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A "Polymer to Polymer" Chemical Recycling of PLA Plastics by the "DE−RE Polymerization" Strategy

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ABSTRACT: Plastics recycling has become an important issue based on the principle of sustainability and circular economy. Therefore, the development of a valuable chemical recycling method, to achieve the recycling process of end-of-life polylactide (PLA) waste without loss of material properties, meets unprecedented opportunities. In this regard, we propose a "DE−RE polymerization" strategy to achieve the recycling process from end-of-life PLA plastic waste to new virgin-quality PLA materials in a "polymer to polymer" mode. This approach improves the efficiency of PLA recycling and promotes the development of plastics reutilization.
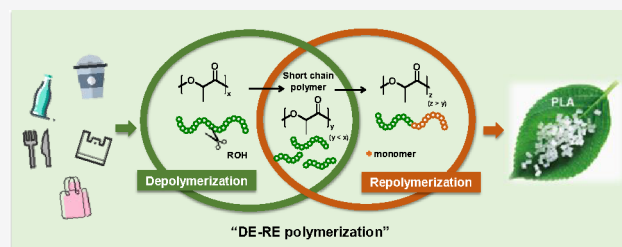
INTRODUCTION

Recently, degradable plastics synthesized from renewable feedstock have been employed as an attractive alternative to the traditional fossil resource-based plastics.[1−4] Among these "green polymers", polylactide (PLA) is arguably the most successful example, which has been used in packaging, textile, and biomedical application areas due to its desirable mechanical and physical properties.[5−7] However, when developing PLA plastics, the end-of-life PLA waste should draw much more attention. If not disposed properly, they could still become a source of environmental contamination because the biodegradation process occurs only under specific environmental conditions.[8,9] On the other hand, through incineration or composting, PLA can be converted to, for example, energy, carbon dioxide, and water, which can be reused to achieve carbon neutrality. But this process requires the reproduction of new PLA to replace the old ones, consuming a lot of land and time. In this regard, there is a great demand for sustainable chemical degradation methods, where useful chemicals are the end-of-life PLA plastic wastes.[10,11]

For most degradable polyester materials, two main strategies have been used to achieve the chemical recycling process.[12−17] One is chemical recycling to their starting monomers;[18−28] the other is chemical upgrading to value-added chemicals.[29−35] Studies have demonstrated that PLA could be hydrolyzed to lactic acid as well as directly converted to lactide. However, harsh reaction conditions such as high temperature (250−280 °C) are usually required.[36] In contrast, the transformation of PLA into lactate esters via the alcoholysis strategy is exceptionally interesting since lactate esters can be used as an environmentally friendly solvent.[37−41] For example, Jones and Wood reported that PLA successfully degraded to methyl lactate catalyzed by an imino monophenolate Zn complex.[42] In addition, Enthaler reported $Zn(OAc)_2$ as the most active state-of-the-art system so far. The high activity (TOF = 45000 h^{-1}) and selectivity (>99%) made it industrially promising.[43] Besides, an organocatalytic recycling of PLA into lactate esters was also achieved by using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as promoter.[44] Another attractive way to utilize lactate esters is to convert back to PLA materials. Progress has been achieved to convert lactate esters to low-molecular-weight PLA.[43] However, to obtain high-molecular-weight PLA materials, hydrolysis of lactate esters to lactic acid, prepolymerization to oligomer, dimerization to lactide, and polymerization to PLA are required, which, while viable, are expensive and inefficient. Therefore, the direct conversion of PLA wastes into new PLA materials is an interesting research topic.

