

CHEMISTRY

Lactate anion catalyzes aminolysis of polyesters with anilines

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Chemical transformation of spent polyesters into value-added chemicals is substantial for sustainable development but still challenging. Here, we report a simple, metal-free, and efficient aminolysis strategy to upcycle polylactic acid by anilines over lactate-based ionic liquids (e.g., tetrabutylammonium lactate), accessing a series of *N*-aryl lactamides under mild conditions. This strategy is also effective for degradation of poly(bisphenol A carbonate), affording bisphenol A and corresponding diphenylurea derivatives. It is found that, with the assistance of water, lactate anion as hydrogen-bond donor can efficiently activate carbonyl C atom of polyesters via hydrogen bonding with carbonyl O atom; meanwhile, as hydrogen-bond acceptor, it can enhance nucleophilicity of the N atom of anilines via hydrogen bonding with amino H atom. The nucleophilic attack of N atom of anilines on carbonyl C atom of polyesters results in cleavage of C–O bond of polymers and formation of the target products.

INTRODUCTION

Chemical recycling of plastics into monomers or value-added chemicals is one of pivotal accesses to achieve a circular economy in the plastic life cycle and also an important way to achieve carbon neutrality (1–5). Polyesters are a kind of major plastics widely applied in our life, among which polylactic acid (PLA), as an environmentally friendly, bio-based, and biodegradable polymer, has become one of the best succedaneum for traditional petroleum-based plastics with production occupying around 32% of global biodegradable plastics (1.23 million tons per year) (6–8). The accumulation of spent PLA is harmful to the environment because its biodegradation in the real environment requires a long time with release of CO₂ (9–10). Therefore, the chemical degradation and transformation of PLA to value-added chemicals have attracted much attention in recent years. To date, PLA has been reported to be decomposed into lactic acid (LA), lactates, or other chemicals (e.g., alanine) via hydrolysis (11, 12), alcoholysis (13–14), and ammonolysis (15) (Fig. 1). In these research studies, acids or bases or metal catalysts and harsh conditions are generally required, and the chemicals produced from spent PLA are still limited.

N-substituted lactamides are a kind of valuable chemicals widely applied in chemical industries, which are generally produced via dehydrative coupling reactions of LA with amines (16–19), suffering from inherent disadvantages such as low efficiency due to the equilibrium reaction and waste production caused by removal of acid or base catalysts. From the viewpoint of sustainable development, green and efficient approach is highly required. Considering its unique chemical structure, spent PLA may act as a feedstock for synthesis of lactamides, which has not been found in a literature survey.

Ionic liquids (ILs), consisted of organic cations and inorganic/organic anions, can be designed with unique properties and thus have been widely used in many areas (20–22). In particular, in chemical reactions, ILs can be used as solvents or catalysts and have shown promising application potentials (23–26). For example, acidic ILs, e.g., *N*-methylimidazolium hydrogen sulfate, efficiently catalyzed esterification reactions of acetic acid with alcohols (24). 1-Butylsulfonic-3-methylimidazolium chloride realized hydrolysis and decomposition of cellulose under mild conditions (26). CO₂-reactive ILs achieved the transformation of CO₂ under metal-free and mild conditions (27, 28). Lactate-based ILs catalyzed reductive amination/cyclization of keto acids under mild conditions (29). Recently, ILs have been reported to be capable of catalyzing the decomposition of polyethylene terephthalate (30–32). Because of their unique structures and properties, task-specific ILs provide opportunity to develop green strategies for degradation of spent polymers.

In our continuous efforts dedicated to the IL-catalyzed chemical reactions (29, 33, 34), here, we report an aminolysis strategy for PLA with anilines over lactate-based ILs (Fig. 1D). With the assistance of water, tetrabutylammonium lactate ([N₄₄₄₄][Lac]) shows the best performance for PLA decomposition with anilines, affording *N*-aryl lactamides in high yields and 100% selectivity. It is found that water can inhibit the formation of hydrogen bonds between two lactate anions, thus strengthening the ability of lactate anion to form hydrogen bonds with other hydrogen bond donor and acceptor. With the assistance of water, the lactate anion as hydrogen-bond donor could activate carbonyl C atom of PLA via hydrogen bonding with carbonyl O atom; meanwhile, as hydrogen-bond acceptor, it could enhance the nucleophilicity of the N atom of anilines via hydrogen bonding with amino H of amines. The nucleophilic attack of the N atom of aniline on the carbonyl C atom of PLA leads to cleavage of the C–O bonds of PLA and formation of *N*-aryllactamides. Combined with water, the lactate ILs could also efficiently upcycle poly(bisphenol A carbonate) (PC) with anilines, producing bisphenol A and corresponding diphenylurea derivatives. In particular, some ureas that are difficult to

