

# How Carbodiimide Modulates Oligomer Migration and Molar Mass in Recycled Poly(lactic acid): A Study Using UPLC-QTOF-MS<sup>E</sup>

Published as part of ACS Applied Polymer Materials special issue "Keeping Carbon from Plastics in Play".

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Cite This: *ACS Appl. Polym. Mater.* 2024, 6, 15230–15241

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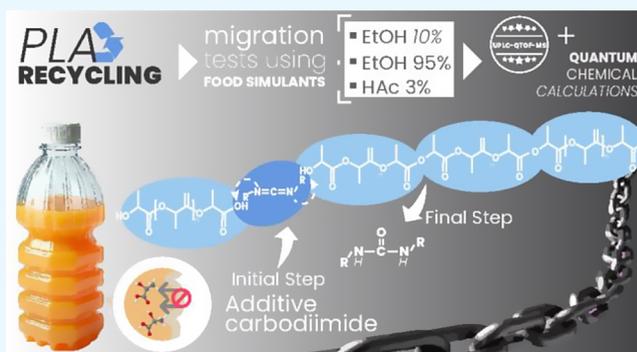
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**ABSTRACT:** The recycling of polymers for direct food contact faces initial challenges due to the loss of molar mass and the generation of Non-Intentionally Added Substances (NIAS), among which oligomers are prominent. In this study, carbodiimide (CDI) was employed as an antihydrolysis agent and chain extender to prevent oligomer formation in the recycling of poly(lactic acid) (PLA). Mechanical recycling was performed on wet and dried PLA with varying concentrations of CDI using corotating intermeshing twin-screw extrusion. CDI contributed to the increase in polymer molar mass and influenced the kinetics of its nonquiescent crystallization. Moisture played a key role in this process, as CDI can react either with water molecules, preventing hydrolytic degradation, or with available sites on the PLA molecule, resulting in increased molar mass and a decrease in the oligomer content. Oligomer migration tests were conducted using three food simulants: ethanol 10%, acetic acid 3%, and ethanol 95%. Ultraperformance liquid chromatography coupled with a quadrupole time-of-flight mass spectrometer was utilized for qualitative and quantitative PLA oligomer analyses. Electronic structure calculations based on the GFN-xTB Hamiltonian were employed for structural optimizations and energies to understand migration and interaction processes in the described systems. Sixteen different PLA oligomers were detected in the food simulant samples. Linear oligomers were identified in all simulants, while cyclic were detected mainly in the 95% ethanol simulant. The antihydrolysis and chain-extending effects of CDI in recycled PLA reduced the total oligomer concentration in both wet and dry samples, improving the physicochemical properties of PLA and ensuring food safety.

**KEYWORDS:** PLA, recycling, carbodiimide, oligomers, migration, UPLC-QTOF-MS<sup>E</sup>, quantum chemical calculations



## 1. INTRODUCTION

New protection and remediation measures have gained prominence in global discussions due to climate change, environmental challenges, and the depletion of nonrenewable resources. The United Nations' 2030 Agenda aims to promote sustainable development, alleviate poverty, protect the environment, and mitigate the impacts of climate change.<sup>1,2</sup> One key strategy for contributing to environmental preservation is the adoption of biodegradable, compostable, and biobased materials for use in single-use plastic products, particularly those intended for food contact and medical applications.<sup>3</sup> Poly(lactic acid) (PLA) is a biodegradable, biobased aliphatic polyester that exhibits processing behavior similar to conventional thermoplastics derived from nonrenewable sources, such as poly(ethylene terephthalate) (PET) and polypropylene (PP).<sup>4–7</sup> In addition, its biocompatibility, origin from renewable sources, and biodegradability make it a promising

alternative to nonrenewable materials in food packaging production.

According to the literature, biobased polymers are classified as biodegradable and/or compostable under specific biodegradation conditions outlined by standards such as ASTM D6400, D5988-18, and ISO 14855. In this context, for example, plastic material is considered compostable if at least 90% of it is decomposed within six months in an industrial composting facility.<sup>8</sup>

While the use of biobased polymers in single-use products can reduce dependence on nonrenewable resources, it does not

**Received:** September 25, 2024

**Revised:** November 25, 2024

**Accepted:** November 27, 2024

**Published:** December 5, 2024



inherently address the environmental impact of postconsumer waste. Improper disposal of these materials continues their accumulation in the environment and landfills, contributing to contamination. One proposed solution to mitigate this issue is recycling, which adds value to postconsumer waste by reintroducing it into the production cycle.

Mechanical recycling has become one of the most used methods for reinserting these materials into the production of food contact products.<sup>9–12</sup> Studies on PLA recycling are proving to be significant for developing a new generation of packaging from renewable sources, as PLA exhibits processability similar to that of conventional polymers.<sup>13–17</sup> In addition, the Food and Drug Administration (FDA), the European Commission (EC), and the Brazilian Health Regulatory Agency (ANVISA) authorize the use of recycled materials in food-contact applications, provided that migration limits of substances within the material are adhered to, ensuring no health risk to consumers from ingestion of these substances.<sup>5,18–21</sup> However, as described in the literature, one of the challenges in the mechanical recycling of PLA is the hydrolytic degradation process, which is accelerated by elevated processing temperatures and high shear rates.<sup>22</sup> This results in a reduction in molar mass and a decline in the PLA's properties, sometimes rendering the polymer unsuitable for reuse in its original application.

Furthermore, concerning the loss of properties after recycling polymers, a new class of substances has gained attention in the context of food safety: Non-Intentionally Added Substances (NIAS). These compounds may arise from the degradation of the polymer matrix, from Intentionally Added Substances (IAS), or as a result of contamination during processing. Several studies have highlighted that NIAS was overlooked for a long time. However, since 2011, European Regulation 10/2011 has included these substances among those found in food-contact packaging that may pose risks to consumer health and compromise the integrity of the materials.<sup>23–29</sup>

To mitigate the degradative processes during the recycling of polyesters, an additive named carbodiimide (CDI) has been studied.<sup>30,31</sup> As described in the literature, CDI is known due to its imide group ( $N=C=N$ ), which can react with water and provide antihydrolysis action. Freitas et al. investigated carbodiimide's effect on increasing PET's molar mass. The results demonstrated that carbodiimide works as an efficient chain extender by reacting with end groups, allowing PET to recover its original properties and enabling its reapplication in the packaging (cradle-to-cradle). These functionalities of CDI could contribute to mitigating degradative processes by reducing polymer chain scission while increasing the molar mass of the polymer.<sup>32–34</sup>

The formation of NIAS, including oligomers, in recycled materials is well documented in the literature and remains a concern regarding the overall benefits of recycling. This issue arises from the potential migration of these substances, which can contaminate food products or the surrounding environment. These concerns highlight the need for more advanced recycling processes and stringent control measures to ensure the safety and sustainability of recycled polymers, particularly in food contact applications.<sup>23,35–37</sup> In this way, European Regulation 10/2011 on materials intended for contact with food establishes specific rules for their use in food packaging, particularly regarding the migration limits that listed substances must maintain. However, oligomers classified as

NIAS are not cataloged/listed as authorized substances and, therefore, cannot exceed the migration limit of 0.01 mg/kg of food.<sup>2026,38</sup>

Given this context, herein it was investigated the influence of carbodiimide content, used as a functional molecule, on the recycling of PLA from two perspectives: (1) the increase of PLA molar mass, allowing the material to return to its original application, and (2) the presence of oligomers, which are classified as NIAS and require their levels to be monitored. Changes in molar mass and flow-induced crystallization were evaluated through rheological measurements. Additionally, two powerful techniques were integrated to quantify cyclic and linear oligomers and predict the interactions between the oligomers and the food simulants.

