

Synergistic Pathways in PLA Breakdown and PTMC Formation: A One-Pot Eutectic-Driven Recycling Mechanism

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Abstract: This study introduces a novel one-pot strategy for the chemical valorization of poly(lactic acid) (PLA), coupling its base-catalyzed depolymerization with the ring-opening polymerization (ROP) of trimethylene carbonate (TMC). The process exploits an eutectic mixture of lactide (LA) and TMC, which lowers the thermal input required for PLA degradation. Using potassium aryloxide (KOAr^{Bu}) as a bifunctional catalyst, the PLA is first quickly hydrolyzed into oligomers or lactic acid, which subsequently initiate the slower polymerization of TMC. Notably, this transformation operates in the presence of residual water, eliminating the need for tedious drying steps. The method achieves selective PLA breakdown conversion and produces (oligo)lactic acid end-capped poly(trimethylene carbonate) (PTMC) with tunable molar mass, depending on water content.

Introduction

As global environmental concerns intensify, the importance of recycling polymers, particularly bio-based ones like poly(lactic acid) (PLA), has gained significant attention.^[1] PLA, derived from renewable resources, offers an alternative to conventional petroleum-based plastics.^[2] However, despite its promise, the accumulation of PLA waste in various environments, where it doesn't readily degrade, poses a significant challenge.^[3] Traditional recycling techniques often fall short, leading to a growing need for innovative approaches to manage PLA waste more efficiently.

Chemical recycling, especially through depolymerization to lactide (LA), emerges as a key solution, allowing the recovery of high-purity monomers and closing the loop on PLA's lifecycle.^[4] This approach aligns with the principles of a circular economy, ensuring that PLA can continue to serve as a sustainable material beyond its initial use.^[5] One of the most significant challenges in depolymerizing PLA to LA lies in the stringent reaction conditions required. The ceiling temperature (T_c) of LA is high (~914 K, in bulk, Fig-

ure 1a),^[6] necessitating harsh conditions and strict drying protocols to prevent side reactions such as epimerization and oligomer formation.^[7] In industrial settings, maintaining an anhydrous environment is particularly challenging, making large-scale implementation difficult. Recently, Odelius et al. have demonstrated that solvent choice plays a crucial role in lowering depolymerization temperatures, with highly polar solvents favoring the equilibrium toward LA formation (Figure 1a).^[4b] For instance, the use of dimethylformamide (DMF) enabled the chemical recycling of high-molecular-weight poly(L-lactic acid) directly to L-lactide (L-LA), achieving over 95 % conversion and 98–99 % selectivity within 1 to 4 hours at 140 °C. While these advancements represent significant progress in the field, the practical challenges associated with solvent recovery and the stringent need for anhydrous conditions highlight the necessity of exploring more practical and scalable alternatives.^[8]

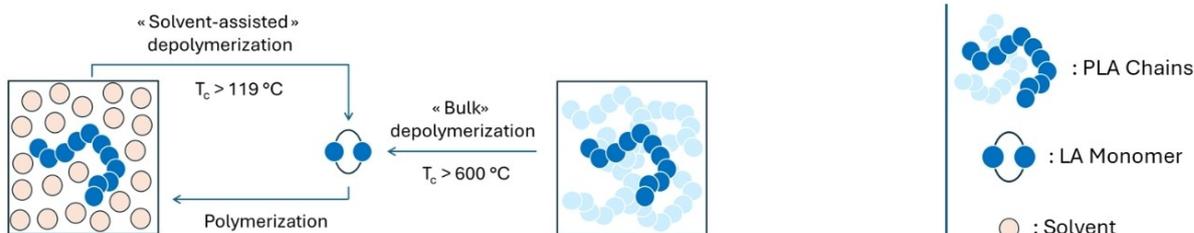
Traditionally, methods such as hydrolysis or alcoholysis of PLA have been considered viable approaches for chemical recycling.^[9] While these methods typically yield lactic acid or alkyl lactates rather than LA, further processing is often required to recover the true monomer. Notably, alcoholysis is regarded as the most suitable method for chemical recovery of PLA, whereas hydrolysis can upcycle lactic acid with lower energy consumption compared to its production from starch fermentation.^[3a] This raises an important question: instead of focusing on recovering lactide, could lactic acid itself serve as a valuable product for the alternative valorization of PLA? Directly generating lactic acid could streamline the recycling process, eliminating the need for additional steps to reconvert it into lactide and providing a new pathway for the production of materials with high industrial value.

