

## RESEARCH ARTICLE

# Selective Low-Temperature Depolymerization of Highly Transesterified P(LLA-co-CL) Copolymers: Efficient Lactide Recovery and PCL Upcycling

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**ABSTRACT**

The selective chemical recycling of copolyesters remains a major challenge for achieving polymer circularity. Here we show that highly transesterified poly(L-lactide-co-caprolactone) (P(LLA-co-CL)) copolymers undergo low-temperature depolymerization with exceptional selectivity for L-lactide (LLA). Statistical copolymers prepared under SnOct<sub>2</sub>/BnOH at 130 °C feature both lactidyl and lactoyl units, reflecting extensive sequence scrambling. Upon vacuum distillation at 230 °C, distillates are recovered that are highly enriched in LLA (up to 96–99 mol%), while the polymer residues reorganize into higher-molar-mass polycaprolactone (PCL) chains sporadically decorated with lactoyl units. Further heating to 250 °C mobilizes these domains, affording controlled release of CL and its dimer. Importantly, no macrocyclic species incorporating caproyl-lactidyl or caproyl-lactoyl motifs were detected, in line with the thermodynamic disfavor of 10- and 13-membered ring formation. Instead, the recycling process combines the selective regeneration of virgin-quality LLA with the generation of unprecedented “upcycled PCL” architectures, distinct from conventional PCL and offering new opportunities for property design. This dual outcome establishes a practical framework for closed-loop and value-added recycling of complex copolyesters.

**1 | Introduction**

Managing plastic waste remains a major barrier to establishing a truly circular materials economy. Among the available strategies, mechanical recycling currently dominates, yet its potential is inherently constrained [1]. In the European Union, less than 9% of plastics re-enter the market as secondary materials, and these are most often downcycled due to degradation processes such as oxidation, chain scission, and cross-linking during reprocessing [2–4]. In contrast, chemical recycling restores the molecular building blocks of polymers and thus enables the production of materials of virtually identical quality to the virgin counterparts [5, 6]. This closes the loop in a theoretically infinite number of cycles without cumulative property degradation. Life cycle assess-

ment (LCA) studies of a representative polyester, i.e. poly(lactic acid) (PLA), have shown that, although mechanical recycling displays the lowest energy demand, chemical recycling consistently outperforms composting, which destroys the material and necessitates de novo polymer production with its associated environmental burdens [7]. Chemical recycling can therefore be regarded as a strategic complement to mechanical routes. While the latter is preferable for short-term, low-impact valorization, chemical depolymerization secures the long-term sustainability of polymer cycles by preserving material value beyond the limits of multiple mechanical reprocessing.

This perspective is particularly relevant for aliphatic polyesters synthesized via ring-opening polymerization (ROP) as their

polymer-monomer equilibrium can be exploited for chemical recycling to monomers (CRM) [8]. In this classical picture, recyclability is assessed through the free energy of polymerization ( $\Delta G_{\text{ROP}}$ ), a one-dimensional descriptor of the equilibrium between polymer and initial monomer. Chemical recycling to rings (CRR), also named cyclodepolymerization, expands this framework into a multi-dimensional thermodynamic landscape [9]. Under catalytic conditions, polyesters can depolymerize not only into their original monomers but also into a distribution of cyclic oligomers via a ring-chain equilibrium (RCE). This highlights that recyclability cannot be understood solely from  $\Delta G_{\text{ROP}}$ , since the formation of larger cycles provides additional depolymerization pathways. CRR thus complements CRM by enabling closed-loop recycling even for polymers that are otherwise poorly suited for monomer recovery, establishing a more general basis for polyester circularity.

Although CRM and CRR provide elegant frameworks for closed-loop recycling, most demonstrations remain limited to purified homopolymers under idealized conditions. In contrast, real-world plastics introduce a much higher level of complexity [10, 11]. Additives such as plasticizers, flame retardants, and pigments affect depolymerization behavior and product purity. Cross-contamination between polymer types hinders selective depolymerization and increases separation costs. Aging phenomena, including oxidation and hydrolysis during use, alter polymer structures and shift equilibrium pathways. Moreover, copolymers and blends introduce mixed sequences that blur thermodynamics and kinetics, often leading to uncontrolled oligomer mixtures rather than clean monomer recovery [12]. These factors illustrate how the apparent recyclability of purified homopolymers can significantly overestimate the practical challenges.

