Accelerating the crystallization kinetics of linear polylactides by adding cyclic poly (L-lactide): Nucleation, plasticization and topological effects

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1. Introduction

Polylactide (PLA) is one of the most versatile biopolymers, but its slow crystallization limits its temperature usage range. Hence finding ways to enhance it is crucial to widen its applications. Linear and cyclic poly (L-lactide) (L-PLA and c-PLA) of similarly low molecular weights (MW) were synthesized by ring-opening polymerization of L-lactide, and ring-expansion methodology, respectively. Two types of blends were prepared by solution mixing: (a) l-PLA/c-PLA, at extreme compositions (rich in linear or in cyclic chains), and (b) blends of each of these low MW materials with a commercial high MW linear PLA. The crystallization of the different blends was evaluated by polarized light optical microscopy and differential scanning calorimetry. It was found, for the first time, that in the c-PLA rich blends, small amounts of c-PLA (i.e., 5 and 10 wt%) increase the nucleation density, nucleation rate (1/τ\(_n\)), spherical growth rate (G), and overall crystallization rate (1/τ\(_{50\%}\)), when compared to neat l-PLA, due to a synergistic effect (i.e., nucleation plus plasticization). In contrast, the opposite effect was found in the c-PLA rich blends. The addition of small amounts of l-PLA to a matrix of c-PLA chains causes a decrease in the nucleation density, 1/τ\(_n\), G, and 1/τ\(_{50\%}\) values, due to threading effects between cyclic and linear chains. Small amounts of l-PLA and c-PLA enhance the crystallization ability of a commercial high MW linear PLA without affecting its melting temperature. The l-PLA only acts as a plasticizer for the PLA matrix, whereas c-PLA has a synergistic effect in accelerating the crystallization of PLA that goes beyond simple plasticization. The addition of small amounts of c-PLA affects not only PLA crystal growth but also its nucleation due to the unique cyclic chains topology.
The crystallization ability and other properties of PLA depend on the ratio L- to D, L-enantiomers [7]. The presence of repeating units of different chirality reduces the crystallinity, crystallization rate, and melting point of PLA [8]. Commercially available PLA materials usually contain a mol % content of D units in the range of 1.5 to 10%. The samples with more than 8% mol cannot crystallize [8].

Many past studies have been devoted to increase PLA crystallization rate. The range of applications for PLA is limited by its low glass transition temperature \(T_g = 50 \text{ to } 80 \, ^\circ \text{C} \) [2,4] unless crystallization can be induced to improve its thermal usage range [9]. Improving PLA crystallization implies modifying its nucleation density and its growth rate. Adding nucleating agents increases the nucleation density [10–17], whereas plasticizer addition increases chain mobility [3,9]. The addition of both nucleating and plasticizers agents has also been reported in the literature [10]. Another alternative to improve the crystallization of PLA is blending with other polymers [14,18,19].

Efficient strategies to enhance PLA crystallization must maintain its biodegradable, non-toxic, and bio-compatible characters. From that point of view, the best nucleating agent and plasticizer could be based on PLA, and PLA stereocomplexes [17,20], or even PLA with different topologies, e.g., cyclic topology.

Cyclic polymers differ from their linear analogs in their lack of chain ends. This provokes unique and improved properties [21]. Different challenges remain [21,22] related to the purity of cyclic polymers (i.e., quantification and identification of non-cyclic impurities), purification methods, and scalability [21,22], but significant advances have been performed in their preparation methods [21–23]. Several potential applications (especially biomedical ones) are recognized, as reported in recent reviews [21,22,24]. The unique cyclic topology seems to be suitable for some biomedical applications. Compared to linear analogs, cyclic polymers exhibit large blood circulation times (improving targeting) and possess faster spherulitic growth rates (gene transfection) efficiency than the linear ones [21]. In the micelle-based drug delivery, the cyclic polymers and copolymers can tune the micelle size and stability due to their self-assembly characteristics [21,22]. Thus, cyclic polymers can have a crucial role in the advancement of the fields mentioned above.

From the crystallization point of view, the comparisons of cyclic and linear polymers in the literature show different and sometimes even opposite trends [1,25–44], hence, their crystallization is still a debated topic [22]. As an alternative for such debate, simulations studies have been performed, but even for them, contradicting results have also been found in their predictions of the relative melting and equilibrium melting temperatures of cyclic and linear polymers [45–47]. However, most studies, both experimental and simulated, employing cyclic and linear polymers, have shown that cyclic polymers exhibit enhanced nucleation [28,29,43], faster spherulitic growth rates (G) [30–33,44] and faster overall crystallization [25,26,34–42] (as determined by DSC, which includes both nucleation and growth) compared to their linear counterparts. Therefore, employing cyclic polymers as an additive to enhance the crystallization of linear PLA seems to be a good strategy.