Building on this idea, several innovative chemical recycling strategies have emerged. For instance, Yang et al. proposed a “depolymerization-repolymerization” (DE-RE) strategy (Figure 1b),^[10] which allows the direct recycling of end-of-life PLA into new, virgin-quality PLA through a controlled two-step process. This approach employs a dual-function zinc-based catalyst that enables both mild depolymerization and subsequent repolymerization, minimizing side reactions and energy. The process offers a notable advantage over traditional methods by avoiding the need for severe reaction conditions and reducing the energy input while maintaining the polymer's original properties.

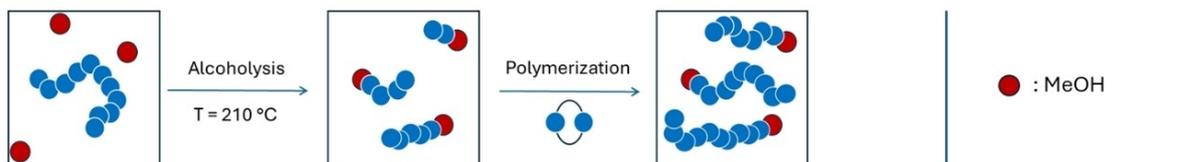
Contemporary methods for PLA hydrolysis primarily rely on the catalytic influence of acids or bases.^[11] Comparatively to acidic conditions, De Jong et al. demonstrated that

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a) « Bulk » PLA Depolymerization vs. « Solvent-assisted » Route : Lactide Valorization



b) PLA « Depolymerization - Repolymerization » Route : A Two-Step Process by Lactide Addition



c) This Work

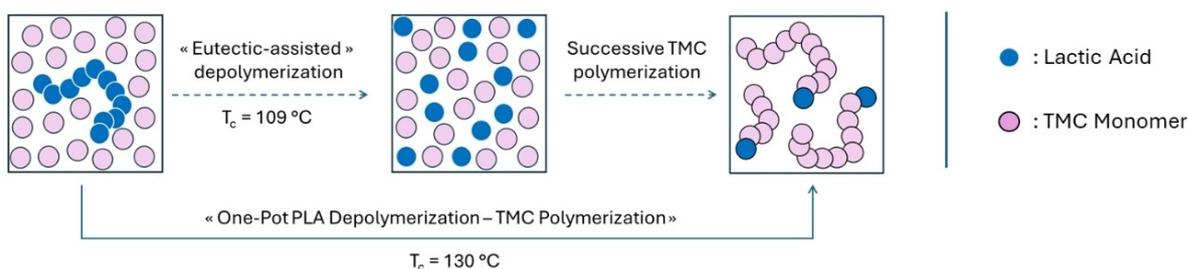
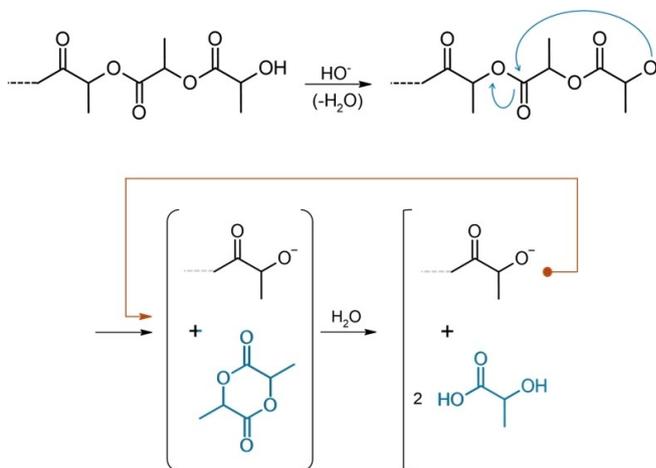


Figure 1. PLA Valorization and Upcycling. a) PLA depolymerization at its ceiling temperatures, either in bulk or via a “solvent-assisted” process. b) Production of PLA homopolymer after alcoholysis of waste PLA and the addition of fresh LA monomers. c) Production of PTMC in a “one-pot” process starting with a “eutectic-assisted” PLA depolymerization in lactic acid, followed by a kinetically slower TMC polymerization.

the base-catalyzed hydrolysis of PLA initiates a nucleophilic attack by hydroxide ions on the hydroxyl groups, leading to the formation of a six-membered lactide ring.^[12] This intermediate, with a very short lifetime under basic conditions, is rapidly converted into lactic acid. The remaining shorter PLA chains continue to undergo the same hydrolysis process, ultimately resulting in complete depolymerization (Scheme 1).

