

# Efficient Hydrolysis of Poly(lactic acid) at Room Temperature to Recycle Self-separated Calcium Lactate

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## Electronic Supplementary Information

**Abstract** Poly(lactic acid) (PLA), a bio-based polymer, is considered to be a sustainable alternative to conventional petroleum-based plastics. However, owing to its widespread use and relatively slow degradation rate in water, PLA still poses potential environmental pollution risks after being discarded. The efficient chemical recycling of PLA represents an attractive approach to addressing both resource reuse and environmental pollution challenges caused by its waste. Hydrolysis is the predominant method of industrial recycling. However, because PLA is insoluble in water, efficient heterogeneous hydrolysis requires high-temperature and high-pressure conditions. In this study, an efficient homogenous hydrolysis method capable of simultaneously dissolving PLA and calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) was developed. Suitable solvents for this method were screened, and it was found that PLA hydrolysis using dioxane and 1,4,7,10,13-Pentaoxacyclopentadecane as solvents achieved conversion rates of 93% and 90%, respectively, within 2 h at room temperature. Notably, the hydrolysis product, calcium lactate, precipitated as a solid from the solvent and therefore self-separated from the reaction solution. The solvent, acid/base conditions, water content, and depolymerization kinetics were investigated. Compared with previously reported hydrolysis methods, the enhanced efficiency observed in this study can be attributed to the concurrent solvation of PLA and  $\text{Ca}(\text{OH})_2$ , which maintains homogeneity throughout the reaction process. Additionally, this method facilitates closed-loop recycling of PLA and is compatible with the highly selective recovery of PLA from various types of PLA products.

**Keywords** Poly(lactic acid); Homogeneous hydrolysis method; Chemical recycling; Closed-loop

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## INTRODUCTION

Lactic acid is usually obtained by acidification of calcium lactate from the fermentation of renewable resources, such as starch and straw. Lactic acid subsequently undergoes dehydration to produce lactide, which finally generates poly(lactic acid) (PLA) via ring-opening polymerization (Fig. 1).<sup>[1,2]</sup> As a life-cycle low carbon footprint polymer, PLA exhibits outstanding mechanical properties, biocompatibility, and biodegradability, and is mass-produced and widely used.<sup>[3–5]</sup> According to the statistical data of European Bioplastics,<sup>[6]</sup> by the end of 2023, the annual output of PLA accounted for 31.0% of the total bio-based plastic production, totaling approximately  $6.7 \times 10^5$  tons. However, for efficient degradation, PLA must be placed under industrial composting conditions, such as 58 °C and high humidity.<sup>[7,8]</sup> The

complete degradation of PLA in soil may take several decades, whereas it undergoes virtually no degradation in seawater.<sup>[9]</sup> Direct disposal of post-consumer PLA products into the environment may cause pollution.<sup>[10]</sup> Therefore, PLA waste should be collected for industrial composting or recycling. In contrast, recycling is preferred because the value of recycled products is higher than that of composted degraded products such as water and carbon dioxide.<sup>[11–13]</sup>

The chemical recycling routes of PLA include pyrolysis,<sup>[14–17]</sup> alcoholysis<sup>[18–21]</sup> and hydrolysis (Fig. 1).<sup>[22–25]</sup> Although the pyrolysis of PLA efficiently recycles lactide, it depends upon the high reaction temperature and high vacuum conditions, and is accompanied by competing side reactions such as isomerization and elimination.<sup>[11,26]</sup> For the alcoholysis of PLA, owing to the incompatibility between PLA and alcohol, the rate of depolymerization is slow, resulting in a low yield and selectivity. Furthermore, the separation and purification processes for depolymerized products are relatively complex because of the presence of lactate, alcohol.<sup>[20,27]</sup> In contrast, hydrolysis is more practical, being applied in global leader PLA companies such as NatureWorks LLC and TotalEn-

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Special Topic: Depolymerizable Polymers

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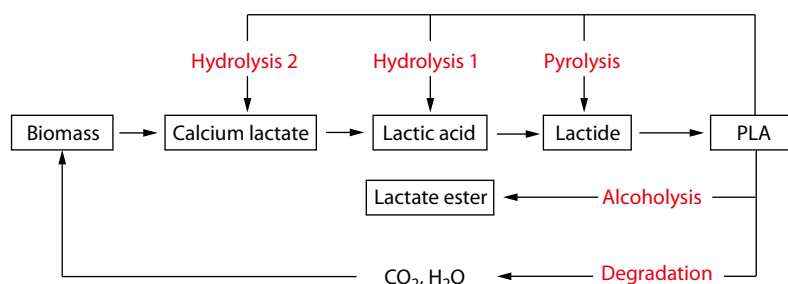


**Fig. 1** The life cycle process of PLA.

ergies Corbion.<sup>[28,29]</sup> The hydrolysis of PLA proceeds via two primary pathways: direct hydrolysis into lactic acid or calcium lactate. Notably, both routes require hydrolysis temperatures that substantially exceed PLA's glass transition temperature of PLA or approach its melting point. At a melting point of 180 °C, the saturated vapor pressure of water can reach as high as 1 MPa. Therefore, it was necessary to increase the pressure in the system. By elevating the temperature and pressure to 180 °C and 1.5 MPa, respectively, the hydrolysis conversion rate of PLA achieved an impressive 98.15% within 3 h.<sup>[30]</sup> In contrast, at 70 °C, the hydrolysis rate of PLA is very slow. The quality loss within five days only reaches 5.1%.<sup>[31]</sup>

Researchers have investigated the utilization of co-solvents and catalysts in order to increase the hydrolysis rate of PLA and reduce energy consumption.<sup>[32,33]</sup> The use of water-ethanol mixtures as a medium for PLA hydrolysis was studied by Auras *et al.*<sup>[34,35]</sup> The inclusion of ethanol caused the polymer to swell, facilitating the sorption of water for hydrolysis. It was estimated that 41 h would be required to achieve a 95% yield of lactic acid at 90 °C. Liu *et al.* utilized a series of ionic liquids as solvents and catalysts.<sup>[36]</sup> [BMIM][OAc] was identified as the best candidate, enabling high conversion to lactic acid within 2 h at 130 °C. The ionic liquid partially dissolved the PLA, resulting in the transformation of PLA from an insoluble solid phase into molecular chains dispersed within the solution. Furthermore, the presence of water molecules significantly enhances the reaction rate by facilitating their attack on the PLA molecular chain. In terms of the catalyst, the hydrolysis efficiency of PLA catalyzed by alkaline is superior to that of PLA subjected to acidic catalysis. Wu *et al.* conducted hydrolysis of PLA in a hydrochloric acid solution at 70 °C with a pH of 1, achieving a retention of 90% PLA mass after 5 days. In contrast, when hydrolysis was performed in sodium hydroxide solution at pH 13, only 30% of the PLA mass was retained after the same period. Furthermore, using 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) as a catalyst resulted in nearly 80% hydrolysis within 5 days.<sup>[31]</sup> Piemonte *et al.* discovered that at a temperature of 180 °C and a pressure of 1.5 MPa, the hydrolysis conversion rate of PLA after 3 h was 98%, while it only took 20 min to complete hydrolysis after adding 0.6 mol/L sodium hydroxide.<sup>[30]</sup> Acids/bases and co-solvents offer considerable advantages in enhancing the hydrolysis rate of PLA, while simultaneously lowering the required reaction temperature and pressure.

In conventional hydrolysis systems, PLA hydrolysis occurs as a multiphase reaction involving two incompatible phases: a PLA phase suspended in aqueous medium. Consequently, water molecules were primarily restricted to interacting with the surface of the PLA phase (Fig. 2a). This process is charac-

terized by heterogeneous depolymerization, specifically heterogeneous erosion, which can be defined as layer-by-layer hydrolysis that progresses from the surface towards the interior.<sup>[37,38]</sup> In contrast, when PLA was dissolved in a mixed aqueous solution, the reaction transitioned from two incompatible phases to a homogeneous phase. This transition significantly enhances the hydrolysis rate. In this study, we propose a method for the efficient hydrolysis of PLA to calcium lactate in a mixed aqueous solution (Fig. 2b). During this reaction, PLA gradually dissolves, thereby markedly accelerating the rate of hydrolysis while simultaneously reducing both the temperature and pressure required for the reaction. Owing to its low solubility, calcium lactate can spontaneously precipitate out of the system. The chemical cycle of calcium lactate, lactic acid, lactide, and polylactic acid is achieved through the recycling of calcium lactate.