Ultraprecise liquid chromatography coupled with a quadrupole time-of-flight mass spectrometry-elevated energy (UPLC-QTOF-MS<sup>E</sup>) was used as a highly sensitive analytical technique to determine and quantify oligomers that may migrate into the food simulants. MSE is a cutting-edge technology that enables thorough, consistent profiling and characterization, standing out as one of the most powerful techniques for identifying nonvolatile compounds. This approach involves a simultaneous collection of low-energy (first function) and high-energy (second function) data, with an energy ramp set between 15 and 30 eV. MSE enables the precise acquisition of both precursor ion masses and fragment ion masses within a single analysis run. Mass precursors and mass fragments are recorded for every detectable compound in the sample. MSE is faster than traditional mass spectrometry or tandem MS techniques, and an added benefit is the reduced need for labor-intensive sample preparation and minimal solvent usage. Furthermore, computational methods were employed to help understand the general trend observed in the interactions between oligomer and food simulants.

Although some studies have explored the antihydrolysis and chain extender potential of carbodiimide in PLA, few focus on evaluating its influence on the molar mass and its crystallization kinetics.<sup>34,39–41</sup> Furthermore, as far as we know, there are no reports in the literature on the role of this molecule in mitigating the migration of oligomers, currently classified as NIAS, which could contribute to improving recycling processes and enhancing food safety.

## 2. EXPERIMENTAL METHODS

**2.1. Chemicals.** The chemicals used for the migration analysis as food simulants were ethanol (HPLC grade, CAS No. 540-84-1) supplied by Scharlau Chemie S. A. (Sentmenat, Spain), acetic acid (99.8%, CAS No. 540-84-1) from Chemie S. A. (Sentmenat, Spain), and ultrapure water sourced from a Milli-Q Ultrametric Wasserlab GR 216071 (Barbatain, Spain). Cyclic  $[LA]_6$  and linear  $OH-[LA]_4-H$  oligomers (both with a purity greater than 90%, where LA stands for lactic acid) were isolated as described in the literature and used as standards for oligomer quantification.<sup>42</sup>

**2.2. Sample.** The commercial biobased polymer used in this study was the PLA Ingeo 4043D (98% L-lactide content), supplied by NatureWorks LLC. The polymer has a melt flow index (MFI) of 6 g/10 min (ASTM D 1238) at 210 °C, with a density of 2.16 g/cm<sup>3</sup> (ASTM D792). A commercial carbodiimide, Carbodilite HMV-15CA, supplied by Nisshinbo Chemical Inc., was used during the PLA recycling.

**2.3. Sample Preparation.** The recycling of PLA was performed using a corotating intermeshing twin-screw extrusion Thermo Scientific Process 11 Parallel Twin-Screw Extruder ( $D = 11$  mm;  $L/D = 40$ ) at 200 °C and 400 rpm. Subsequently, the recycled PLA was reprocessed with varying concentrations of CDI (0.5, 1.0, and 3.0 m/

m %). Before incorporating CDI, the PLA samples underwent either a drying step in a vacuum oven (*dry samples*) or were reprocessed without drying (*wet samples*) to ensure the presence of moisture during the reprocessing. The drying was conducted in a vacuum oven at 80 °C for 4 h. Afterward, the samples were thermo-pressed at 200 °C for 3 min at 0.2 Torr to form PLA films. Table 1 describes the sample after the preparation.

**Table 1. Nomenclature Employed in This Study**

samples	nomenclature
PLA reprocessed	PLA <sub>r</sub>
dried PLA reprocessed + 0.5 m/m% CDI	PLA <sub>0.5%<sub>d</sub></sub>
dried PLA reprocessed + 1.0 m/m % CDI	PLA <sub>1%<sub>d</sub></sub>
dried PLA reprocessed + 3.0 m/m % CDI	PLA <sub>3%<sub>d</sub></sub>
wet PLA reprocessed + 0.5 m/m % CDI	PLA <sub>0.5%<sub>w</sub></sub>
wet PLA reprocessed + 1.0 m/m % CDI	PLA <sub>1%<sub>w</sub></sub>
wet PLA reprocessed + 3.0 m/m % CDI	PLA <sub>3%<sub>w</sub></sub>

**2.4. Rheological Characterization.** The rheological measurements were performed on an Anton Paar MCR 302 at 200 °C, using 25 mm diameter plates with a gap distance of 1 mm, under an inert nitrogen atmosphere. Complex viscosity ( $\eta^*$ ) was measured via dynamic frequency sweep tests performed in the linear viscoelasticity regime at 1% strain amplitude within the angular frequency range of 0.1–500 rad/s. The time sweep measurements were also performed, and details about measurements can be found in the Supporting Information.

The nonquiescent (shear flow-induced) crystallization of PLA with varying levels of CDI was conducted on the same rheometer under an inert nitrogen atmosphere. The samples were heated to 200 °C for this analysis and then cooled to 115 °C. Once stabilized at this temperature, a shear rate of 0.1 s<sup>-1</sup> was applied while monitoring the shear stress ( $\tau$ ) as a function of time. The onset of crystallization under shear flow, referred to as the “induction time,” was identified by the sudden increase in shear stress.

**2.5. Migration Tests.** The PLA film samples were subjected to migration experiments using food simulants (6 dm<sup>2</sup> of material per 1 kg of simulant) according to European Regulation 10/2011.<sup>20</sup>

All samples (5.4 × 1 cm) were tested in triplicate for migration using ethanol 10% (simulant A), acetic acid 3% (simulant B), and ethanol 95%, substitute simulant of D2 (vegetable oil) as it is indicated in EU 10/2011, for fatty simulant in the food category. These simulants represent hydrophilic foods capable of extracting hydrophilic compounds, foods with a pH below 4.5, and lipophilic foods, respectively. The vials were filled with 18 g of simulant and subjected to migration testing for 10 days at 60 °C, simulating worst-case conditions that packaging might encounter. The samples were then analyzed using UPLC-QTOF-MS<sup>E</sup>. Gravimetric control was conducted to determine the mass of the simulant used precisely to express the results as indicated in EU 10/2011.<sup>20</sup>

**2.6. Analytical Instrumental Conditions.** UPLC-QTOF-MS<sup>E</sup> was carried out in an Acquity system using an Acquity UPLC BEH C18 column (2.1 mm × 100 mm × 1.7 μm particle size), both from Waters (Milford, MA, USA). The solvents used as mobile phases for positive mode were water and methanol with 0.1% formic acid (solvents A<sub>1</sub> and B<sub>1</sub>). The column flow was 0.3 mL/min at 40 °C. Gradient elution was carried out with mobile phase A/B varying from 98/2 to 0/100% over 15 min, followed by a return to the initial conditions within 2 min. The sample injection volume was 10 μL.