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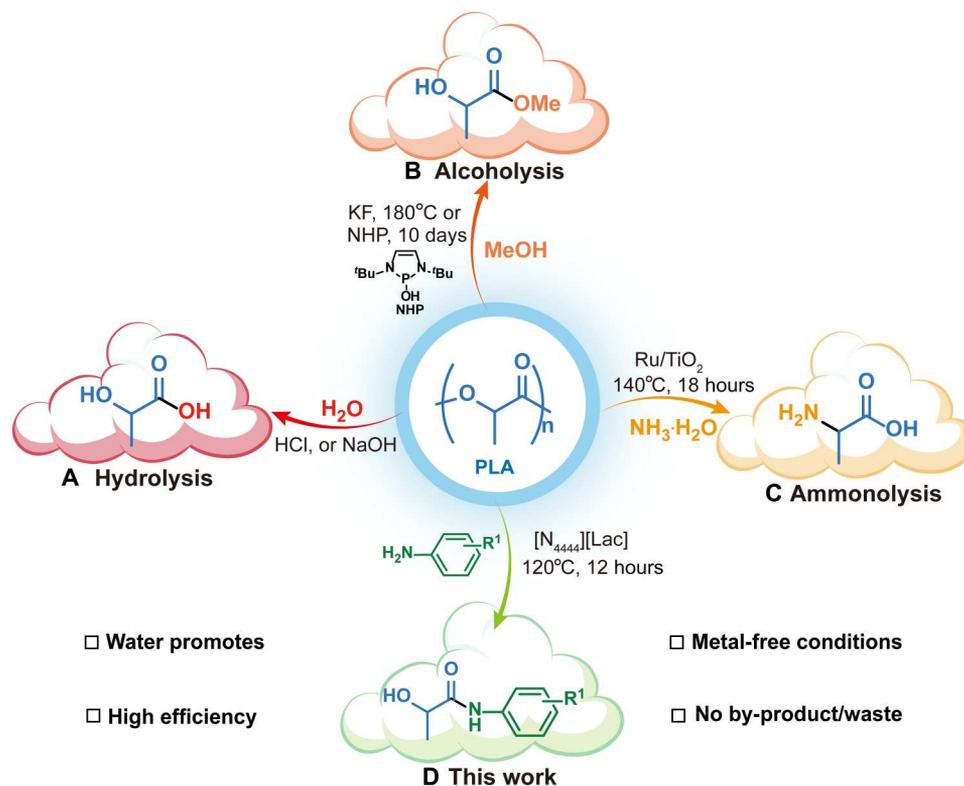


Fig. 1. Transformation of PLA to chemicals via different approaches. (A) PLA hydrolysis. (B) PLA alcoholysis. KF, potassium fluoride; NHP, 1,3-di-*tert*-butyl-1,3-dihydro-2*H*-1,3,2-diazaphosphol-2-ol. (C) PLA ammonolysis. (D) Present work for PLA aminolysis.

synthesize via conventional routes can be produced. This lactate anion catalysis strategy is simple and highly efficient to depolymerize PLA and PC and also provides green and metal-free routes to produce *N*-aryl lactamides and diphenylurea derivatives, respectively.

RESULTS

Our exploration was begun with the decomposition of PLA by aniline (**2a**), and various ILs were examined. As shown in Fig. 2A, PLA could not be depolymerized by **2a** in the absence of any catalyst. Brønsted acidic ILs [SO₃H-PMIm][OTf] and [SO₃H-PMIm][HSO₄] ([SO₃H-PMIm] = 1-propylsulfonate-3-methylimidazolium, [OTf] = trifluoromethanesulfonate; fig. S1) were ineffective. The halogen anion-based ILs, e.g., [EtMIm][Cl] and [EtMIm][Br] ([EtMIm] = 1-ethyl-3-methylimidazolium; fig. S1) displayed activity for the reaction, but affording product **3a** in low yields. The ILs with acetate or lactate anions such as [EtMIm][OAc], [EtMIm][Lac], [N₁₁₁₁][Lac], [N₂₂₂₂][Lac], and [N₄₄₄₄][Lac] ([Lac] = lactate, [N₁₁₁₁] = tetramethylammonium, [N₂₂₂₂] = tetraethylammonium, [N₄₄₄₄] = tetrabutylammonium; fig. S1) were very effective for the reaction, producing **3a** in 100% selectivity and high yields. In particular, [N₄₄₄₄][Lac] showed the best performance without any by-product, probably ascribing to its strongest ability to form a hydrogen bond with the carbonyl O atom of PLA reflected by the Kamlet-Taft parameters of the ILs (table S1). Different from the lactate ILs, ammonium lactate was found to be ineffective for the reaction. The above findings indicate that the acetate or lactate anions play crucial role in decomposition of

PLA by **2a**, and the cations of the ILs influence the activities of the anions. In contrast, in the case using [EtMIm][OAc] as the catalyst, *N*-phenyl acetamide was detected as a by-product (fig. S2), which implies that acetic acid may be generated from the reaction that the [OAc][−] anion abstracts one proton from −NH₂ of **2a** (35), and the resultant acetic acid further reacts with **2a** to form *N*-phenylacetamide (fig. S3).

After extensive experimentation (fig. S4), it was found that [N₄₄₄₄][Lac] in combination with suitable amount of water showed good performance for decomposition of PLA with **2a** under the optimized conditions: PLA (50.0 mg), **2a** (2.0 mmol), H₂O (1.0 mmol), and [N₄₄₄₄][Lac] [20 mole percent (mol %)], at 120°C for 12 hours. Notably, water played an important role in mediating the catalytic activity of [N₄₄₄₄][Lac] (Fig. 2B). In the absence of water, a low **3a** yield of 45% was achieved, while the addition of small amount of water into the reaction system apparently increased **3a** yields, reaching a high value of 88% at the water amount of 1.0 mmol. However, further increasing the water amounts resulted in a gradual decrease in the **3a** yields. In particular, at the water amount of 16.0 mmol, the **3a** yield declined to 45%. As known, water has a strong ability to form hydrogen bonds with various hydrogen-bond donors and acceptors, which has widely been applied in chemical reactions as solvent, cosolvent, or cocatalyst (36–37). In this work, a small amount of water markedly improves the catalytic activity of [N₄₄₄₄][Lac], which may result from the hydrogen bonding interaction between water and the lactate anion. From the chemical structure of lactate anion, it is obvious that one lactate anion as hydrogen-bond donor and acceptor tends to form hydrogen bonds with another lactate anion, which could be destroyed by