## MATERIALS AND METHODS

### Materials

Dioxane (Dio, >99.9%) was purchased from Tianjin Zhiyuan Reagent Co., Ltd. The PLA pellets were supplied by Anhui BBKA Biochemical & Futerra PLA Co., Ltd., BBKA FUTERRA PLA FY801 (the crystallinity of PLA was 31.5%, and the average inner diameter of the PLA pellets was 3.51±0.33 mm). Sodium acetate and pyrazine were purchased from Aladdin (Nuclear Magnetic Resonance internal standard >99%). PLA cups are essentially free of additives, whereas PLA cup lids exhibit a mass ratio of 0.87/0.13 for PLA/CaCO<sub>3</sub>. PLA straws have a mass ratio of 0.8/0.02/0.18 for PLA/PBAT/CaCO<sub>3</sub>. Calcium hydroxide (Ca(OH)<sub>2</sub>), potassium hydroxide (KOH), and sodium hydroxide (NaOH) were purchased from Aladdin (>95% purity). Calcium L-lactate, which incorporates five molecules of crystalline water, was purchased from Aladdin. It was dried in a vacuum oven at 120 °C for 12 h to effectively remove the contained crystal water, and utilized as a standard reference substance.

### Methods

#### Calcium lactate from the hydrolysis of PLA

Typically, 0.2 g of PLA pellets were dissolved in 8.8 g of Dio. The PLA solution was subsequently placed on a magnetic stirrer, where it was magnetically stirred at 1000 r/min. Subsequently, 0.6 g of water and 0.1 g of Ca(OH)<sub>2</sub> were added, and the reaction was carried out for 12 h. Following the completion of the reaction, the solid product and solution were obtained by filtration (Fig. S1 in the electronic supplementary information, ESI). Subsequently, the product was washed with ethanol and dried under vacuum.

The PLA conversion was calculated in accordance with the

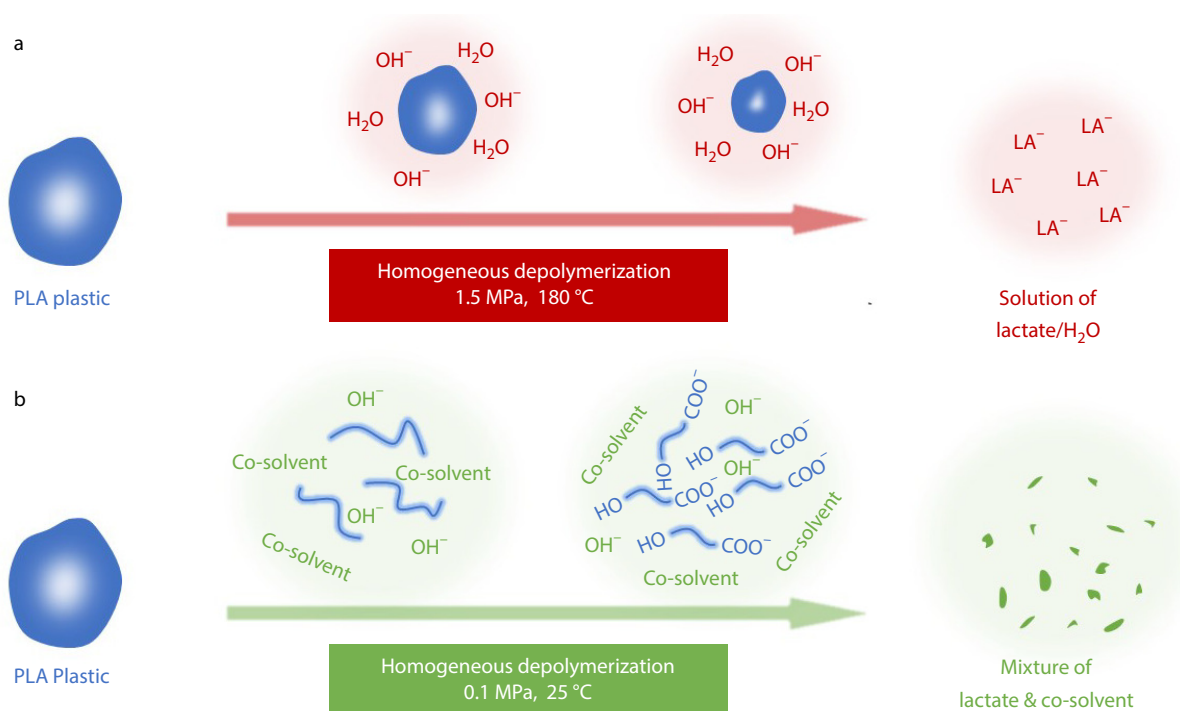


**Fig. 2** (a) The mechanism of traditional heterogeneous depolymerization of PLA during hydrolysis; (b) the mechanism of homogeneous depolymerization in this work of PLA during hydrolysis.

formula provided in Eq. (1), where  $m_{\text{PLA}-t}$  and  $m_{\text{PLA}-0}$  are the masses of PLA at time  $t$  and the initial time, respectively;  $A_{\text{PLA}-t}$  and  $A_{\text{PLA}-0}$  represent the areas of integration of the NMR hydrogen spectra of  $-\text{CH}_3$  before and after the reaction in solution, respectively. When PLA was completely dissolved,  $A_{\text{PLA}-t}/A_{\text{PLA}-0}$  was equal to  $m_{\text{PLA}-t}/m_{\text{PLA}-0}$ . Calcium lactate is soluble in water; therefore, deuterated water was utilized as the deuterated reagent, and sodium acetate served as the internal standard for  $^1\text{H}$ -NMR. This allowed the calculation of the calcium lactate yield. The calcium lactate yield was calculated according to the following Eq.(2): where  $A$ ,  $n$ , and  $M$  denote the integral area, number of protons, and molar mass of the respective substance, respectively. The error in this internal standard calculation method was approximately 1% (Table S1 in ESI).

$$\text{PLA conversion (\%)} = \left(1 - \frac{m_{\text{PLA}-t}}{m_{\text{PLA}-0}}\right) \times 100\% = \left(1 - \frac{A_{\text{PLA}-t}}{A_{\text{PLA}-0}}\right) \times 100\% \quad (1)$$

$$\text{Yield (\%)} = \frac{A_{\text{calcium lactate}} \times n_{\text{sodium acetate}} \times M_{\text{calcium lactate}}}{A_{\text{sodium acetate}} \times n_{\text{calcium lactate}} \times M_{\text{sodium acetate}}} \times 100\% \quad (2)$$

#### Dynamic experiment of PLA homogeneous depolymerization process

Numerous studies have classified the hydrolysis process as a first-order reaction in the study of PLA depolymerization kinetics. Consequently, in the present study, concerning the hydrolysis kinetics of PLA, a first-order kinetic model was adopted. The relationship between the hydrolysis rate and PLA concentration is expressed by Eq. (3):

$$\frac{d(C_{\text{PLA}})}{dt} = -kC_{\text{PLA}} \quad (3)$$

where  $k$  represents the rate constant and  $C_{\text{PLA}}$  represents the PLA concentration at  $t$ .

$$C_{\text{PLA}} = C_{\text{PLA}0} (1 - X) \quad (4)$$

where  $X$  represents the PLA conversion rate; consequently, Eq. (4) can be reformulated as Eq. (5):

$$\frac{dX}{dt} = k(1 - X) \quad (5)$$

Eq. (5) is integrated with time to derive the corresponding Eq. (6).

$$\ln \frac{1}{1 - X} = kt \quad (6)$$

#### Economic and environmental evaluation

The energy efficiency coefficient  $\varepsilon$  directly compares the proposed method with other methods to verify its efficiency, which is defined by Eq. (7), where  $t$  is the reaction time (in minutes),  $T$  is the reaction temperature in degrees Celsius, and  $Y$  is the yield of the main monomer as a mass fraction. The lower the temperature and reaction time, the higher the relative value of  $\varepsilon$ . The  $E$  factor is based on the environmental factor ( $E$ ) proposed by Prof. Sheldon in 1992<sup>[39]</sup>, which has been successfully used in green chemistry metrics and corresponds to a simple mathematical relation defining the amount of waste generated per unit of the product. The solvent could be recycled and the solvent recovery rate was  $X\%$ . The modified  $E$  factor can be calculated through Eq. (8), based on the recyclability of the solvent, and used to compare the  $E$  factor of different PLA depolymerization studies in the literature and the one presented here. The environmental energy impact corresponds to the combined effect of mass input and energy economy, as described in Eq. (9).

$$\varepsilon = \frac{Y}{T \times t} \quad (7)$$

$$E = \frac{\left[ \frac{\text{Solvent}}{\text{PLA}} \times (1 - X\%) \text{ratio} + \frac{\text{Cat}}{\text{PLA}} \text{ratio} + \text{other} \frac{\text{Subst}}{\text{PLA}} \text{ratio} \right] \times m_{\text{PLA}}}{\text{Yield}_{\text{product}} \times \frac{MM_{\text{product}}}{MM_{\text{PLA mere}}} \times m_{\text{PLA}}} \quad (8)$$

$$\xi = \frac{E}{\varepsilon} \quad (9)$$

### Characterization

(1) Fourier transform infrared (FTIR) spectroscopy. FTIR analyses were performed using a Nicolet 6700 spectrophotometer scanning from 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$ .