In the previous work, polymers with one or more hydroxyl groups at the chain end could be used as macromolecular initiators to initiate the polymerization of subsequent monomers.[45−48] Therefore, polymers with different structures or composition units could be synthesized (Scheme 1A). On the other hand, by use of alcohols as a transesterification reagent for chain cleavage, macromolecules can be modified to have controlled molecular weight and functionality or converted into small molecules (Scheme 1B).[31−33,49] Inspired by these two methodologies, we propose a "DE−RE polymerization" strategy to achieve the recycling process
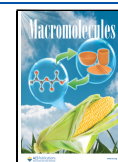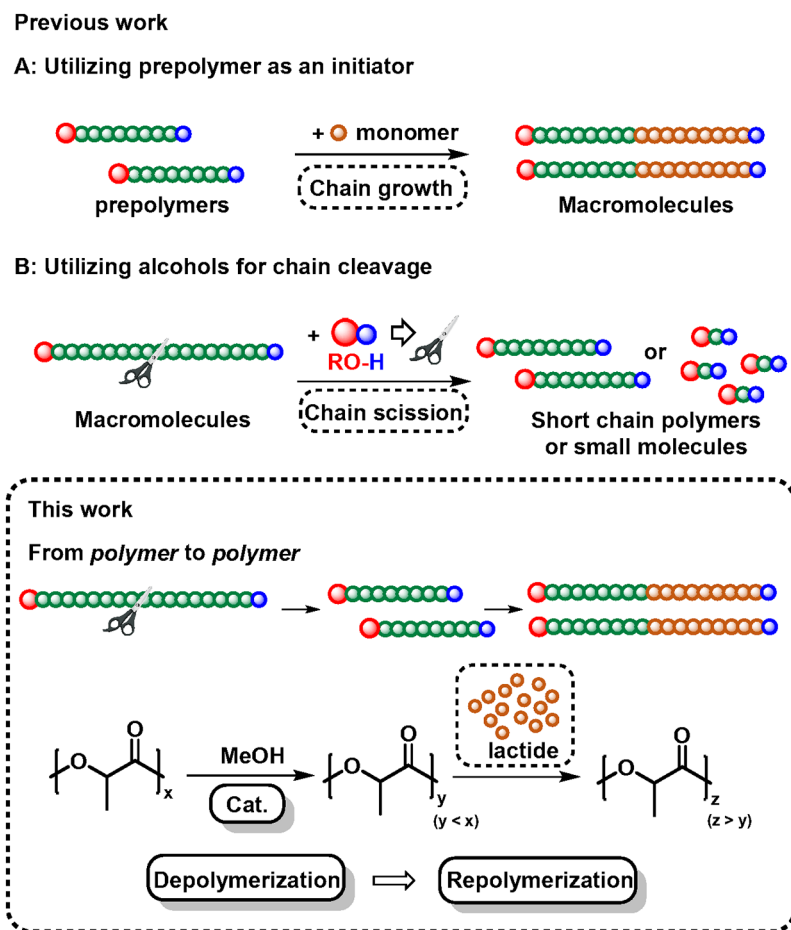
Scheme 1. Chemical Recycling of PLA Plastics by the "DE−RE Polymerization" Strategy

from end-of-life PLA wastes to new virgin-quality PLA materials (Scheme 1). In this strategy, the discarded PLA plastics are first depolymerized to obtain short PLA chains and then repolymerized with newly added lactide (LA) to generate new PLA materials with good quality. It is worth noting that to achieve this idea, the following important points should be taken into full account. (1) A versatile catalyst that not only achieves the high-efficiency depolymerization under mild conditions but also catalyzes controllable repolymerization in one pot, even with a small amount of chain transfer reagent, is crucial. (2) Different types of commercial PLA plastics, varying in molecular weight and dispersity, should be suitable for this strategy. (3) The quality of the newly produced PLA material should be the same as or better than the original one. (4) The catalyst preferably has the characteristics of nontoxicity, biocompatibility, and commercial availability. However, very limited catalyst has the potential to achieve the "DE−RE polymerization" process in one pot under mild conditions. For example, $Sn(Oct)_2$ is a good catalyst for the polymerization of LA monomers,[50] but $Sn(Oct)_2$-mediated depolymerization conditions (140−180 °C) of PLA are rather harsh.[51] Recently, our group reported a supporting ligand-free transesterification catalyst, zinc bis[bis(trimethylsilyl)amide] ($Zn(HMDS)_2$), that enables catalytic capability for both polyester synthesis and degradation under mild conditions.[52] Inspired by this result, a "polymer to polymer" chemical recycling of end-of-life PLA plastics by the "DE−RE polymerization" strategy might be achieved. In this context, influences of different operating

conditions on this strategy were explored in detail. Furthermore, various commercial PLA plastics were applied in the strategy, and the properties of the recovered polymers were also investigated. This approach might be a new idea for plastics reutilization.