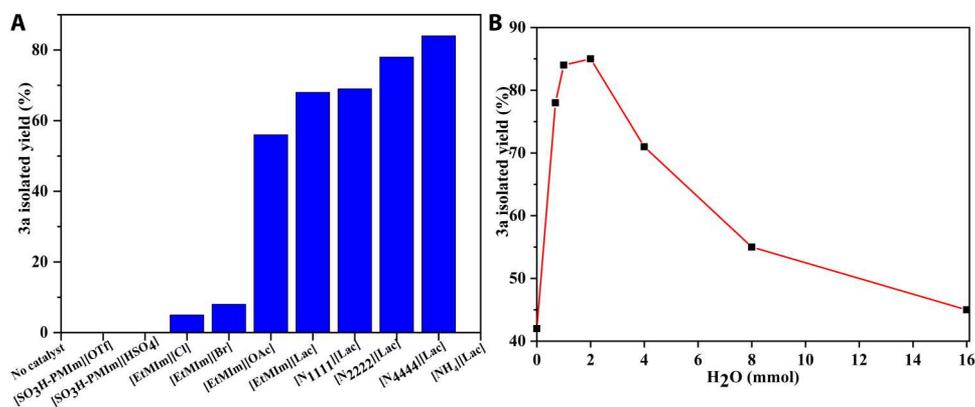


Fig. 2. Screening conditions for decomposition of PLA with aniline. (A) IL-catalyzed aminolysis of PLA with aniline. Reaction conditions: PLA (50.0 mg, 0.694 mmol structural unit), **2a** (2.0 mmol), H₂O (1.0 mmol), and IL [20 mole percent (mol %) based on PLA], at 140°C for 6 hours. (B) Effect of H₂O amounts on aminolysis of PLA with aniline. Reaction conditions: PLA (50.0 mg, 0.694 mmol structural unit), **2a** (2.0 mmol), and [N₄₄₄₄][Lac] (20 mol % based on PLA), at 140°C for 6 hours. Note that the obtained product yields were average of three replicates with a reproducibility of $\pm 3\%$.

water because water can form strong hydrogen bonds with lactate anion, thus tuning its activity to form hydrogen bonds.

To explore the reaction pathway, in situ nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) analysis (fig. S5) and control experiments (Fig. 3) were performed. From the in situ ¹³C NMR spectra of the reaction solutions of PLA with **2a** over H₂O/[N₄₄₄₄][Lac] performed at 120°C (fig. S5A), it is obvious that the altitude of ¹³C NMR resonances assigning to the carbonyl C [$\delta = 173.8$ parts per million (ppm)] and phenyl C ($\delta = 138.0$ ppm) linking to N atom of **3a** gradually increased with reaction time, indicating the formation of the target product (fig. S5A). However, there was no signal ascribing to LA intermediate that may be generated from hydrolysis of PLA. The in situ FTIR spectra provided similar information (fig. S5B), in which the IR stretching vibration absorbance of the carbonyl C at $\delta = 1754$ cm⁻¹ in PLA (38) gradually decreased and the stretching vibration absorbance of the carbonyl C at $\delta = 1683$ cm⁻¹ (39) in **3a** gradually increased with reaction time, while no signal assigning to LA was observed. It seems that, from the above results, PLA was directly aminolyzed by **2a** over [N₄₄₄₄][Lac]. Considering that PLA can be hydrolyzed to LA (11) and LA can react with **2a** to form **3a** (16) under the catalysis of suitable catalysts, [N₄₄₄₄][Lac] was examined for catalyzing hydrolysis of PLA and reaction of LA with **2a**, respectively. It was indicated that [N₄₄₄₄][Lac] was effective for both

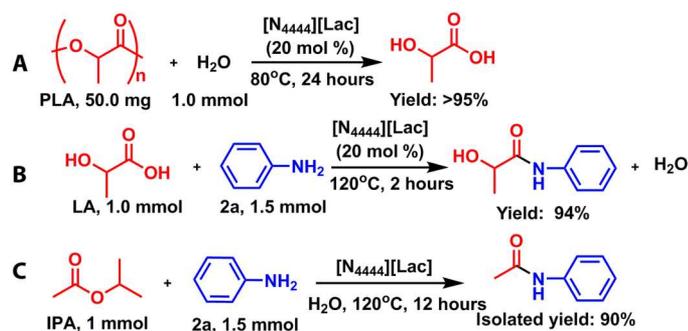


Fig. 3. Control experiments. (A) Reaction between PLA and H₂O. (B) Reaction of LA and PhNH₂. (C) Reaction of IPA and PhNH₂.

reactions, producing corresponding LA and **3a** in high yields (Fig. 3, A and B). From these two control experiments, it can be deduced that even LA could be produced from PLA hydrolysis in the decomposition of PLA with **2a**, it could further react with **2a** to form **3a**, which also could explain why no LA was detected by in situ NMR and FTIR analysis.

To further explore the reaction mechanism of PLA decomposition over H₂O/[N₄₄₄₄][Lac], isopropyl acetate (IPA) that could be decomposed with **2a** catalyzed by [N₄₄₄₄][Lac] to form *N*-phenylacetamide **3sb** (Fig. 3C) was selected as a model compound for structural unit of PLA to investigate interaction among IPA, **2a**, IL, and water via NMR spectroscopy and density functional theory (DFT) calculations. From the ¹⁷O NMR spectra of IPA, IPA-[N₄₄₄₄][Lac], and IPA-[N₄₄₄₄][Lac]-H₂O mixtures, it is clear that the chemical shifts assigning to the carbonyl O atom of IPA in the mixtures shifted from 366.74 ppm for pure IPA to 363.87 ppm for the IL-IPA mixture and further shifted upfield to 351.49 ppm for the IL-H₂O-IPA mixture (Fig. 4A). These findings indicate that the electron cloud density of the carbonyl O atom of IPA was enhanced in the IPA-IL mixture, ascribing to the strong hydrogen bonding with the lactate anion, and it was further improved in the presence of water, which suggests that water also involved in the formation of hydrogen bond between IPA and the lactate anion.