(2) Nuclear magnetic resonance (NMR) spectroscopy. The NMR spectra of PLA and calcium lactate were recorded on a Bruker Avance III spectrometer operating at 400 MHz in  $\text{CDCl}_3$  and  $\text{D}_2\text{O}$ .

(3) Scanning electron microscopy (SEM). The solid material separated after the reaction was taken on Prox manufactured in Phenom to determine its structure and characterize the particle size of the separated solid product.

(4) UV Absorbance Photometer. The solubility of  $\text{Ca}(\text{OH})_2$  in different solvent ratios was tested using Cary 50 (Agilent Technologies Inc). When a certain concentration of turbid  $\text{Ca}(\text{OH})_2$  solution was diluted to a transmittance of 100%, it was determined that  $\text{Ca}(\text{OH})_2$  was completely dissolved to test its solubility.

(5) Polarimeter. The specific rotation values of calcium lactate in deionized water were measured using a polarimeter (SGW<sup>®</sup>-2) at a temperature of 20 °C and wavelength of 589 nm. The ratio of L-configuration in the samples was calculated using the following Equation:

$$\text{L ratio (\%)} = \frac{[\alpha]_{\text{D}}^{20} \pm [\alpha]_{\text{D}}^{20}}{2[\alpha]_{\text{D}}^{20}} \times 100\% \quad (10)$$

where  $[\alpha]_{\text{D}}^{20}$  is the measured specific rotation value,  $[\alpha]_{\text{D}}^{20}$  is the specific rotation value reported in the literature, or the specific rotation value of the standard.

(6) High-performance liquid chromatography (HPLC). The chemical purity of the recycled calcium lactate was determined using HPLC (Agilent1260). The HPLC system was equipped with a C18 column and a UV detector at 210 nm. Methanol and 0.05% aqueous phosphoric acid were used as the mobile phases. The LC column and oven temperature were maintained at 30 °C. The flow rate of the mobile phase was maintained at 0.5 mL/min. The elution program (0.05% aqueous phosphoric acid/methanol, V/V) was as follows: (90/10) from 0 min to 12 min, linear ramp to (60/40) from 12 min to 16 min, (90/10) from 16 min to 20 min.

## RESULTS AND DISCUSSION

### Homogeneous Depolymerization versus Heterogeneous Depolymerization

A comparative study of the heterogeneous and homogeneous depolymerizations of PLA using  $\text{Ca}(\text{OH})_2$  was conducted at various temperatures. As illustrated in Fig. 3, at room temperature, the hydrolysis of PLA in an aqueous heterogeneous system exhibited extremely low efficiency, with a conversion rate of only 0.7% within 12 h. Even when the temperature was increased to 90 °C, the conversion rate remained relatively low (8.3%). In contrast, in a homogeneous system, the hydrolysis conversion rate

reached 93% within 2 h at room temperature. Furthermore, increasing the temperature to 70 °C resulted in nearly complete hydrolysis of PLA within 5 min. These experimental results highlight a significant difference in the PLA hydrolysis processes between the two systems. This discrepancy can be attributed to the compatibility between PLA and water, which significantly affects the mass transfer during the reaction process. In a heterogeneous reaction involving two incompatible phases (PLA suspended in an aqueous phase), there is a mass-transfer limitation that reduces the reaction rate. In contrast, homogeneous depolymerization ensures full contact between the two phases, enhancing mass transfer and accelerating the reaction rate.

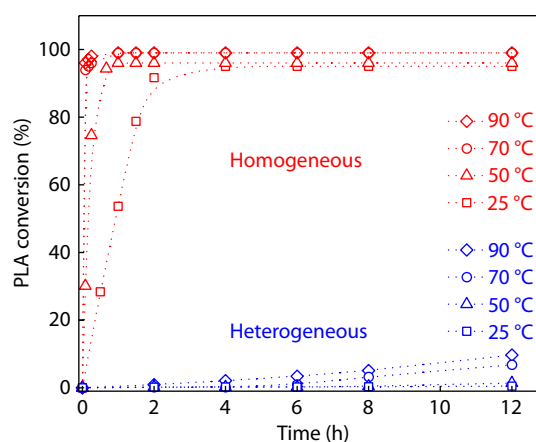


**Fig. 3** PLA hydrolysis conversion curves at different temperatures in homogeneous and heterogeneous systems. The feed mass ratio of PLA/alkali/water was fixed at 2:1:48.

Under standard atmospheric pressure, with the feed mass ratio of PLA/alkali/water fixed at 2:1:6, the conversion and molecular weight changes during both homogeneous and heterogeneous depolymerization processes were investigated. In the heterogeneous depolymerization process, PLA exhibited a significantly slower depolymerization rate, achieving only 7.5% conversion within 12 h (Fig. 4a). As the hydrolysis conversion rate of PLA increased, the molecular weight of residual PLA gradually decreased (Fig. 4b, Table S2 in ESI). Notably, even at higher conversion rates, the molecular weights remained relatively high. Owing to its immiscibility with water, PLA undergoes surface erosion, where water continuously erodes the PLA surface layer-by-layer from the exterior to the interior, leading to increased degradation primarily on the surface. In contrast, during the homogeneous process, the molecular weight of PLA decreases rapidly in the initial stage of the reaction, reaching an  $M_n$  of 18 kDa within 0.5 h, despite the low conversion rate at this stage. After 2 h, the molecular weight stabilized at approximately 6 kDa and did not change significantly with further increase in the PLA conversion rate (Figs. 4c and 4d, Table S3 in ESI). At the onset of the reaction, the solution contained significant concentrations of alkali anions and PLA molecular chains. These alkali anions randomly

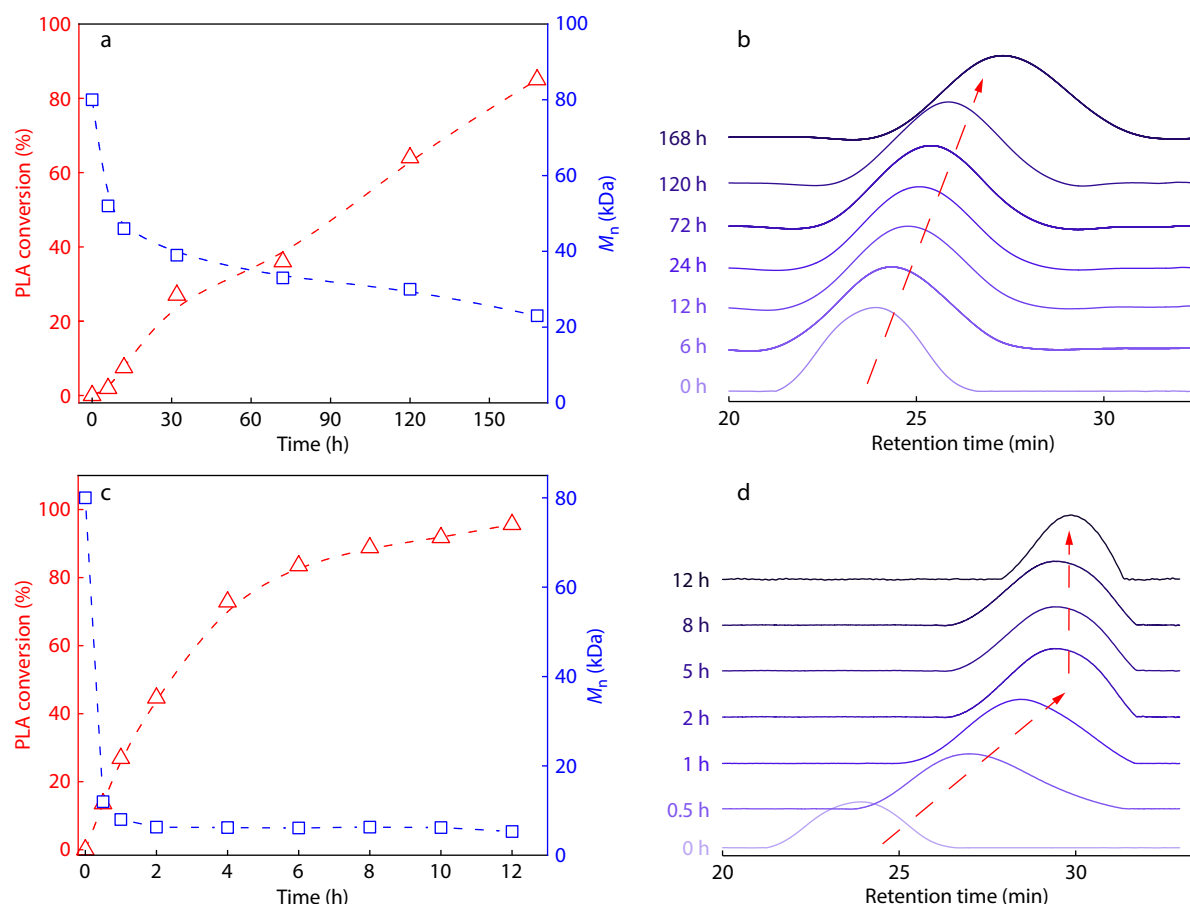


**Fig. 4** (a, c) PLA conversions and (b, d) GPC analysis in (a, b) heterogeneous systems at 70 °C and (c, d) homogeneous systems at room temperature.

