[b]	M_n^{th}[c] (KDa)	L_{LA}[d]	L_{CL}[e]
6	10/90	100/100	9	11	66.5	1.48	54.7	1.0	12.2
7	30/70	100/88	25	33	60.0	2.25	57.5	1.3	3.1
8	50/50	100/100	54	53	58.0	2.06	60.3	2.7	1.9
9	70/30	100/85	69	70	69.7	1.46	63.1	3.2	2.6
10	90/10	100/100	90	86	48.6	1.41	65.9	11.1	1.0

[a] All reactions were carried out in the melt at 110 °C for 1 h using $1.2 \cdot 10^{-5}$ mol of **1**, [ε-CL + LA]/[**1**] /[^{i}PrOH] = 1400:1:2.
[b] Experimental M_n and Đ values determined by GPC in THF using polystyrene standards.
[c] Theorical M_n = [(L-LA /^{i}PrOH) × (% conversion of L-LA) × (mol wt of L-LA)] + [(ε-CL/^{i}PrOH) × (% conversion of ε-CL) × (mol wt of ε-CL)].
[d] Average sequence length of the lactidyl unit in the copolymer as determined by ^{13}C NMR.
[e] Average sequence length of the caproyl unit in the copolymer as determined by ^{13}C NMR.

the copolymer composition. For all the polymer chains, the calculated percentages of lactide (see fourth column in Table 2) and ε-caprolactone units were corresponding to the monomer feed ratios [LA]/[CL] (see second column in Table 2).

The conversion of lactide was ever quantitative, while the conversions of ε-caprolactone ranged from 85 to 100 % (see third column of Table 2). This is consistent with the reactivity scale observed in the corresponding homopolymerization reactions.

The fraction of CL-LA heterodiads in the copolymers were calculated by comparing the intensity of the signals of the methylene protons close to the ester functional group (–CH$_2$–C=O and –COOCH$_2$-, α and ε protons, respectively) of the CL-LA heterosequences with the same methylene protons for the CL-CL homosequences (Figure 5).

The percentage of ethero-linkages CL-LA increased coherently with the amount of L-lactide (from 10 to 90 %) in the monomer feed as showed by intensity of the signals assigned to ε(CL-LA) and α(CL-LA) sequences (see Figures S4–S8 of SI). The highest concentration of heterodiads (86 %) was observed for sample [LA]/[CL] = 90/10, thus the microstructure of this polymer can be defined as a chain of polylactide in which prevailingly isolated caprolactone units are dispersed (run 10, Table 2).

The carbonyl region (between 175 and 165 ppm) of the ^{13}C NMR spectra furnished additional information about the microstructures of the obtained copolymers. As example, the ^{13}C NMR spectrum of the copolymer obtained in run 8 of Table 2 is shown in Figure 6 where the resonances described were assigned according to the previously published literature (Kasperczyk and Bero 1991, 1993; P. Vanhoorne et al., 1992).

In the ^{13}C NMR spectrum of Figure 6, no signal was detected at 171.1 ppm. This resonance is indicative of a sequence in which a single "lactic"

ester unit is allocated between two units of caprolactone. The same was observed for the samples obtained by runs 8–10 of Table 2.

Thus, the achieved structures were not a consequence of side trans-esterification processes of but a result of the catalyst ability to efficiently incorporate both the monomers.

Differently, this resonance was evident in the samples obtained at higher concentrations of caprolactone (run 6 and 7 of Table 2, see Figure S8 of SI). Reasonably, in the presence of an excess of the less reactive CL monomer, side transterification reactions between PLA sequences before the insertion of the scarcely reactive ε-CL become more recurrent and should play a crucial role to increase the randomization degree during statistical copolymerization (Shao et al., 2020).

The average length of the lactidyl unit blocks was evaluated from the triads sequences signals. The average lengths of (L_{LA}) and caproyl unit (L_{LC}) were determined from the equations by Kasperczyk and Bero (1993).