The ¹³C NMR analysis provides more information on the interactions among IPA, IL, and water (Fig. 4B). The ¹³C NMR spectra show that the chemical shifts assigning to the carbonyl C atom of IPA in the mixtures shifted from 168.25 ppm for pure IPA to 168.65 ppm for the IPA-IL mixture and further to 170.66 ppm for the IPA-IL-H₂O mixture (Fig. 4B), which should be ascribed to the hydrogen bonding interactions of the carbonyl O of IPA with the lactate anion or with the lactate complexing with water. The ¹³C NMR results indicate that the electron cloud density of the carbonyl C atom of IPA decreases and its electrophilicity enhances due to the interactions with the IL or to the cooperative effect of the IL and water. As a result, it can be deduced that the electrophilicity of the carbonyl C atom of IPA can be enhanced by the IL and be further improved by the cooperative interaction of the IL and water. That is, IPA can be activated by the IL, especially, with the assistance of water, which makes the carbonyl C atom of IPA be easily attacked by

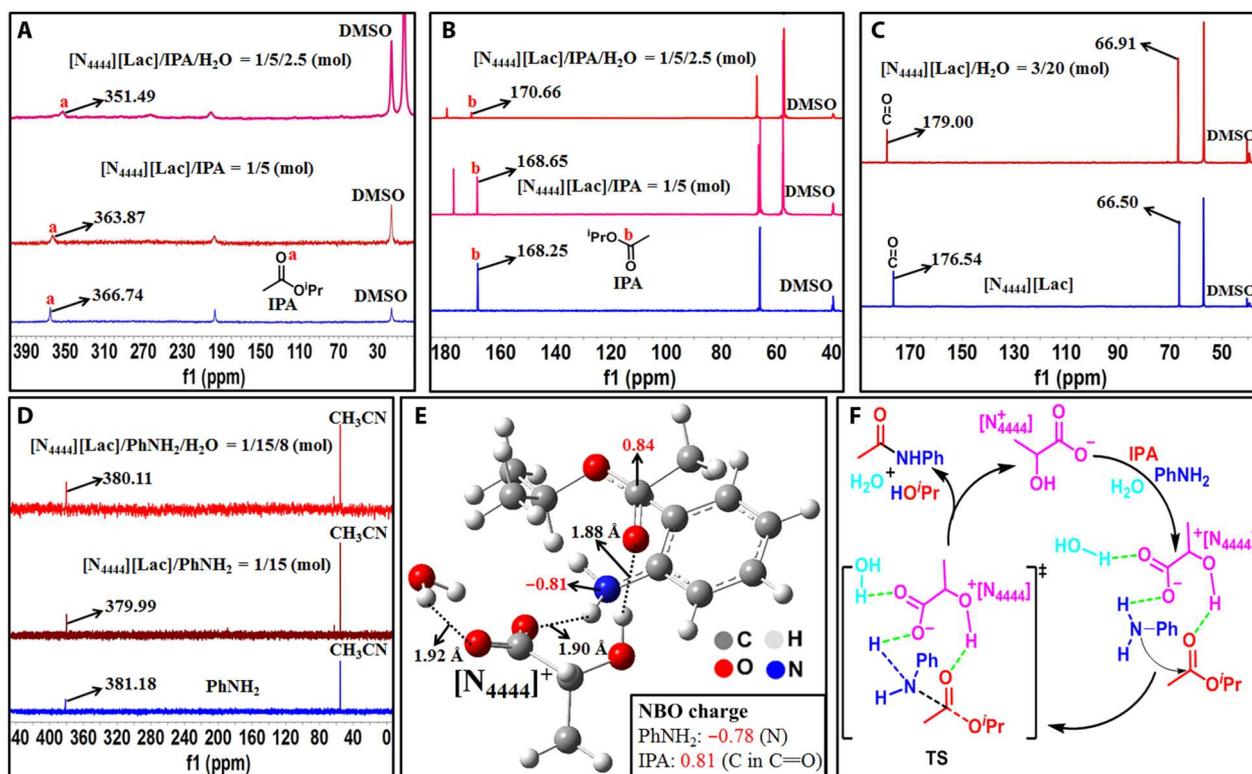


Fig. 4. Mechanism investigation. (A) ^{17}O NMR spectra of IPA, IL-IPA and H_2O -IPA-IL recorded at 60°C (16.0 ppm of O in DMSO as the internal standard). (B and C) ^{13}C NMR spectra recorded at 60°C (39.5 ppm for C in DMSO as the internal standard). (D) ^{15}N NMR spectra recorded at 60°C (55.3 ppm for N in CH_3CN as the internal standard). (E) Optimized geometries of $[\text{N}_{4444}][\text{Lac}]$ interacting with PhNH_2 , H_2O , and IPA (black font: atom distance; red font: NBO charges). (F) Proposed reaction mechanism for the transformation between IPA and PhNH_2 .

nucleophiles. The above results and discussion may explain why the presence of a suitable amount of water in the reaction system could improve the activity of the IL to catalyze PLA decomposition with **2a**.

The chemical shifts assigning to the carbonyl C atom of lactate anion in the H_2O -IL mixture shifted from 176.54 ppm for pure $[\text{N}_{4444}][\text{Lac}]$ to 179.00 ppm and the chemical shifts assigning to the C atom linking with OH group in lactate anion in the mixture shifted from 66.50 ppm for pure $[\text{N}_{4444}][\text{Lac}]$ to 66.91 ppm (Fig. 4C). This indicates that water can form a strong hydrogen bond with the lactate anion, which could influence ability of the lactate anion to interact with IPA.

The ^{15}N NMR spectra indicate that the chemical shift assigning to the N atom of **2a** in the **2a**-IL mixture shifted from 381.18 ppm for pure **2a** to 379.99 ppm (Fig. 4D), indicating that **2a** can be activated by IL via forming hydrogen bond; whereas, for the IL-water-**2a** mixture, it hardly changed compared to that for the IL-**2a** system (Fig. 4D), suggesting that water played a little role in activating **2a**. The strong hydrogen bonding interaction between the IL and **2a** strengthens the nucleophilicity of the N atom in amine, which is favorable for it to attack electrophilic carbonyl C atom of IPA, thus catalyzing the cleavage of C—O bond in IPA to form *N*-phenylacetamide and isopropyl alcohol.