The research related to cyclic and linear polymer blends is scarce, and in most of the cases, has been focused on molecular dynamic simulations [46,48–54] and diffusion studies [55], in which, ring and linear chain sizes are important factors. Shin et al. [56] blended cyclic and linear PLLA and PDLA to study stereocomplexation. It has been recognized that small amounts of linear chains dramatically affect the properties of the cyclic polymers due to threading effects. Threading refers to the action of linear chains that can rephase and thread through cyclic chains, thereby joining several chains together thus affecting diffusion and relaxation times. Threading effects have been reported by Kapnistos et al. [57], López et al. [36], and Pérez et al. [35] in cyclic-linear polyethylene (PS) blends, cyclic-linear poly (e-caprolactone) (PCL) blends, and cyclic/multi-walled carbon nanotubes-grafted-linear-PCL (MWCNT-g-I-PCL) nanocomposites, respectively.

In the work of López et al. [36], it was found that small amounts of linear PCL cause a deviation with respect to a simple mixing law. Only when the linear PCL content is increased, the experimental points follow a linear mixing law. However, the influence of small amounts of cyclic PCL on a linear PCL matrix has not been investigated yet. The different works of cyclic linear blends focus on adding small amounts of linear polymer to a cyclic matrix. None of these works have explored the opposite case, leaving pending questions: What happens when small amounts of cyclic chains are added to a linear matrix? Is the threading effect still present? Are molecular weight differences between linear and cyclic chains relevant for the blends behavior?

In the present work, we will answer these questions by studying linear/cyclic PLLA blends, which maintain the exceptional characteristics of the PLA, in a composition range where small amounts of cyclic chains are added to a mixture of linear chains and vice-versa. As far as the authors are aware, this is the first time that both composition ranges (i.e., linear rich and cyclic rich blends) have been explored. We will also investigate for the first time, the topological influence of low MW linear and cyclic PLLAs as additives for a commercial PLA (with high MW), and thus design fully biobased, biodegradable, and biocompatible thermoplastic blends. We show that chain topology can have dramatic effects on the nucleation and crystallization rates of linear/cyclic PLA blends.

2. Experimental part

2.1. Materials

The cyclic PLLA (c-PLLA) used in this work was synthesized by ring-expansion. According to Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) mass spectrometry experiments, there are 98% of c-PLLA chains in the sample, with a number average molecular weight \(M_n = 9 \, \text{kg/mol} \). The cyclic nature of the c-PLLA was proved by confronting the experimental MS chromatogram (MALDI-TOF analysis) to an isotopic model (see Fig. S1). Furthermore, Size Exclusion Chromatography (SEC) analysis were performed, obtaining \(M_n = 13.5 \, \text{kg/mol} \), dispersity index of 1.33, and the absent of significant linear traces (see Fig. S2). An analogous linear PLLA (I-PLLA) was synthesized by ring-opening polymerization of L-lactic acid, obtaining a I-PLLA with a \(M_n = 15.5 \, \text{kg/mol} \) and a dispersity index of 1.5. Both c- and I-PLLA were obtained from 100% L-lactide monomers with a controlled synthetic procedure that avoids racemization [58–59]. Details on the methods used to produce cyclic and linear PLAs are reported in ref. [58] and [59], respectively.

Linear/Cyclic (I-PLLA/c-PLLA) blends were prepared in solution, using chloroform, CHCl₃, as a solvent. In all the cases, 4 mg of solid material were dissolved in 1 mL of CHCl₃. Small amounts, 5 and 10 wt%, of c-PLLA (i.e., around 0.2 mg) were added in a I-PLLA matrix (i.e., around 3.8 mg) and vice-versa. The mixture was placed directly in DSC pans, dried in a vacuum oven (to avoid any solvent), at 60 °C, until obtaining a constant weight (this process can take several hours). The prepared blends are shown in Table 1.

A commercial high molecular weight (MW) linear PLA, synthesized by ring-opening polymerization of lactide, was provided by

<table>
<thead>
<tr>
<th>Material</th>
<th>c-PLLA content (wt%)</th>
<th>I-PLLA content (wt%)</th>
<th>c-PLLA content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-PLLA</td>
<td>–</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>c-PLLA</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>PLA</td>
<td>100</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>I-PLLA/c-PLLA 95/5</td>
<td>–</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>I-PLLA/c-PLLA 90/10</td>
<td>–</td>
<td>90</td>
<td>10</td>
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<td>I-PLLA/c-PLLA 5/95</td>
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<td>95</td>
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<tr>
<td>PLA/I-PLLA 95/5</td>
<td>95</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>PLA/c-PLLA 95/5</td>
<td>95</td>
<td>–</td>
<td>5</td>
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</table>

Table 1: List of prepared blends.
NatureWorks (commercial name 4032D). This PLA has a L-lactide content of 2% mol, an $M_n = 123$ kg/mol, and a dispersity index of 1.72. The PLA was blended (i.e., following the procedure described above), in solution, with 5 wt% of c- or l-PLLA, as is indicated in Table 1.

2.2. Polarized light optical microscopy (PLOM) experiments: crystallization from the melt state

Morphological observations, as well as nucleation density, and spherulitic growth rate experiments were performed by filming spherulites growing in an Olympus BX51 PLOM, equipped with a λ plate (i.e., a red tint plate) between the polarizers at 45°. The samples were prepared by solving-casting, with 1.3% of the weight of the materials dissolved in CHCl3. One drop of this solution was placed in a glass cover, and then the solvent was evaporated. The samples were heated in a temperature-controlled hot stage (Mettler FP82HT). The thermal history of the samples was erased at 190 °C for 3 min, and then the samples were cooled at 50 ºC/min until the desired crystallization temperature ($T_c$). In the case of nucleation density experiments, a constant $T_c$ and a constant crystallization time were selected for comparison purposes. For spherulitic growth rate experiments, we selected $T_c$ in a range of 105 to 130 ºC, with intervals of 5 ºC.