The detector was an API source (atmospheric pressure ionization) with ESI (electrospray ionization) coupled to a mass spectrometer (Xevo G2) consisting of a quadrupole, a collision cell, and a time-of-flight (QTOF) detectors, all supplied by Waters (Milford, MA, USA). The electrospray probe was operated in positive (ESI+) mode and in sensitivity analyzer mode. The mass ranged from 50 to 1200 Da, and the capillary voltage was 2.5 kV. The sampling cone voltage was also set to 30 and 70 V for positive mode. The source temperature was

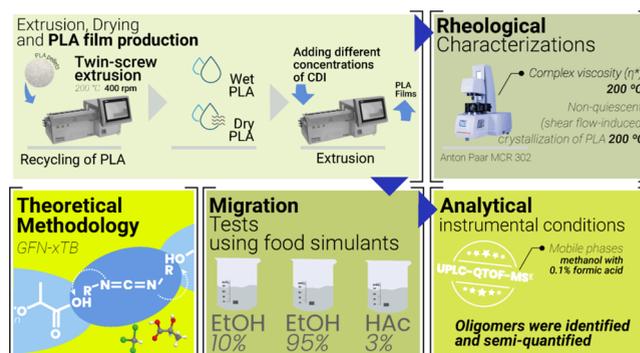
120 °C, and nitrogen was used as the desolvation gas, with a flow rate of 450 L/h at 400 °C. The cone gas flow rate was 20 L/h.

The acquisition was performed in MS<sup>E</sup> mode to allow low and high collision energy (CE) use in the collision cell during the same run. The mass spectrum at low energy (CE 4 V) provided information about the fragment ions. Mass correction was ensured by infusion of a LockSpray solution of leucine-enkephalin (2 ng/mL in water/acetonitrile with 0.1% formic acid) at a flow rate of 5 μL/min. Test mix solution of known standards were injected every 20 injections to ensure accurate mass readings. MassLynx v.4.1 (Waters, Milford, MA, USA) was used for sample analysis.

The PLA oligomers were semi-quantified using a calibration curve for cyclic oligomers with [LA]<sub>6</sub> and linear oligomers with OH-[LA]<sub>4</sub>-H.<sup>42</sup> The instrumental limits of quantification (LOQ) were 3.6 μg/g for [LA]<sub>6</sub> and 0.45 μg/g for OH-[LA]<sub>4</sub>-H, and the instrumental limits of detection (LOD) were 1.2 and 0.15 μg/g for the respective oligomers.

**2.7. Theoretical Methodology.** To help understand the interaction between oligomers and simulants, electronic structure calculations using the GFN-xTB<sup>43</sup> approach was carried out in the ORCA program.<sup>44,45</sup> The interaction with the simulants was considered using the implicit analytical linearized Poisson–Boltzmann (ALPB) solvation model.<sup>46</sup> As the EtOH 95% medium is basically ethanol, this was the solvent defined in the ALPB model. For EtOH 10% and HAC 3%, which are mainly composed of water, the implicit solvent considered in the ALPB computations was water. Therefore, we have simulated two conditions, named EtOH or H<sub>2</sub>O, within the theoretical data.

Finally, Figure 1 shows the flowcharts of the work from the PLA recycling step to sample preparation, the rheological analysis, and the



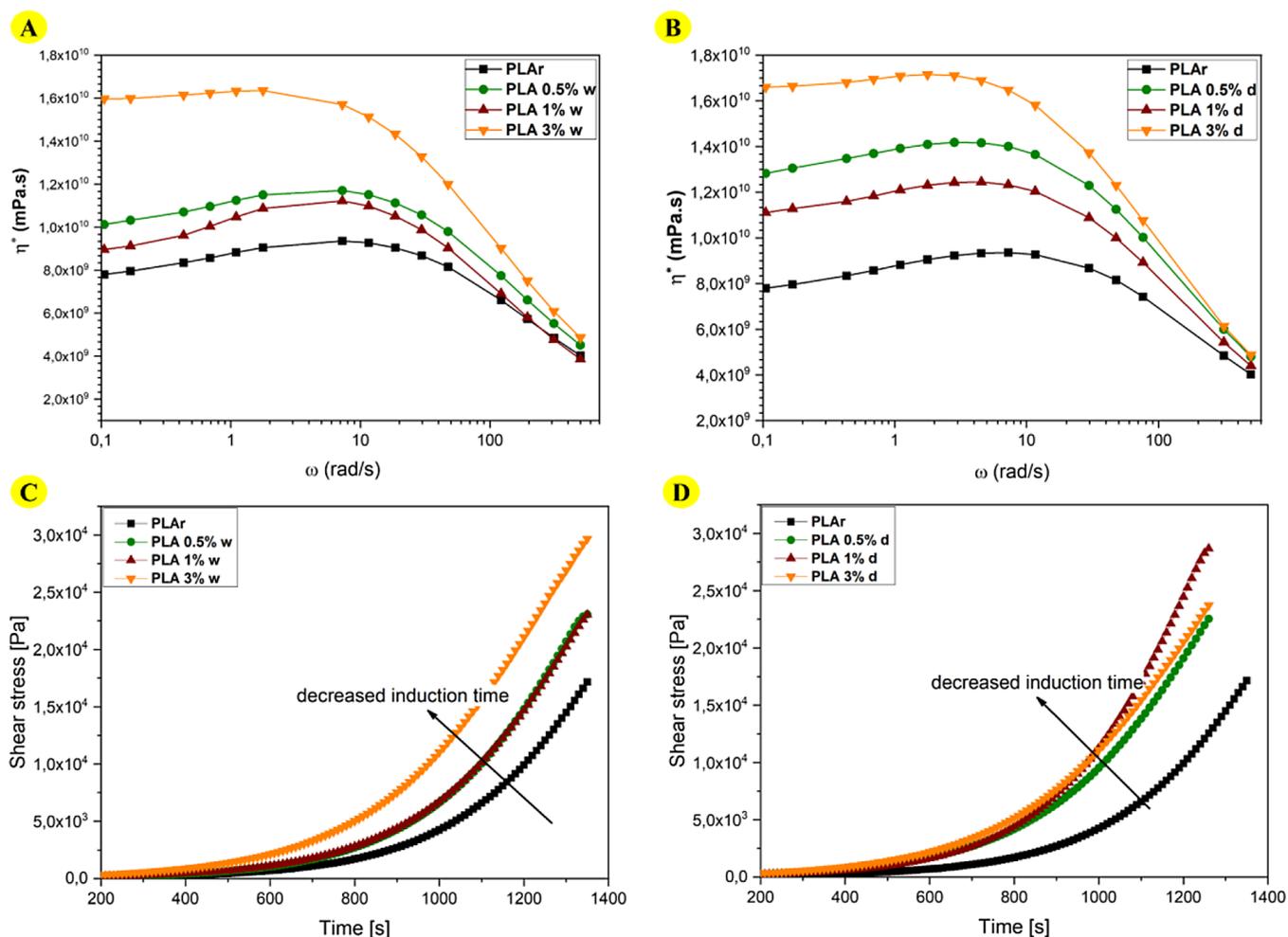
**Figure 1.** Flowcharts of the work: Samples preparation, rheological characterization, migration tests, analytical procedures, and theoretical methodology.

determination of oligomer by UPLC-QTOF-MS<sup>E</sup> and, the theoretical-computational analysis.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Carbodiimide Content on PLA Molar Mass and Nonquiescent Crystallization.

