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A new and efficient lactic acid polymerization by multimetallic cerium complexes: a poly(lactic acid) suitable for biomedical applications†

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Among many, poly(lactic acid) (PLA) has received significant consideration. The striking price and accessibility of L-lactic acid, as a naturally occurring organic acid, are important reasons for poly-(L)-lactic acid (PLLA) improvement. PLLA is a compostable and biocompatible/bioresorbable polymer used for disposable products, for biomedical applications, for packaging film, in the automotive industry, for electronic device components, and for many other applications. Formerly, titanium and other metals have been used in different orthopaedic screws and plates, but they are not degradable and therefore remain in the body. So, the development of innovative and eco compatible catalysts for polyester synthesis is of great interest. In this study, an innovative and eco sustainable catalyst was employed for PLLA synthesis. The combined $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ –NaI system has been demonstrated to be a very valuable and nontoxic catalyst toward PLLA synthesis, and it represents a further example of how to exploit the antibacterial properties of cerium ions in biomaterials engineering. A novel synthesis of poly-(L)-lactic acid was developed in high yields up to 95% conversion and with a truly valuable molecular weight ranging from 9000 to 145 000 g mol^{-1} , testing different synthetic routes.

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Introduction

The development of bio-based polymers to substitute or decrease the use of polymers from petrochemical resources continues to show an increasing growth. In recent years in fact, the enlargement of degradable polyester syntheses, became more popular due to both environmental and strategic reasons. First of all, biopolymers are a well-known class of materials derived from organic products like milk derivatives and cellulose, which show a very easy degradation pattern. Furthermore, they are really important materials in the biomedical field,¹ and the advent of these polymers has significantly influenced the development and rapid growth of various technologies in modern medicine.² This involves greater attention both in their preparation and in their use and disposal (reuse, recycling, and recovery). Thus, the susceptibility of aliphatic polyesters to bio degradative processes,³ and the presence of contaminants due to the promoters employed in their industrial production, must be carefully considered.⁴ For

this reason, practical and feasible catalytic systems, which allow minor contamination of the polymeric material especially when it may be potentially applied in biomedicine are welcomed. With this paper we wish to make available our efforts on the use of non-toxic and low environmental impact catalysts in the development of strategies useful for the preparation of polyesters.⁵

Poly-L-(lactic acid) (PLLA) belongs to the family of polymers commonly made from α -hydroxy acids such as lactic acid (2-hydroxypropionic acid). Three are the main routes usually used to synthesize PLA, depending on the molecular weight of the resulting aliphatic polymer, namely, a direct condensation polymerization, a combined melt polycondensation with a Solid State Process (SSP) starting from oligomers in the presence of tin, titanium or zinc based catalysts,^{6–11} and the last is the ring-opening polymerization (ROP),¹² starting from a purified lactide structure.^{13,14}

Lewis acids have significantly increased their use, and eco-friendly Lewis acid catalysts are available, but particular attention must be directed to their toxicity and to the contamination of the final polymer product especially in the biomedical field. In recent years, multimetallic catalysts are receiving increasing attention in the catalysis of polycondensation reactions that can lead to the formation of polymeric structures.¹⁵ A very interesting example is the recent methodology developed by J. A. Garden *et al.*¹⁶ in the use of heterometallic complex catalysts to obtain aliphatic polyesters such as poly(lactic acid). It is a typical academic demonstration of what has been studied in these last decades and namely, that the multimetallic catalysis