2.3. Non-isothermal differential scanning calorimetry (DSC) experiments

Standard non-isothermal DSC tests, as well as isothermal tests, were performed in a Pyris 1 DSC of PerkinElmer with an Intracooler 2P as a cooling device. The DSC was operated with an ultrapure N2 atmosphere, maintaining a constant flow of 20 mL/min, and it was calibrated with indium and tin standards. For the standard non-isothermal test, as received samples were encapsulated in aluminum DSC pans and heated at 10 °C/min until 190 ºC. Their thermal history was erased by holding at 190 ºC for 3 min. Subsequently, the samples were cooled, at 5 or 20 ºC/min, until 0 ºC, registering the crystallization (i.e., in those cases in which it occurred). A holding step, of 1 min, at 0 ºC, was used. Then a heating scan, at 20 ºC/min was performed to register the different thermal transitions.

2.4. Isothermal DSC experiments: crystallization from the glassy state

The isothermal crystallization of the PLA samples employed in this work was too slow to follow them from the melt state. In order to increase the overall crystallization rate, the samples were first cooled from the melt to a temperature below the glass transition temperature, $T_g$, to allow for vitrification and nucleation during cooling. Then, the sample was quickly heated from the glassy state up to the selected $T_c$ value, where the crystallization was followed by isothermally recording the heat evolved as a function of time with the DSC. The following steps were applied to the samples:

a. Erase of the thermal history at 190 °C for 3 min.

b. Cooling from 190 °C to 0 °C, at 60 °C/min. Note that the temperature of 0 °C is below $T_g$ of the PLA, which is around 60 °C.

c. Hold the sample at 0 °C for 1 min.

d. Heat the sample from 0 °C to the selected $T_c$ (a range of 85 to 130 °C, with increments of 5 °C was employed), at 60 °C/min (a rate at which no crystallization can occur during heating).

e. Hold the sample at $T_c$ enough time to complete its crystallization under isothermal conditions. Often, a time of 30 min was enough to complete the crystallization process.

f. Heat the sample from $T_c$ to 190 °C at 20 °C/min to register the heating behavior after the isothermal crystallization.

3. Results and discussion

In this work, we have evaluated the behavior of two different kinds of blends:

(a) low MW l-PLLA with small amounts of c-PLLA and vice-versa (Section 3.1) and

(b) commercial high MW linear PLA with small amounts of low MW l-PLLA or c-PLLA (Section 3.2).

The different effects generated in these blends are discussed below.

3.1. Topological effect in cyclic and linear low MW PLLA blends

In this section, the blends of l-PLLA with small amounts of c-PLLA, and mirror compositions (i.e., c-PLLA with small amounts of l-PLLA, see compositions in Table 1) are analyzed with different techniques.

3.1.1. Polarized light optical microscopy results: isothermal crystallization from the melt state

Fig. 1 shows the spherulitic morphology (i.e., negative spherulites for the neat materials and their blends) obtained after the samples were crystallized from the melt at a $T_c = 115$ °C for 10 min for both l-PLLA, c-PLLA and their blends.

By using the same conditions of isothermal crystallization temperature ($T_c = 115$ °C) and time (10 min), it is possible to compare qualitatively the nucleation density in Fig. 1, and analyze the different effects caused by the addition of cyclic and linear PLLA in the blends.

3.1.1.1. Nucleation: threading vs. nucleation effect. Fig. 1a and d show that c-PLLA has a much higher nucleation density than its linear analog (i.e., l-PLLA). This is in line with the results reported in the literature for l-PLLA and c-PLLA and PDLA [27], of slightly higher MW (~14 kg/mol (c-PLLA) and 16.7 kg/mol (l-PLLA)), and other linear and cyclic polymers, such as polyethylene (PE) [29], PTHF [28,43], and PCL [25,34].

The differences in nucleation have been attributed to the cyclic topology (note that the MWs of the l-and c-PLLA employed in this work are similar) since it is characterized by a lack of chain ends and more collapsed coil conformations in the melt. Therefore, it is expected that cyclic chains nucleate faster than linear chains of similar MWs [25,26].

Fig. 1b and c show that as the c-PLLA content increases in the l-PLLA/c-PLLA blends (i.e., from 5 to 10 wt%), the number of nuclei increases. Thus, the small amount of c-PLLA acts as a nucleating agent of the l-PLLA, despite the fact that their presence might lead to threading events with the linear chains. It has been reported that small amounts of cyclic chains do not affect the overall conformation and dynamics of the linear chains [50]. The reason for this behavior is that a large fraction of linear chains do not experience any interactions with cyclic chains [50].

