Structure of Poly(l-lactic acid)s Prepared by the Dehydropolycondensation of L-Lactic Acid with Organotin Catalysts

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ABSTRACT: The synthesis of low-molecular-weight (weight-average molecular weight < 45,000 g/mol) lactic acid polymers through the dehydropolycondensation of L-lactic acid was investigated. Polymerizations were carried out in solution with solvents (xylene, mesitylene, and decalin), without a solvent using different Lewis acid catalysts (tetraphenyl tin and tetra-$n$-butyldichlorodistannoxane), and at three different polymerization temperatures (143, 165, and 190 °C). The products were characterized with differential scanning calorimetry, size exclusion chromatography, vapor pressure osmometry, $^{13}$C NMR, and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF). The resulting polymers contained less than 1 mol % lactide, as shown by NMR. The number-average molecular weights were calculated from the ratio of the area peaks of ester carbonyl and carboxylic acid end groups via $^{13}$C NMR. The stereosequences were analyzed by $^{13}$C NMR spectroscopy on the basis of triad effects. Tetraphenyl tin was an effective transesterification catalyst, and the randomization of the stereosequence at 190 °C was observed. In contrast, the distannoxane catalyst caused comparatively less transesterification reaction, and the randomization of the stereosequences was slow even at 190 °C. The l-lactic acid and n-lactic acid isomers were added to the polymer chain in a small, blocky fashion. The MALDI-TOF spectra of poly(l-lactic acid) (PLA) chains doped with Na$^+$ and K$^+$ cations showed that the PLA chains had the expected end groups. The MALDI-TOF analysis also enabled the simultaneous detection of the cyclic oligomers of PLA present in these samples, and this led to the full structural characterization of the molecular species in PLA. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 43: 2164–2177, 2005

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INTRODUCTION

Poly(l-lactic acid) (PLA) has recently been recognized as an environmentally benign polymer because of its facile biodegradability. Achieving high-molecular-weight PLA polymers through the direct dehydropolycondensation of l-lactic acid (LLA) is rather difficult because of various factors, such as kinetic control, limited and inappropriate catalyst activity, and lack of suppression of depolymerization. The water byproduct formed by the condensation of the carboxylic and hydroxyl end groups induces reverse reactions that result in the hydrolysis of the ester linkages. Moreover, commercially available LLA produced by ferme-
tation contains approximately 12% water (w/w). Hence, a water-tolerant catalyst is needed for dehydration.

In comparison with the well-established method for the catalytic ring-opening polymerization of L-lactide, the direct dehydropolycondensation of LLA has received less attention. Yamaguchi et al. studied the direct polycondensation of LLA with various Bronsted and Lewis acid catalysts through continuous azeotropic dehydration, in which the recycled solvent was passed through a tube packed with molecular sieves to keep the concentration of water in the solvent at less than 3 ppm. Moon et al. examined the melt/solid polycondensation of LLA catalyzed by a tin chloride dihydrate/p-toluenesulfonic acid binary system. Otera et al. showed that distannoxanes could be effective catalysts for the direct dehydropolycondensation of LLA to PLA. Appropriately substituted distannoxanes are hydrophobic in nature because of bulky alkyl groups around the tin atoms and, therefore, can act as water-tolerant catalysts.

On the basis of a study of the variation of the substituents \( \text{Sn}_2\text{Cl}_2 \) on the distannoxane ladder structure, it has been concluded that the molecular weights of the obtained polymers are relatively insensitive to the nature of the substituents. However, no detailed characterization of the structure and properties of such polymers has been published.

Tetraphenyl tin (2) has been widely used in the ring-opening polymerization of lactides. However, there is no report of the use of 2 as a catalyst for direct dehydropolycondensation.

The objective of this study was to examine, in depth, the dehydropolycondensation reaction of LLA with 2 and distannoxane as water-tolerant catalysts. A detailed characterization of the structures of PLA oligomers was performed with various techniques, such as matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), quantitative \( ^{13} \text{C} \) NMR analysis, size exclusion chromatography (SEC), wide-angle X-ray diffraction (XRD) analysis, and vapor pressure osmometry (VPO). The nature of the end groups of PLA in the oligomers prepared by dehydropolycondensation was determined with MALDI-TOF MS and quantitative \( ^{13} \text{C} \) NMR spectroscopy.