attack multiple ester bonds and terminal carboxyl groups, resulting in the formation of calcium lactate and generation of short PLA chains enriched with carboxyl anions. The synergistic action between the carboxyl and base anions accelerates the depolymerization of these short chains, ultimately producing calcium lactate.

The solvent plays a crucial role in the homogeneous depolymerization process. We compared the effects of various solvents on PLA hydrolysis efficiency. Organic solvents, such as chloroform ( $\text{CHCl}_3$ ), tetrahydrofuran (THF), 1,4,7,10,13-pentaoxacyclopentadecane (POPCE), acetone (AC), toluene (TL), dimethyl carbonate (DMC), and Dio, can effectively dissolve PLA under certain conditions. At room temperature, the use of Dio as the solvent resulted in a PLA conversion rate of 93% within 2 h. In contrast, the use of  $\text{CHCl}_3$  led to a significant decrease in the conversion rate, reaching only 28%. (Fig. 5a). The hydrolysis conversion rate of PLA was approximately 1% for the AC, TL, and THF solutions and 8% for the DMC solution during the same time frame. As a solvent for the homogeneous hydrolysis method, Dio significantly enhanced hydrolysis efficiency owing to its excellent compatibility with both PLA and water. The broad applicability of the homogeneous hydrolysis method was validated through comprehensive solvent screening. The capacity of POPCE, as a green solvent, to synergistically dissolve both PLA and water enabled the system to achieve a conversion of 90% under identical reaction

conditions within 2 h. These findings indicate that the pivotal factor in enhancing the efficiency of PLA hydrolysis is the homogeneous reaction rather than relying exclusively on Dio. This strategy holds considerable promise for the development of environment-friendly solvents.

Acids or bases have been demonstrated to effectively increase the hydrolysis rate of PLA. In the homogenous depolymerization process, acids and bases with high conversion and selectivity were chosen, including organic and inorganic acids or bases. PLA hydrolysis is significantly more effective under alkaline conditions than under acidic conditions. The yield of PLA hydrolysis over a period of one hour was less than five percent when using p-toluene sulfonic acid (PTSA), hydrochloric acid (HCl), and diphenyl phosphate (DPP) were used. Unlike acids, bases exhibit greater hydrolysis efficiency. As shown in Fig. 5(b), under NaOH and KOH conditions, PLA was nearly fully hydrolyzed within one hour. Furthermore, under  $\text{Ca}(\text{OH})_2$  conditions, the conversion rate of PLA hydrolysis reached 53% within the same time frame. The hydrolysis of esters is an equilibrium reaction, and inorganic bases promote a positive shift of the equilibrium by further acid-base neutralization reactions with lactic acid, which is produced after the breaking of the PLA ester bonds. The veracity of this mechanism can be corroborated by the discrepancy in the hydrolysis products observed under varying acidic and basic conditions. The hydrolysis product of PLA, in the presence of

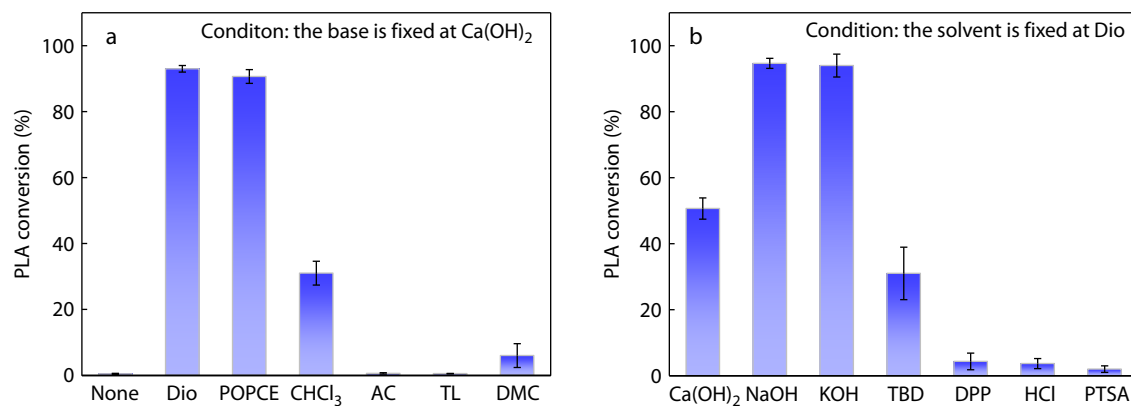


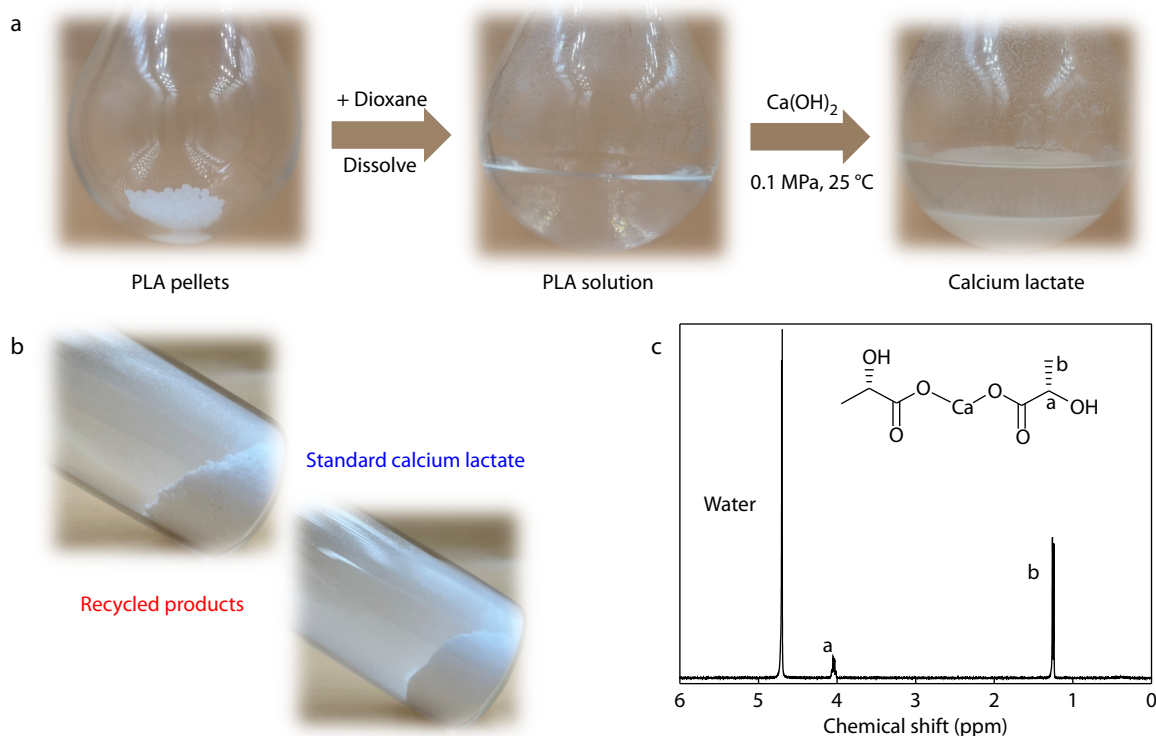
**Fig. 5** Influence of (a) solvents and (b) acid/base on the hydrolysis conversion of PLA. The feed mass ratio of PLA/alkali/water was fixed at 2:1:48.

inorganic bases, contained lactate (Figs. S2 and S3 in ESI). This result provides evidence that inorganic bases accelerate hydrolysis by participating in the reaction.