In contrast, adding small amounts of l-PLLA to the c-PLLA matrix generated the opposite effect. Fig. 1e shows that small amounts of l-PLLA lead to a reduction in the number of nuclei of the l-PLLA-c-PLLA 5/95 blend. Thus, the small amounts of l-PLLA act as an anti-nucleating agent of the c-PLLA as these linear chains thread through the cyclic ones, creating extra entanglement points that hinder the nucleation and diffusion of cyclic chains (see the illustration in Scheme 1b and its discussion below). This chain threading effect has been reported before for cyclic/linear PS and PCL blends by López et al. [36] and Kapnistos et al. [57], respectively, and for cyclic/MWCNT-g-l-PCL blends by Pérez et al. [35].

3.1.1.2. Spherulitic growth kinetics: plasticization vs. threading effects. By measuring the growth of the spherulites by PLOM in a wide $T_c$ range, we have evaluated the influence of blending linear and cyclic chains on spherulitic growth (G) kinetics. Fig. 2 shows the G values (i.e., spherulitic growth rates) vs. $T_c$ for all the materials examined in this work. Fig. 2a shows the typical bell-shape behavior of the G vs. $T_c$ curves caused by the competition between secondary nucleation (high temperatures or low supercoolings) and diffusion (low temperatures or high
supercoolings) [27]. By comparing the $G$ vs. $T_c$ curves of the $l$-PLLA and $c$-PLLA, it is obvious that significantly higher $G$ values are obtained for $c$-PLLA. Such difference (also reflected on energetic parameters obtained by fits to the Lauritzen and Hoffman theory, as shown in Table S7) is caused by the faster diffusion rate at high supercoolings (i.e., related to compact coil conformation, lower entanglement density, and enhanced supercooling degree [36]) of the cyclic chains in comparison to linear ones [26,44]. Yamazaki et al. [44] determined that the term proportional to the diffusion constant, $G_0$ [60,61], is higher for cyclic PCLs than for linear analogs in a wide range of MW. In the present work, our results suggest that in the low supercooling temperature range (right hand side of the bell shape curve in Fig. 2a), the increase in $G$ values for PLLA cyclic chains is due to the higher secondary nucleation rate of the ring like chains in comparison with linear ones.

Sample purity can affect the results of spherulitic growth rate. Zaldua et al. [27] reported similar $G$ values for $l$- and $c$-PLLA. The results were explained by the presence of a small fraction of linear or higher MW cycles detected by SEC. Such impurities retard spherulitic growth rates of $c$-PLLA, in such a way that they can be comparable to those of $l$-PLLA. Hence, the higher difference between $G_c$, $G_l$ found here (Fig. 2a) is probably related to a small amount of linear impurities in the samples used in the present work.

For clarity, we plotted $G$ values measured at constant $T_c$ (for two temperatures, $T_c = 115$ °C, and 117.5 °C) versus $c$-PLLA content in Fig. 2b. As $c$-PLLA is added to $l$-PLLA, a remarkable increase in $G$ values is observed. When 10 wt% of $c$-PLLA is added, the $G$ value of the $l$-PLLA/ $c$-PLLA 90/10 blend is comparable to the value for neat $c$-PLLA. Thus, small amounts of $c$-PLLA cause a plasticization-like effect on the $l$-PLLA matrix, explaining the increase in $G$ values observed (see Scheme 1a). An acceleration of the diffusion of linear chains in the presence of rings was predicted by Subramanian and Shanbhag [53], who studied symmetric and asymmetric cyclic/linear blends of polymers by simulations. However, this had never been corroborated experimentally until now, thanks to the results presented here. They have also reported that in some cases, the linear chains remain practically unaffected by the ring ones, whereas, as expected, ring chains always show slower diffusion in the

![Fig. 1. PLOM micrographs taken after crystallization from the melt of the samples at 115 °C for 10 min. Circles are used in 1a and 1e to indicate the spherulites present in the micrographs.](image)

![Scheme 1. Schematic representation of different effects on chain diffusion in blends rich in (a) $l$-PLLA, and (b) $c$-PLLA.](image)
blends [50].

An opposite effect is obtained when \( l \text{-PLLA} \) is added to \( c \text{-PLLA} \). This behavior is explained by the threading effect of small amounts of \( l \text{-PLLA} \) on \( c \text{-PLLA} \), which hinders both secondary nucleation and diffusion of cyclic molecules (see Scheme 1b). This trend corroborates the findings of previous works [35,36]. Fig. 2b also shows a solid black line (representing the mixing law) indicating that both, plasticization-like and threading effects will be diluted as the \( T_c \) increases, and hence, the mixing law will be recovered, as were found in previous works [35,36]. Fig. 2b also shows a solid black line (representing the mixing law) indicating that both, plasticization-like and threading effects will be diluted as the \( T_c \) increases, and hence, the mixing law will be recovered, as were found in previous works [35,36].