**EXPERIMENTAL**

**Materials**

LLA was obtained from Purac (United States) as an 88% (w/w) aqueous solution and was used without further purification. 2 was obtained from Aldrich (United States) and was used without further purification. \( p\)-Xylene, mesitylene, and decahydropaphthalene were obtained from Aldrich (United States) and were also used without further purification.

1,3-Dichloro-1,1,3,3-tetra-n-butyldistannoxane catalysts were prepared through the condensation of equimolar amounts of di-n-butyldichloride and di-n-butyldioxine in benzene for 10 h. The crude product was obtained through the evaporation of benzene and was purified by crystallization from a minimum amount of hot \( n\)-hexane.

Yield: 88%. mp: 109–111 °C (lit. 110–112 °C). ELEM. ANAL. Calcd. for \( \text{C}_{16}\text{H}_{36}\text{Sn}_{2}\text{OCl}_{2} \) (552.42): C, 34.75%; H, 6.52%; Sn, 42.98%. Found: C, 33.62%; H, 6.93%; Sn, 43.47%.

**General Procedure for the Synthesis of PLA by Direct Dehydropolycondensation**

With a quartz reactor vessel equipped with a Dean–Stark-type condenser, 40.2 g of 88% LLA was azeotropically dehydrated with 40 mL of a nonpolar, aprotic solvent for 6 h at the reflux temperature of the corresponding azeotrope without any catalyst. After the removal of water in the trap of the Dean–Stark condenser, the reaction vessel was cooled to 50 °C, the required amount of catalyst was added, and this was followed by the slow heating of the reaction mixture to the refluxing temperature of the solvent under mild stirring with the help of a mag-
nomic stirring bar. The reaction time was 15 h in all cases. The reaction mixture was cooled to room temperature, and 100 mL of chloroform was added to dissolve the resultant mixture. The resultant solution was poured into 400 mL of n-hexane for the precipitation of the polymer. The polymer was collected by filtration and further purified by repeated dissolution and precipitation.

Characterization

Molecular Weights

The molecular weights [number-average molecular weight ($M_n$) and weight-average molecular weight ($M_w$)] and polydispersity ($M_w/M_n$) were determined with respect to polystyrene standards by SEC on a Waters 150 C machine at 25 °C with eluting PLA solutions (10 mg/mL of CHCl$_3$), with toluene as an internal standard, through a series of five 30-cm-long μ-Styragel columns with pore sizes of 10$^5$, 10$^4$, 10$^3$, 500, and 100 Å. CHCl$_3$ was used as the mobile phase (flow rate = 1 mL/min), and a refractive-index detector was used for the detection of different molecular weight fractions. The $M_n$ and intrinsic viscosity ($\eta$) values were determined with the help of a Knauer K-7000 vapor pressure osmometer (25 °C) and a three-arm Ubbelohde viscometer (Schott Gerate) at 30 °C.

NMR

For the NMR measurements, the samples were dissolved in chloroform-$d$ in 5-mm-diameter NMR tubes at room temperature. The sample concentration for the $^{13}$C NMR measurements was 10 wt %. Proton-decoupled $^{13}$C NMR spectra (nuclear Overhauser effect) were recorded on a Bruker DRX 500-MHz NMR spectrometer working at 125 MHz for $^{13}$C. $^{13}$C NMR spectroscopy was also performed on a Bruker DRX 500-MHz NMR spectrometer in 10-mm-o.d. sample tubes. A digital resolution of 32,000 data points, an 18,000-Hz spectral width, a pulse angle of about 30 °, and a relaxation delay of 2 s were used; $10^3$–$10^4$ transients were accumulated. CDCl$_3$ served as a solvent and tetramethylsilane served as an internal standard for all $^{13}$C NMR measurements. The relative peak areas were proportional to the number of carbon atoms. The peak areas were calculated by the deconvolution method with WIN NMR software.

Thermal Analysis

Differential scanning calorimetry (DSC) measurements were performed on a PerkinElmer DSC-7 thermal analyzer in a nitrogen atmosphere. The measurements were run from −40 to 200 °C at a heating rate of 10 °C/min and at a cooling rate of 100 °C/min. The glass-transition temperature ($T_g$) and the crystallinity data were recorded from the second and first heating curves, respectively. Crystallinity values for different polymers were calculated through the integration of the normalized area of the melting endotherm, the determination of the heat involved, and the rating of it to the reference 100% crystalline polymer (93.6 J/g).$^{12}$

X-Ray Analysis

Wide-angle X-ray scattering patterns of the samples were obtained in the reflection mode with a Rigaku Dmax 2500 diffractometer and Ni-filtered copper radiation. The samples were scanned in the 2θ range of 10–35 °, and the generator was operated at 40 kV and 150 mA. The full width at half-maximum of the 110 peak was determined with peak-fitting software available with the diffractometer.