The products obtained from hydrolysis by NaOH and KOH were colorless viscous liquids that were miscible with the solvent. The product requires additional separation *via* distillation. Conversely, a white solid precipitated from the solution when  $\text{Ca(OH)}_2$  was used for PLA hydrolysis (Fig. 6a), indicating that the resulting product was insoluble in the solvent. A pure solid product was obtained through a simple solid-liquid separation and washing-drying process (Fig. 6b). The structure and purity of the solid were characterized and tested using  $^1\text{H-NMR}$ , FTIR, EDS, HPLC, and polarimeter. Structural analysis confirmed that the product was calcium lactate (Ca-Lac). The chemical and optical purity of calcium lactate derived from hydrolysis exceeded 99%. (Figs. 6c–6e, Figs. S4

and S5, Tables S4 and S5 in ESI). Compared to  $\text{Ca(OH)}_2$ , although PLA exhibits a faster hydrolysis rate in the presence of KOH and NaOH than  $\text{Ca(OH)}_2$ , we opted for  $\text{Ca(OH)}_2$  because of its ability to allow self-separation of the hydrolyzed products. In addition, calcium lactate serves as a crucial intermediate in the production of PLA and is an essential raw material for lactic acid synthesis.<sup>[40]</sup>

The conversion of PLA as a function of the base ratio was monitored to determine the optimal concentration to achieve homogeneous depolymerization with maximal energy efficiency. The conversion rate of PLA relative to the molar ratio of  $\text{OH}^-$  to lactic acid units in the depolymerization solution over a reaction duration of 12 h at room temperature is illustrated in Fig. 7. The results indicated that the PLA conversion rate increased with increasing ratio of  $\text{OH}^-$  to lactic acid units, reaching a peak at a molar ratio of 1:1. Further increasing the



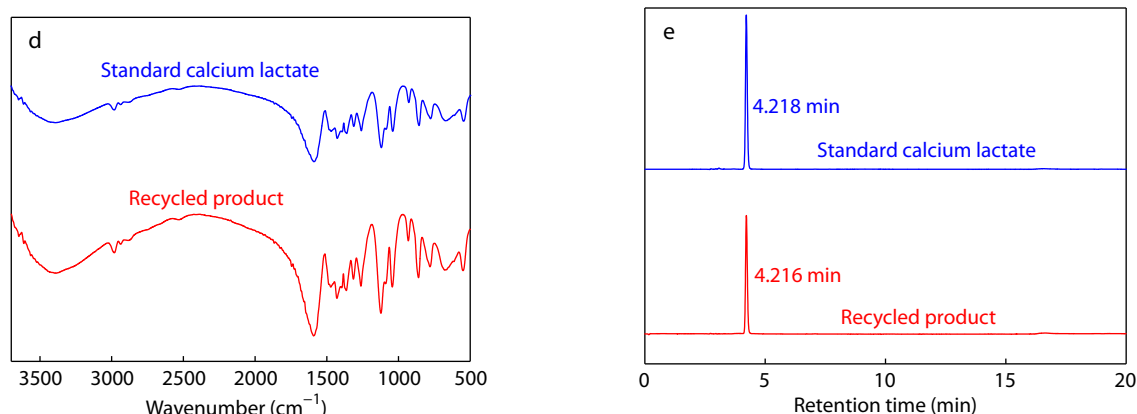


**Fig. 6** (a) Digital photographs obtained from PLA hydrolysis process; (b) Photographs of the hydrolysed product and standard calcium lactate; (c) The <sup>1</sup>H-NMR spectrum of recycled product; (d) The FTIR spectra of recycled product and standard calcium lactate; (e) The HPLC curves of recycled product and standard calcium lactate.

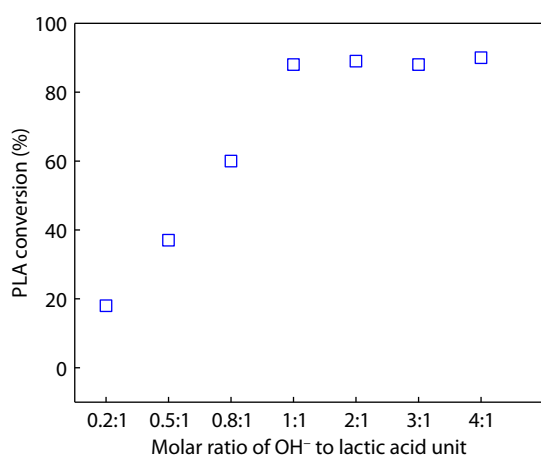


**Fig. 7** PLA conversion rate as a function of the molar ratio of OH<sup>-</sup> to lactic acid unit. The feed mass ratio of PLA/alkali/water was fixed at 2:1:6.

OH<sup>-</sup> ratio did not enhance the PLA conversion rate and remained constant. This trend implies the active involvement of Ca(OH)<sub>2</sub> in the reaction mechanism, and it was confirmed that Ca(OH)<sub>2</sub> is consumed during this process, as evidenced by the solid product being calcium lactate. Given that PLA conversion appears to be maximized at approximately a 1:1 molar ratio, subsequent experiments were conducted using this specific ratio.

In the system with a mass ratio of PLA/H<sub>2</sub>O/Dio at 2/6/88, PLA was initially dissolved in Dio, followed by the addition of H<sub>2</sub>O and Ca(OH)<sub>2</sub>, achieving a 94% conversion rate within 12 h. Direct mixing of PLA, Dio, H<sub>2</sub>O, and Ca(OH)<sub>2</sub> resulted in a conversion of 39% within 12 h and 92% within 34 h. In contrast, in the heterogeneous system (direct mixing of PLA, Ca(OH)<sub>2</sub>, and H<sub>2</sub>O), the hydrolysis conversion of PLA reached approximately 0.7% within 12 h, and 1.3% within 34 h. The hydrolysis rates observed under both feeding modes were significantly enhanced compared with those in the heterogeneous systems. Additionally, the pre-dissolution of PLA led to a substantial enhancement in the hydrolysis rate when compared to direct mixing, an effect that can be attributed to the dissolution process of PLA. While factors such as particle size

and crystallinity are known to significantly influence the dissolution process,<sup>[41]</sup> these effects were effectively mitigated in a homogeneous system.

### Equilibrium and Kinetic Investigation of Phase Behavior

Chemical recycling of PLA was successfully achieved by incorporating Ca(OH)<sub>2</sub> at room temperature and atmospheric pressure using Dio and water as co-solvents. The water-to-Dio ratio in the co-solvent also had a significant influence on the hydrolysis rate. By maintaining a constant mass of Dio, the water content was gradually adjusted to determine its effect on the hydrolysis rate. As the water content increased, PLA transitioned from total to partial dissolution (Fig. S6 in ESI). Additionally, the hydrolysis yield of PLA exhibited a trend of initially increases and subsequently decreasing within 1 h. Specifically, when the water-to-Dio ratio reached 1:1, a noticeable decline in the hydrolysis conversion rate was observed (Fig. 8a). It is worth noting that increasing the water ratio to 0.7:1 may result in some calcium lactate dissolving in the co-solvent, which is not conducive to self-separation (Fig. S7 in ESI). Therefore, maintaining a water ratio of 0.5:1 is recommended for ideal experimental conditions. This phenomenon can be attributed to the reaction between PLA and Ca(OH)<sub>2</sub> in the co-solvent. As the water content increased, the solubility of PLA decreased, whereas that of calcium hydroxide increased. Consequently, this led to an improvement in the hydrolytic conversion rate of PLA to some extent. However, when the water content becomes excessively high, PLA becomes largely insoluble in the co-solvent, resulting in a decline in its hydrolytic conversion rate.

The solubility of PLA and Ca(OH)<sub>2</sub> was quantitatively assessed (Figs. S8–S12 in ESI), the results are presented in Fig. 8(b). With increasing water content, the solubility of Ca(OH)<sub>2</sub> increased, reaching 32.26×10<sup>-4</sup> g/g under the optimal reaction conditions. However, the solubility of PLA rapidly declined, reaching only 43.2×10<sup>-4</sup> g/g under ideal circumstances. Despite their low solubility, the dissolution equilibrium presented in the co-solvent accelerates the dissolution of both PLA and Ca(OH)<sub>2</sub> by consuming them within it, thereby advancing the reaction equilibrium. Kinetic tests further confirmed the reactant dissolution equilibrium during homogeneous depolymerization.