Building on this understanding of PLA hydrolysis, the current work explores a novel approach to further enhance PLA recycling through the use of eutectic systems. In 2012, we demonstrated that L-lactide (L-LA) can form a eutectic mixture with trimethylene carbonate (TMC), creating a melt at just 21.3 °C in a 50:50 wt % mixture.^[13] All together, it is hypothesized that the LA formed during the base-catalyzed hydrolysis of PLA can act synergistically with TMC, significantly reducing the thermal input required for PLA breakdown. The LA-TMC eutectic not only facilitates the depolymerization of PLA, but also serves as both a solvent and reactant, promoting the transesterification of PLA in the presence of residual water, conditions far more compatible with industrial applications.

As highlighted in this manuscript, the depolymerization of poly(L-lactide) (PLLA), in the presence of residual water, facilitated by the eutectic mixture, proceeds with a reaction



Scheme 1. Mechanism of alkali-based PLA hydrolysis as proposed by De Jong.^[12]

kinetics significantly faster than the subsequent polymerization of TMC. This allows for the efficient degradation of PLLA before initiating the polymerization of TMC, all within a “one-pot” process (Figure 1c). By leveraging these properties, the current approach aims to lower the break-

down temperature while reducing the need for stringent drying protocols. This offers a more energy-efficient and environmentally sustainable solution for PLA recycling, with potential applications in the production of high-value polymers such as poly(trimethylene carbonate) (PTMC).^[14] Building on these principles, it is proposed that the valorization of PLLA into high-value polymers such as PTMC is not only chemically viable but also strategically justified. With an estimated global production of 190,000 tons of PLA annually as of 2019, and a broader polycarbonate market reaching 4.51 million metric tons in 2022, the integration of PLLA recycling into PTMC production aligns with the growing demand for sustainable alternatives within this polymer family. Moreover, the PTMC market is projected to expand from \$72 billion in 2024 to \$113.89 billion by 2031, driven by a compound annual growth rate (CAGR) of 6.77%, highlighting both the strategic relevance and the economic potential of integrating recycled PLA into PTMC production.^[15]

Results and Discussion

The choice of catalyst and experimental conditions for poly(lactic acid) (PLA) depolymerization is critical, particularly when aiming to accurately determine a ceiling temperature (T_c). Defined as the temperature at which the rates of polymerization and depolymerization are in equilibrium, T_c marks the point beyond which no net polymerization occurs. Experimentally, T_c is determined by conducting polymerization reactions across a range of temperatures and identifying the threshold at which polymerization ceases to proceed efficiently. However, a direct determination of T_c in a lactide-trimethylene carbonate (LA-TMC) mixture is not feasible because TMC not only polymerizes independently but can also copolymerize with LA.^[13,16]

To address this challenge and achieve a more accurate estimate of the depolymerization temperature, ethylene carbonate (EC), a five-membered analog of TMC whose polymerization is thermodynamically forbidden,^[17] was selected as a substitute. The use of EC allows for the determination of a T_c value for PLA under conditions analogous to those with TMC, while avoiding any risk of copolymerization. This approach simulates TMC-like conditions without introducing competing polymerization reactions.

It was first verified that LA and EC indeed form an eutectic mixture, as this is critical for replicating the eutectic behavior observed in the LA-TMC system. Differential scanning calorimetry (DSC) analyses were performed to study the eutectic behavior of different mixtures of L-lactide (L-LA, melting temperature, T_m ~98.3°C) and EC (T_m ~40.1°C). Both melting points and enthalpies were recorded after pretreatment of all blends at 100°C for 5 min (Supporting Information, Table 1). As shown in Figure 2a, except for the pure components and mixtures with a L-LA molar fraction between 0.17 and 0.3, all mixtures exhibit two melting points: one corresponding to the eutectic mixture at around 15.1 (± 2.1)°C, and the other to the noneutectic