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based on the combined action of different metals in a chemical transformation, amplifies the activity of the single metal. Thus, the proximity between the metal centers, seems to provide favorable conditions for the occurrence of enhanced catalytic properties.¹⁷ Up to date, however, this greater catalytic activity, consequence of the heterometallic cooperativity of multimetallic catalysts, is followed by two major application difficulties. First, the assessment of the environmental effects of multimetallic substances requires information on potential combination effects.¹⁸ Secondly, the long-term stability of the molecular structures of heterometallic complexes is an omnipresent and pressing concern in industrial processes.¹⁹ For the latter reason the most used catalysts in PLA synthesis are the tin(II) salts and the most used are the commercially available SnCl_2 or $[\text{Sn}(\text{Oct})_2]$.^{20–23} So, the search for useful catalysts for aliphatic polyesters synthesis is a truly big challenge. In the last years, inexpensive, water tolerant, non-toxic,²⁴ and easy to handle cerium trichloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) has attracted considerable attention because of its diverse applications as a Lewis acid catalyst in organic synthesis.²⁵ In line with our research interests in exploring new and more concise procedures for polymer formation promoted by Lewis acids, we have increased the potentialities of the combination of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ with NaI,²⁶ capable of transforming the typical aggregates of metal halides such as CeCl_3 into the corresponding more reactive monomeric structures.²⁷ In addition to our knowledge on the efficiency of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI system, Fedynshkin *et al.* reported the oligo-lactic acid thermal decomposition promoted by $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$,²⁸ suggesting us that the use of an appropriate amount of catalyst $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI can facilitate the synthesis of the corresponding polyester. Thus, we tested a new, efficient and eco-sustainable $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI catalyst following two different reaction processes. Our catalytic procedure (Scheme 1) demonstrated to be very efficient in a two-step synthesis of poly(L-lactic acid) **4** starting from a polycondensation step in which a prepolymer oligo(L-lactic acid) (OLLA) **2** has been obtained, followed by a $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI melt-solid state (SSP) polycondensation that provides PLLA **4** with a molecular weight ranging between 2000 and 146 000 g mol^{-1} . Furthermore, we defined a new strategy for PLLA synthesis, starting from L-lactide **3**, using the same cerium(III)-NaI catalytic system for the ring opening polymerization

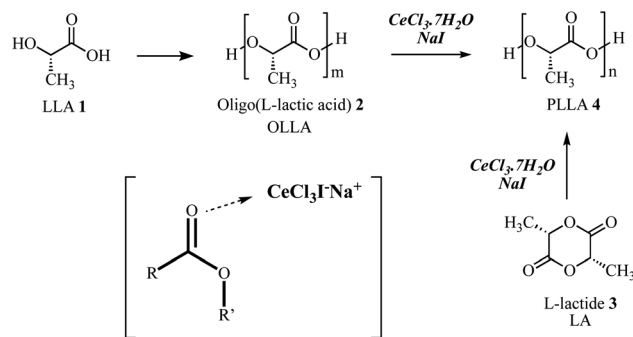
reaction under microwaves irradiation, which provides a polymer in a high percentage of conversion and very good molecular weights, boosting the reaction rate up to 1 hour.

Results and discussion

$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI physical characterization

The XPS technique has been applied for the characterization of the multimetallic $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI catalyst. The typical structure of the commercially available cerium trichloride is $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, where the CeCl_3 molecule incorporate seven water molecules. The structure of this heptahydrate cerium trichloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) consists of dimers $[\text{CeCl}_3(\text{H}_2\text{O})_7]_2$, as shown by L. A. Boatner *et al.*^{31,32} (Fig. 1).

This remarkable ability of water of crystallization can find explanation in its coordination that makes easy the disaggregation of the crystal lattice of cerium salt which might lead to a notable increase in the Lewis acidity of the cerium available at the particle surface.³³ This hydrophobic amplification concept³⁴ have been shown in several catalyzed $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ organic transformations.^{35,36} To confirm the mechanistic role of the NaI we have analyzed the interaction between $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ with NaI by X-ray photoelectron spectroscopy, in order to analyze the chemical shift in the core level binding energies.³⁷ Fundamental reasons for this are the inherent element specificity of the associated element core level binding energies, and also the sensitivity both to the amount of the element present and its localization at the surface, the latter characteristic caused by the short mean free path of low energy (30–1000 eV) photoelectrons in the solids.^{38,39} We have started from a belief that CeCl_3 is a rare-earth trihalides whose initial state is f^1 ($\text{Ce} = [\text{Xe}] 4f^1 5d^1 6s^2$) as no promotion of f electron is required for a trivalent bonding with chlorine. Nevertheless, in the final state the charge transfer energy defined as the energy required to take an electron from the ligand p level to the unoccupied 4f level (about 9.7 eV)⁴⁰ ($f^2\nu$) is less than the value of the 4f-core hole Coulomb attraction (12.2 eV). This leads to a $f^2\nu$ satellite (where ν is the hole in the valence) at about 3.4 eV lower binding energy. Intensity and energy of this satellite are sensitive to the degree of hybridization of



Scheme 1 General synthesis of PLLA using $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI as catalytic system with $m < n$, and cerium(III) salts-sodium iodide activation of the ester group reported by Marcantoni *et al.*^{29,30}

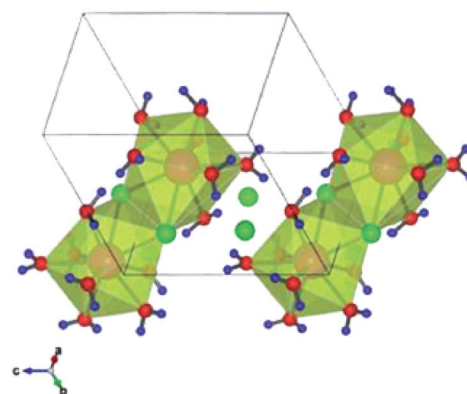


Fig. 1 Crystal structure of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. The Ce coordination polyhedral are shaded in yellow, oxygen atoms are in red, chlorine atoms are in green, and hydrogen atoms are in blue.