On the basis of the NMR analysis results, DFT calculations were performed to explore the interaction among $[\text{N}_{4444}][\text{Lac}]$, H_2O , IPA, and **2a** using a simple system that contains one molecule of each component. The calculated Gibbs free energy changes ΔG

for forming hydrogen bonds demonstrate that lactate anion is preferable to form hydrogen bond with H_2O than with another lactate anion, and the hydrogen bond network among lactate anion, H_2O , IPA, and **2a** shows the lowest ΔG (table S2). From the optimized geometries of the IL interacting with H_2O , IPA, and **2a** (Fig. 4E), it is clear that the lactate anion can simultaneously form hydrogen bonds with **2a** and IPA. The length of hydrogen bond formed between the carbonyl O atom of IPA and hydroxyl H atom of lactate was calculated to be 1.88 Å, and the calculated natural bond orbital (NBO) charges of carbonyl C atom of IPA changed from 0.81 for pure IPA to 0.84 in the mixture (Fig. 4E), demonstrating the increased electrophilicity of this carbonyl C atom. The length of hydrogen bond formed between the negative O atom of lactate and one H atom in NH_2 of **2a** was 1.90 Å, and the NBO charges of N atom of **2a** changed from -0.78 for pure **2a** to -0.81 in the **2a**-IL-IPA- H_2O mixture (Fig. 4E), indicating the enhanced nucleophilicity of the N atom in **2a**.

The above NMR analysis and DFT calculation results demonstrated that water can strengthen the ability of the lactate anion to activate the carbonyl C atom in PLA via weakening the hydrogen bonding between two lactate anions. The lactate anion can simultaneously activate carbonyl C atoms of PLA and the N atom of PhNH_2 via strong hydrogen bonding interaction, which is thus capable of catalyzing the aminolysis of PLA.

On the basis of the above results and discussion, a possible reaction pathway is proposed (Fig. 4F). Initially, the lactate anion interacted with H_2O forms two strong hydrogen bonds with the carbonyl

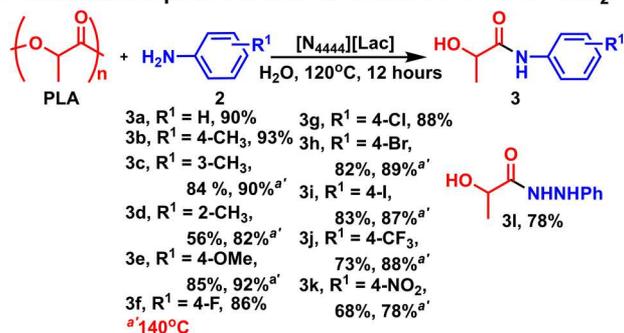
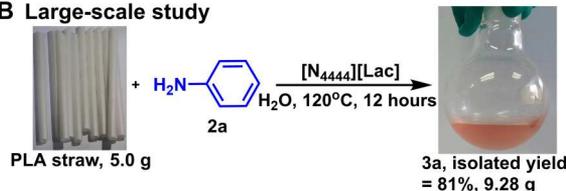
A The substrate scope of the reaction between PLA and PhNH₂**B Large-scale study**

Fig. 5. [N₄₄₄₄][Lac]/H₂O-catalyzed aminolysis of PLA with various anilines and scale-up study. (A) Substrate scope of the reaction between PLA and PhNH₂. (B) Large-scale study.

O atom in IPA and one H atom of -NH₂ in 2a, respectively. Subsequently, the activated N atom of 2a attacks the activated carbonyl C in IPA, resulting in breakage of the C—O bond of IPA and formation of transition state TS. Last, *N*-phenyl acetamide is formed, and the IL is regenerated.

Inspired by the above results, we tried to use various anilines to degrade PLA, and the results are shown in Fig. 5A. As indicated, all the tested anilines could efficiently react with PLA under catalysis of [N₄₄₄₄][Lac]/H₂O, generating *N*-aryl lactamides in good to excellent yields. Notably, the anilines with electron-rich groups exhibited higher reactivity than those with electron-poor groups (3b and 3e versus 3j and 3k). The methyl-substituted aniline derivatives showed the reactivity following the order: aniline ≈ *p*-methyl aniline > *m*-methyl aniline > *o*-methyl aniline, probably due to the steric effects (3a–3d). The halogen-substituted anilines are also tolerant to the catalytic system, which can deconstruct PLA into corresponding lactamides in high yields (3f–3i). In particular, phenylhydrazine could decompose PLA over [N₄₄₄₄][Lac]/H₂O, affording the desired product 3l in high yield. These results indicate that [N₄₄₄₄][Lac]/H₂O can efficiently catalyze the reactions of PLA with anilines in the presence of water, which provides a simple route for the synthesis of *N*-aryl lactamides. Alkyl amines were also examined; however, they showed no reactivity under the similar conditions.

In addition, large-scale decomposition of PLA straw with 2a was performed using 5.0 g of PLA as feedstock, and 9.28 g of 3a was obtained under the optimized conditions (Fig. 5B). This indicates that [N₄₄₄₄][Lac]-catalyzed aminolysis of PLA can be scaled up, which presents application potential.