The understanding of the molar mass increase as a function of carbodiimide content in PLA was analyzed. The study was designed to (i) assess the effect of varying carbodiimide concentrations on molar mass and (ii) determine how the presence of moisture influences this process. Figure 2A,B presents the viscosity complex as a function of angular frequency for all samples that exhibit a clear Newtonian plateau at low frequencies regardless of the presence of moisture. The incorporation of CDI leads to a significant increase in complex viscosity, accompanied by a slight decrease in the length of the Newtonian plateau, indicating a more pseudoplastic behavior.



**Figure 2.** Complex viscosity ( $\eta^*$ ) versus angular frequency at 200 °C under (A) wet and (B) dry conditions, and shear stress ( $\tau$ ) versus time at 115 °C under (C) wet and (D) dry conditions for PLAr and PLA with CDI concentrations of 0.5, 1.0, and 3.0 m/m %.

The time sweep measurements were performed (Supporting Information—Figure S1) to verify the stability of the samples. A slight linear decrease was observed until 1250 s, which means that the degradation reactions may occur during the experiment resulting in chain scission.<sup>14</sup> Although this, an increase in the molar mass was observed with the addition of carbodiimide, corroborating the results of the frequency sweep.

The alteration in molar mass affects the kinetics of PLA crystallization; therefore, an investigation into noncrystallization conditions was carried out. Figure 2C,D shows the stress ( $\tau$ ) as a function of time under nonquiescent conditions at a shear rate of 0.1 s<sup>-1</sup>. The onset time can be determined by observing when the viscosity increases abruptly. At this point, the viscosity tends to infinity, indicating that the material begins to behave as a solid. It has been indicated that the induction time is approximately proportional to the inverse of the nucleation rate.<sup>47</sup> At a constant temperature, the free energy associated with the flow depends solely on the entanglement density and the Deborah number. Since the crystallization rate is the result of the product between nucleability and transportability, it is highly influenced by the mobility and diffusivity of the polymer chains. Despite the increase in molar mass, a reduction in flow-induced crystallization time is observed with increased carbodiimide content.

Table 2 shows the results of the degree of crystallinity ( $X_c$ (%)) for the PLA with the addition of carbodiimide, for the

**Table 2. Enthalpy of Melting and Degree of Crystallinity Results for the PLA Without and With Carbodiimide Addition in Wet and Dry Samples**

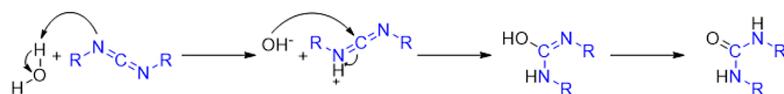
sample	$\Delta H_m$ (J/g)	$X_c$ (%)
PLAr	24.81 ( $\pm 3.67$ )	26.67 ( $\pm 3.94$ )
PLA0.5%w	27.51 ( $\pm 1.03$ )	29.60 ( $\pm 1.10$ )
PLA1%w	21.58 ( $\pm 2.37$ )	23.20 ( $\pm 2.53$ )
PLA3%w	20.05 ( $\pm 0.75$ )	21.56 ( $\pm 0.84$ )
PLA0.5%d	26.85 ( $\pm 0.58$ )	28.87 ( $\pm 0.63$ )
PLA1%d	20.24 ( $\pm 0.50$ )	21.77 ( $\pm 0.54$ )
PLA3%d	17.89 ( $\pm 0.74$ )	19.23 ( $\pm 0.79$ )

wet and dry samples, compared to recycled PLA. The  $X_c$  was obtained from eq 1:

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (1)$$

where  $\Delta H_m$  is the enthalpy of melting obtained by DSC analysis for each sample and  $\Delta H_m^0$  is the theoretical enthalpy of melting assuming 100% crystalline PLA with a value of 93 J/g.

## Anti-hydrolysis



## Chain-extending

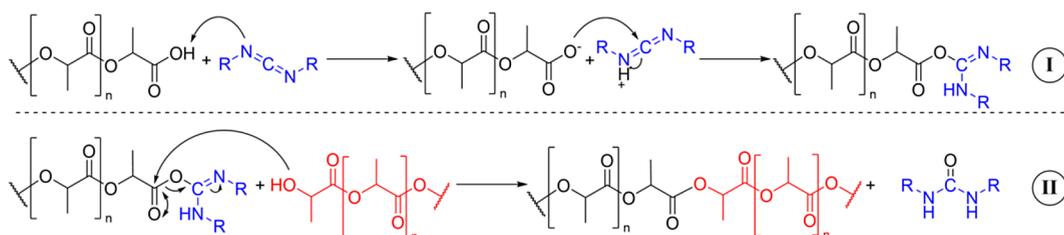


Figure 3. Proposed mechanism illustrating the antihydrolysis and chain-extending action of CDI.

Table 3. Candidate Oligomers Classified by Retention Time ( $t_r$ ), Sodium Molar Mass [ $MNa^+$ ], and Molecular Formula (MF) for Each Food Simulant