MALDI-TOF MS Analysis

MALDI-TOF MS analysis was performed on a Kratos Kompact MALDI IV spectrometer equipped with 0.7-m linear and 1.4-m reflection flight tubes as well as a 337-nm nitrogen laser with a pulse width of 3 ns. All experiments were carried out at an accelerating potential of 20 kV. In general, mass spectra from 200 shots were accumulated to produce a final spectrum. The obtained data were smoothened to reduce the spikiness by the average method; the smoothening filter moved along the collected data channels, adding together a number of channels and dividing by that number to give an average signal. This smoothening, however, did not eliminate or hide minor signals distinct from the baseline noise. The samples were dissolved in tetrahydrofuran (1 mg/mL) and mixed with the matrix (15 mg/mL of tetrahydrofuran) before being dried on the sample plate. 2,4,6-Trihydroxyacetophenone was used as the matrix. The sample plate was in-
inserted into the apparatus under a high vacuum (∼10⁻⁵ Pa).

RESULTS AND DISCUSSION

Molecular Weights

The SEC elugrams of the PLA oligomer samples are shown in Figure 1. All molecular weight data correspond to polystyrene standards, with a refractive-index detector, and so are only apparent values. PLA-1, PLA-2, and PLA-3 polymers were prepared by dehydropolycondensation with 2 as a catalyst and with various solvents (p-xylene, mesitylene, and decalin), as shown in Table 1. PLA-4 was prepared in the absence of a solvent with the same catalyst. PLA prepared in the presence of decalin at 190 °C and in the absence of a solvent at 190 °C showed an unusually broad $M_w/M_n$ value. This was presumably due to the presence of macrocyclics. A similar observation was made by Kricheldorf et al. for PLA macrocyclics containing tin atoms in their chains.

Figure 1. SEC elugrams of PLA oligomers: (a) PLA-1, (b) PLA-2, (c) PLA-3, (d) PLA-4, (a’) PLA-5, (b’) PLA-6, (c’), PLA-7, and (d’) PLA-8.
PLA-1 [Fig. 1(a)] showed a broad peak, whereas a bimodal peak was observed for PLA-2 [Fig. 1(b)]. PLA-3 [Fig. 1(c)] and PLA-4 [Fig. 1(d)] showed unimodal peaks.

Similar observations were also made when 1,3-dichloro-1,1,3,3-tetra-n-butyldistannoxane was used as a catalyst (Table 1). PLA-5 [Fig. 1(a')] showed a broad peak corresponding to \( M_n = 500 \) and \( M_w = 900 \). PLA-6 [Fig. 1(b')] showed a bimodal distribution, the first peak corresponding to \( M_n = 2600 \) and \( M_w = 3600 \) and the second peak corresponding to \( M_n = 500 \) and \( M_w = 600 \). PLA-7 [Fig. 1(c')] showed a single peak corresponding to \( M_n = 6400 \) and \( M_w = 24,700 \), whereas for PLA-8 [Fig. 1(d')], the \( M_n \) and \( M_w \) values were 3600 and 17,000, respectively. The molecular weights increased with the temperature for both catalysts. At lower temperatures, large number of very low-molecular-weight oligomeric species predominated. An increase in the temperature beyond 165 °C resulted in a single peak of relatively high-molecular-weight species.

Thermal Characterization

The results of the thermal characterization are shown in Table 2. \( T_g \) varied from 40 to 60 °C for the polymers prepared with 2 and dichlorodistannoxane as catalysts.

The melting temperature (\( T_m \)) of the polymers prepared with the 2 catalyst increased from 146 to 149 °C, whereas those prepared with the distannoxane catalyst showed a monotonic increase in \( T_m \) from 142 to 162 °C that depended on the temperature of the reaction.