■ RESULTS AND DISCUSSION

Influences of Operating Conditions on the "DE−RE Polymerization" Strategy. Before exploring this "DE−RE polymerization" strategy, we also conducted the chemical recycling of end-of-life PLA plastic waste back to lactide monomer. Using $Zn(HMDS)_2$ and methyl lactate as the catalytic system, we achieved the depolymerization process under 210 °C and 0.05 mbar conditions (see the Supporting Information, Figures S1 and S2). The proportions of L-LA, D-LA, and meso-LA in the degradation products were 87%, 2%, and 11%, respectively. Like the industrial production of L-LA, the inevitable racemization side reaction leads to the formation of meso-LA and D-LA in products, which greatly decreases the purity of the L-LA.[53,54] To obtain high purity L-LA, multiple purification processes are necessary. However, the tedious postprocessing not only reduces the yield of L-LA but also decreases the production efficiency. Moreover, the high temperature and vacuum make it an energy-consuming and uneconomic process. Therefore, the disadvantages of uncontrollable racemization side reactions and harsh reaction conditions in this strategy stimulated us to find a new strategy
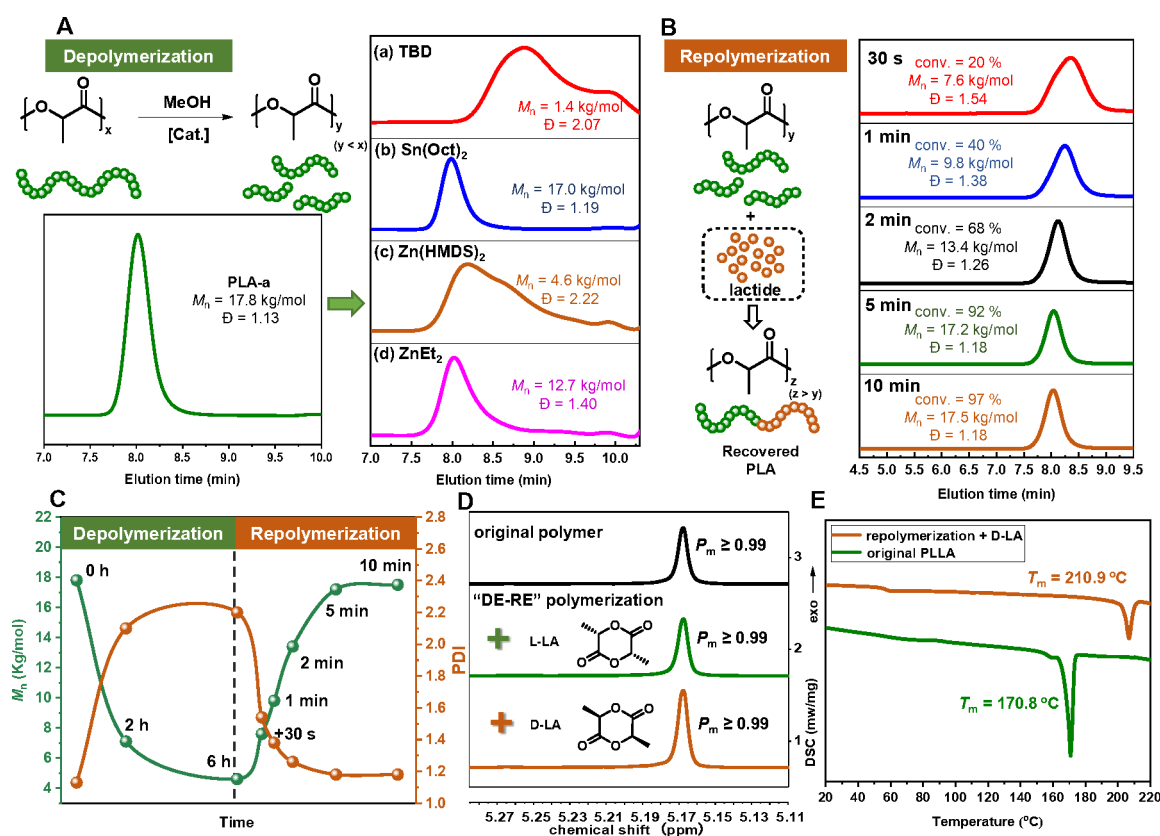
Figure 1. Results for depolymerization—repolymerization of PLA. (A) GPC analysis of the depolymerization of PLA using different catalysts (Table 1, entries 1−4). (B) GPC analysis of the repolymerization of *rac*-LA at different times catalyzed by $Zn(HMDS)_2$ (Table 1, entry 3). (C) Plots of M_n and Đ versus time during the depolymerization—repolymerization of PLA catalyzed by $Zn(HMDS)_2$ (Table 1, entry 3). (D) Partial homonuclear decoupled ^1H NMR spectrum of PLA before and after the "DE−RE polymerization" (Table 1, entries 13 and 14). (E) DSC traces of PLA before and after the "DE−RE polymerization" (Table 1, entry 14).
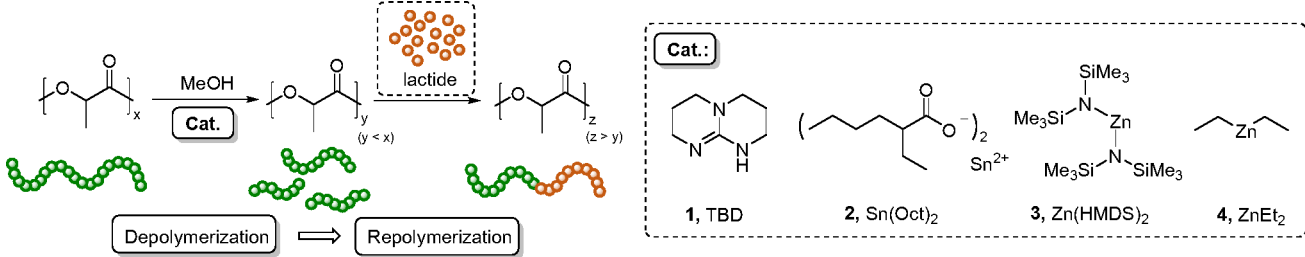
to improve the recovery efficiency of PLA wastes under mild conditions.