Encouraged by the above results, we extended the [N₄₄₄₄][Lac]-catalyzed aminolysis strategy of PLA with anilines to degradation of PC that is an important plastic widely applied in our life. Its upcycling is also substantial, especially for the synthesis of value-added chemicals. It was found that [N₄₄₄₄][Lac] in combination with water could also efficiently catalyze the PC degradation by anilines,

affording the monomer bisphenol A (40) and various diphenylurea derivatives in 100% selectivity. In particular, some diphenylurea derivatives that are difficult to produce by conventional routes could be obtained via this strategy. As shown in Fig. 6A, most of the tested anilines reacted well with PC to produce bisphenol A and corresponding diphenylurea derivatives in good to excellent yields (4a–4i). Notably, the anilines with electron-rich groups gave the corresponding ureas in better yields than those with electron-poor groups (4b and 4e versus 4f and 4j), which may be ascribed to the steric hindrance effects. Similar to degrading PLA, the methyl-substituted anilines presented the similar reactivity to

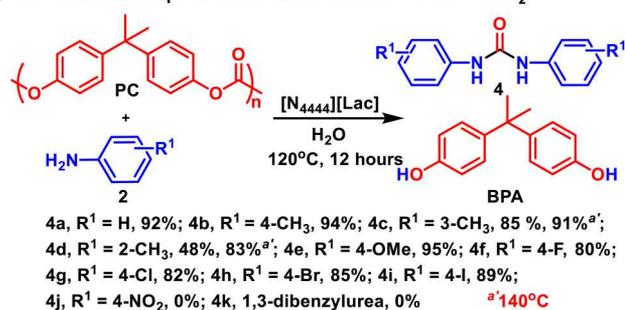
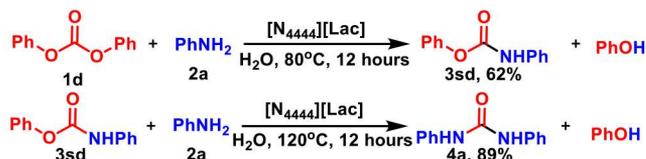
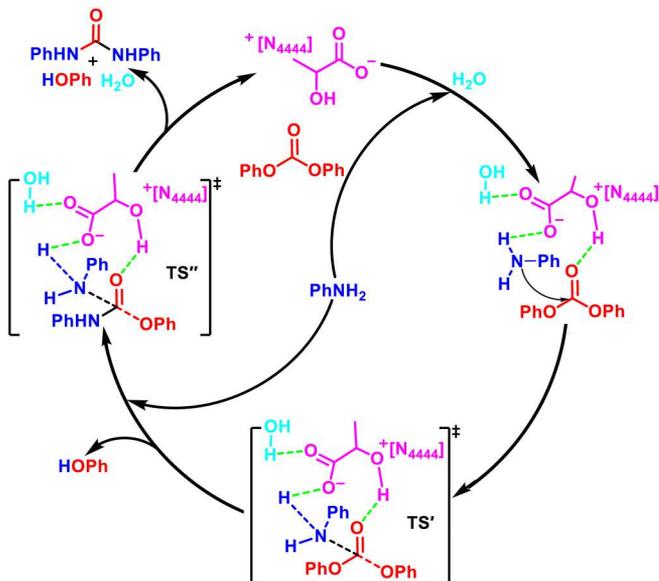
A The substrate scope of the reaction between PC and PhNH₂**B The control reactions for exploring the reaction mechanism of PC and 2a****C The proposed reaction mechanism for the conversion of DPC and PhNH₂**

Fig. 6. [N₄₄₄₄][Lac]/H₂O-catalyzed aminolysis of PC with various anilines and study on reaction mechanism. (A) Substrate scope of the reaction between PC and PhNH₂. (B) Control reactions for exploring the reaction of PC and 2a. (C) Proposed reaction mechanism for the conversion of DPC and PhNH₂. Note that the obtained product yields were average of three replicates with a reproducibility of ±3%.

decompose PC, following the order: aniline \approx *p*-methyl aniline > *m*-methyl aniline > *o*-methyl aniline (**4a–4d**). The halogen-substituted anilines also could decompose PC well, producing bisphenol A and the desired ureas in high yields (**4f–4i**). However, benzylamine and 4-nitroaniline (NA) were examined to show no reactivity for PC degradation under the catalysis of [N₄₄₄₄][Lac] (**4j**, **4k**).

Using diphenyl carbonate (DPC) as the structural unit of PC to explore the possible reaction pathway of PC decomposition by aniline, it was found that DPC could react with aniline to form phenyl phenylcarbamate **3sd** (**4l**) accompanied with phenol under the catalysis of [N₄₄₄₄][Lac]/H₂O and **3sd** could further react with another aniline molecule to form diphenyl urea and phenol (Fig. 6B). These findings suggest that [N₄₄₄₄][Lac] could efficiently activate the carbonyl C atoms in DPC and in **3sd** via hydrogen bonding interactions, thus making them be easily attacked by aniline to form C–N bond. The decomposition of PC by **2a** may follow the possible reaction pathway as illustrated in Fig. 6C. With the aid of water, the lactate anion activates the carbonyl O atom of DPC and the N atom of **2a** via hydrogen bonding interaction, and the N atom of **2a** attacks the carbonyl C in DPC to form intermediate **3sd** via transition state **TS'** with release of one phenol molecule. Then, another activated **2a** attacks intermediate **3sd** to form the desired product **4a** via transition state **TS''**, with release of another phenol molecule and regeneration of the IL.

Diphenylurea derivatives are a kind of important subunits prevalent in organic synthesis, bioscience, transmembrane, agrochemicals, and pharmaceuticals (**42–47**), which could be produced via the reactions of anilines with CO₂ (**48**), urea (**49**), or isocyanate (**50**), suffering from their inherent drawbacks. Aminolysis of PC with anilines provides unique strategy to produce symmetrically aryl ureas (**51**), which not only achieves decomposition of PC (**52–54**) but also produces valuable ureas. The lactate-based IL catalytic systems developed in this work is green, low-cost, and highly efficient for degradation of PC to monomer bisphenol A and for synthesis of diphenyl ureas, which has promising application potentials.