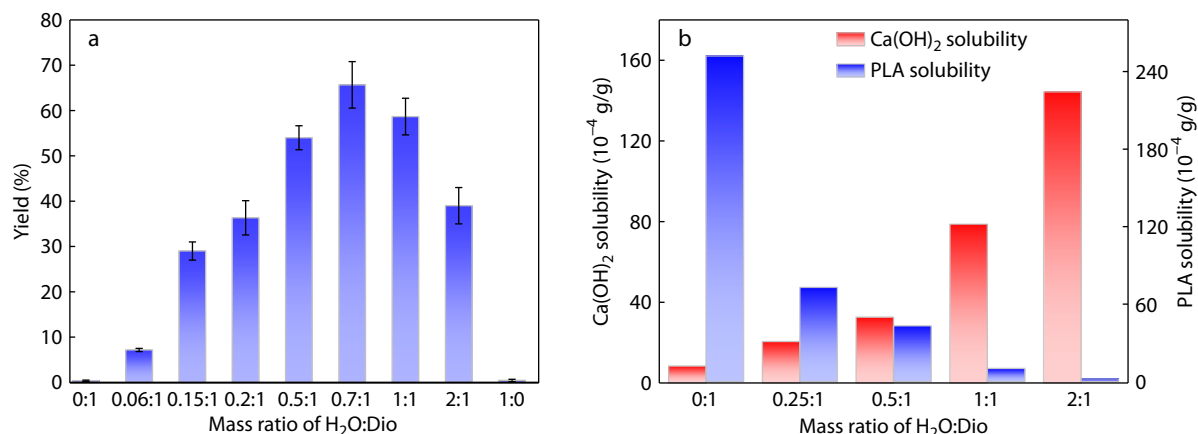


**Fig. 8** (a) The hydrolysis yield of PLA fluctuates in accordance with the water ratio; (b) The solubility of Ca(OH)<sub>2</sub> and PLA in solution as a function of different proportions of co-solvent.

With increasing water content, PLA transitioned from complete dissolution to partial dissolution. Therefore, it is essential to conduct kinetic experiments under these two conditions to validate the principles of dissolution equilibrium in a solution. When PLA is partially dissolved in the solution, the temporal change in the hydrolysis conversion rate of PLA is illustrated in Fig. 9(a), and shows a straight line with correlation coefficients greater than 0.99 when plotting the inverse of the conversion of PLA, indicating that depolymerization was a first-order reaction. Working at two different PLA con-

centrations, the curves also demonstrated first-order kinetic behavior (Figs. S13 and S14 in ESI). This can be explained by the dissolution equilibrium of PLA and calcium hydroxide during the reaction. When PLA is completely dissolved in the co-solvent, the dissolution equilibrium of Ca(OH)<sub>2</sub> exists in the whole system. The solubility of calcium hydroxide was constant, and as the reaction time increased, the concentration of PLA decreased. Therefore, the rate of hydrolysis was solely dependent on the concentration of PLA present in the solution, thus exhibiting first-order kinetics. When PLA was partially

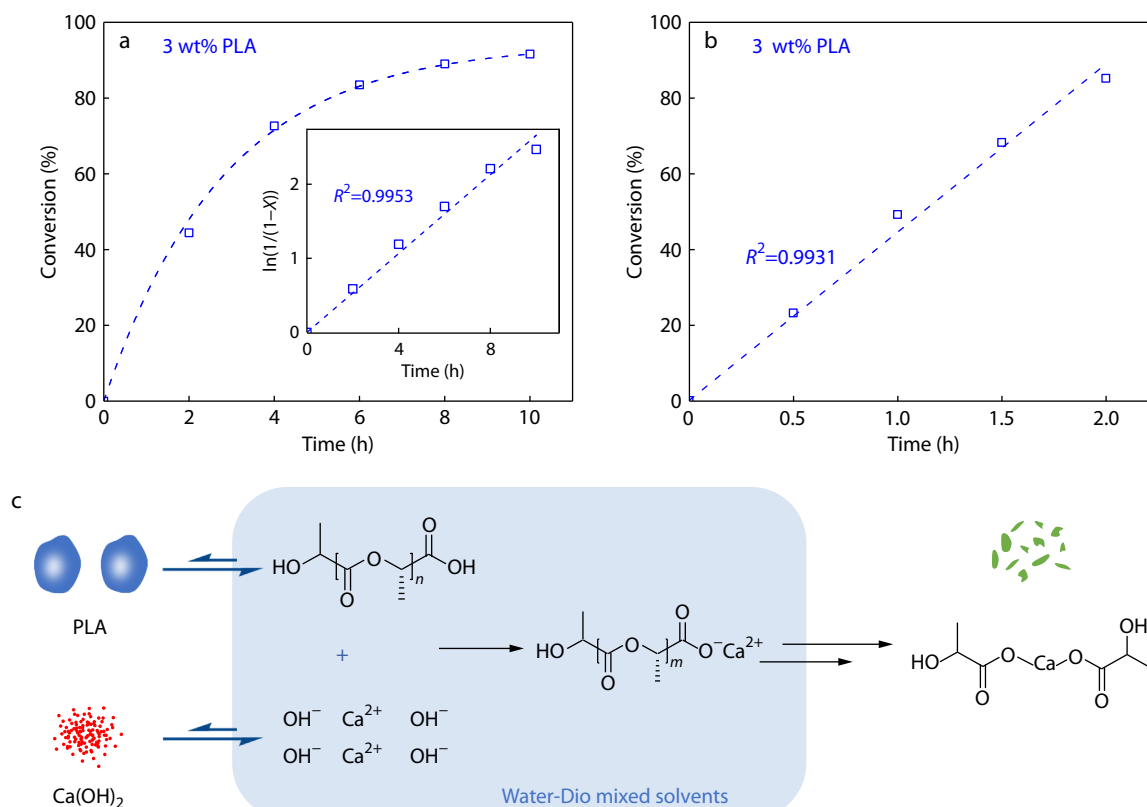


**Fig. 9** The kinetics curves of the PLA hydrolysis process in the homogenous systems (a) with the mass ratio of PLA/alkali/water being fixed at 2:1:6 within 10 h, (b) with the mass ratio of PLA/alkali/water being fixed at 2:1:48 within 2 h; (c) Sequential dissolution and reaction process of PLA and calcium hydroxide in the homogeneous system.

dissolved, drawing the change curve of PLA conversion rate with time revealed a straight line with a good linear relationship, and the correlation coefficient was greater than 0.98, suggesting that PLA depolymerization was a zero-order reaction at this point (Fig. 9b, Fig. S15 in ESI). When PLA is partially dissolved, equilibrium is established between PLA and  $\text{Ca}(\text{OH})_2$  in the solution. As PLA and calcium hydroxide in the solution are consumed, the undissolved PLA and calcium hydroxide will be dissolved in the solution (Fig. 9c). Consequently, as the reaction progressed, the concentrations of PLA and calcium hydroxide in the solution remained constant. This is reflected in the kinetic model, which demonstrates a zero-order level, in accordance with the observed behavior.

### Exploration towards the Practical Applications and Selective Depolymerization

To further verify the applicability of the homogeneous depolymerization method, the degradation of different commercial PLA products (tumblers and straw) was evaluated. All PLA products could be depolymerized under the same optimization conditions, and the product was calcium lactate (Fig. S16 in ESI). PLA is mixed with common packaging plastics such as poly(ethylene terephthalate) (PET) and polyethylene (PE). PET and PE do not hydrolyze because of their insolubility in dio. PLA can be se-

lectively depolymerized using this method, and these non-recycled plastics are easily recycled *via* simple filtration. PLA can be selectively depolymerized using this method, and these non-recycled plastics are easily recycled *via* simple filtration. Under these hydrolysis conditions, the properties of the other plastics remained essentially unchanged before and after the hydrolysis process (Figs. S17 and S18 in ESI).