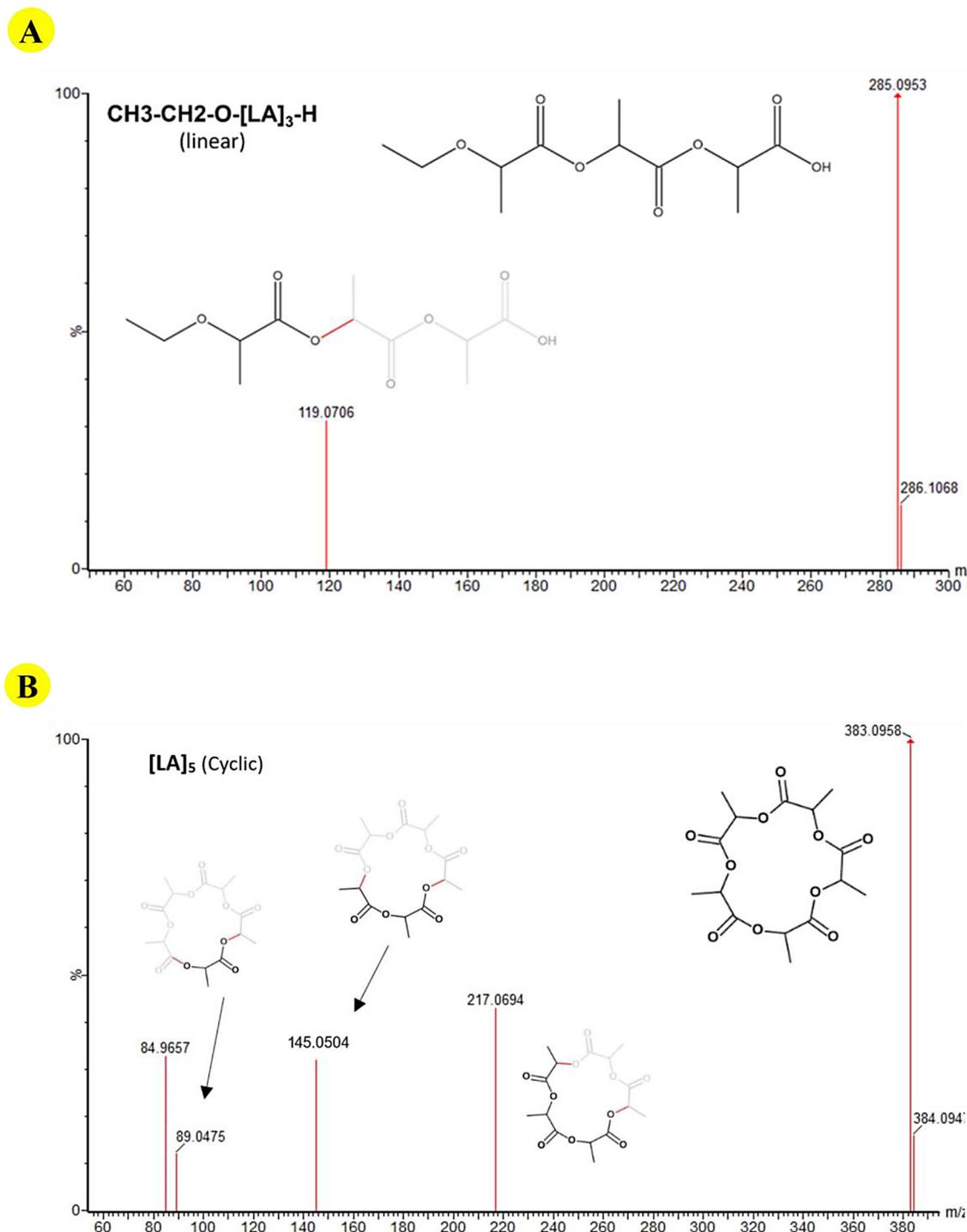
Number#	$t_r$ (s)	Mass [ $MNa^+$ ]	MF	Candidate oligomer	Simulant		
					EtOH 10%	EtOH 95%	HAc 3%
1	5.417	213.0732	C8H14O5	CH <sub>3</sub> -CH <sub>2</sub> -O-[LA] <sub>2</sub> -H			
2	5.719	329.0844	C12H18O9	OH-[LA] <sub>4</sub> -H			
3	6.279	285.0953	C11H18O7	CH <sub>3</sub> -CH <sub>2</sub> -O-[LA] <sub>3</sub> -H			
4	6.461	401.1059	C15H22O11	OH-[LA] <sub>5</sub> -H			
5	6.801	473.1282	C18H26O13	OH-[LA] <sub>6</sub> -H			
6	6.920	357.1167	C14H22O9	CH <sub>3</sub> -CH <sub>2</sub> -O-[LA] <sub>4</sub> -H			
7	7.04	383.0936	C15H20O10	CYCLIC [LA] <sub>5</sub>			
8	7.151	545.1475	C21H30O15	OH-[LA] <sub>7</sub> -H			
9	7.342	429.1367	C17H26O11	CH <sub>3</sub> -CH <sub>2</sub> -O-[LA] <sub>5</sub> -H			
10	7.448	617.1697	C24H34O17	OH-[LA] <sub>8</sub> -H			
11	7.46	455.1160	C18H24O12	CYCLIC [LA] <sub>6</sub>			
12	7.655	501.1591	C20H30O13	CH <sub>3</sub> -CH <sub>2</sub> -O-[LA] <sub>6</sub> -H			
13	7.760	527.1376	C21H28O14	CYCLIC [LA] <sub>7</sub>			
14	7.900	573.1780	C24H32O16	CYCLIC [LA] <sub>8</sub>			
15	7.99	645.1978	C26H38O17	CH <sub>3</sub> -CH <sub>2</sub> -O-[LA] <sub>8</sub> -H			
16	8.18	671.1790	C27H36O18	CYCLIC [LA] <sub>9</sub>			

The literature widely acknowledges that, under quiescent conditions, molar mass significantly influences the rate of nuclei formation.<sup>47,48</sup> Polymer chains with lower molar mass require less time for nucleus formation and subsequent crystal growth. This behavior was observed in wet and dry samples (Table 2), which means that the lower the molar mass, the higher the degree of crystallinity. However, the crystallization behavior of polymers is often influenced by the application of shear flow to the sample. Under real processing conditions, this effect becomes crucial, as crystallization typically occurs in a flowing environment. By examining flow-induced crystallization, it is possible to determine the induction time, revealing how shear flow impacts crystalline structure formation. It is well established that the crystalline structures formed under shear differ from those formed under quiescent conditions. Shear flow can align polymer chains, promoting the formation of primary nuclei precursors. The crystallization efficiency is closely linked to (i) the formation of shear-induced nuclei and (ii) the relaxation time of the polymer chains. Therefore, polymers with higher molar mass present longer relaxation times and exhibit greater chain alignment, which enhances the efficiency of the crystallization process, as observed in Figure 2.

Figure 3 presents a mechanism proposal for the reaction of CDI with water molecules and the reaction of CDI with meres

of PLA. It illustrates the hydrolysis mechanism between water and carbodiimide, where carbodiimide abstracts a proton from water molecules via electrophilic attack, leading to the formation of hydroxyl, which will react with carbon in the carbodiimide group ( $R'-N=C=N-R'$ ). This nucleophilic attack forms a transition state and a subsequent intermediate, which undergoes proton transfer and rearrangement. Ultimately, the reaction forms a urea derivative ( $R-NH-C(=O)-NH-R'$ ), a common outcome when carbodiimides are exposed to water. In this manner, carbodiimide functions as an antihydrolysis agent, protecting the PLA polymer chain from degradation through hydrolysis.

In addition, CDI can act as a chain extender, as illustrated in the mechanism shown in Figure 3, which is divided into two stages. As described by Schotman,<sup>49</sup> carboxylic acid groups can react with carbodiimides through an electrophilic attack, initiating coupling reactions. Initially, the proton from the carboxylic acid group at PLA structure is abstracted by the carbodiimide, which subsequently reacts with the nucleophilic carbon of the protonated carbodiimide intermediate (I). This is followed by the coupling of another terminal carboxyl group of PLA in the same reaction, resulting in polymer chain extension and the formation of a urea derivative (II).



**Figure 4.** High-energy collision and fragmentation spectra of candidate (A) linear and (B) cyclic oligomers identified in food simulants.