While our study does not claim to resolve all these issues, we take a step forward by addressing the chemical recycling of more complex architectures. Recent advances have shown that copolymer recycling is feasible when sequence distribution provides favorable thermodynamic pathways. For example, perfectly alternating epoxide/anhydride copolyesters undergo catalytic depolymerization into thermodynamically stable 16- and 18-membered macrolactones, which can be repolymerized into the pristine polyester [13]. In another approach, triblock copolymers from  $\delta$ -valerolactone and its  $\alpha$ -alkylated derivatives were designed to depolymerize cleanly into their monomers, which could then be repolymerized directly into thermoplastic elastomers with virgin-like properties [14]. These studies highlight that recyclability in copolymers is achievable but relies critically on sequence control or block compatibility.

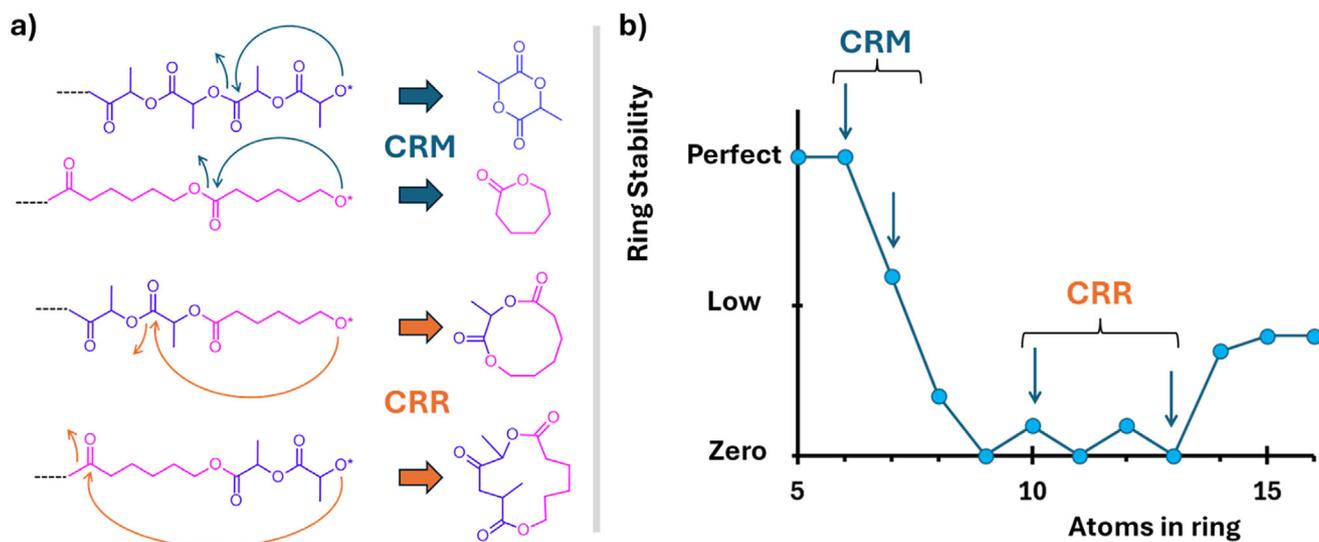
Despite recent advances in monomer design toward chemically recyclable polymers [15], systematically evaluating substitution effects and structure-property relationships remains highly challenging and labor-intensive. In parallel, certain copolymers of broad biomedical interest offer a compelling opportunity for study. Poly(lactide-*co*-caprolactone) (P(LA-*co*-CL)), for example, is widely used in resorbable sutures, tissue engineering scaffolds, drug delivery devices, and other medical applications [16, 17]. Classical analyses of ring formation established that macrocycle stability is strongly dependent on ring size, with medium-sized rings (8–14 atoms) destabilized by steric congestion and conformational constraints [18]. In P(LA-*co*-CL), the most likely CRR

closures during thermal scission would generate 13-membered (caproyl-lactidyl) or 10-membered (caproyl-lactoyl) rings, both situated in this strained regime (Figure 1a,b). Consequently, unlike homopolyesters derived from six- or seven-membered lactones, such copolymers lack accessible pathways to stable macrocycles. More recent studies further demonstrate that depolymerization rates are dictated by ring size, with six-membered polyesters depolymerizing up to two orders of magnitude faster than seven-membered analogues [19]. These insights indicate that P(LA-*co*-CL), even when highly transesterified, could be efficiently converted into its constituent lactide and  $\epsilon$ -caprolactone monomers. Subtle differences in depolymerization barriers may even be exploited to selectively recover one monomer over the other, positioning this copolymer as a stringent and instructive model for precision chemical recycling (Figure 2).