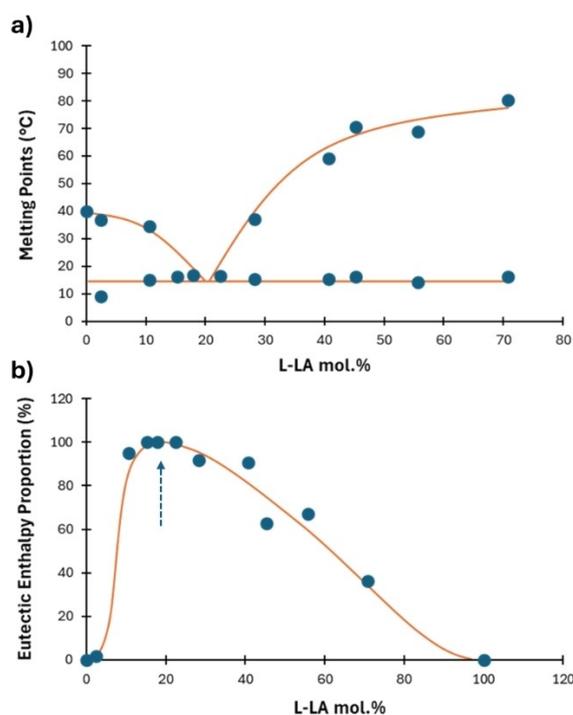


Figure 2. a) Melting points of various L-LA/EC mixtures; b) relative percentage of the eutectic melting enthalpy recorded for different L-LA/EC mixtures. The arrow marks the speculated perfect eutectic mixture.

product. The ideal eutectic composition was determined based on the ratio of the enthalpy of the eutectic ($\Delta H_{\text{eutectic}}$) to the sum of the enthalpies of the eutectic and noneutectic components ($\Delta H_{\text{eutectic}}/(\Delta H_{\text{noneutectic}} + \Delta H_{\text{eutectic}})$). As shown in Figure 2b, a maximum is observed at around 20 mol.% L-LA, suggesting an ideal composition of one L-LA molecule for every 4 EC molecules.

Having confirmed that the L-LA/EC mixture forms a eutectic, it was hypothesized that this eutectic environment could influence the LA-PLA equilibrium, potentially lowering the T_c for PLA depolymerization. To validate this hypothesis, it was essential to identify an effective depolymerization catalyst. Given the high polarity of the medium, the use of Lewis acids, which are commonly employed for PLA depolymerization, appeared impractical. The carbonyl functionalities in the mixture can strongly stabilize these transition metal-based catalysts, rendering them inactive for this study. Notably, a representative catalyst such as tin(II) octanoate ($\text{Sn}(\text{Oct})_2$) was tested but failed to initiate LA ROP in the L-LA/EC mixture under various polymerization conditions. This prompted us to explore another catalyst class capable of operating in such an environment while maintaining adequate selectivity for PLA depolymerization. Notably, since the generation of LA is essential for the eutectic degradation of PLA, and following the mechanisms outlined by De Jong,^[12] it became clear that a basic catalyst would be required for this process. Based on prior research showing the activity of aryloxide-based catalysts in ring-opening polymerization (ROP) of LA,^[18] the 2,4,6-tri-*tert*-

butyl-phenolate of potassium (KOAr^{Bu}) was selected as a promising candidate. This catalyst benefits from steric hindrance, minimizing undesirable side reactions such as transesterification, while being basic and robust enough to perform under the highly polar environment of the L-LA/EC system.

In line with the strategy of utilizing residual water present in the reaction medium, the efficiency of the catalyst and its inactivity toward EC were verified. Karl-Fischer titration revealed a water content of 0.106 μL per gram of EC, confirming the presence of sufficient water to act as an initiator for LA ROP. It should also be noted that, as with the eutectic mixture studies, the L-isomer of LA (L-LA) was used throughout the remainder of this study.

Polymerizations of L-LA were therefore carried out in EC with a monomer concentration of 0.5 M, resulting in a $[\text{L-LA}]_0/[\text{H}_2\text{O}]_0$ ratio of 69, using 0.5 molar equivalent of KOAr^{Bu} as activator compared to the water initiator molar content ($[\text{H}_2\text{O}]_0/[\text{KOAr}^{\text{Bu}}]_0=2$). Polymerizations were performed at four different temperatures, ranging from 40 to 95 °C. Since the maximum temperature was set to 95 °C, the stability of EC under these conditions was first verified. Specifically, an undried batch of EC containing water was heated at 95 °C for over 12 hours, and subsequent ^1H NMR analysis confirmed that no ring-opening of EC occurred (Supporting Information, Figure 1). The dependence of $[\text{L-LA}]_{\text{eq}}$ on temperature is shown in Figure 3a (Supporting Information, Table 2). Across the temperature range, $[\text{L-LA}]_{\text{eq}}$ increases in a non-linear pattern from 0.195 to 0.427 $\text{mol}\cdot\text{L}^{-1}$. The standard thermodynamic parameters for