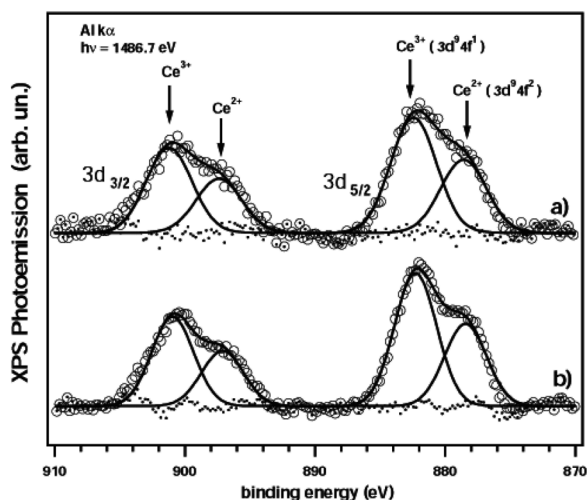


Fig. 2 The XPS spectra of fine powdered samples of: (a) $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and (b) $\text{CeCl}_3 \cdot 7\text{H}_2\text{O-NaI}$.

Table 1 Screening of iodide source in $\text{CeCl}_3 \cdot 7\text{H}_2\text{O-M}_x\text{I}_y$ catalysts

Entry	Catalyst	M_n^a (g mol^{-1})	M_n^b (g mol^{-1})	T_{on}^c ($^\circ\text{C}$)	Yield (%)
2a	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$	650	500	260	42.1
2b	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O-NaI}$	1300	2000	270	54.7
2c	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O-CuI}$	600	400	270	45.8
2d	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O-KI}$	100	350	261	45.6

^a $^1\text{H-NMR}$ analysis. ^b GPC analysis (detector RI, refractive index). ^c TGA analysis.

the f states with the conduction states.⁴¹ We reported the XPS measurements⁴² of the 3d core level in $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O-NaI}$ (Fig. 2 in (a) and (b) respectively).

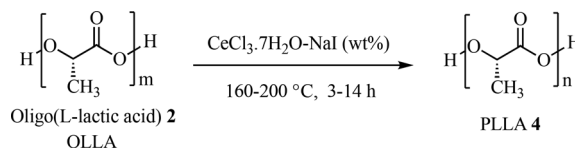
From the present study we cannot observe a variation within few percent in the intensity of the f^2 satellite, indicating that the introduction of the NaI in the system does not vary the degree of the hybridization of the f states with conduction states. Such as hybridization is certainly enhanced for both samples with respect to the only CeCl_3 molecular structure,⁴³ but this property is conserved after the insertion of NaI. Furthermore, it can be excluded the presence of an initial f^0 (metallic) state due to the promotion of the “f” electron in the valence bond (Fig. 2). Such a peak is in general observed at 10 eV higher binding energies. These results, thus, suggest us that there is not a direct interaction between cerium(III) site and iodide ion. The activity of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O-NaI}$ system is mainly exerted in the heterogeneous phase and, above all, we believe that a chloro-bridged oligomeric structure of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ is easily broken by donor species such as iodide ion. The resulting monomeric $\text{CeCl}_3 \cdot 7\text{H}_2\text{O-NaI}$ complex is a more active Lewis acid promoter.