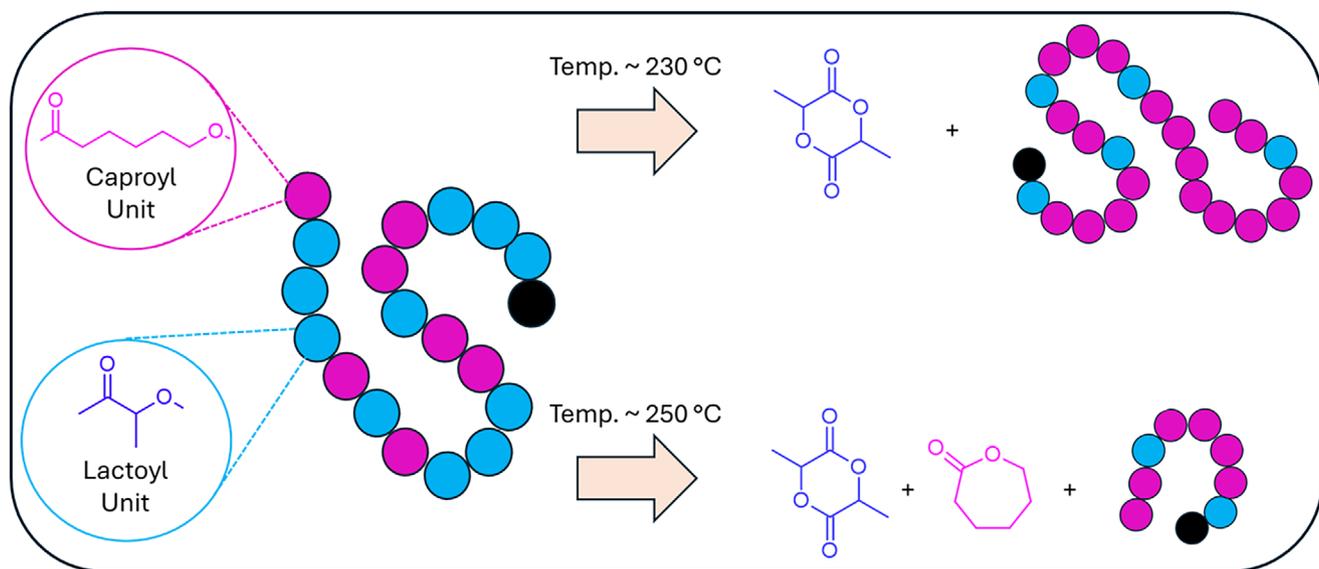
## 2 | Results and Discussion

Copolymerizations of L-lactide (LLA) and  $\epsilon$ -caprolactone (CL) with coordination-insertion catalysts are dominated by the higher reactivity of LLA [20–22]. The resulting blocky sequences can be randomized at elevated temperature and prolonged reaction time through transesterification [22–24]. Polymerizations were therefore carried out in bulk at 130°C for 3-to-4 days using tin(II) 2-ethylhexanoate ( $\text{SnOct}_2$ ) and benzyl alcohol (BnOH) as the initiating system ( $[\text{LLA}+\text{CL}]_0/[\text{BnOH}]_0/[\text{SnOct}_2]_0 \sim 500/10/1$ ). To assess the effect of composition on the recycling process, three representative LLA/CL ratios were targeted. Table 1 summarizes the molecular characteristics of the copolymers. Copolymer notation such as P(LLA28/CL72) means that the initial comonomer feed consists of 28 mol% in LLA and 72 mol% in CL. The LLA mole fraction in the feed ( $f_{\text{LLA}} = 0.28, 0.5, \text{ and } 0.66$ ) perfectly matched the final copolymer compositions ( $F_{\text{LLA}}$ ), determined from the integration of LLA methine and CL methylene signals, confirming the quantitative co-insertion of both LLA and CL monomers (Figures S1 and S2). Further insight into the copolymer microstructure was obtained by analyzing the carbonyl region of the  $^{13}\text{C}$  NMR spectra (168–174 ppm). In all samples, a distinctive resonance at 170.86 ppm was detected, assigned to lactoyl carbonyls generated by cleavage within a lactidyl unit during transesterification (Figure 3a; Figures S3–S5) [25]. This observation unambiguously demonstrates the coexistence of lactidyl and lactoyl sequences, consistent with an effective second-mode transesterification that effectively randomizes the distribution of lactoyl units along the copolymer backbone [25–27]. Notably, the fraction of lactoyl units decreases as the LLA content in the copolymer increases (37.5% for P(LLA28/CL72), 8.9% for P(LLA50/CL50), and 2.6% for P(LLA66/CL34); Table 1), consistently with lactoyl formation occurring predominantly from transformations involving caproyl-containing sequences. Importantly, the molar mass dispersities ( $M_w/M_n = D_M \sim 2$ , Figures S6–S8) indicate that the copolymers adopt a statistical rather than blocky microstructure, confirming that the applied polymerization conditions led to sufficiently randomized copolymers for the subsequent recycling studies.