The copolymer obtained from [LA]/[CL] ratio = 50:50 showed L_{CL} = 1.9 and L_{LA} = 2.7, these values not far from 2 suggest a structure close to a random one.

The reactivity ratios for lactide (r_{LA}) and caprolactone (r_{CL}) were evaluated by the composition data of the copolymers obtained NMR and the monomer compositions in the feeds.

The values for r_{LA} and r_{CL} were in range of 1.3–4.1 and 1.5–2.5, respectively. For the ε-CL/LA copolymerization, the reactivity ratios r_{LA} and r_{CL} can be defined as $r_{LA} = k_{LALA}/k_{LACL}$ and $r_{CL} = k_{CLCL}/k_{CLLA}$, where k_{CLLA} is the kinetic constant related to the addition of the CL unit to a growing chain ending with a LA monomer unit and vice versa. The reactivity ratios can be calculated as r_{LA} (1/f) = 2 [LA-LA]/[LA-CL] and
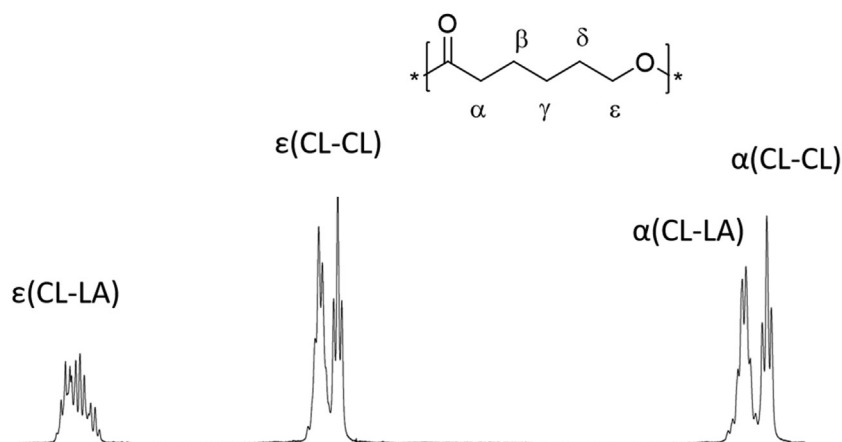

Figure 5. Methylene region of the ^{1}H NMR spectrum of a P(CL-co-LLA) sample obtained in run 8 Table 2.
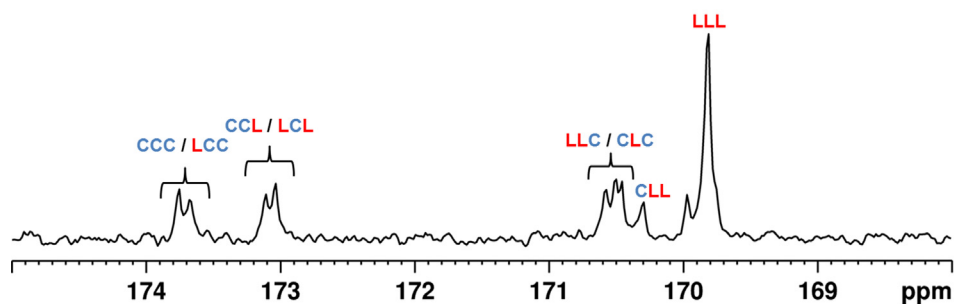
Figure 6. ^{13}C NMR spectrum of a P(CL-*co*-LLA) sample obtained in run 8 Table 2.

r_{CL} f = 2 [CL-CL]/[CL-LA] where f is the composition in the of the monomer feed and it is defined as f = [CL]/[LA].

The r_{LA} values were larger that r_{CL} ones, coherently with the activities showed towards the two monomers in the related homopolymerizations. The reactivity ratio products r_{LA} r_{CL} > 1 suggests a nonideal, non-azeotropic copolymerization.