Two-step synthesis of poly(lactic acid) by a melt polycondensation – solid state process (SSP)

The prepolymer was first synthesized by direct polycondensation of LLA and several different catalysts were investigated (Table S1†), using 0.1 mol% of the catalyst. As reported $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O-NaI}$ (1 : 1 ratio) system were compared, resulting in a more active catalytic activity of the latter, with a weight average molecular weight, $M_w = 3600 \text{ g mol}^{-1}$. The M_n of oligolactic acid 2 (OLLA) was determined by $^1\text{H-NMR}$ analysis and the results were compared with those obtained with a gel permeation chromatography (GPC). From the $^1\text{H-NMR}$ analysis the degree of polymerization (DP) and the M_n of the prepolymer were determined by obtaining the ratio of proton integrals of the oligomeric chain (Fig. S1,† peak a and peak c) to that of end-groups as reported in eqn (1).⁴⁴

$$\text{DP}(\text{CH}) = \frac{\sum \int \text{CH} (5.1 \text{ ppm})}{\sum \int \text{CH} (4.5 \text{ ppm})} \quad (1)$$

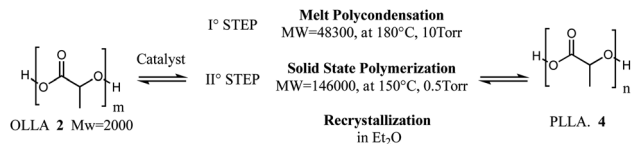
Table 2 Optimization of the reaction conditions of the melt-solid state polymerization steps



Entry	Catalyst ^b (wt%)	Temp. ($^\circ\text{C}$)	Time (h)	M_n^c (g mol^{-1})	M_w^c (g mol^{-1})	T_{on}^d ($^\circ\text{C}$)	Yield ^e (%)	DP ^c
2a	—	180	7	7500	8000	241	95	1.10
2b	0.3	180	7	8000	8300	291	92	1.03
2c	0.7	180	7	44 500	48 300	300	92	1.08
2d	0.7	160	7	16 100	30 000	277	93	1.85
2e	0.7	180	3	24 300	28 900	269	95	1.20
2f	1.3	180	7	11 500	14 500	284	92	1.25
2g	0.7	200	7	7300	33 700	306	79	4.70
2h	0.7	180	14	16 500	29 900	281	93	1.81
2l ^a	—	150	16	52 400	94 500	305	92	1.80
2m ^a	—	150	29	23 200	146 000	310	92	6.30

^a Solid state polymerization (SSP) starting from entry 2c $M_w = 48\,300 \text{ Da}$. ^b Wt% of OLLA : $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$: NaI (100 : 0.7 : 0.7). ^c GPC analysis (triple detector). ^d TGA analysis. ^e Yield (%) calculated by the equation $\text{yield} = [\text{g PLLA}/\text{g LLA}] \times 100$.



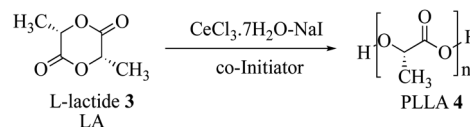
Scheme 2 Melt-solid state polymerization steps with $m < n$.

The polymerization conversions are reported in Table S1† with different Lewis acids. In Table S1† it is also reported the onset temperature (T_{on}) (Fig. S2†). The highest value obtained was around 270 °C, confirming the low molecular weight of **2**. The best results were obtained with monomeric $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI combination (Table S1,† entry S1g) being this catalyst able to coordinate oxygen atoms and to push the reaction to the elimination of water. Then, different iodide sources were screened in order to ensure the high catalytic activity of cerium(III) Cl_3 -NaI couple, KI and CuI gave lower efficiency than that of the $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI system (Table 1).

The NaI gave the optimal results, so then the ratio between $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and NaI was tested and an equimolar ratio allowed to reach the best result (Fig. S3,† $\text{CeCl}_3 \cdot 7\text{H}_2\text{O} : \text{M}_x\text{I}_y \rightarrow 0.1 : 0.1 \text{ mol}\%$).

The optimized catalytic procedure with $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI was subsequently employed in melt-solid polycondensation,^{45,46} starting from oligolactic acid **2** (OLLA) and carrying out the polycondensation of OLLA in the presence of our $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI catalytic system. Through a screening of the ratio between $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and NaI (Table 2) it was possible to prepare the aliphatic polyester with high molecular weight and with excellent conversions. The thermal dehydration without a catalyst did not result in a high molecular weight PLLA (Table 2, entry 2a). A high amount of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI (Table 2, entry 2f-h), was able to activate the dehydrative equilibrium. However, due to the hard reaction conditions, such a high concentration of the catalyst, relatively high temperature and long reaction time, induced L-lactide formation and relevant polymer decomposition rather than polycondensation. The results indicated in Table 2 entry 2c, show a weight average molecular weight of $M_w = 48\,300 \text{ g mol}^{-1}$ as the highest molecular weight obtained in the melt polycondensation with a degree of polymerization (DP) equal to 1.08. This value was obtained after 7 h at 180 °C keeping pressure at 1333 Pascal and 0.7 wt% of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. In Table 2 is also reported the onset degradation temperature (T_{on}) obtained from TGA. PLLA with the highest molecular weight showed a value around 300 °C (Table 2, entry 2c). T_{on} of the other polymers were lower except when the temperature of polymerization was 200 °C (Table 2, entry 2g). This behaviour could be explained considering all the degradation processes that might occur at high temperatures which led to the formation of shorter chains but also to the subsequent crosslinking of polymer matrixes. PLLA synthesized by melt polycondensation underwent a second step of Solid State Polymerization (SSP).