The recyclability of our P(LLA-*co*-CL) copolymers was investigated without prior purification, relying on the residual  $\text{SnOct}_2$  catalyst already present in the materials ( $[\text{LLA}+\text{CL}]_0/[\text{SnOct}_2]_0 = 500$ ). This choice was made to exploit the residual tin species as an



**FIGURE 1** | (a) Hypothetical chain fragments of a statistical P(LA-co-CL) copolymer with an -O\* active chain end. Blue arrows: chemical recycling to monomers (CRM) regenerates lactide (LA) and  $\epsilon$ -caprolactone (CL). Orange arrows: possible formation of 10- and 13-membered macrolides through cyclodepolymerization of caproyl-lactoyl or caproyl-lactidyl sequences. (b) Relative stability of (macro)cycles as a function of ring size, adapted from ref. [18]. Arrows indicate the pathways considered: CRM toward 6- and 7-membered lactones, CRR toward disfavored 10- and 13-membered rings.



**FIGURE 2** | Our work: Low-temperature selective depolymerization of LLA from highly transesterified P(LLA-co-CL) copolymers, accompanied by caproyl block rearrangement into heavier PCL chain decorated with lactoyl units (Temperature: 230 °C).

**TABLE 1** | Molecular characterizations of P(LLA-co-CL) copolymers.<sup>a</sup>

Entry	$f_{LLA}^b$	$F_{LLA}^c$	Lactoyl fraction <sup>d</sup> (%)	$M_n$ , SEC <sup>e</sup> (g/mol)	$\bar{D}_M^e$
P(LLA28/CL72)	0.28	0.29	37.5	6,200	1.96
P(LLA50/CL50)	0.5	0.5	8.9	9,200	2.03
P(LLA66/CL34)	0.66	0.66	2.6	7,200	2.07

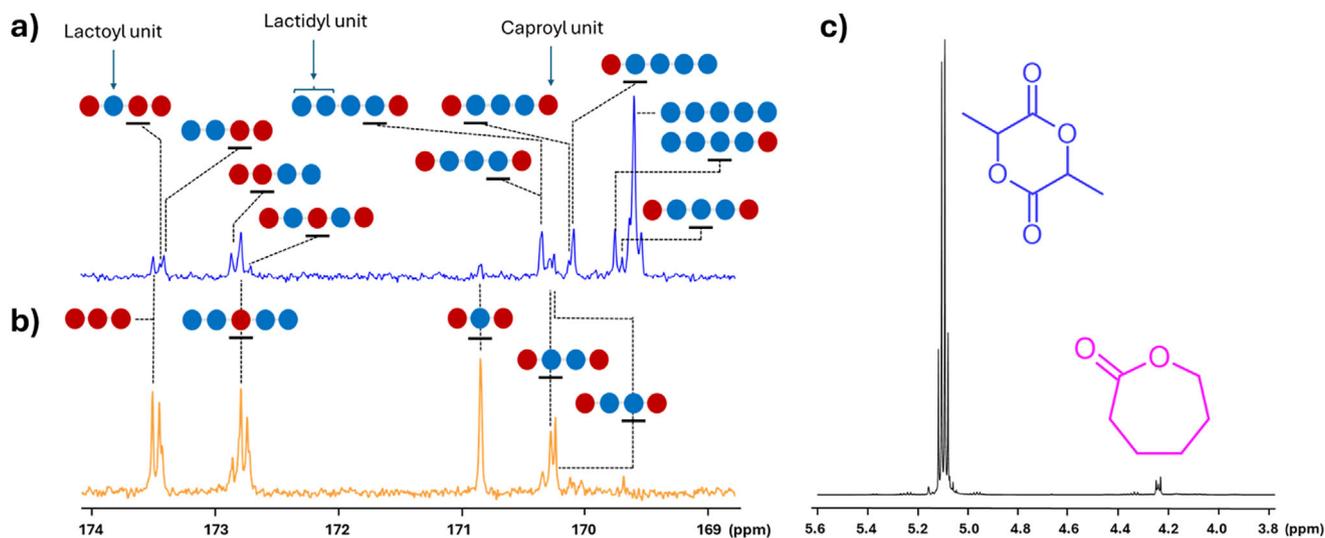
<sup>a</sup>Polymerization conditions:  $[LLA+CL]_0/[BnOH]_0/[SnOct_2]_0 = 500/10/1$ ; 130 °C; 3-to-4 days;