L-LA polymerization in EC were then determined from the dependence of $R^*(\ln[\text{L-LA}]_{\text{eq}}/[\text{L-LA}]_0)$ on the reciprocal of the absolute temperature (Figure 3b).^[19] Analysis of the experimental data using the least-squares method yielded $\Delta H_p^\circ = -13.5 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S_p^\circ = -35.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, from which a T_c value of 109 °C was determined. Lower than that observed by Odelius et al.,^[4b] it still remains within the same range, supporting the hypothesis that an eutectic mixture can also play a significant role in the thermodynamics of poly(L-lactide) PLLA depolymerization. Although the critical temperature for the polymerization process was determined to be 109 °C, it was chosen to perform the remainder of our study at 130 °C. This slightly higher temperature should ensure more efficient depolymerization kinetics, while still remaining within a reasonable range for the thermal stability of PLLA.

To assess the efficiency of KOAr^{Bu} in catalyzing PLLA depolymerization, even in the presence of oxygen, thermogravimetric analysis (TGA) was performed. To that end, a PLLA with a size exclusion chromatography (SEC)-based number average molecular weight (M_n SEC) of 20,600 $\text{g}\cdot\text{mol}^{-1}$ ($M_w/M_n = \mathcal{D}_M = 1.09$) was synthesized using a benzyl alcohol (BnOH) initiator and a 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) organic catalyst. Once the PLLA was free of any DBU residues, following a purification via a liquid/liquid extraction,^[20] a film comprising KOAr^{Bu} at a fixed loading of 1:1000 (where 1000 represents the number of lactidyl repeat units) was prepared by solvent casting in THF. The chemical recycling of PLLA was then evaluated under a nitrogen/air (80/20) flow (20 mL/min) at 130 °C. Even under presence of oxygen, the catalyst demonstrated its effectiveness in PLLA depolymerization, with a linear polymer mass loss over time, showing a rate of ca. 0.4 % per minute (Supporting Information, Figure 2).

Following the evaluation of KOAr^{Bu} in catalyzing the depolymerization of laboratory-synthesized PLLA under controlled conditions, including the presence of oxygen, the investigation was extended to assess its performance under more demanding conditions. The focus shifted to high molecular weight, highly crystalline commercial PLLA, a material recognized for its stability and mechanical robustness. High molar mass PLLA is known to undergo intermolecular transesterification with alcohols or water, forming lower molar mass chains that can subsequently depolymerize more rapidly.^[21] To this end, a degradation test was performed on NatureWorks PLLA 4043D (Relative M_p SEC = 145,000 $\text{g}\cdot\text{mol}^{-1}$), known for its elevated crystallinity and mechanical robustness, in EC at 130 °C for 1 hour. Notably, neither the PLLA nor the EC was dried prior to the reaction, allowing the full influence of residual moisture to be accounted for, and the reaction was performed under the air. Based on the amount of water determined by Karl-Fisher in the EC, a lactic acid (lactoyl) unit concentration of 6 M was deliberately employed to expose the PLLA to a 5-fold excess of water molecules, thereby promoting transesterification and chain scission.

While the presence of water is known to induce hydrolysis of the PLLA into shorter chains, the SEC analysis before and after the reaction provided evidence of a

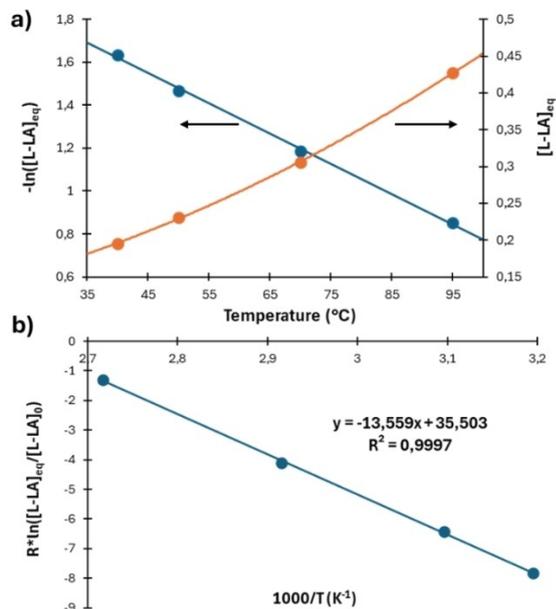


Figure 3. Polymerization thermodynamics of L-LA in EC ($[\text{L-LA}]_0 = 0.5 \text{ M}$, polymerization degree = $[\text{L-LA}]_0/[\text{H}_2\text{O}]_0 = 69$, $[\text{H}_2\text{O}]_0/[\text{KOAr}^{\text{Bu}}]_0 = 2$) a) Dependences of the equilibrium concentration of L-LA ($[\text{L-LA}]_{\text{eq}}$, orange curve) and the corresponding negative natural logarithm values of $[\text{L-LA}]_{\text{eq}}$ (blue line) on the temperature; b) Dependence of $R^*(\ln[\text{L-LA}]_{\text{eq}}/[\text{L-LA}]_0)$ on the reciprocal of the absolute temperature.