Fig. 3b shows that the melting point values for \( c \text{-PLLA} \) are slightly larger than those of \( c \text{-PLLA} \) in agreement with values reported in the literature by Louisy et al. [1] and Shin et al. [56]. Zaldua et al. [27], on the other hand, found slightly higher values for \( T_m \text{-c-PLLA} \) (148.6 °C) in comparison with \( T_m \text{-l-PLLA} \) (146.8 °C). Higher \( T_m \) values of linear polymers with respect to its cyclic counterparts have also been reported for other linear and cyclic polymers [26]. Such a trend has been attributed to higher melting entropies of the cyclic polymers in comparison with the linear ones [28,43]. However, other factors should be considered, as the differences in \( T_m \) values could be influenced by:

1. differences in the synthetic methods (i.e., ring closure click chemistry [27] vs. ring expansion (in this work), zwitterionic ring-opening polymerization [56], and reactive extrusion [1]),
2. differences in MWs (i.e., 13 kg/mol (in this work), and 15, 16, and 29 kg/mol in the works of Shin et al. [56], Zaldua et al. [27], and Louisy et al. [1], respectively). Note that in Fig. 3b, the highest value of the equilibrium melting temperature, \( T^* \) (i.e., 217 °C) is that detected for the commercial linear PLA with a much higher MW than any of the other samples.
3. the critical issue of purity of the cyclic chains, which always contain even a very small amount of linear chains.

In this work, we also determined the \( T^* \) for \( l \text{-PLLA} \), \( c \text{-PLLA} \) and their blends (see Table S5 on the SI). Remarkably, Fig. 3b shows that \( T^* \text{-c-PLLA} \) > \( T^* \text{-l-PLLA} \) and that the trend with composition is a straight line consistent with a simple linear mixing law, except for the \( l \text{-PLLA/c-PLLA} \) 5/95 blend, where the threading effects produced a melting point depression. Please note that Zaldua et al. [27] also reported a similar trend with \( T^* \text{-c-PLLA} \) > \( T^* \text{-l-PLLA} \). This is an interesting result.
considering that in other cyclic polyesters, like PCL, it has also been reported that the \( T_m \) of the cyclic chains is higher than that of the linear ones, assuming that in the crystalline state, the entropy is the same in both cases [26]. In this work, the apparent (kinetic) melting points determined by non-isothermal crystallization of the linear chains seem to be lower than that of \( c \)-PLLA, see Scheme 1. In the low supercooling range, the secondary nucleation is also facilitated by cyclic chains addition.

Fig. 3a shows that as the \( c \)-PLLA content increases in the blends, the \( T_m \) values decrease compared to that of \( l \)-PLLA, indicating an increase in the nucleation density. In the \( l \)-PLLA addition to the \( c \)-PLLA matrix, the expected \( T_m \)-nucleation density qualitative relationship is not observed since the \( l \)-PLLA/\( c \)-PLLA 5/95 shows a slightly lower \( T_m \) than that of \( c \)-PLLA. As we mentioned before, the \( T_c \) determination is made from non-isothermal tests, and in some cases, this can generate deviations concerning the expected behavior. The nucleation results obtained from the DSC scans in non-isothermal conditions (except for the \( l \)-PLLA/\( c \)-PLLA 5/95) are nevertheless consistent with the PLOM observations that also show similar differences in nucleation density during isothermal crystallization from the melt.

The results obtained by DSC and PLOM show that adding small amounts of \( c \)-PLLA to a linear PLLA matrix increases both the nucleation density (Figs. 1 and 3) and the spherulitic growth rates (Fig. 2). In contrast, the opposite effect is obtained (by PLOM) by adding small amounts of \( l \)-PLLA in the cyclic PLLA matrix.
a simple mixing law) as a result of the threading effects.

As far as the authors are aware, this is the first time that synergistic and antagonistic effects in the extremes of cyclic/linear PLLA blends and cyclic/linear polymers are obtained, offering the complete picture regarding the crystallization behavior of cyclic/linear blends. Both effects are schematically illustrated in Scheme 1, as explained above.

3.1.3.1. Understanding the plasticization-like and threading effects. Scheme 1a shows that in the l-PLLA-rich blends, the addition of c-PLLA accelerates l-PLLA chain diffusion due to a plasticization-like effect (produced by the peculiar topology of cyclic chains with compact coil conformations). Even though some threaded chains might be present (see the bottom part of Scheme 1a), the much larger fraction of unthreaded chains determine the properties of these blends.

In Scheme 1b, the threading effect of c-PLLA by l-PLLA chains in c-PLLA-rich blends is shown. In this case, the threading effect slows down the diffusion of cyclic chains, and we can consider that linear chains thread most of the cyclic ones. We can assume that a cyclic chain is equivalent to two covalently connected linear chains; therefore, each threaded chain will affect two chains (instead of one, as in a linear matrix). Also, it has been found, with simulations, that one linear chain can thread more than one cyclic molecule [50]. Therefore, the threading effect of the linear chains on the ring molecules has a larger influence when the matrix of the blend is made up of cyclic chains than in the opposite case.

Further analysis of the overall crystallization behavior from the glassy state was performed by using the Avrami [62,63] and the Lauritzen and Hoffman [64,65] (LH) theories (see details on Sections S4 and S6 of the SI).