<sup>b</sup> $f_{LLA}$ , LLA mole fraction in comonomer feed;

<sup>c</sup> $F_{LLA}$ , LLA mole fraction in the P(LLA-co-CL) copolymer;

<sup>d</sup>Lactoyl fraction (%) as determined by  $^{13}C$  NMR =  $100 \times I_{170.86}/I_{\Sigma 170.86-169.54}$  (excluding caproyl);

<sup>e</sup>As determined by SEC analysis in THF at 35 °C using PS standards.



**FIGURE 3** | Expanded carbonyl carbon regions of the <sup>13</sup>C NMR spectra of P(LLA66/CL34) copolymer before (a) and after thermal depolymerization at 230°C for 4 h (b). (c) Enlarged <sup>1</sup>H NMR region ( $\delta = 3.8$  and 5.6 ppm) of the species distilled from the P(LLA66/CL34) at 230°C for 4 h.

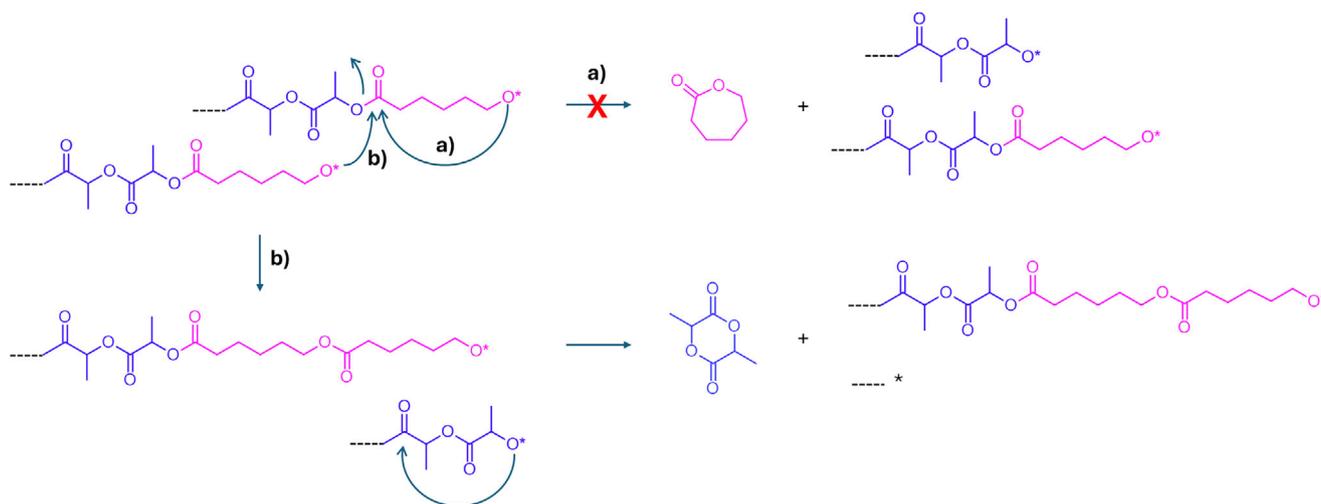
internal catalytic probe, allowing us to directly assess the thermodynamic and sequence-dependent selectivity of depolymerization without additional reagents. SnOct<sub>2</sub> is also a well-established and highly efficient catalyst for polyester depolymerization under bulk conditions, making it an appropriate model system for mechanistic studies of chemical recycling [28–31]. Thermogravimetric analysis (TGA) was first employed to determine the onset degradation temperatures and thereby select an optimum depolymerization temperature [28, 32–35]. While purified P(LLA-co-CL) copolymers typically display a single degradation step [27], all three samples exhibited multi-step degradation profiles, reminiscent of those observed for block copolymers (Figures S9–S11) [27]. DTG curves revealed a clear two-step degradation for both P(LLA66/CL34) and P(LLA50/CL50), whereas P(LLA28/CL72) displayed a slightly more complex behavior with an additional mass loss at higher temperature. The mass losses observed in the first degradation step did not exactly match the theoretical LLA mass fractions but nevertheless revealed a clear qualitative correlation with copolymer composition (Table S1). This qualitative trend suggests that, upon heating, the copolymers could undergo a sequence rearrangement, most likely through transesterification, which leads to the preferential release of lactide derivatives, while the multi-step profiles suggest that chain rearrangements may convert caproyl into lactidyl end groups, thereby enabling repeated lactide regeneration (Figure 4).