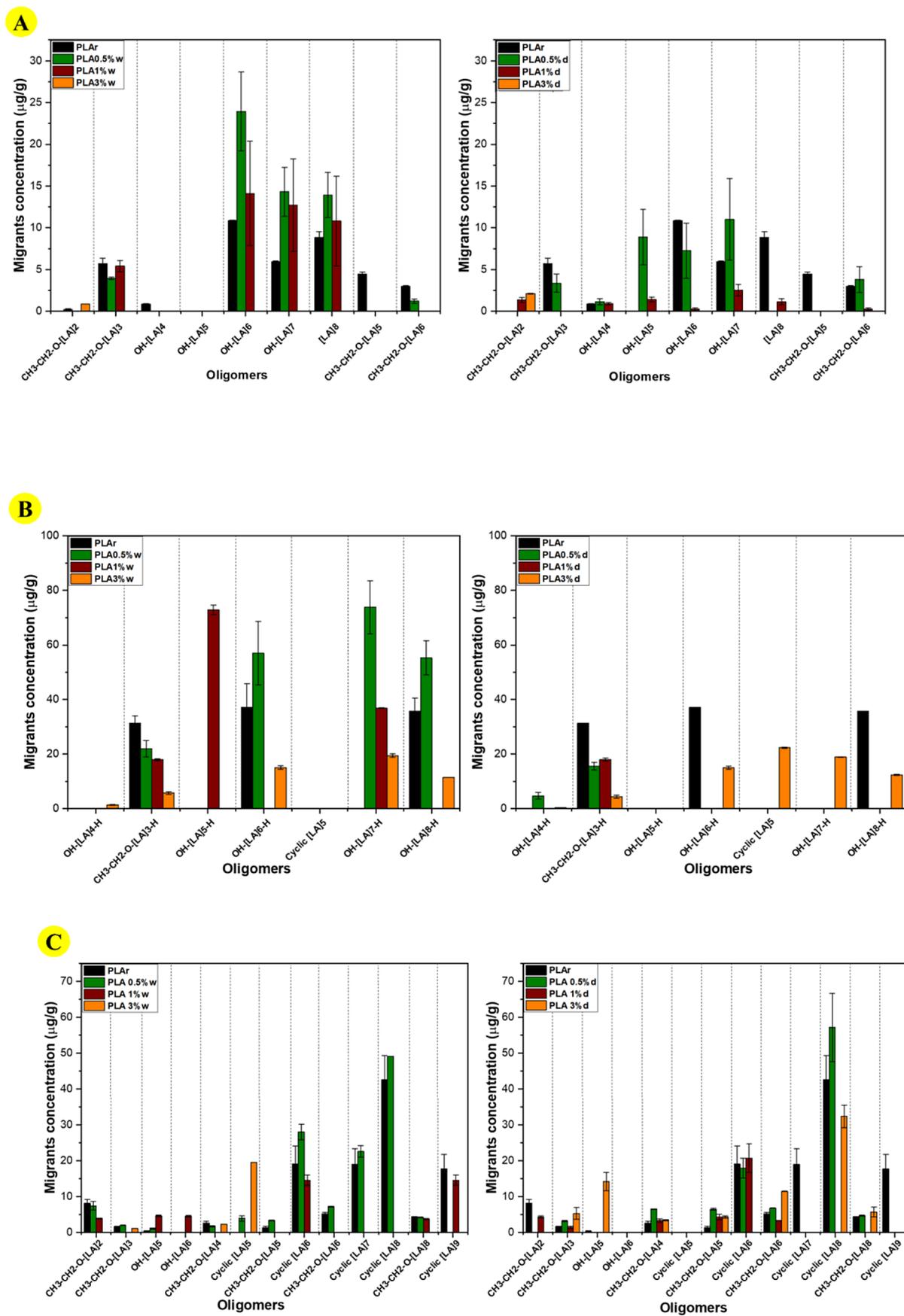
### 3.2. Identification of Oligomers in Recycled PLA.

Table 3 shows the total number of candidate oligomers identified in all the PLA samples, with and without the addition of the CDI, for the three different food simulants. Sixteen (16) oligomers were identified, including those initially present in the PLA, where 69% were linear chains, while 31% were cyclic structures.

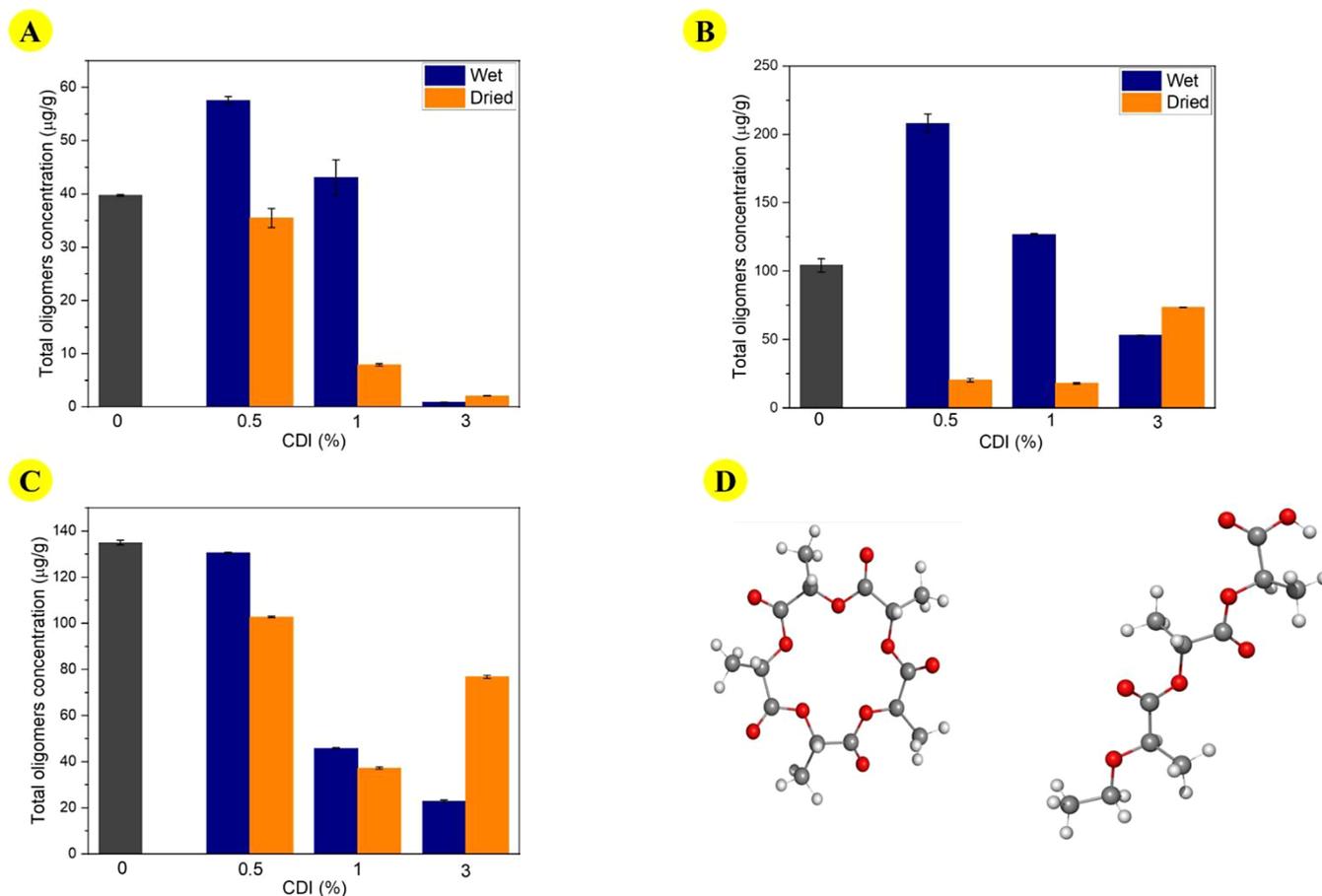
As described in the literature, many of these oligomers have been previously cataloged in some studies,<sup>23–25,50,51</sup> mainly employing and involving PLA for food contact applications. Additionally, the sodium ion adducts [MNa<sup>+</sup>] were detected

for all oligomers. Each oligomer contained the single monomer [LA], corresponding to the formula C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>, as also reported by Aznar et al. in their study on the migration of PLA oligomers in PLA/polyester blend employed in packaging.<sup>25</sup> The oligomer candidates were identified based on their retention time, molar mass with the sodium ion adduct, molecular formula, and chemical structure, as described in Table 3 and Figure 4.