subsequent unzipping process. Figure 4 reveals a monomodal but broad polymer signal, a significant decrease in M_p , and the appearance of the characteristic LA monomer signal at 20.35 mL, highlighting the occurrence of unzipping. Note that, given the ultimate goal of this work is to break down PLLA into lactic acid molecules capable of promoting subsequent cyclic carbonate polymerization, the isomeric form of the LA generated at this stage, i.e., *L*-, *D*-, *rac*- or *meso*-LA, was not determined. The broad dispersity ($\mathcal{D}_M = 5$) confirms that KOAr^{tBu} can effectively induce depolymerization, even in the presence of residual moisture in a high molecular weight, highly crystalline PLLA. This broad dispersity value is likely associated with the limited solubility of the commercial PLLA 4043D in EC at 130 °C. To address this limitation and enhance the effectiveness of the interaction between the PLLA and the KOAr^{tBu} catalyst, it was chosen to utilize PLLA with a molecular weight of 20,600 $\text{g}\cdot\text{mol}^{-1}$ (Relative $M_n\text{SEC}$) for the remainder of our investigation into TMC polymerization.

Finally, prior to the “PLLA depolymerization – TMC polymerization” one-pot process attempt, the efficiency of KOAr^{tBu} to catalyze the TMC ROP from an exogenous protic initiator was also demonstrated. To this end, TMC was polymerized in bulk at 130 °C from BnOH with an initial molar ratio of $[\text{TMC}]_0/[\text{BnOH}]_0/[\text{KOAr}^{\text{tBu}}]_0$ of 420/1/1. After 2 hours, a conversion of 78 % was recorded, yielding PTMC with a $M_n\text{SEC}$ of 33,500 $\text{g}\cdot\text{mol}^{-1}$ ($\mathcal{D}_M = 1.9$).

Following this demonstration of KOAr^{tBu} 's efficiency in catalyzing both the PLLA eutectic-driven depolymerization from remaining water and the TMC ROP, it was decided to test both processes in a one-pot approach. It was hypothesized that, in the presence of KOAr^{tBu} at 130 °C, PLLA chains would be preferentially cleaved over TMC ring-opening. This assumption is grounded in thermodynamic, kinetic, and structural considerations. Firstly, the linear structure of PLLA makes its ester linkages more accessible to nucleophilic attack by water activated by KOAr^{tBu} than the cyclic TMC, which benefits from the inherent stability of

its ring structure.^[22] Ester linkages in a linear polymer are under minimal conformational strain, allowing efficient cleavage without the need to overcome additional energy barriers associated with ring tension, as would be required to initiate TMC ring-opening. Moreover, the formation of lactide as a product of PLLA depolymerization generates a eutectic mixture with TMC, enhancing the solubility and reactivity of these components. This eutectic formation could stabilize lactide in the reaction medium, creating a thermodynamically favorable environment that promotes further PLLA degradation over TMC polymerization. By forming an intermediate eutectic state, the reaction may effectively “delay” the TMC polymerization, providing a kinetic advantage for PLLA cleavage. Consequently, KOAr^{tBu} -activated water is more likely to catalyze PLLA breakdown as a kinetically and thermodynamically accessible process, prior to engaging in TMC ring-opening polymerization.