To further test this hypothesis and characterize the reaction products, ~1 g of each copolymer was depolymerized on a larger scale using a Kugelrohr distillation apparatus. The temperature was initially set to 230°C, i.e., 10°C above the degradation onset of the most stable copolymer but still below the temperature at which the second degradation step begins. The reaction was allowed to proceed for 4 h, followed by an additional 2-h distillation at 250°C. Both the distillate and the polymer residue were subsequently collected and analyzed for each temperature (Table 2).

As anticipated, vacuum distillation at 230°C for 4 h provided distillates highly enriched in LLA, with selectivities up to 96–

99 mol% for P(LLA50/CL50) and P(LLA66/CL34) (Table 2; Figure 3c and Figures S12–S14). Even for the more caprolactone-rich P(LLA28/CL72) sample, lactide remained the dominant species (80 mol%), demonstrating the strong preference for LLA regeneration under these conditions. In line with the non-basic character of the SnOct<sub>2</sub> catalyst, only minor amounts of meso-lactide ( $\leq 2.5$  mol%) were detected [36–39]. Small fractions of caprolactone (16.5 mol% for P(LLA28/CL72)) and traces of its dimer (di-CL) were observed, the latter in agreement with earlier work of Höcker on the thermal depolymerization of PCL at 260°C in the presence of a tin catalyst [40]. Importantly, the overall recovery yields increased with the initial lactide content of the copolymers, further underscoring the efficiency and selectivity of the depolymerization process.

Such preferential release of LLA at the early stage of the recycling process can be explained by depolymerization of copolymer chains terminated by lactidyl units (activated by the catalyst) but also intermolecular transesterification reactions between chains end-capped by caproyl units (Figure 4). Rather than liberating CL synthons via back-biting, chains terminated by a caproyl unit appear to undergo transesterification, thereby converting the terminal group into a lactidyl chain-end, which in turn promotes LLA formation. Consistent with this interpretation, SEC analysis of the residues revealed an increase in molar mass for all three samples (Table 2). Even more strikingly, <sup>13</sup>C NMR analysis provided unambiguous evidence for extensive sequence rearrangements. Compared to the pristine copolymers, the carbonyl region (168–174 ppm) of the distillation residues displayed only very low remaining signals associated with lactidyl units (Figure 3b; Figures S15 and S16). Only resonances attributable to lactoyl carbons ( $\delta = 170.86$  ppm) and CL triads ( $\delta = 173.52$  ppm) were clearly detected, along with two additional signals at  $\delta = 173.47$  and 172.81 ppm. The former can be confidently assigned to CL-lactoyl-CL-CL sequences, whereas the latter is more ambiguous. Although traditionally attributed to LA-LA-CL-LA-LA sequences, the overall spectral features rather suggest an assignment to CL-lactoyl-CL-lactoyl-CL sequences, usually reported near  $\delta = 172.73$  ppm [25–27].



**FIGURE 4** | Proposed low-temperature pathway for lactide regeneration from P(LLA-*co*-CL) copolymers. Two caproyl-terminated chains (O\*, the active chain end) with lactidyl–caproyl units are shown. Intramolecular back-biting (a) is disfavored (crossed out), whereas intermolecular transesterification (b) generates lactidyl-terminated chains capable of releasing lactide (LA) via back-biting.