DISCUSSION

In summary, we present a strategy to decompose spent PLA and PC with anilines over lactate-based ILs in the presence of H₂O. It is found that water can inhibit lactate anions to form strong hydrogen bonds between themselves, thus strengthening its ability to form hydrogen bonds with other hydrogen bond donor and/or acceptor. In combination with water, the lactate anion as hydrogen-bond donor can efficiently activate the carbonyl C atoms in the polyesters via hydrogen bonding interaction with carbonyl O atoms; meanwhile, as hydrogen-bond acceptor, it can enhance nucleophilicity of the N atom in anilines via hydrogen bonding with the N atom of amines. The nucleophilic attack of the N atom of anilines on the carbonyl C atom of polymers achieves the cleavage of C–O bond in the polymers and the formation of C–N bond in the target products. The [N₄₄₄₄][Lac]-catalyzed aminolysis of PLA and PC also provides green and metal-free routes to produce N-substituted lactamides and diphenylurea derivatives under mild conditions, which shows high performance and can produce some lactamides and ureas that are difficult to synthesize by conventional approaches. This work provides a simple and green strategy for degradation of PLA and PC and also provides green routes to produce N-substituted

lactamides and diphenylurea derivatives, which may have promising applications.

MATERIALS AND METHODS

Materials

Anilines including aniline (99%), *p*-toluidine (99%), *m*-toluidine (99%), *o*-toluidine (99%), *m*-anisidine (99%), *p*-anisidine (99%), 4-fluoroaniline (99%), 4-chloroaniline (99%), 4-bromoaniline (99%), and 4-iodoaniline (99%) were purchased from J&K Scientific Co. Ltd. 4-Aminobenzotrifluoride (99%), NA (99%), phenylhydrazine (98%), LA (> 85%), tetrabutylammonium hydroxide [>40 weight % (wt %) in water], tetramethylammonium hydroxide pentahydrate (97%), and tetraethylammonium hydroxide (>40% in water) were purchased from Beijing Innochem Science & Technology Co. Ltd. PLA (power, *M_w*: 60,000) and PC (power, *M_w*: 26,000) were purchased from Shanghai Macklin Biochemical Co. Ltd. Sodium hydroxide (97%) and silver nitrate (99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Silica gel (200 to 300 mesh) was purchased from Qingdao Haiyang Chemical Co. Ltd.

The ILs including [SO₃H-PMIm][OTf] (99%), [SO₃H-PMIm][HSO₄] (99%), [EtMIm][Cl] (99%), [EtMIm][Br] (99%), and [EtMIm][OAc] (99%) were provided by Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. [EtMIm][Lac] was synthesized according to the procedures reported in literature (**55**, **56**), and other lactate-based ILs including [N₁₁₁₁][Lac], [N₂₂₂₂][Lac], and [N₄₄₄₄][Lac] were synthesized via the neutralization of corresponding bases with LA (**29**). The chemical structures of the as-synthesized lactate ILs are shown in fig. S1.

Procedures for synthesis of tetraalkylammonium lactate ILs ([N₁₁₁₁][Lac], [N₂₂₂₂][Lac]), and [N₄₄₄₄][Lac])

In a typical experiment to synthesize [N₄₄₄₄][Lac], tetrabutylammonium hydroxide (10.0 mmol, 6.48 g), H₂O (5 ml), and LA (10.0 mmol, 10.6 g) were mixed in a 50-ml glass tube reactor, equipped with a magnetic stirring bar and sealed with a cap. Then, the mixture was stirred at room temperature for 24 hours. After the reaction, the mixture was dried for removing most water in vacuo. Then, the residue was put in a vacuum drying oven for 48 hours at 60°C, and [N₄₄₄₄][Lac] was obtained. [N₁₁₁₁][Lac] (**57**) and [N₂₂₂₂][Lac] (**58**) were synthesized following the analogous procedures. Their physicochemical properties are shown in the Supplementary Materials.

Procedures for synthesis of [EtMIm][Lac]

LA (10.6 g, 10.0 mmol) was added to a solution of NaOH (10.0 mmol, 0.4 g) in MeOH (5 ml), and the mixture was stirred for 5 hours at 30°C. Then, the resulting clear, colorless solution was added to the solution of 1-ethyl-3-methylimidazolium bromide (10.0 mmol, 1.91 g) in MeOH (10 ml), and the mixture was stirred at 30°C for 12 hours. Five milliliters of Et₂O was then added to the solution when a white precipitate immediately formed. The resulting slurry was stirred at 30°C for another 24 hours. Anhydrous Na₂SO₄ (2.0 g) was added in to the mixture, and the mixture was put in the refrigerator for 12 hours. The resultant precipitate of sodium bromide was removed using filtration, and the solvent was evaporated under vacuum. Anhydrous Et₂O (5 ml) was added into the product, and the mixture was stirred

for another 12 hours. After filtration and evaporated under vacuum, the product [EtMIm][Lac] was obtained. Its physiochemical properties are shown in the Supplementary Materials.

General procedures for aminolysis of PLA or PC with anilines

In a typical experiment to decompose PLA with aniline, PLA (50.0 mg), H₂O (1.0 mmol), and aniline (2.0 mmol) were mixed with [N₄₄₄₄][Lac] (20 mol %) in a 10-ml glass tube reactor, and the reactor was equipped with a magnetic stirring bar and sealed with a cap. Then, the mixture was stirred at 120°C for 12 hours. After the reaction, the mixture was extracted with ethyl acetate (5 ml each time) 3 for three times. The combined organic solutions were washed with water and brine, dried over anhydrous Na₂SO₄, and further dried in vacuo. The residue was purified by flash column chromatograph on silica gel to afford the target product **3a**. Similarly, PLA could be degraded by other anilines under the catalysis of [N₄₄₄₄][Lac] in the presence of water, affording corresponding lactamides **3b-3l**, **4a-4i**, and **6a**. The scale-up study was performed using PLA straw as the feedstocks via an analogous procedure. Note that the PLA straw was cut into species as far as possible. The ratio of **5a** to **2a** was 1:1 when **6a** was prepared. Note that the isolated yield wt % = mass of the isolated product/ theoretical mass of the product from complete conversion of PLA. (Warning! Because the reaction was performed at 120°C, higher than the boiling point of water, the auto-generated pressure inside the glass reactor was higher than atmospheric pressure due to the vaporization of water and organic compounds. Therefore, pay attention to the safety as performing the reaction.)