The degree of crystallinity calculated from powder XRD patterns is shown in Table 1. Typically, the degree of crystallinity was between 70 and 80%, except for PLA-3 and PLA-7, which were abnormally low. This observation can be attributed to the racemization of LLA to d-lactic acid and its incorporation into the polymer chain. The percentage of crystallinity, as determined by DSC, was lower than that determined by XRD. A similar observation was reported for PLA prepared by ring-opening polymerization.14

The crystallinity percentage and microscopic morphology of PLA vary with its thermal history (e.g., annealing) and stereosequence distribution (e.g., S-length distribution). According to theories of polymer chain folding, the lamellar thickness is dependent on the crystallization temperature. Some kinds of structural defects due to the stereoconfiguration are rejected from crystalline domains, and this results in a reduction of the lamellar thickness. The distribution of S-lengths in the polymer causes some fraction of the defects, which may be incorporated into the crystalline domains. The presence of defect structures is reflected in the value of enthalpy of fusion of crystallization (\( \Delta H_{crys} \)).

In the case of XRD, measurements of the d-spacing indicate an expansion (110) plane of the PLA lattice, and all other planes such as (020) and (002) are invariant; this leads to the conclusion that only a parameter of the unit cell is changing.15 Therefore, the crystallinity percentage data obtained from XRD and DSC provide considerably different values.

### Table 2. Thermal Characterization Results of PLA Oligomers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_g ) (°C)</th>
<th>( T_m ) (°C)</th>
<th>( \Delta H_f ) (J/g)</th>
<th>Crystallinity at ( T_m ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-A</td>
<td>44</td>
<td>146</td>
<td>42</td>
<td>45.0</td>
</tr>
<tr>
<td>PLA-A'</td>
<td>42</td>
<td>192</td>
<td>48</td>
<td>51.3</td>
</tr>
<tr>
<td>PLA-B</td>
<td>42</td>
<td>144</td>
<td>44</td>
<td>47.0</td>
</tr>
<tr>
<td>PLA-B'</td>
<td>55</td>
<td>154</td>
<td>37</td>
<td>39.5</td>
</tr>
<tr>
<td>PLA-C</td>
<td>60</td>
<td>149</td>
<td>25</td>
<td>26.7</td>
</tr>
<tr>
<td>PLA-C'</td>
<td>59</td>
<td>162</td>
<td>47</td>
<td>50.2</td>
</tr>
<tr>
<td>PLA-D</td>
<td>57</td>
<td>153</td>
<td>47</td>
<td>50.2</td>
</tr>
<tr>
<td>PLA-D'</td>
<td>55</td>
<td>145</td>
<td>40</td>
<td>42.7</td>
</tr>
</tbody>
</table>

\( \Delta H_f \) = enthalpy of fusion.

End-Group Analysis by \( ^{13} \)C NMR

\( ^{13} \)C NMR is a useful tool for determining \( M_n \). Besides end-group determination, this technique has also been used for the determination of the residual LLA, lactide formed by the unzipping of chain ends,16,17 and the optical purity of the polymer. \( ^1 \)H NMR has also been used for the quantitative determination of end groups of PLA with a degree of polymerization (DP) of less than 18.16 However, in this case, the method proved to be inadequate because the DP of PLA was 15–170.

In this study, the NMR technique was used to determine the effects of the catalysts and temperature on the end groups and to estimate the amount of lactide and residual lactic acid in the PLA samples. Figure 2 shows the NMR spectra corresponding to polymers PLA-1, PLA-2, PLA-3, PLA-4, PLA-5, PLA-6, PLA-7, and PLA-8.

In the spectrum of PLA-1 [Fig. 2(a)], the peaks appearing from 168.5 to 169.7 ppm are
due to ester carbonyl groups, and peaks arising from 172.9 to 173.1 ppm are due to carboxylic acid end functional groups. In the region of 172.9–173.1 ppm, two absorption peaks can be observed. A similar observation was made by earlier workers.\textsuperscript{16,17} The greatest influence on the cochemical shift of the end units of PLA was the long-distance interaction, and this suggested a particular conformation and arrangement of the stereoisomers.\textsuperscript{16} The degree of polymerization (\(DP_n\)) was estimated from the relative integral ratio of these groups of signals. The small amount (<1%) of the cyclic fraction was not taken into account for calculating \(M_n\) by NMR. There were no peaks due to lactide in this polymer. The calculated \(DP_n\) and \(M_n\) values were 16 and 1100 for PLA-1 and 45 and 3300 for PLA-2.
The peak at 167.6 ppm was assigned to lactonic carbonyl groups of the L-lactide. The proportion of formed lactide in the sample was determined from the integral ratio of the peaks for the lactone carbonyl and ester carbonyl. The lactide concentration was 1.6 mol %.