**TABLE 2** | Molecular characterizations of P(LLA-*co*-CL) copolymers before and after distillation under a two-step thermal treatment.

Sample	Before Distillation		Residue	Distillate				Yield <sup>d</sup> (wt.%)
	$M_n$ , SEC <sup>a</sup> (g/mol)	Distillation temperature (°C) <sup>b</sup>		$M_n$ , SEC <sup>c</sup> (g/mol)	LLA (mol.%)	mesoLA (mol.%)	CL (mol.%)	
P(LLA28/CL72)	6,200	230	20,200	80	2.5	16.5	<1	30.8
		250	24,000	45.6	1.3	44.4	8.6	45.3
P(LLA50/CL50)	9,200	230	10,600	98.6	0.7	0.7	<1	45.3
		250 <sup>e</sup>	8,300	35	2	62.9	<1	54
P(LLA66/CL34)	7,200	230	14,400	96	1.3	2.1	<1	53
		250	14,000	84.1	3.3	11.4	1.2	61.4

<sup>a</sup>Number-average molar mass ( $M_n$ ) of the copolymers before distillation, determined by SEC in THF at 35°C against PS standards;

<sup>b</sup>Distillation performed in two successive steps: first at 230°C for 4 h, followed by 250°C for 2 h;

<sup>c</sup>Number-average molar mass ( $M_n$ ) of the copolymers after distillation, determined by SEC in THF against PS standards;

<sup>d</sup>Calculated based on the mass of copolymer charged prior to distillation;

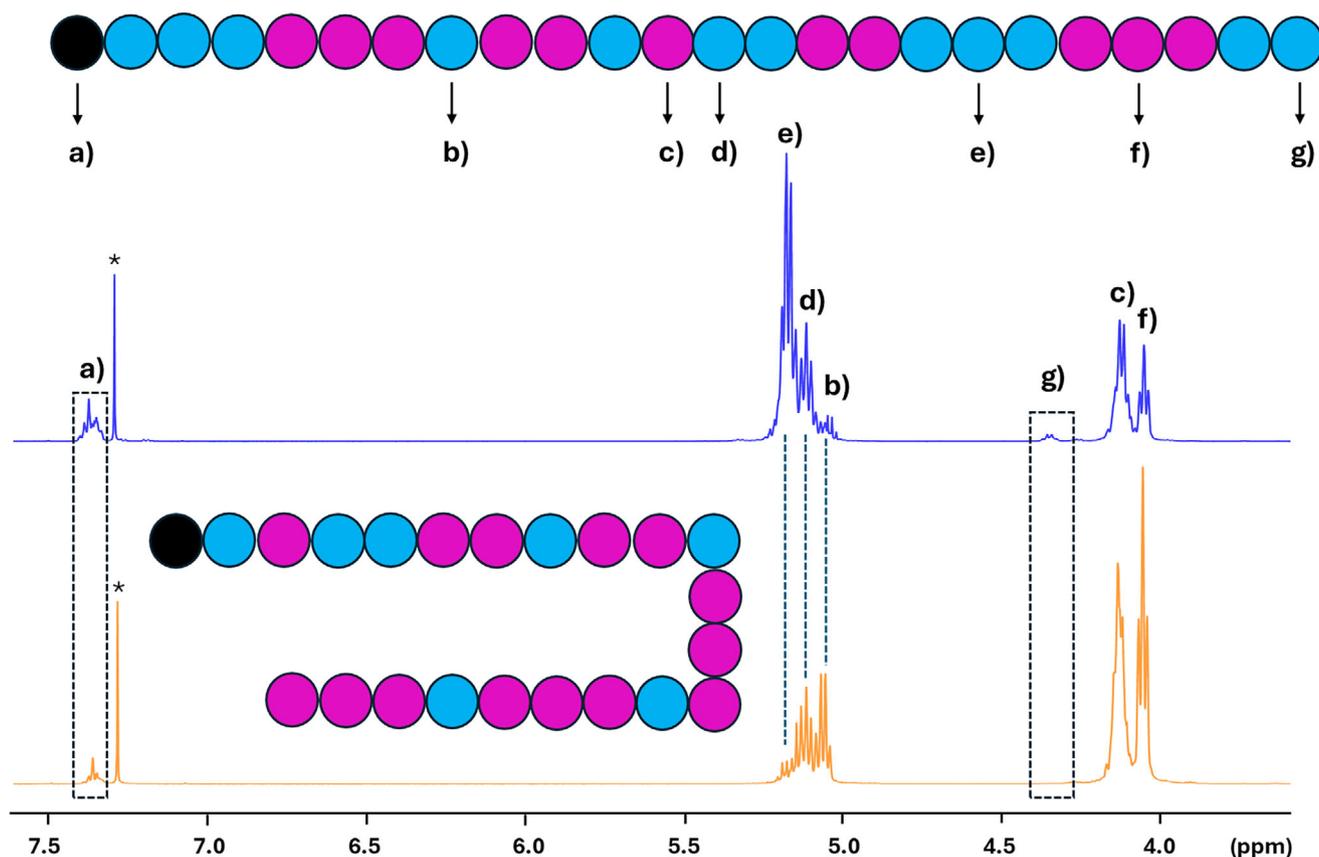
<sup>e</sup>3 h of thermal treatment.