3.1.3.2. Avrami and Lauritzen and Hoffman theories: threading vs. synergistic effect. The Avrami index ($n$) and the constant proportional to the overall crystallization rate ($K$) were obtained [62]. The obtained $n$ values, in some cases are low (see Table S4 on the SI) as the isothermal
crystallization was performed from the glassy state, enhancing the nucleation density [27]. However, they can be approximated to \( n = 3 \), in many cases, indicating that instantaneously nucleated 3D spherulites have been obtained. The \( n \) values do not show specific trends regarding the topology. The \( K \) values (expressed in \( \text{min}^{-1} \)) were transformed to \( K^{1/3} \) (expressed in \( \text{min}^{-1/3} \)) for comparison purposes. The \( K^{1/3} \) vs. \( T_c \) curves follow the same trend as the \( 1/T_{50\%} \), indicating the goodness of the fit (see Fig. S6). For more details, see Section S4 on the SI.

From the heating DSC traces, after the isothermal crystallization experiments, we have determined the \( T_m \) using the Hoffman-Weeks (HW) extrapolation (see Section S5 on the SI). We found that \( T_m \) for c-PLLA (150.8 °C to 148.4 °C), which is in line with previous studies on PLAs [27], as well as on other cyclic and linear polymers [26] (e.g., PCL [34,44]), even in a wide range of MWs [44]. When small amounts of c-PLLA are added to the l-PLLA matrix, the \( T_m \) remains within a linear simple mixing law line (see Fig. 3b). In contrast, due to threading effects, small amounts of l-PLLA cause a \( T_m \) depression (i.e., from 150.8 °C to 148.4 °C) in the l-PLLA/c-PLLA 5/95 blend.

The LH theory allows us to quantify energetic parameters related to the crystallization process. Applying the LH theory with the Origin plug in developed by Lorenzo et al. [62] (now converted into an Origin App, see ref. [66]), we have obtained the \( K_g \) values, using for its calculation the \( T_m \) values obtained by the HW extrapolation and the parameters indicated in Section S6 of the SI. The \( K_g \) is a parameter proportional to the energy barrier that the polymer needs to overcome for the overall crystallization (as it is obtained by isothermal DSC studies, which include both nucleation and growth). The obtained \( K_g \) values are plotted in Fig. 5 for l-PLLA, c-PLLA and their blends. It is worth noting that the obtained values are lower than those reported in the literature because of the low MW of the samples; for more details, see reference [8].

Fig. 5 shows that the \( K_g \) value for c-PLLA is lower (indicating a lower energy barrier for overall crystallization) than that for l-PLLA because of the topological differences between the samples. The addition of c-PLLA to a l-PLLA matrix causes a decrease in the \( K_g \) value, attributed to a synergistic effect. Such synergistic effect is due to the dual action of cyclic chain addition: nucleation plus plasticization effects. In contrast, the addition of l-PLLA to a c-PLLA matrix increases the \( K_g \) values that are even higher than that of neat l-PLLA, evidencing the strong influence of the threading effect when small amounts of l-PLLA are added to a matrix of cyclic chains. Table S7 on the SI shows that \( K_g \) (growth only) values (obtained from PLOM data), are lower than \( K_g \) (nucleation plus growth) values (obtained from DSC data), as expected [67,68].

### 3.2. Plasticization of l-PLLA and c-PLLA on commercial high MW PLA: role of topology

Small amounts of l-PLLA and c-PLLA of low MWs (i.e., the same materials employed in the previous section), were blended with a commercial PLA (i.e., with a much higher MW). The addition of low MW PLA chains is expected to cause a plasticization effect of the commercial PLA sample employed. But, will there be any influence of chain topology? In this section, we answer this question by analyzing, for the first time, the effect of f-PLLA and c-PLLA addition on the crystallization of a commercial PLA matrix.

#### 3.2.1. Polarized light optical microscopy (PLOM) results: crystallization from the melt state

Fig. 6 shows PLOM micrographs taken at the same \( T_c \) and time conditions for the commercial PLA and their blends with 5 wt% of l-PLLA and 5 wt% of c-PLLA, respectively.

Fig. 6 shows, qualitatively, a relatively similar nucleation density (or slightly higher) between the PLA matrix (Fig. 6a) and the PLA/l-PLLA 95/5 blend (Fig. 6b). In contrast, there is a large increase in the nucleation density of PLA when 5 wt% c-PLLA (Fig. 6c) is added. Once again (as in the blend with l-PLLA of low MW), the small amount of cyclic PLLA is acting like a nucleating agent for PLA, as c-PLLA can nucleate much faster than PLA, subsequently triggering its nucleation.

#### 3.2.1.1. Spherulitic growth rate: plasticization-like effect and topological influence

Fig. 7a shows the differences in the spherulitic growth rates for the neat components. Fig. 7b shows that despite these differences, c-PLLA produces more significant changes when added to the PLA matrix.

In Fig. 7a, the differences between c-PLLA and l-PLLA have already been discussed above. The lower spherulitic growth rate for PLA at temperatures below 125 °C stems from its slower chain diffusion caused by its much higher MW. It has been reported that for linear PLA with \( M_n \) ranging from 1 to 200 kg/mol, \( G_s \) increases as \( M_n \) decreases [8]. Also, due to the MW effect, the maximum in \( G_s \) occurs at higher \( T_g \) values than that for l-PLLA and c-PLLA. In the case of the blends, Fig. 7b shows that both PLA/l-PLLA 95/5 and PLA/c-PLLA 95/5 blends have higher \( G_s \) values compared to neat PLA. As in the nucleation case (Fig. 6), the 5 wt% c-PLLA addition has a stronger influence on neat PLA (in comparison with 5 wt% l-PLLA addition), causing the highest \( G_s \) values. Considering the similar MW between l-PLLA and c-PLLA, the enhanced nucleation and crystallization values reached by adding c-PLLA (in comparison with l-PLLA) can be attributed to its cyclic topology, a remarkable result.