To verify the feasibility of the "DE−RE polymerization" strategy, the catalytic process of different catalysts was first explored. At the beginning, the organocatalyst TBD was employed to catalyze the depolymerization of PLA synthesized in our laboratory (Table S1, M_n = 17.8 kg/mol, Đ = 1.13). The loading of catalyst was 1 mol % compared with polymeric ester, and 3 times the amount of methanol with respect to the polymer chain was involved. GPC monitoring showed that the polymer chain quickly cleaved into short chain polymer within 2 h (Figure 1A(a), M_n = 1.4 kg/mol, Đ = 2.07), which indicated TBD can catalyze transesterification efficiently. When it comes to the repolymerization process, 3 mmol of *rac*-LA was added to the reaction system for chain growth. However, the efficient transesterification characteristic made the repolymerization uncontrollable, the molar weight of the recovered polymer was much lower than the expected (Table 1, entry 1, 7.9 vs 17.8 kg/mol), and the dispersity (Đ = 1.82) was wide due to uncontrollable transesterification reaction (Figure S3). Therefore, TBD is an inferior candidate for "DE−RE polymerization". Besides, in the previous study, the industrially relevant catalyst $Sn(Oct)_2$ has been proved to achieve the degradation of PLA at high temperature. However, when it was utilized in this strategy at room temperature, the reaction failed. The molecular weight of the polymer hardly changed under depolymerization step (Figure 1A(b), M_n = 17.0 kg/mol, Đ = 1.19), and the repolymerization process also

remained stagnant (Table 1, entry 2). This result showed that $Sn(Oct)_2$ has low activity under mild conditions.

Next, the catalytic performance of $Zn(HMDS)_2$ was explored (Table 1, entry 3). It is encouraging that the molecular weight of PLA was cracked to a quarter of the initial polymer in a controlled and predicted manner after adding 3 times the amount of methanol with respect to the polymer chain (from 17.8 to 4.6 kg/mol, Figure 1A(c)). Subsequently, in the repolymerization stage, the polymer chain rapidly increased to the original in <10 min (Figures 1B and Figures S4−S5, M_n = 17.5 kg/mol, Đ = 1.18). This breakthrough indicated the practicability and maneuverability of the "DE−RE polymerization" strategy. Likewise, diethylzinc ($ZnEt_2$) was also taken into consideration. However, low activity was observed during chain scission (from 17.8 to 12.7 kg/mol, Figure 1A(d)) and chain growth steps (Table 1, entry 4). It took up to 90 min to consume the monomer upon repolymerization. Besides, the molecular weight of the resulting PLA was higher than the theoretical values (22.9 vs 17.8 kg/mol), which indicated that part of the chain transfer reagent did not form the new polymer chain end. These results above could be explained by the fact that only a part of alkyl groups in $ZnEt_2$ convert into highly active metal zinc alkoxyls as well as aggregation state in $Zn(OMe)_x(Et)_y$.[55] Finally, by comparison, $Zn(HMDS)_2$ took the top spot for this polymer recycling strategy. Therefore, more systematic studies about $Zn(HMDS)_2$ were performed next.