Consistent with the concentration used to determine T_c in EC, a lactidyl unit concentration of 0.5 M was employed, corresponding to 0.1 g of PLLA in 1.7 g of TMC. Importantly, similar to the EC used to verify PLLA depolymerization, it is anticipated that TMC could facilitate similar, if not more efficient, depolymerization kinetics under the previously established temperature and concentration conditions. While TMC has the potential to induce the depolymerization of PLLA into lactide, the varying presence of water in the system may also lead to hydrolysis reactions of PLLA facilitated by TMC. To ensure a limited amount of water, the TMC used was dried, whereas the PLLA was not. Given the unknown quantity of water present, the reaction was conducted using a 1/150 molar equivalent of KOAr^{tBu} relative to the PLLA lactidyl content ($[\text{L-LA}]_0/[\text{KOAr}^{\text{tBu}}]_0 = 150$). As shown in Figure 5a, although PLLA degradation is already observed after 40 minutes (Relative $M_n\text{SEC} = 1,300 \text{ g}\cdot\text{mol}^{-1}$), no apparent modification of the TMC signal is detected. ^1H NMR of the crude medium reveals a conversion in TMC limited to 3.5 mol.%, supporting the hypothesis that, driven by the water activated by KOAr^{tBu} , PLLA chains degrade more rapidly than TMC polymerizes (Supporting Information, Figure 3). After 3 hours, the relative TMC signal completely disappears, replaced by a new one characterized by a relative $M_n\text{SEC}$ of 12,000 $\text{g}\cdot\text{mol}^{-1}$. The ^1H NMR analysis of the precipitated sample unambiguously confirms a structure corresponding to an ω -hydroxyl PTMC, end-capped in the α position with an average of two lactidyl units (Figure 5b). The ^{13}C NMR analysis confirms the very short length of the lactidyl-based segment. Figure 5c shows a zoomed-in view of the carbonyl carbon region (150–172 ppm) specifically from the ^{13}C spectrum, complementing the ^1H NMR data shown in Figure 5b. In this region, distinct signal assignments allow for the identification of LA and TMC-based triad sequences. A peak at 154.92 ppm is attributed to a TMC triad sequence, while additional signals at 154.36 and 170.27 ppm, characterizing the carbonyls of the LA-TMC linkage, and the absence of LA triads at 169.6 ppm, confirm the oligomeric nature of the lactidyl-based initiating block.^[23]

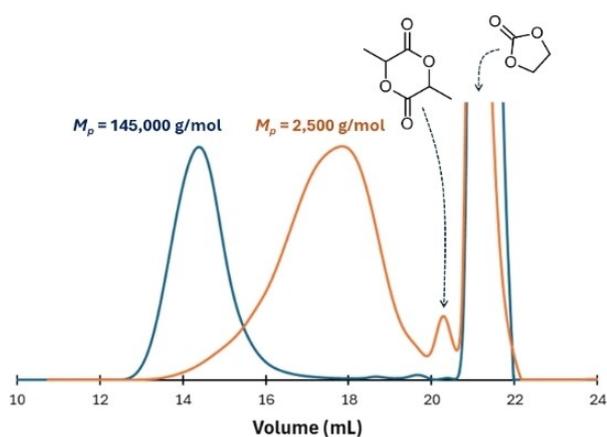


Figure 4. SEC molecular weight data of commercial PLLA (4043D, Natureworks) before (blue curve) and after depolymerization test (orange curve) in EC at 130 °C for 1 hour ($[\text{PLLA}]_0/[\text{H}_2\text{O}]_0 = 1/5$; $[\text{Lactic acid}]_0 = 6 \text{ M}$; catalyst loading 1/1000).