In the spectrum of polymer PLA-3 [Fig. 2(c)], the ester carbonyl peak appears between 168.9 and 169.6 ppm. However, there is no peak due to the carboxylic end groups. The peak at 167.3 ppm was assigned to the carbonyl group of the lactide. The absence of any peak due to carboxylic acid end groups indicates the presence of macrocyclic oligomers of PLA. The proportion of formed lactide in this sample was calculated to be 1 mol %.

The spectrum of PLA-4 [Fig. 2(d)] shows peaks between 169.2 and 169.8 ppm and between 173.0 and 173.3 ppm for ester carbonyl and carboxylic acid end functional groups, respectively. The DPₙ and Mₙ values were 23 and 1600, respectively. There were no peaks corresponding to the cyclic lactide.

A comparison of Figure 2(a–c) and Figure 2(d) indicates that, when 2 was used as the dehydropolycondensation catalyst, linear oligomers formed exclusively at 143 °C, whereas cyclic oligomers formed exclusively at 190 °C in the solvent decalin. However, when dehydropolycondensation was performed at the same temperature in the absence of a solvent, only linear polymers formed.

For PLA-5 [Fig. 2(a’)], the ester carbonyl and carboxylic acid end group peaks arose between 169.5 and 169.7 ppm and at 173.3 ppm, respectively. DPₙ and Mₙ values were 40 and 2900, respectively. No lactide was detected in this sample.

Figure 2(b’) presents the spectrum of polymer PLA-6; the ester carbonyl peak appears between 169.2 and 169.5 ppm. No peak was found corresponding to the carboxylic acid end group. Therefore, the formation of macrocyclics was implied. There was no peak for the lactide carbonyl.

Polymer PLA-7 [Fig. 2(c’)] also consisted completely of macrocycles because the spectrum shows only ester carbonyl peaks between 169.2 and 169.6 ppm and no peak for the carboxylic acid end group. The lactide was present in a 0.5 mol % concentration.

Polymer PLA-8 [Fig. 2(d’)] was once again found to be a mixture of linear and cyclic oligomers because the spectrum contains peaks from both ester carbonyl and carboxylic acid end groups between 169.3 and 169.7 ppm and between 173.7 and 173.8 ppm, respectively. The calculated DPₙ and Mₙ values were 18 and 1300, respectively.

A comparison of Figure 2(a’–c’) and Figure 2(d’) shows that the oligomers synthesized with distannoxane as a catalyst were structurally similar to the oligomers synthesized with 2 as a catalyst. Both the solvent and temperature had profound effects on the end groups of the oligomers. The rate of polymerization was proportional to the boiling of the solvents. It was assumed that the removal of water was efficiently achieved with a high-boiling-point solvent. Although the oligomers prepared at 143 and 165 °C showed the presence of carboxylic acid end groups, the oligomers synthesized at 190 °C in the solvent decalin showed an absence of such end groups, and this indicated the exclusive formation of cyclic oligomers. However, at 190 °C, oligomers with carboxylic acid end groups were observed when the reaction was performed in the absence of any solvent.

Effect of the Temperature on the Racemization of LLA

The polymerizations with both catalysts, 2 and the dichlorodistannoxane, produced highly crystalline oligomers at 143 °C. However, when the polymerization reaction temperature was increased to 190 °C, the crystallinity decreased from 79 to 37%. This was suspected to be due to the racemization of LLA.

The extent of racemization at 143 and 190 °C was examined with 13C NMR. The spectrum for oligomer PLA-3, synthesized at 190 °C with 2 as a catalyst, showed five characteristic signals at 169.20, 169.21, 169.31, 169.39, and 169.54 ppm [Fig. 3(a)]. According to the theoretical stereoquence distributions, the signal at 169.54 ppm was assigned to the isotactic (i, mm) sequence of the carbonyl carbon atom of successive LLA units. The peaks in the region between 169.31 and 169.39 ppm were tentatively assigned to the heterotactic (h, rm) sequence, and the peak at 169.20 ppm was assigned to the syndiotactic (s, rr) sequence. 13C NMR spectra of copolymers of L-lactide and D-lactide were studied by Chabot and Vert and the fine structures in the carbonyl were discussed. Considering different components, these authors divided the carbonyl spectrum into three regions. The unique peak at the downfield was attributed to the isotactic triad. On the basis of such an analysis, the extent of D-lactic acid units in the backbone was estimated to be
about 22 mol %. The spectrum of PLA-7 synthesized with 1,3-dichloro-1,1,3,3-tetra-n-butyl-distannoxane as the catalyst at 190 °C is shown in Figure 3(b). A significantly higher level of noise is apparent in the spectrum, and this makes quantification somewhat difficult. A value of 12% of d-lactic acid units in the PLA chain was estimated from Figure 3. For the characterization of stereosequences, the average length of an isotactic block \( L_i = L_{1L} \times L_{DD} \) is a useful term. It was calculated from dyad probabilities of methane carbon with the Bernoullian equation.