#### 3.2.2. DSC non-isothermal experiments

Fig. 8 shows the non-isothermal scans for the PLA and their blends with l- and c-PLLA.

Fig. 8a shows an exothermic peak for the PLA and their blends during cooling from the melt, at around 99 °C. The enthalpy (\( \Delta H_c \)) of this peak significantly increases in the blends (see Table S3 on the SI), evidencing the enhanced crystallization process triggered by the addition of the low MW l-PLLA and c-PLLA samples. The \( T_g \) obtained for the PLA/c-PLLA blend is higher than that of the PLA/l-PLLA blend due to the topological effect.

Fig. 8b shows that neither l-PLLA nor c-PLLA affect the \( T_m \) values of the PLA. The \( T_{50\%} \) values of the blends are significantly lower than the \( T_c \), indicating the higher number of nuclei active in the blends, especially in the PLA/c-PLLA blend, that shows the lowest \( T_c \) value. Also, it is observed that the addition of c-PLLA to neat PLA generates the lowest \( T_g \) value (note that the \( T_g \) PLA/l-PLLA is higher) compared to the PLA (see Tables S1 and S2). This indicates the higher chain mobility in this blend as a result of the plasticization-like effect.

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![Fig. 5](image_url)  
**Fig. 5.** \( K_g \) values as a function of the c-PLLA content for l-PLLA, c-PLLA and their blends. The arrows indicate the influence of the different effects (synergistic effect and threading effect) on the \( K_g \) values.
3.2.3. Overall isothermal crystallization: crystallization from the glassy state

Fig. 9 shows a comparison of $1/\tau_0$ and $1/\tau_{50\%}$ values as a function of $T_c$ for neat PLA, $l$-PLLA, and $c$-PLLA (Fig. 9a and c), and a comparison of the neat PLA with the PLA/$l$-PLLA and PLA/$c$-PLLA blends (Fig. 9b and d).

Fig. 9a and c show that PLA has a higher $1/\tau_0$ and $1/\tau_{50\%}$ values than low MW $l$-PLLA and $c$-PLLA. It must be remembered that in this case, the crystallization has been determined from the glassy state. Commercial high MW linear PLA (with a 2% mol of D stereoisomer) nucleates and crystallizes slowly from the melt. However, when it is crystallized from the glassy state, its nucleation density and nucleation rate are greatly enhanced. This is reflected in the high values of $1/\tau_0$ in comparison with the low MW samples ($l$-PLLA and $c$-PLLA). At a constant $T_c$, it is expected that the primary nucleation rate (expressed as $1/\tau_0$) increases as the MW increases [69], either at low or high $T_c$, whereas the $1/\tau_{50\%}$ vs. MW behavior is more complex. At low $T_c$, the diffusion plays a key factor, and hence the low MW chains will have a faster overall crystallization. At high $T_c$, the nucleation favors the high MW chains.

Fig. 9a and c reflect that the maximum $1/\tau_0$ and $1/\tau_{50\%}$ values of the PLA occur at higher $T_c$ values than for $l$-PLLA and $c$-PLLA, due to the MW differences. The faster overall crystallization kinetics of the PLA is explained by the strong influence of its nucleation capacity from the glassy state. The high MW PLA has a higher nucleation density and higher nucleation rate (see Fig. 9a) compared to the $l$-PLLA and $c$-PLLA. However, the $l$-PLLA and $c$-PLLA have a higher diffusion capacity due to their low MWs, and this is reflected in their higher $G$ values, shown in Fig. 7a.

Fig. 9d shows how by adding only 5 wt% of $l$-PLLA or $c$-PLLA to the PLA matrix, a significant increase in the overall crystallization rate is obtained. Both PLA/$l$-PLLA 95/5 and PLA/$c$-PLLA 95/5 blends crystallize faster than neat PLA, even when the neat minority components were slower (see $l$-PLLA and $c$-PLLA in Fig. 9c).
To illustrate the significant increases caused by the addition of 5 wt% of l-PLLA or c-PLLA, we have taken the $1/\tau_{50\%}$ values, at selected $T_c = 112$ °C and 122 °C, and plotted them as a function of the l-PLLA and c-PLLA content, for the corresponding blends, as shown in Fig. 10. Fig. 10a and b show that both l-PLLA and c-PLLA can increase $1/\tau_{50\%}$ by a factor of 1.8 and 2.5, respectively. By comparing both Figures, it is interesting to note that c-PLLA addition causes a higher increase than l-PLLA addition, independently of the selected $T_c$. Considering that both l- and c-PLLA have similar MWs, the higher capacity of c-PLLA to accelerate the overall crystallization kinetics of PLA can be attributed to a topological effect. The l-PLLA only acts as a plasticizer agent of the PLA since it does not affect the PLA nucleation rate (see Fig. 9b), but it does affect its diffusion (see higher $G$ of the PLA/l-PLLA blend compared to the PLA in Fig. 7b). In contrast, adding c-PLLA to the PLA matrix has a synergistic effect since c-PLLA accelerates both the nucleation rate (see Fig. 9b, and the higher number of nuclei in Fig. 6c) and the spherulitic growth rate (see Fig. 7b). Scheme 2 illustrates this situation.