NMR measurements

NMR spectra were recorded on a Bruker Avance III 400 HD or 500 WB spectrometer equipped with 5-mm pulsed-field-gradient probes. Chemical shifts are given in parts per million relative to tetramethylsilane. To eliminate the effect of solvent, Wilmad coaxial insert NMR tubes were used for ¹H, ¹³C, ¹⁹F, ¹⁵N, and ¹⁷O NMR analysis at 333.2 or 393.2 K. Dimethyl sulfoxide (DMSO)-*d*₆ or deuterated water (D₂O) was added in the inner tube, and the sample was in the outer tube. For ¹H, ¹³C, and ¹⁹F NMR analysis, pure products were dissolved in DMSO-*d*₆ or D₂O and were recorded on Bruker Avance III 400 HD or 500 WB.

For ¹³C and ¹⁷O NMR analysis, pure IPA, [N₄₄₄₄][Lac], and IPA with a molar ratio of 1:5 and the mixture of [N₄₄₄₄][Lac], IPA, and H₂O with a molar ratio of 1:5:2.5 were, respectively, recorded. Each sample (0.3 ml) was added into the outer tube, and the inner tube containing DMSO was inserted.

For ¹⁵N NMR analysis, pure PhNH₂, and the mixture of [N₄₄₄₄][Lac] and PhNH₂ with a molar ratio of 1:15 and the mixture of [N₄₄₄₄][Lac], PhNH₂, and H₂O with a molar ratio of 1:15:8 were, respectively, recorded. Each sample (0.3 ml) was added into the outer tube, and the inner tube containing CH₃NO₂ in DMSO was inserted.

For in situ ¹³C NMR analysis, the mixture of PLA (25 mg), PhNH₂ (1 mmol), H₂O (0.5 mmol), and [N₄₄₄₄][Lac] (20 mol %) was prepared. The mixture (0.5 ml) was added into the NMR tube, and the spectra were recorded every 0.5 hours from 0 to 7 hours at 393.2 K. Seven representative in situ ¹³C NMR spectra were selected to analyze the intermediates during the reaction.

ATR-FTIR characterization

The mixture of PLA (25 mg), PhNH₂ (10 mmol), H₂O (5 mmol), and [N₄₄₄₄][Lac] (20 mol %) was prepared. FTIR spectra of the liquid samples were collected in the attenuated total reflect (ATR) mode on a Bruker Vertex 70 infrared spectrometer at a resolution of 1 cm⁻¹, and the spectra were recorded every 0.5 hours from 0 to 7 hours at 393.2 K. Seven representative scans were collected for both the samples.

GC-MS characterization

The products were dissolved in EtOH and put into the gas chromatography–mass spectrometry (GC-MS) analysis instrument performed using GC-MS (SHIMADZU-QP2010) with a packed column DB-5 ms.

DFT calculations

All calculations were performed with the Gaussian 09 package (59). Geometry optimizations were carried out at the M06-2X (60)/def2-TZVP (61) level at 298.15 K. The free energy of solvation of gas-phase optimized structures was calculated using the solvation model density-generic ionic liquid solvation model (62, 63). Vibrational frequency analysis was performed to estimate thermochemical data.

Note that the DFT calculation was performed to understand the interactions of [N₄₄₄₄][Lac] with H₂O, aniline, and IPA as a model compound of structural unit for PLA. Our DFT data presented have some limitations, which do not include greater numbers of cations and anions to demonstrate the effect of cluster size and, nonetheless, support the experimental results as they stand.

Measurement of water contents in ILs

ILs were first freeze-dried for 72 hours. Their water contents were determined using a Karl Fischer moisture meter (KLS701). Note that the value of water content is an average of three replicates.

Elemental combustion analysis on ILs

ILs were first freeze-dried for 72 hours. Their elemental compositions were determined using a Thermo Flash EA1112 instrument. Note that the element content is an average of three replicates.

General procedure for determination of Kamlet-Taft parameters for ILs (64, 65)

For testing Kamlet-Taft polarity parameters of the lactate-based ILs, *N,N*-diethyl-4-nitroaniline (DNA) was used to determine the value of π^* that reflects the dipolarity/polarizability of ILs. Reichardt's dye (RD) and NA were, respectively, used as probes to determine the values of α and β , which reflect hydrogen bond acidity and hydrogen bond alkalinity, respectively. The concentrations of dyes DNA and NA in IL were 2.5×10^{-5} and 1.0×10^{-5} M, respectively, and that of RD was 1.0×10^{-4} to 4.0×10^{-4} M. The adsorption spectra of the dye-IL mixture were recorded on a PE1050 ultraviolet-visible spectrophotometer. The Kamlet-Taft parameters were calculated using the equations: $= 14.57 - 4270/\lambda_{\max, \text{DNA}}$; $\beta = 11.134 - 3580/\lambda_{\max, \text{NA}} - 1.125 \times \pi^*$; $\alpha = (19.9657 - 1.0241 \times \pi^* - \nu_{\text{RD}})/1.6078$; $\nu_{\text{RD}} = 1/(\lambda_{\max, \text{RD}} \times 10^{-4})$, and the results are listed in table S1. Note that the obtained values of α , β , and π^* were average of three replicates with a reproducibility of $\pm 3\%$, respectively.

Supplementary Materials

This PDF file includes:

Supplementary Text

Figs. S1 to S5

Tables S1 and S2

NMR Data and Spectra

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Acknowledgments

Funding: This work was financially supported by the National Natural Science Foundation of China (22233006, 21890761, and 22121002). **Author contributions:** Z.L. and Y.Z. designed the project and prepared the manuscript for publication. F.W. and Y.Z. carried out the experiments and collected the data. Y.W. performed the calculations. All authors analyzed the data and contributed to the writing of the manuscript. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

Submitted 8 September 2022

Accepted 30 December 2022

Published 1 February 2023

10.1126/sciadv.ade7971