These conclusions are further supported by <sup>1</sup>H NMR analysis. For instance, in the case of P(LLA66/CL34), integration of the aromatic protons of the benzyl ester end-group revealed a substantial increase in  $M_n$ ,NMR (14,400 g.mol<sup>-1</sup> after distillation vs. 6,800 g.mol<sup>-1</sup> before). Three additional features are worth noting: (i) the complete disappearance of the quartet at  $\delta$  = 5.18 ppm, characteristic of PLLA sequences, together with the near disappearance of the  $\delta$  = 5.12 ppm signal assigned to lactidyl units embedded within caproyl sequences, while the weak quartet at  $\delta$  = 5.06 ppm became predominant after distillation; (ii) a marked decrease in the aromatic signals at  $\delta$  = 7.35 ppm relative to the caproyl resonances ( $\delta$  = 4.00–4.21 ppm), indicating that the chain rearrangements responsible for the molar mass increase occur preferentially at chain-ends originally rich in lactidyl units; and (iii) the complete disappearance of the  $\delta$  = 4.35 ppm signal, characteristic of PLA methine protons, further demonstrates that LLA release also proceeds from chain termini. (Figure 5).

Taken together, analyses consistently indicate that the recycling process generates PCL chains sporadically decorated with lactoyl units. Such rearrangements demonstrate that LLA release occurs from both internal segments and chain termini. Upon subsequent heating at 250°C for 2 h, these lactoyl-decorated PCL chains preferentially undergo further rearrangements, leading to the enhanced regeneration of CL (and its dimer). Apart from minor amounts of di-CL, no macrocyclic species incorporating caproyl–lactidyl or caproyl–lactoyl motifs were detected, indicating that the cyclodepolymerization pathways leading to 10- or 13-membered rings are strongly disfavored, at least at such temperatures (Figures S17–S19).

### 3 | Conclusions

We demonstrate that highly transesterified P(LLA-*co*-CL) copolymers undergo selective lactide recovery at 230°C, while the



**FIGURE 5** |  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , r.t., 500 MHz) of P(LLA66/CL34) copolymer, zoomed between  $\delta = 3.5$  and 7.5 ppm, before (blue, top) and after distillation at  $230^\circ\text{C}$  for 4 h (orange, bottom). Residual  $\text{CHCl}_3$  is marked by an asterisk. Hypothetical structures are shown above the spectra, with blue spheres denoting lactoyl units and orange spheres denoting caproyl units. Note that two lactoyl units form a lactidyl group.

residue reorganizes into higher- $M_n$  PCL chains incorporating lactoyl units. Unlike purely lactidyl segments, caproyl/lactidyl or caproyl/lactoyl junctions cannot cyclize into stable macrolides, which rationalizes the persistence of these sequences in the residue and their incorporation within the upgraded PCL backbone. This unique structure defines an “upcycled PCL” material, distinct from conventional PCL, and highlights the potential of transesterification-driven rearrangements to generate interesting architectures. Structurally different than copolyesters synthesized from direct condensation of L-lactic acid and 6-hydroxyhexanoic acid [41], such materials warrant further investigation, both to characterize their properties and to evaluate their broader relevance in polyester recycling and upcycling strategies.

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#### Conflicts of Interest

The authors declare no conflicts of interest.

#### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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### Supporting Information

Additional supporting information can be found online in the Supporting Information section.

**Supporting File:** marc70148-sup-0001-SuppMat.docx