PLA oligomers prepared at lower temperatures, 143 and 165 °C, did not show any d-lactic acid incorporation.

The racemization reactions are most likely due to a dynamic equilibrium of ester interchange reactions occurring between the polymer chains. During the ester interchange reactions, there are two ways in which the ester linkages between successive lactic acid units can cleave and reform. One is acyl–oxygen cleavage, which does not involve the chiral carbon in question. The other is alkyl–oxygen cleavage, in which the covalent bond between oxygen and the chiral carbon breaks and subsequently reforms; this results in an inversion of the configuration. The change from LLA (the L-form) to the D, \( \text{D,L}-\text{form} \) in the presence of the tin chloride dihydride catalyst partially through racemization has been observed with DSC and XRD.\(^{19}\) The strong proton acid assists with the breaking of the ester bond through typical carbonyl–oxygen bond breaking.

The results indicate that as the temperature increased, the probability of alkyl–oxygen cleavage increased, and this resulted in the formation of the inverted configuration. \( \text{2} \) promoted greater inversion than dichlorodistannoxane. In the case of the dehydropolycondensation reaction catalyzed by \( \text{2} \), the d-lactic acid units seemed to be incorporated into the backbone in a purely random manner, whereas in the distannoxane-catalyzed reaction, the LLA and d-lactic acid isomers were added to the polymer chain as small blocks separated from each other. The splitting pattern of these signals is identical to those reported earlier in the literature.\(^{18}\)

Intensive transesterification caused randomization of the stereosequences, with the result that \( L_i \) values tended to 2.0. For distannoxane, transesterification was comparatively less than that for \( \text{2} \). Isotactic block \( (L_i) \) values of 3.3–3.5 were found for the distannoxane catalyst at 190 °C and confirmed the presence of small, blocky groups.

MALDI-TOF MS Analysis

MALDI-TOF MS has been employed for the determination of molecular weights and the nature of end groups.\(^{20,21}\)

With dehydropolycondensation reactions, only low-molecular-weight oligomers can be prepared. Such oligomers are quite amenable to analysis by MALDI-TOF. Therefore, the oligomers prepared during this study were subjected to MALDI-TOF MS analysis.
The results of the analysis are shown in Figure 4(a–e) and Figure 5(a–d). Figure 4(a) presents the MALDI-TOF mass spectrum of sample PLA-1. The oligomer contained chains terminated by OH on one side and COOH on the other. The MALDI spectrum is dominated by a series of intense peaks ranging from a mass of 500 Da to a mass of 1500 Da, corresponding to oligomers doped with Na\(^+\) ions of type H—[O—CH(CH\(_3\))\(_2\) CO]\(_n\)—OH—Na\(^+\) (mass = 72\(n\) + 18 + 23); \(n\) values varying from 7 to 20 were detected, 23 being the mass number of sodium. The five most intense peaks belonging to this series, corresponding to oligomers with \(n\) values of 9–13, are labeled in the spectrum and reported as enlarged in the inset. The spectrum also displays other peaks of lower intensity, which desorbed as oligomers doped with K\(^+\) ions (K\(^+\) adduct molecular ions, mass = 72\(n\) + 18 + 39; see the peaks at 705, 777, 849, 921, and 992 in the inset).