3.2.3.1. Understanding the plasticization-like and synergistic effect. The main difference between linear and cyclic polymers is the lack of chain ends in the latter. This lack of chain ends causes a faster diffusion in the cyclic polymers as compared to the linear ones, as cyclic chains tend to have a significantly more compact coil conformation. If we consider a blend, the chain ends of the linear PLLA of low MW can be entangled with PLA high MW chains, as shown in the bottom part of Scheme 2a. Although the presence of these low MW linear chains improves the mobility of the high MW chains, such mobility is lower in comparison with the one caused by the cyclic chains (see Scheme 2b).

When we have cyclic chains, their lack of chains ends endows them with more compact coil conformations that enhance their diffusion and make them more effective plasticizers, even if some threading effects could exist between cyclic and linear chains. Our results are in agreement with recent molecular dynamics simulations performed by Tsalikis and Mavarantzas [50]. They simulated PEO blends of linear and cyclic chains. They found that short rings were less susceptible to threading by much longer linear chains, and therefore can preserve their highly compact conformations with much faster diffusion than comparable size linear chains.

3.2.3.2. LH theory: plasticization-like vs. synergistics effect. As in the
previous section, we applied the LH theory to the experimental data of Fig. 9. We employed the $T_m$ obtained by the HW extrapolation, in which values around 217 °C were obtained (see Table S5), in line with the values reported in the literature [20]. The $K_g$ values for the neat PLA and its blends are plotted in Fig. 11.

Fig. 11 shows the reduction of the $K_g$ value of the PLA compared with its blends indicating that either $l$-PLLA and $c$-PLLA facilitates the crystallization of the PLA (a similar trend is obtained for the $K_g$ values in Table S7). The lower $K_g$ of $c$-PLLA compared to $K_g$ of $l$-PLLA suggests the influence of the topology (note that $l$- and $c$-PLLA have a similar MW and the same content in the blend). The $c$-PLLA provokes higher nucleation and higher diffusion of the PLA matrix chains, thereby accelerating $1/\tau_0$, $G$, and $1/\tau_{50\%}$ values.

4. Conclusions

Linear and cyclic low MW PLLAs were blended with small amounts of their counterparts. For the $l$-PLLA rich blends, it was found for the first time that small amounts of $c$-PLLA cause a synergistic effect (i.e., nucleation plus plasticization effects) since the nucleation density, nucleation rate ($1/\tau_0$), spherulitic growth rates ($G$), and overall
crystallization rates (1/1500) increase compared to the values obtained for neat l-PLLA. These effects were found to be higher when the c-PLLA content increased from 5 to 10 wt%. In contrast, in the c-PLLA rich blends, adding small amounts of l-PLLA caused opposite effects: reductions in nucleation density, 1/τp, G, and 1/τ50% values, due to threading of the linear chains through the cyclic ones.

Low MW l-PLLA and c-PLLA in small amounts were blended, for the first time, with a commercial high MW PLA, causing different effects, depending on the topology (i.e., linear vs. cyclic) on the spherulitic growth rate, nucleation rate, and overall crystallization kinetics without depressing the melting temperatures. The l-PLLA acts only as a plasticizer of the PLA matrix, as expected, accelerating its spherulitic growth rate but without affecting the nucleation density or the nucleation rate. In contrast, the c-PLLA has a remarkable synergistic effect on the high MW PLA matrix. The c-PLLA not only accelerates the spherulitic growth rate but also the nucleation rate, and hence the overall crystallization rate of the PLA matrix. These rate enhancements on the PLA matrix caused by adding c-PLLA, reported also for the first time, are explained by the unique topology of cyclic polymers.

CRediT authorship contribution statement

M.B.R carried out the preparation of most blends and characterization by non-isothermal and isothermal DSC, and PLOM. E.P.C and J.V.I supported the blends preparation and characterization. R.A.P.-C supervised the DSC experiments and carried out relevant data elaboration and interpretation. A.M. conceived this research work with A.J.M, contributed to the elaboration and interpretation of the experimental results, and coordinated the project. O.C synthesized and characterized the materials chemically and interpreted and elaborated the chemical results. A.J.M. designed methods for investigating crystalline structure, provided interpretation of results and coordinated the project. R.A.P.-C and A.J.M mainly wrote the manuscript with contributions from all other authors.

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Appendix A. Supplementary data

SEC and MALDI-TOF curves for c-PLLA, additional DSC curves and data Tables and Hoffman-Weeks extrapolations are included. Data pertaining the application of the Avrami and Laurtizen and Hoffman crystallization theories (using the Crystalization Fit App, see ref. [66]) are also included. Supplementary data to this article can be found online at https://doi.org/10.1016/j.jbiomac.2021.07.028.

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