Similar results were described for CL/LA copolymerizations initiated by simple Al (iOPr)$_3$ (Vanhoorne et al., 1992) or by phenoxy-imine aluminum complexes(Pappalardo et al., 2009).

For all samples, the molecular weights of the produced copolymers were coherent with their theoretical values. The dispersity values ranged between 1.41 and 2.25; higher values were observed for the polymerizations performed with a higher content of CL. Reasonably, in the presence of a large amount of the less reactive CL monomer, transesterification phenomena became competitive with the propagation thus causing an enlargement on the distribution of the molecular masses.

2.4. Thermal analyses

Thermal analysis of copolymers were performed by differential scanning calorimetry (DSC). Thermal parameters (glass transition temperature, T_g, melting temperature and enthalpy, T_m, ΔH_m, crystallization temperature and enthalpy, T_c, ΔH_c) are reported in Table 3 and the thermograms of the second DSC heating are shown in Figure S10 of SI.

As expected, the thermal behavior is strictly dependent on copolymer composition, even if some discrepancies are apparent. In detail, the copolymers having a low comonomer content (entry 6 and 10 of Table 3), are both crystalline at the first DSC heating run. The observed T_m values, 44 and 156 °C, are consistent with a crystallinity due to the presence of long sequences of the prevailing monomer, LA (L_{LA} = 11.1) and CL (L_{CL} = 12.2), respectively. WAXD spectra (shown in Figure S10 of the SI) confirm the presence of the typical crystalline phases of PCL and PLLA (α-form) (Chatani et al., 1970; Sasaki and Asakura 2003). The observed T_m values, which are lower compared to the commonly reported values of the respective homopolymers (Crescenzi et al., 1972; Doi and Steinbuchel 2001), are due to the presence of the relative comonomers which disturb the crystallization process and reduce crystallite sizes and

therefore T_m. The thermal behavior is a consequence of distribution of the comonomers along the chain for which reaction time is a critical parameter because transesterification reactions post polymerization can occur. All the polymerization reactions were performed for 1 h. For copolymerizations in which the LA content is higher, because of the higher reactivity of LA, the full conversion occurred in less time; thus, during the residual time transesterification reaction could occur increasing the disorder degree of the chain.

As for copolymers with composition 70/30 (entry 9 and 7), a low crystallinity is observed for the copolymer with LA as predominant monomer (entry 9, LA = 70), while the copolymer with CL predominant (entry 7, CL = 70) is amorphous. The WAXD spectrum (shown in Figure S11 of the SI) confirms that a small amount of crystal phase is present in the sample 9. Furthermore, the width of the only two well-evident spectrum reflections point out that very small crystallites are present in the sample and justify the observed low melting temperature of the sample. Likewise, the only large halo detected in the WAXD spectrum of sample 7, confirms the presence of only amorphous phase in this sample. These results are in good agreement with the data reported by Vanhoorne for LA-CL copolymers which show a PLLA crystal phase even in samples having CL units up to 40 %. Conversely, PCL crystalline phase is observable only for LA-CL copolymers containing less than 25 % of LA units.

As for the copolymer with composition 50/50, the presence of a melting endotherm centered at T = 158 °C (see Figure S9 in SI) and a clear reflection in the WAXD spectrum (even if wide and of low intensity) at 2theta ≈17° indicates that a small amount of PLLA crystal phase is present in this sample. It is worth noting that, the observed average lengths of (L_{LA}), 2.7, is comparable with that of the 70/30 sample (L_{LA} = 3.2) in which a similar amount of crystal PLLA phase is present (compare the ΔH_ms in Table 3).

The DSC, WAXD and NMR data suggest that in this sample there are some few sequences of LA units, longer than the average length evaluated by NMR analysis, capable of crystallizing.

Therefore, rather than a perfect random microstructure this sample could have a rough "gradiented" microstructure, which has CL sequences too short to crystallize in the CL rich segments while in the LA rich

Table 3. Thermal parameters of CL-LA random copolymers. Homopolymer data are also reported for comparison.