Figure 4(b) shows the MALDI spectrum of polymer PLA-2. The most intense peaks belonging to this series, corresponding to oligomers with \(n\) values of 14–27, are labeled in the spectrum and reported as enlarged in the inset. The spectrum shows the chemical heterogeneity, which consists of linear and cyclic oligomers. Macrocyclic structures with \(n\) = 14–27 (mass = 72\(n\) + 23) can be observed. The macrocyclic structures were
formed by intramolecular transesterification or esterification between chain ends. The spectrum also shows oligomers doped with $K^+$ ions (mass $= 72n + 39$; see peaks at 1048–1983 Da), which overlap the linear polymers doped with sodium ions, of masses ranging from 1050 to 2000. The linear chains doped with potassium ions appear as peaks at 1568, 1640, and 1712 Da (see the inset).

Figure 4(c) shows the MALDI spectrum of polymer PLA-3. The spectrum is dominated by a series of intense peaks of masses ranging from 600 to 3000 ($n \geq 10$). In this region, the spectrum also shows two mass series of higher intensity that can be assigned to cyclic oligomers of PLA, which appear as oligomers doped with sodium or potassium ions with masses of $72n + 23$ and $72n + 39$, respectively. The intensity of the peaks due to cyclics falls off sharply at higher molecular masses. No peaks corresponding to linear polymers doped with sodium or potassium ions were found.

Figure 4(d) shows the MALDI-TOF mass spectrum of polymer PLA-4. The spectrum is dominated by a series of intense peaks ranging from 800 to 2000 Da with $n < 10$. In the region between masses of 800 and 1100 Da, this spectrum shows one series of higher intensities and two mass series of lower intensities. The peaks at higher intensities, ranging from 800 to 1100 Da, correspond to cyclic polymers doped with sodium ions and also overlap with peaks of the doped potassium ions of linear oligomers at lower intensities.
The sample expected to be formed by oligomers bearing CO\textsubscript{2}CH\textsubscript{3} and OH as terminal groups, corresponding to the general formula CH\textsubscript{3}CO—[O—CH(CH\textsubscript{3})—CO]—OH—Na\textsuperscript{+}, shows peaks in the region between 800 and 1020 Da, from which the molecular mass of each oligomer can be calculated as 72\textsubscript{n} + 60 + 23. The peaks ranging from 1200 to 1450 Da correspond to two different formulas: HO—Sn(O)—O—CH(CH\textsubscript{3})—CO—OCH(CH\textsubscript{3})—OCH\textsubscript{2}CH\textsubscript{3} and CH\textsubscript{3}O[COO—CH\textsubscript{3})OO]\textsubscript{n}O Sn(O)[OOC(H(CH\textsubscript{3}))OCO]OOC\textsubscript{3}. These peaks most likely appear in the spectrum because of the presence of impurities such as methanol, ethanol, and acetic acid in the L-LA monomer, which reacted during polymerization and formed chain ends of PLA. Such chains also have residual catalysts attached at the end in different forms, though in small concentrations. Cyclic polymers varying from \( n = 10 \) to \( n = 16 \) were also found. The tin-containing fragment of the spectrum in the range of 1200–2000 Da was expanded and is shown in Figure 4(e). Distinct isotropic peaks were also observed because of the presence of tin at 1127 and 1415 Da, which corresponded to the formula \((\text{C}_6\text{H}_5)_3\text{Sn}[O—CO—CH—(CH\textsubscript{3})_n]—OH—K\textsuperscript{+}\). The peak at 1262 Da was due to a cyclic-ring-containing tin atom doped with potassium ions of mass 72\textsubscript{n} + 118 + 154 + 16 + 39. The peak at 1551 Da was due to the formula \((\text{C}_6\text{H}_5)_3\text{Sn}[O—CO—CH—(CH\textsubscript{3})_n]O—Sn—(\text{C}_6\text{H}_5)_3—K\textsuperscript{+}\).

Figure 5(a) depicts the MALDI-TOF mass spectrum of PLA-5. As expected, the MALDI-TOF mass spectrum of this sample in Figure 2(a) shows a series of intense molecular ion peaks ranging from a mass of 500 to a mass of 2900 Da, which are assigned to the oligomers doped with sodium ions, denoted by the structure H—[O—CH(CH\textsubscript{3})—CO—]\textsubscript{n}OH—Na\textsuperscript{+}. In the region from 1200 to 1400 Da, the MALDI spectrum shows some other mass series of lower intensity. These peaks are assigned to CH\textsubscript{3}CO—[O—CH (CH\textsubscript{3})—CO—]\textsubscript{n}OH oligomers desorbing without the formation of any doped ions with either sodium or potassium. The peaks ranging from 1600 to 2700 Da show a mass series of higher intensity. These peaks correspond to oligomers of the structure H—[O—CH(CH\textsubscript{3})—CO—]\textsubscript{n}OCH\textsubscript{3}, with a molecular mass of 72\textsubscript{n} + 32, once again desorbing without adduct formation. In the region from 1700 to 2400 Da, the lower intensity peaks correspond to oligomers doped with sodium ions and terminated with OCH\textsubscript{3} and H, most likely generated from the impurities present in LLA.