The linear oligomers were identified in the EtOH 10%, and Hac 3% simulants, although at lower levels in the acid simulant. In contrast, both linear and cyclic oligomers were



**Figure 5.** Oligomer migration for the samples with different concentrations of CDI (0.5, 1, and 3%), wet and dry, and each food simulant: (A) EtOH 10%, (B) HAc 3%, and (C) EtOH 95%.



**Figure 6.** Total oligomer concentration as a function of carbodiimide concentration for each simulant: (A) EtOH 10%, (B) HAC 3%, and (C) EtOH 95%, for dry and wet samples; and (D) model systems used in computational investigations, considering cyclic and linear oligomers.

detected in the EtOH 95% simulant. Figure 4A shows the high-energy collision spectrum for one of the linear oligomers identified in the three food simulants. This oligomer, with the structure formula  $\text{CH}_3\text{-CH}_2\text{-O-}[\text{LA}]_3\text{-H}$ , was identified by its mass of 285.0953  $m/z$ , corresponding to the molecular formula  $\text{C}_{11}\text{H}_{18}\text{O}_7$ . Additionally, the cyclic oligomer with the structure formula  $\text{OH-}[\text{LA}]_5\text{-H}$ , having a mass of 383.0936  $m/z$ , corresponding to the molecular formula  $\text{C}_{15}\text{H}_{20}\text{O}_{10}$  is shown in Figure 4B and was identified in the EtOH 95% simulant.

As shown in Figure 4, the identified fragments demonstrated a high degree of reliability in confirming the structure of the proposed oligomers. However, the Lactide monomer ( $\text{C}_6\text{H}_8\text{O}_4$ ) cannot be identified due to the difficulties in its ionization and detection by mass spectrometry, as reported in the literature.<sup>23</sup>

**3.3. Migration of PLA Oligomers and the Influence of the Presence of Carbodiimide.** Figure 5 presents the migration data for each identified oligomer listed in Table 3, covering both wet and dry conditions for each food simulant, EtOH 10%, HAC 3%, and EtOH 95%. To ensure consistency, comparisons of oligomer concentrations were conducted exclusively on reprocessed PLA samples, with recycled PLA as the control. In addition, the results compare samples without the CDI to those containing three different concentrations (0.5, 1.0, and 3.0 m/m %) across the various food simulants. The oligomer migration levels are expressed in  $\mu\text{g/g}$ , clearly comparing and illustrating how the presence and

concentration of the CDI influence migration behavior in each simulant.

As described in the methodology, the samples were reprocessed under dry and wet conditions to evaluate the influence of humidity on the hydrolysis degradation process.

As stated, linear oligomers were identified in the EtOH 10% and HAC 3% simulants, totaling 9 and 7, respectively, as shown in Figure 5A,B. A cyclic oligomer ( $[\text{LA}]_5$ ) was identified for HAC 3%. The concentration of oligomers in dried samples decreases compared to wet samples for both the EtOH 10% and HAC 3%. However, although the number of oligomers detected was higher for the samples exposed to the EtOH 10% simulant, their concentration was lower when compared to the HAC 3% simulant. This behavior is observed for dry and wet samples, as shown in Figure 5A,B.

On the other hand, linear and cyclic oligomers were quantified for the EtOH 95% simulant, totaling 13 oligomers, as shown in Figure 5C. In this case, the difference between the dry and wet samples was less pronounced than the other simulants.

Figure 6A–C shows the total oligomer concentration as a function of CDI concentration for the three food simulants, evaluating both wet and dry samples. This compilation includes the total concentration of all oligomers that migrated to each food simulant, encompassing both cyclic and linear forms. These results enable us to assess the influence of CDI concentration on the migration of PLA oligomers present in the samples.

Figure 6 shows that, in general, the wet samples exhibit higher concentrations of oligomers. Additionally, it was observed that for the EtOH 10% simulant, the total oligomer concentration tended to decrease as the CDI concentration increased for wet and dry samples. Samples containing 0.5 and 1.0% CDI show higher total oligomer values than the control sample. This phenomenon can be explained by the fact that the control PLA was reprocessed after undergoing the typical drying process for this type of polymer. However, for the wet material, CDI incorporation occurred without the drying step, which may have led to hydrolytic reactions, as previously described, increasing total oligomer content, especially at lower CDI concentrations. However, increasing the CDI concentration to 3.0% causes a substantial reduction in this value.

For CDI concentrations between 0.5 and 1.0 m/m%, the decrease in total oligomer concentration is more pronounced in the dry samples because the presence of water is minimal, which hinders the process of degradation by hydrolysis and the presence of CDI also acts as an antihydrolysis agent, preventing further formation of oligomers that could migrate to the simulants. On the other hand, at a 3% CDI concentration, a significant reduction is observed, with virtually no difference between the two sample types.

A similar trend was observed for the samples exposed to the HAc 3% simulant, especially in the wet condition. However, there was an initial reduction in the detected values for the dry samples, followed by an increase as the CDI concentration increased. A similar behavior was noted in the samples exposed to EtOH 95%. As described in the literature,<sup>32,33,49</sup> CDIs are recognized for their bifunctionality, acting as an antihydrolysis additive and a chain extender. This functional duality is evident in the individual oligomer migration results and the total oligomer analysis as a function of CDI content. In both wet and dry samples, there is a downward trend in the concentration of oligomers migrating to the simulants as the concentration of CDI increases.

However, the wet samples have a higher concentration of oligomers than the dry ones, due to hydrolytic reactions. In addition, the efficiency of CDI as a chain extender is more pronounced in the dry samples, as verified in the rheological analysis, because the lower the concentrations of water in the system, the more available CDI is to react with the end groups of the molecules present in the PLA.<sup>49,52</sup>

As described in European Regulation 10/2011, food contact materials are subject to strict rules regarding the migration of IAS and NIAS.<sup>20,53</sup> The EU recognizes lactic acid as an authorized monomer for the biobased polymer PLA with no restrictions on its migration in contact with food. However, cyclic lactide, along with linear and cyclic oligomers are not included in this positive list and are classified as NIAS. Therefore, their migration limit must not exceed 0.01 mg/kg ( $\mu\text{g/g}$ ). As shown in Figure 6, some of the oligomers exceed the specific migration limits, while others meet or are below the limit stipulated by the EU.