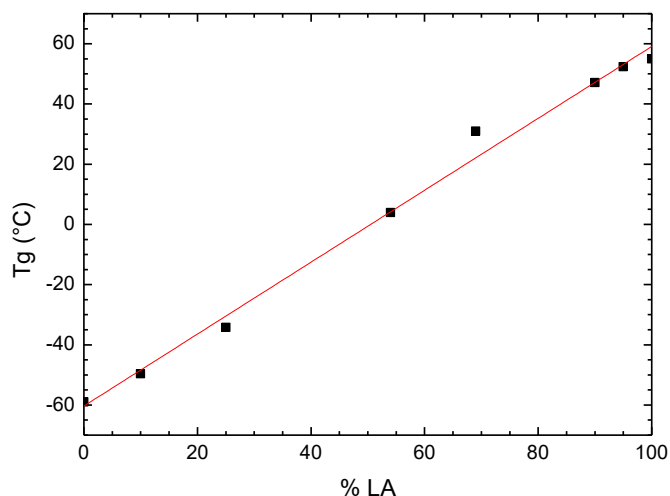| Entry	LA (%)	First DSC heating run				Second DSC heating run				
		T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PCL[a]	0	nd	nd	nd	nd	-59	-	-	58	68
6	10	-	-	44	50	-50	-	-	39	39
7	30	-	-	-	-	-34	-	-	-	-
8	50	117	3	158	3	4	124	2	158	2
9	70	-	-	134	4	52	116	1.3	141	2
10	90	-	-	156	36	47	120	25	158	25
PLA[a]	100	nd	nd	nd	nd	55	-	-	163	40

nd = not detected.

Figure 7. T_g values of the copolymers of Table 3 as a function of the LA mol % content. T_g values of PLLA and PCL homopolymers are also reported.

segments LA sequences are long enough to allow the crystallization of PLLA, even if in small and defective crystals.

As for the copolymer glass transition (T_g), the dependence of unique observed T_g of each sample vs lactide (LA) mol % content in the copolymers is reported in Figure 7. T_g values increase linearly from -59 °C (T_g of polycaprolactone homopolymer) to 55 °C (T_g of polylactide homopolymer) with increasing the LA units in the copolymer, showing the typical trend observed in random copolymers (for which T_gs follows Fox's law) (Li et al., 2012; Pilone et al., 2015) These data confirm the hypothesis (based on NMR data) that the microstructure of the copolymers is substantially random.

3. Conclusions

Pincer zinc complexes **1** and **2** revealed to be efficient catalysts for homopolymerization and copolymerization of L-lactide and caprolactone. Both catalysts, after activation with isopropanol, showed higher activity in the homopolymerization of lactide than of caprolactone. Different abilities in controlling the polymerization reactions depending on the structure of the substituents (phenyl or isopropyl groups) on the neutral phosphorous donors of the pincer ligands emergerged. Complex **1** revealed to control with high efficiency the molecular masses of the obtained polymers while complex **2** produced polymers with molecular masses higher than those theoretically expected.

Complex **1** efficiently promoted the copolymerization of L-lactide and ε-caprolactone in a variable range of compositions that were coherent with the monomers ratio in the feed. The NMR analysis suggested random microstructures. In some cases, transesterification reactions contributed to the redistribution of the monomers along the polymer chain giving microstructures with more randomized distributions. The thermal analysis showed single glass transition temperatures, indicating the amorphous nature of the copolymers, in accordance with a random distribution of the monomers along the polymer chain.

3.1. Experimental section

All details about NMR analysis of polymers and metal complexes (instruments and methods), GPC analysis (instruments and methods), thermal analysis (instruments and methods) and Wide-angle X-ray diffraction of polymers and copolymers, are reported in the supporting information. All experimental details about purification of solvents and monomers, the synthesis and characterization of zinc complexes, the

description of the polymerization and copolymerization procedures were reported in the supporting information.

Declarations

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