Degradable plastic bags are among the most commonly utilized PLA-based products and are typically composed of PBAT, PLA, and  $\text{CaCO}_3$ . In this study, PLA/PBAT/ $\text{CaCO}_3$  plastic bags composed of mass ratios of 0.45/0.50/0.05 were utilized as representative examples for the hydrolytic recycling of PLA plastics in practical applications. The process involves the dissolution of plastic bags using Dio as a solvent, followed by filtration to yield a solution containing dissolved PLA and PBAT alongside undissolved solid calcium carbonate (Figs. 10a and 10b). The solution containing the dissolved PLA and PBAT underwent hydrolysis under typical conditions ( $\text{Dio}/\text{H}_2\text{O}$  mass ratio of 88/6). After a reaction period of 12 h, the resulting mixture was filtered to yield a clear solution and insoluble solid powder. The  $^1\text{H}$ -NMR spectrum of the clarified solution exhibited only the characteristic peaks of PBAT with no resonance corresponding to PLA (Fig. 10c). Furthermore, solid analysis revealed that the  $^1\text{H}$ -NMR spectrum was consistent

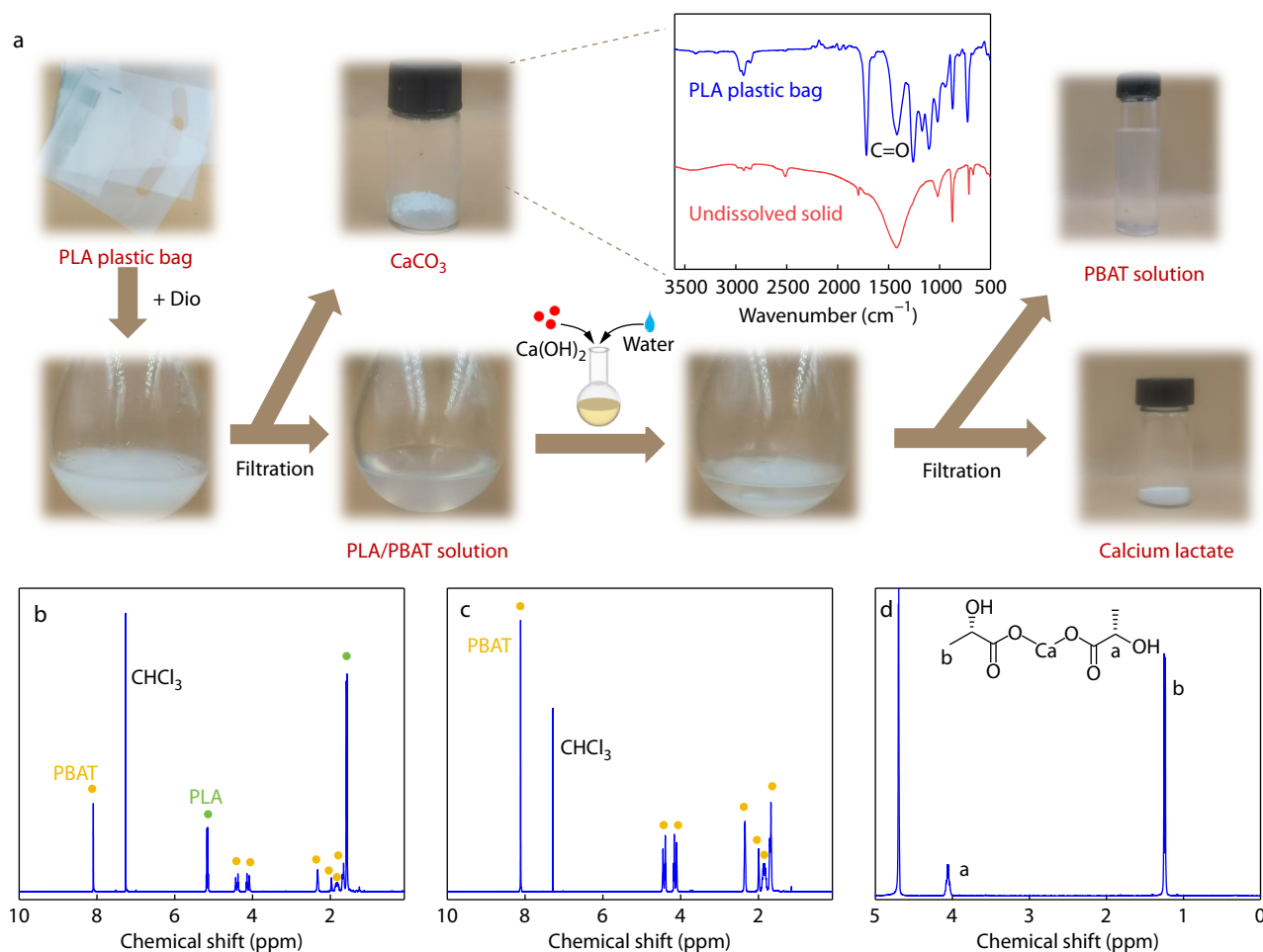


**Fig. 10** (a) Digital photographs of products at different stages of the PLA hydrolysis process and embedded FTIR spectra of  $\text{CaCO}_3$ ;  $^1\text{H}$ -NMR spectroscopy of the (b) solution containing dissolved PLA and PBAT, (c) clarified solution after hydrolysis and (d) hydrolysis products.

with calcium lactate, with no resonance associated with the hydrolyzed products of PBAT (Fig. 10d). These findings suggest that PLA underwent selective hydrolysis, whereas PBAT remained largely intact. The hydrolysis conversion rate of PLA was > 99%, and the yield of calcium lactate was 91% within 12 h. Selective hydrolysis originates from structural divergence between PLA and PBAT. This phenomenon can be attributed to the higher susceptibility of the aliphatic ester groups in PLA to nucleophilic attack by  $\text{OH}^-$  compared to the aromatic ester groups present in PBAT. In the context of the PLA products employed in practical applications, the inorganic filler components present within them are inherently insoluble in conventional solvents. Consequently, these fillers were efficiently removed during the initial filtration step. Furthermore, the process demonstrated the selective hydrolysis of PLA, even in the presence of soluble additives within the system. Consequently, this method has the potential to selectively recycle PLA from various PLA products.

### The Closed Loop Recycling

The PLA hydrolysis recycling system developed in this study facilitates the regeneration of PLA throughout its life cycle *via* a closed-loop process of "Calcium Lactate  $\rightarrow$  Lactic Acid  $\rightarrow$  Lactide  $\rightarrow$  PLA" (Fig. 11a). Calcium lactate is the initial feedstock for the synthesis of PLA and is converted into lactic acid through an

acidification process. Subsequently, lactide is produced through a cyclization process involving a dehydration-condensation reaction. PLA was successfully synthesized *via* ring-opening polymerization. Throughout this process, the chemical structures of the products at each stage were characterized by  $^1\text{H-NMR}$  spectroscopy (Figs. 11b–11d). In this cycle, calcium lactate functions as both the terminal product of the hydrolysis reaction and initiation point for recycling. This method facilitates the chemical recycling of calcium lactate and establishes a closed loop among "calcium lactate  $\rightleftharpoons$  PLA".

### Economic and Environmental Evaluation of Homogeneous Depolymerization

The PLA recycling process is shown in Fig. 12. PLA undergoes hydrolysis in the presence of Dio,  $\text{Ca}(\text{OH})_2$ , and water at ambient temperature. Upon completion of the reaction, crude calcium lactate solid and a co-solvent ( $95.2\% \pm 0.5\%$ ) were obtained through filtration. Subsequent washing and drying of the crude calcium lactate resulted in the production of a small quantity of co-solvent ( $4.2\% \pm 0.3\%$ ) and fine calcium lactate powder. The recycled co-solvents can be reused directly. This process ensures the complete conversion of both  $\text{Ca}(\text{OH})_2$  and PLA into calcium lactate, eliminating the need for additional consumption during production. To mitigate the potential solvent volatility arising from issues related to system tightness, the implementation of a

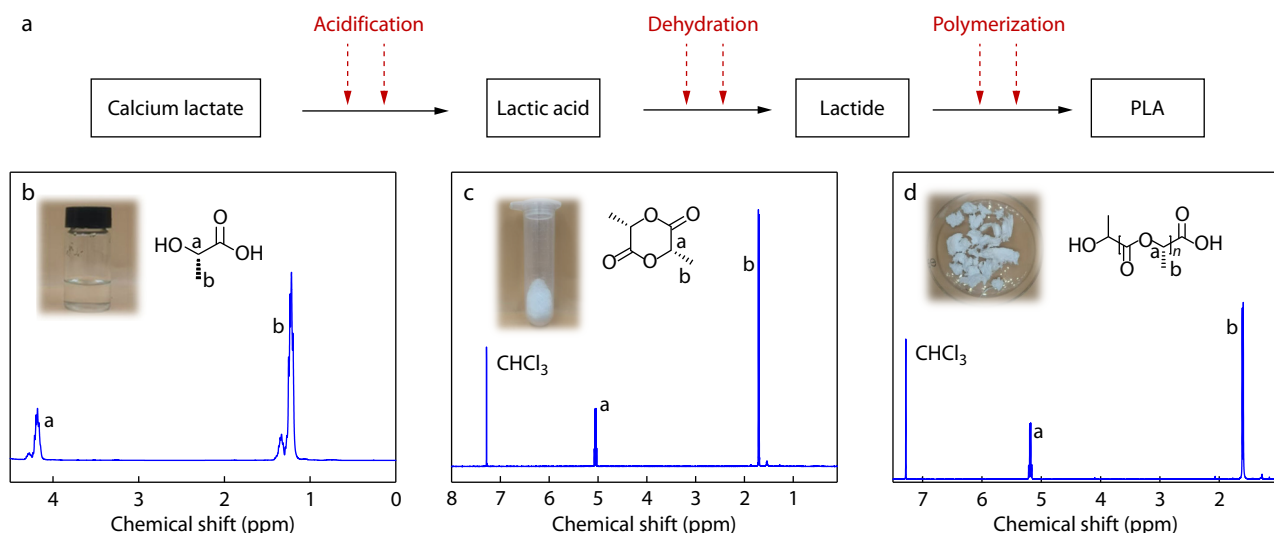


Fig. 11 (a) Routes for synthesizing PLA from calcium lactate, the  $^1\text{H-NMR}$  spectra of (b) the lactic acid (c) lactide, and (d) PLA.