The MALDI spectrum of PLA-6 is presented in Figure 5(b). The most intense peaks, ranging from 700 to 2100 Da, correspond to doped sodium ions of cyclic oligomers with a mass of 72\textsubscript{n} + 23 (\( n \) varies from 10 to 28). The corresponding cyclic oligomers doped with potassium ions can also be seen as peaks of a mass of 72\textsubscript{n} + 39. These peaks of cyclic oligomers doped with potassium ions
overlap a series of corresponding peaks of linear oligomers doped with sodium ions of a mass of $72n + 18 + 23$. The results, therefore, indicate a mixture of linear and cyclic oligomers in PLA-6.

Figure 5(c) depicts the MALDI spectrum of polymer PLA-7. The most intense peaks, arising in the region from 1600 to 2000 Da, correspond to cyclic oligomers doped with sodium ions ($n$ varies from 9 to 37). The doped potassium ions that appear in the same region are also of the cyclic oligomers. This confirms that exclusively macrocyclic oligomers were present in this sample.

Similarly, the MALDI spectrum of polymer PLA-8 is shown in Figure 5(d). The spectrum is dominated by a series of intense peaks ranging from 500 to 3000 Da, corresponding to linear oligomers doped with sodium ions (mass $= 72n + 18 + 23$, where $n$ ranges from 9 to 30). The most intense peaks in this series are reported and enlarged in the inset, which shows peaks in the region between 600 and 1500 Da. The oligomers doped with sodium ions in the region from 600 to 1800 Da overlap the doped sodium ion peaks of the type $\text{HO}-\text{CH(CH}_3\text{)}_2\text{-CO-}[\text{OCH}_3\text{]Na}^+$, that is, linear polymer molecules with a methyl ester end group in-
stead of carboxylic acid (again, mass = 72n + 34 + 23). The oligomers doped with potassium ions corresponding to this series can also be seen clearly in the mass region between 600 and 1900 Da. The molecular ion peaks in the region between 1600 and 2400 Da correspond to the K⁺ adduct ion peaks of cyclic oligomers (n ranges from 21 to 30).

The results show that cyclization effectively competes with propagation during dehydropolycondensation, especially at temperatures greater than 165 °C. These results agree with similar conclusions drawn from NMR studies. Thermodynamically controlled polycondensation tends to end up with ring–ring equilibria and not with the formation of one giant chain in equilibrium with a few cycles. According to the ring–ring equilibria, either higher molar mass, rigid polymers or low-molar-mass cycles may be the main reaction prod-

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Figure 5. (Continued from the previous page)
ucts. The experimental results in this work support the simultaneous occurrence of both thermodynamically and kinetically controlled polycondensation.22

CONCLUSIONS

The structure and properties of low-molecular-weight PLA oligomers produced by dehydropolycondensation are determined by the nature of the catalyst and the polymerization temperature. Results show that linear PLA oligomers with $M_n \sim 6000–9000$ can be prepared with organotin catalysts. The failure to obtain high-molecular-weight polymers in bulk or in the presence of a solvent can be attributed to the competitive formation of macrocycles. The structure of oligomers changes from linear to macrocyclic as the reaction temperature is increased. When dehydropolycondensation is performed in the absence of a solvent, some linear polymer is also obtained. The oligomer crystallinity varies between 37 and 85%, depending on the nature of the catalyst and solvent. No racemization reaction occurs at temperatures below 165 °C. However, 12–22 mol % d-lactic acid incorporation has been observed in oligomers prepared at 190 °C. The LLA and d-lactic acid isomers are added to the polymer chain in a small, blocky fashion in the presence of the distannoxane catalyst, whereas the randomization of stereosequences has been observed for 2. MALDI-TOF also has confirmed the presence of linear oligomers at 143 °C, a mixture of linear and cyclic oligomers at 165 °C, and predominantly cyclic oligomers at 190 °C.

REFERENCES AND NOTES