One reason the total concentration of oligomers exceeds the specific limit is related to the conditions of the migration tests. These migration tests simulate the extreme conditions a packaging may experience, and it is near the glass transition temperature of PLA (55–60 °C). At this temperature, the amorphous chain gains mobility, facilitating the migration of substances. Additionally, the interaction between the simulant and the PLA, as well as between the simulant and the oligomers, plays a crucial role in understanding the migration

process, impacting both food safety and quality. However, the total oligomer migration shows a clear tendency to decrease with increasing CDI concentration in all the simulants, with a reduction of up to 98.5% observed for samples containing 3% CDI in the EtOH 10% simulant.

**3.4. Understanding Oligomer's Migration to Food Simulants.** As described above, the oligomers present in PLA can originate from prior processing and the recycling stages of these materials. The degradative processes, primarily hydrolysis, significantly increase oligomer formation, which can render PLA unsuitable for use in food contact packaging. In this context, understanding oligomer migration and employing strategies to mitigate this mass transfer process is crucial for effecting PLA that is suitable for direct food contact and enhancing safety.

Literature suggests that the diffusion process is strongly influenced by the molar mass of the compounds and the polymer's glass transition temperature.<sup>54</sup> However, these are not the primary factors in the analysis of the contaminant migration process. As noted by Paiva et al., other factors, especially the characteristics and interactions between the systems, must also be considered when evaluating compound migration.<sup>55</sup> In this context, the triple interaction between the polymeric matrix, oligomers, and food simulants plays a crucial role in migration. Furthermore, the conditions under which migration tests are conducted can significantly influence diffusion processes.

Another aspect not yet addressed in the literature is the influence of carbodiimide on oligomer migration. As reported, carbodiimides possess two critical properties in the processing and recycling of polymeric materials: their antihydrolysis effect and their function as polymer chain-extending agent.<sup>30,32–34</sup> As an antihydrolysis additive, carbodiimide can react with water in the system (Figure 3), preventing the polymer chain from undergoing degradation and reducing the formation of oligomers and other NIAS. In this context, the additive's potential is more significant in wet PLA samples.

On the other hand, as previously mentioned, CDI can act as a chain extender by reacting with the end groups of PLA. Compared to PLA chains, oligomers' lower molar mass facilitates the diffusion process. In short polymers, movement follows Brownian diffusion, whereas in long-chain polymers, reptation governs the diffusion process, leading to significantly slower mobility.<sup>56</sup> Consequently, oligomers are expected to have higher diffusivity, which favors their reaction with CDI. As a result, the presence of CDI reduces the formation of free oligomers in the sample and inhibits their migration to the simulants. As described previously, a proposed mechanism illustrating the dual action of CDI, both as an antihydrolysis chain-extender agent (Figure 3).

**3.5. Understanding Oligomer's Migration to Food Simulants through Molecular Modeling.** As described in the theoretical methodology, the structure of each oligomer, cyclic (OH-[LA]<sub>5</sub>-H) and linear (CH<sub>3</sub>-CH<sub>2</sub>-O-[LA]<sub>3</sub>-H), was optimized using the GFN-xTB method, as can be seen in Figure 6D. The solvation energy,  $\Delta E$ , which describes the affinity between the oligomer and its medium (simulant) was obtained by eq 2:

$$\Delta E = E_{\text{medium}}^{\text{oligomer}} - E_{\text{vacuum}}^{\text{oligomer}} \quad (2)$$

$E_{\text{medium}}^{\text{oligomer}}$  is the energy of the oligomer (cyclic or linear) in a specific solvent (ethanol or water) and  $E_{\text{vacuum}}^{\text{oligomer}}$  is the energy of

an oligomer in gas-phase. Therefore, to calculate  $\Delta E$ , the models for the cyclic and linear (Figure 6D) oligomers were optimized in gas-phase and each medium. The more negative  $\Delta E$  is, the greater the affinity of the oligomer with the simulant. All structures were confirmed as a minimum in the explored potential energy surface by vibrational frequencies analysis.

To understand the overall trend in why linear oligomers were identified in EtOH 10%, EtOH 95%, and HAc 3% simulants, while the cyclic oligomer was detected in EtOH 95% simulant only, the interaction between oligomer and simulants, through the solvation energy ( $\Delta E$ ), was estimated and collected in Table 4. The more negative  $\Delta E$  is, the more

**Table 4. Solvation Energy,  $\Delta E$  (kJ/mol) for Each Oligomer in Ethanol and Water**

oligomer	$\Delta E$ (EtOH)	$\Delta E$ (H <sub>2</sub> O)
cyclic	−110.0	−60.6
linear	−134.3	−89.5

significant the affinity of the oligomer with the simulant. Due to its favorable interactions with the solvent, about −134.3 kJ/mol in EtOH and −89.53 kJ/mol in H<sub>2</sub>O, the linear species appear more in any solution than the cyclic one. In the EtOH simulant,  $\Delta E$  for the cyclic oligomer becomes greater, about −110.0 kJ/mol, and this species is now experimentally identified in this medium. It is worth noting that although real cyclic and linear oligomers exhibit varying repeating length distributions, incorporating all possible variations would be impractical for electronic structure calculations. Hence, the employed model provides an initial view of the systems and an upper-bound estimate for the solvation energies.

#### 4. CONCLUSIONS

The antihydrolysis and chain extension effects of carbodiimide in PLA were achieved by incorporating it via corotating intermeshing twin-screw extrusion. After this, the PLA samples were subjected to migration tests in three food simulants: 10% ethanol, 3% acetic acid, and 95% ethanol (fatty simulant), and oligomers from PLA were qualitatively and quantitatively determined by UPLC-QTOF-MS<sup>E</sup>.

The addition of carbodiimide directly increased PLA physical properties such as complex viscosity, influencing PLA molar mass and molar mass distribution and enhancing the nucleation rate of shear flow-induced PLA crystals.

Moreover, carbodiimide was beneficial for food safety, as the total migration of oligomers exhibited a clear tendency to decrease with increasing CDI concentration. This is attributed to CDI's ability to prevent the degradation of PLA chains, which reduces the formation of oligomers and other non-intentionally added substances, while also acting as a chain extender.

The theoretical methodology allows the identification of the linear species as more prevalent in both solutions compared to the cyclic one, due to its favorable interactions with the solvent. In the ethanol simulant, the energy difference for the cyclic oligomer increases, making this species experimentally identifiable in this medium.

Finally, this study provides valuable insights into the dual role of carbodiimide in enhancing both the physical properties and safety profile of PLA for food packaging applications. By improving the polymer's resistance to hydrolysis and reducing the migration of potentially harmful oligomers, this work

advances the development of safer, more sustainable biobased materials suitable for direct contact with food.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.4c03030>.

Details of time sweep analysis parameters and results in graph format (PDF)

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##### Funding

The Article Processing Charge for the publication of this research was funded by the Coordination for the Improvement of Higher Education Personnel - CAPES (ROR identifier: 00x0ma614).

##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

The authors are grateful for financial support in part by the Coordenação de Aperfeiçoamento de Nível Superior—Brazil

(CAPES)—Finance Code 001, Conselho Nacional de Desenvolvimento Científico e Tecnológico—CNPq—Brasil (200096/2022-2), and São Paulo Research Foundation (FAPESP) for Grant 2021/08224-1 and Grant 2022/12043-5. The authors also wish to thank the Government of Aragon and the European Social Fund for financial support (T-53-20R) to the GUIA Group.

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