In particular, PLLA with the highest $M_w = 48\,300 \text{ g mol}^{-1}$ (Table 2, entry 2c), was then underwent the last step (Scheme 2), a solid state process, at 150 °C under reduced pressure. A

Scheme 3 General ring opening polymerization reaction using $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI system.

further recrystallization with diethyl ether (Et_2O) was carried out at room temperature. Kinetic studies were performed, after 16 h the PLLA **4** obtained reached an $M_w = 94\,500 \text{ g mol}^{-1}$ with a DP value of 1.80 (Table 2, entry 2l) while, increasing to 29 h this value was equal to 6.30, due to an important decrease in $M_n = 23\,300 \text{ g mol}^{-1}$, even if the M_w increases up to the value of $M_w = 146\,000 \text{ g mol}^{-1}$ (Table 2, entry 2m) (Fig. S4†).

It was shown that the PLLA polymer synthesized by a two-step condensation polymerization of L-lactic acid in the presence of our $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI system had significantly higher molecular weight and crystallinity as compared with PLLA produced with the conventional stannous-based catalyst. Discoloration was effectively inhibited by our cerium(III) catalytic system, and there was no significant change in its T_g .

Ring opening polymerization of L,L-lactide (LA) catalyzed by $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI system

The poly(lactic acid) synthesis was also performed starting from L-lactide (LA) in order to verify the catalytic activity of the $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI (Scheme 3).

Following the previous study, we carried out the reaction in batch conditions comparing the only $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ with the multimetallic system (0.1 mol%), without the need of any co-initiator, obtaining a better result with the second one, $M_w = 11\,500 \text{ Da}$ and $M_w = 15\,300$ respectively (Table 3), in 12 h at 165 °C.

Table 3 Comparative study of cerium(III) derivatives

Entry	Cat.	M_n^a (g mol^{-1})	M_w^a (g mol^{-1})	DP^a	T_{on}^b (°C)	Conv. ^a (%)
3a	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$	11 300	11 500	1.02	283	92
3b	$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ - NaI	12 700	15 300	1.20	287	97

^a GPC analysis (triple detector). ^b TGA analysis.

Table 4 Screening of several co-initiators

Entry	Co-init. ^a (mol%)	M_n^b (g mol^{-1})	M_w^b (g mol^{-1})	DP^b	T_{on}^c (°C)	Conv. ^b (%)
4a	1-Dodecanol	4700	6700	1.40	273	96
4b	Benzyl alcohol	16 700	18 100	1.20	283	93
4c	Ethylene glycol	4700	8300	1.70	281	95
4d	1,4-Butandiol	1500	3300	2.10	274	94

^a 3 mol% of co-initiator. ^b GPC analysis (triple detector). ^c TGA analysis.



application in the field of biomaterials. The known antibacterial properties of cerium ions, make them suitable for the production of biomaterials and PLA polymers as well as in our procedure. Our $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI catalytic system, not only bypassed the problem of contamination from toxic metal catalysts, but its beneficial properties might be exploited for the bioactivity of the prepared biopolymers. Thus, it seems to be very reasonable to look for new efficient and eco-friendly catalysts. Indeed, the $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI catalytic system allowed to obtain a PLLA with an intermediate molecular weight, which made the final polymer suitable for biomedical applications but to a less extent for mechanical ones. So, given the trend of a broadening of the spectrum of the PLA-based biomaterials with additional biological, physicochemical, or biomechanical properties, PLLA produced in these processes may be used for biomedical purposes such as drug delivery and for production of microcapsules. Further studies are in progress in our laboratories in order to link this biocompatible polyester with antimicrobial agents, antioxidants and drugs, for the use in medical fields.

Author contributions

All authors listed have made a substantial, direct, and intellectual contributions to the work, and approved it for publication.

Conflicts of interest

There are no conflicts to declare.

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