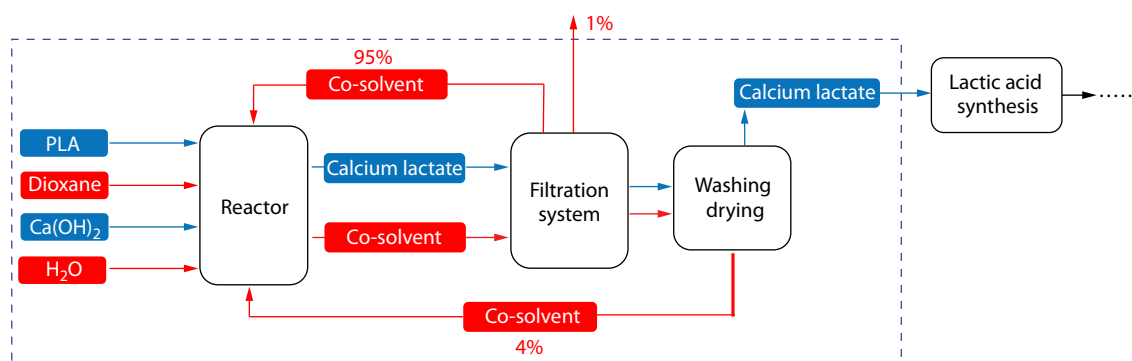


Fig. 12 The process flow chart of PLA hydrolysis.

closed filtration system ensures that the solvent loss per cycle is limited to within 1%. A comprehensive evaluation and analysis of the energy loss throughout the process was conducted. The reaction occurred at room temperature, thus eliminating the need for additional energy input. The separation of calcium lactate and the solvent can be accomplished through a straightforward filtration method, thereby circumventing the necessity for high-energy-consuming steps, such as distillation in the separation process. The primary energy consumption in this procedure is concentrated in stages, such as mechanical transfer and filtration separation, which exhibit relatively low energy requirements.

Solvent recycling of the dioxane-water mixture per cycle maintained the hydrolysis conversion of PLA and calcium lactate yield at 95% over five consecutive cycles, confirming the stability of the recycling protocol (Fig. 13). The three green chemical parameters— $E$ ,  $\epsilon$ , and  $\xi$ —reported in various studies<sup>[31,32,36,42,43,44]</sup> are compared in Table 1. At 70 °C, the  $\epsilon$  factor reported in this study was at least 10 times greater than the best results documented in the literature. The remarkable properties of  $\epsilon$  can be attributed to its extremely high efficiency and selectivity, with the homogeneous hydrolysis reaction typically completed within 5 min at 70 °C. Under these conditions, considering both  $E$  and  $\epsilon$ , this work achieves a satisfactory  $\xi$  value ( $2.2 \times 10^3$  °C·min). At room temperature, the  $E$  fac-

tor presented here approaches solvent-free conditions, as it can be recycled at least 5 times while generating virtually no waste; concurrently, it also maintains a very favorable  $\xi$  value ( $2.8 \times 10^2$  °C·min). After 5 cycles, the recovery rate of the solvent was approximately 92%, and at this time, the  $E$  factor increased to 2.96 and the  $\xi$  value ( $5.7 \times 10^4$  °C·min) is also satisfactory.

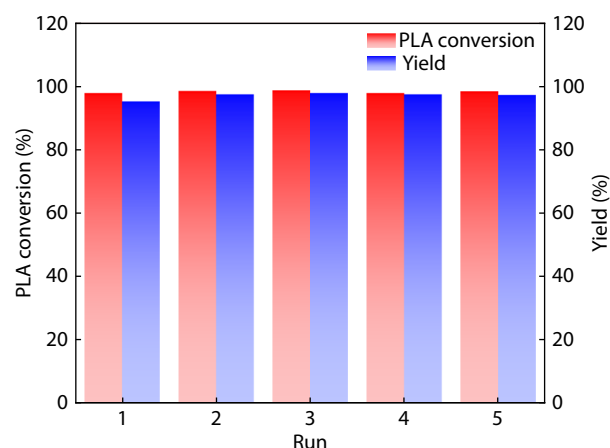


Fig. 13 Reusability of the co-solvent for PLA hydrolysis.

Table 1 Summary of the PLA hydrolysis conditions and green chemical factors in this work and literatures<sup>a</sup>.

| Ref.      | Catalyst            | Temp. (°C)       | $P$ (MPa) | Time (h) | $E$ factor (a.u.) | $\epsilon$ (°C <sup>-1</sup> ·min <sup>-1</sup> ) | $\xi$ (°C·min)    |
|-----------|---------------------|------------------|-----------|----------|-------------------|---------------------------------------------------|-------------------|
| [32]      | NaOH                | 180              | 1.8       | 0.33     | 5.95 <sup>b</sup> | $2.7 \times 10^{-4}$                              | $4.5 \times 10^3$ |
| [32]      | None                | 180              | 1.8       | 3        | 5.95              | $3.0 \times 10^{-5}$                              | $5.0 \times 10^4$ |
| [31]      | DPP                 | 160              | 0.1       | 3.5      | 0.21              | $2.5 \times 10^{-5}$                              | $8.7 \times 10^3$ |
| [44]      | ZnO                 | 130              | 0.1       | 24       | 400               | $5.3 \times 10^{-6}$                              | $7.5 \times 10^7$ |
| [36]      | IL                  | 130              | 0.1       | 2        | 1.15              | $4.8 \times 10^{-5}$                              | $2.3 \times 10^4$ |
| [42]      | None                | 250              | 0.1       | 0.33     | 1.77              | $1.8 \times 10^{-4}$                              | $9.8 \times 10^3$ |
| [43]      | None                | 170 <sup>b</sup> | 0.1       | 13.3     | 0.058             | $3.3 \times 10^{-6}$                              | $1.7 \times 10^4$ |
| This work | Ca(OH) <sub>2</sub> | 70               | 0.1       | 0.083    | 5.72              | $2.6 \times 10^{-3}$                              | $2.2 \times 10^3$ |
|           | Ca(OH) <sub>2</sub> | 25               | 0.1       | 12       | 0.0147            | $5.2 \times 10^{-5}$                              | $2.8 \times 10^2$ |

<sup>a</sup> In the calculation, all the water, organic solvents, and ionic liquid are designated as the reaction solvent; <sup>b</sup> Microwave heating.

## CONCLUSIONS

In an alkaline environment at ambient temperature and pressure, a homogeneous hydrolysis system with excellent compatibility with both PLA and water can markedly enhance the hydrolysis efficiency of PLA. For instance, the Dio solvent system can achieve 93% hydrolysis conversion within 2 h, whereas the POPCE system can attain a 90% conversion rate. Compared with conventional hydrolysis methods, this approach significantly enhances the hydrolysis efficiency. Moreover, when commercial PLA products (*e.g.*, plastic bags) containing PLA, PBAT, and CaCO<sub>3</sub> were hydrolyzed using this method, PLA was selectively hydrolyzed, whereas calcium carbonate and PBAT remained largely unaffected. In addition, the calcium lactate recovered via this method enabled the closed-loop cycle of the PLA. Through kinetic studies and systematic investigations of the solvent type, acid-base ratio, alkali concentration, and water content, it was demonstrated that the high hydrolysis efficiency observed in this study is attributed to the gradual dissolution of PLA and calcium hydroxide in the co-solvent system, thereby maintaining a homogeneous reaction phase throughout the process. We pro-

pose a novel and efficient chemical recycling strategy for treating mixed waste plastics, which offers advantages such as minimal waste generation, simple equipment requirements, and low energy consumption, thereby contributing to the sustainable waste management.

## Conflict of Interests

The authors declare no interest conflict.

## Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3378-7>.

## Data Availability Statement

The data that support the findings of this study are available

from the corresponding authors upon reasonable request.

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