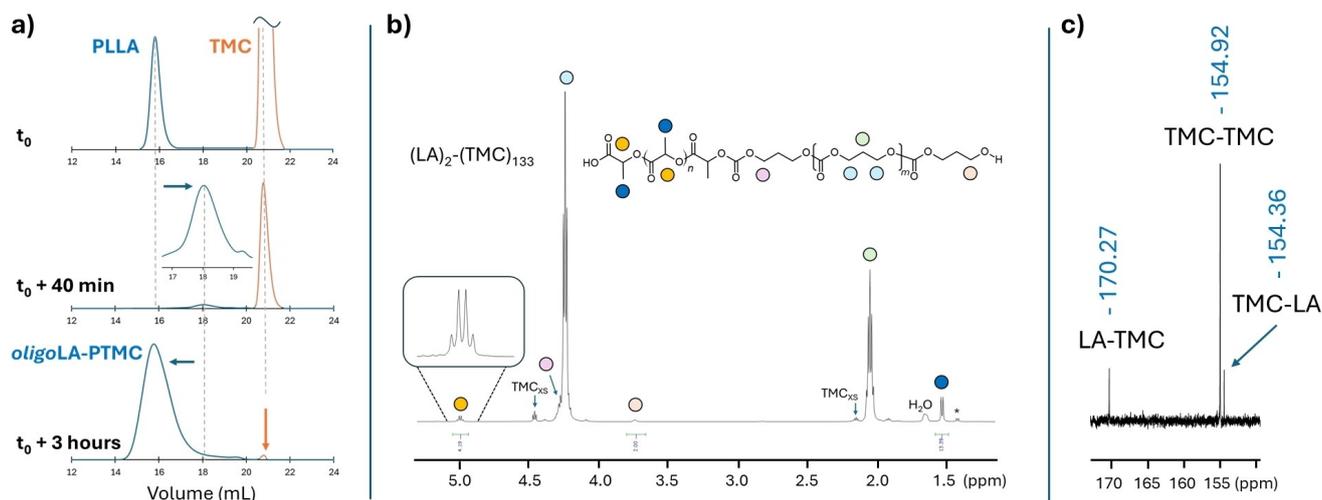


Figure 5. Analysis of the stages in the process of PLLA depolymerization and TMC polymerization. a) Molecular weight profiles over time measured by SEC, illustrating the evolution of PLLA depolymerization alongside TMC polymerization. b) ^1H NMR spectrum of the final product, showcasing the chemical characteristics of the protons present (* impurities). c) Zoom into the carbonyl region of the ^{13}C NMR spectrum, highlighting the signals associated with the carbonyl groups in the final product.

As determined by SEC, by reference to a polystyrene standard calibration, using the Mark-Houwink relationship $[\eta] = KM^a$ for PS and PTMC ($K_{\text{PS}} = 1.25 \times 10^{-4} \text{ dL} \cdot \text{g}^{-1}$, $a_{\text{PS}} = 0.707$, $K_{\text{PTMC}} = 2.77 \times 10^{-4} \text{ dL} \cdot \text{g}^{-1}$, $a_{\text{PTMC}} = 0.677$), a M_n of $9,400 \text{ g} \cdot \text{mol}^{-1}$, characterized by a D_M of 1.9, was calculated. Based on the intensity of the methylene hydroxyl end-groups, the degrees of polymerization for LA and TMC were determined by ^1H NMR to be 2 and 133, respectively (Figure 5b). This gives a M_n^{NMR} of $13,800 \text{ g} \cdot \text{mol}^{-1}$, a value that does not align with the absolute molar mass obtained by SEC. This discrepancy could stem either from the high dispersity or from the influence of the *oligoLA* sequence on the hydrodynamic volume of PTMC. Interestingly, when repeating the “PLLA depolymerization – TMC polymerization” process with a deliberate addition of $8 \mu\text{L}$ of water, an α -lactic acid-terminated PTMC is obtained (Supporting Information, Figure 4), resulting in a M_n^{NMR} of $3,900 \text{ g} \cdot \text{mol}^{-1}$ and an absolute M_n^{SEC} of $3,200 \text{ g} \cdot \text{mol}^{-1}$, minimizing the observed discrepancy.

Conclusion

This work advances polymer recycling by introducing a one-pot eutectic-assisted mechanism for PLA depolymerization and PTMC formation. The LA-TMC eutectic system, combined with KOAr^{tBu} , creates a selective environment for PLLA breakdown without requiring stringent drying, addressing a critical barrier for industrial scalability. Although the PTMC molar mass depends on the residual water content, this approach enables efficient PLLA degradation and facilitates subsequent TMC polymerization in a more energy-efficient process. Beyond PLLA, the method holds promise for other bio-based polymers, representing a meaningful step toward more sustainable and industrially viable polymer recycling within a circular economy framework.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: PLA • Eutectic mixtures • Depolymerization • PTMC • Recycling

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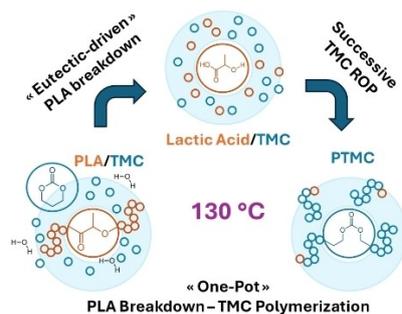
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Research Article

Polymer Chemistry

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Synergistic Pathways in PLA Breakdown and PTMC Formation: A One-Pot Eutectic-Driven Recycling Mechanism



PLA is efficiently depolymerized in a one-pot process. LA formed during degradation creates an eutectic mixture with TMC, enabling milder recycling conditions without extensive drying. The 2,4,6-tri-tert-butyl-phenolate of potassium catalyzes selective depolymerization, followed by TMC polymerization, yielding lactic acid end-capped PTMC with high efficiency.