Table 1. Results for Depolymerization−Repolymerization of PLA

entry[a]	PLA	cat.	depolymerization				repolymerization			recovered polymer	
			$[\text{cat.}]^b$ (mol %)	$n_{\text{MeOH}}/n_{\text{PLA−OH}}{}^c$	t (h)	$M_{\text{n,GPC}}$ $(Đ)^g$	$n_{\text{LA}}{}^d$ (mmol)	t (min)	conv^e (%)	$M_{\text{n,theor}}{}^f$ (kg/mol)	$M_{\text{n,GPC}}$ $(Đ)^g$
1	a	1	1	3	2	1.4 (2.07)	3	1	99	17.8	7.9 (1.82)
2	a	2	1	3	6	17.0 (1.19)	3	720	<10		
3	a	3	1	3	6	4.6 (2.22)	3	10	96	17.8	17.5 (1.18)
4	a	4	1	3	6	12.7 (1.40)	3	90	96	17.8	22.9 (1.21)
5	a	3	1	3	6	4.7 (2.20)	5	10	97	26.7	26.1 (1.15)
6	a	3	1	3	6	4.6 (2.32)	1	10	97	8.9	8.8 (1.38)
7	a	3	1	3	2	14.3 (1.27)/1.3 (1.48)	1	5	98	8.9	21.8 (1.12)/6.8 (1.22)
8	a	3	1	3	12	3.2 (2.97)	1	5	96	8.9	9.2 (1.48)
9	a	3	0.35	1	6	8.8 (2.11)	1	90	91	17.8	18.7 (1.27)
10	a	3	0.15	0.5	6	14.9 (1.45)	0.5	420	91	17.8	18.4 (1.33)
11	b	3	1	7	6	7.8 (2.68)	7	20	98	40.0	40.2 (1.21)
12	a+b	3	1	5	6	5.9 (2.13)	5	20	98	28.9	30.1 (1.17)
13[h]	c	3	1	3	6	6.8 (2.17)	3	10	93	24.6	23.1 (1.14)
14[i]	c	3	1	3	6	5.9 (2.39)	3	5	96	24.6	22.7 (1.14)
15[j]	a′	3	1	3	0.5	2.6 (2.08)	3	15	98	13.5	13.4 (1.76)
16	a′	3	1				1	4 h	90	26.4	24.9 (1.13)

[a]Polymers: **a**, PLA, M_n = 17.8 kg/mol, $Đ$ = 1.13, DP_0 = 100; **b**, PLA, M_n = 40.0 kg/mol, $Đ$ = 1.16, DP_0 = 250; **c**, PLLA, M_n = 24.6 kg/mol, $Đ$ = 1.18, DP_0 = 100, P_m = 0.99; **a′**, PLA, M_n = 13.5 kg/mol, $Đ$ = 1.13, DP_0 = 100; depolymerization conditions: 144 mg of PLA (1 mmol) in 1.5 mL of DCM, 25 °C. The amount of chain-end hydroxyl in the polymer chain $n_{\text{PLA−OH}}$ = 1 mmol/DP_0. [b]Loading of catalysts was relative to the polymeric ester. [c]Loading of MeOH (n_{MeOH}) was relative to the amount of chain-end hydroxyl in the polymer chain ($n_{\text{PLA−OH}}$). $M_{\text{n,depoly}} = M_{\text{n,PLA}}/[1 + (n_{\text{MeOH}}/n_{\text{PLA−OH}})]$. [d]rac-Lactide was added to repolymerization. DP upon repolymerization = $n_{\text{LA}}/(n_{\text{MeOH}} + n_{\text{PLA−OH}})$. [e]Monomer conversion was determined and calculated by the ^{1}H NMR spectrum of the crude product in CDCl$_3$. [f]$M_{\text{n,theor}} = M_{\text{n,depoly}} + M_{\text{n,repoly}}$; $M_{\text{n,repoly}}$ = (DP upon repolymerization/DP_0) × $M_{\text{n,PLA}}$. [g]Apparent number-average molar mass (M_n, kg/mol) and dispersity ($Đ$) values were determined by GPC in THF using polystyrene standards for calibration and corrected by using the factor 0.58 for polylactide. [h]L-Lactide was added to repolymerization. [i]D-Lactide was added to repolymerization. [j]Reaction was conducted without solvent, 130 °C.

To clarify the concrete details in the course of "DE−RE polymerization" promoted by Zn(HMDS)$_2$, the change trend of molecular weight was constantly monitored. As demonstrated in Figure 1C, after methanol was acted on the polymer, the decrease in molecular weight appeared (from 17.8 to 4.6 kg/mol), which illustrated that all the polymers have been cut into short chains. Concomitantly, the dispersity of the polymer also broadened ($Đ$ changed from 1.13 to 2.22), which implied that the polymers were not cut neatly but were uneven. Focusing on the repolymerization step, the dispersity of newly formed polymers gradually narrowed ($Đ$ changed from 2.22 to 1.18), which indicated that the propagation rate varied between long and short polymer chains; the growth rate of long chains lagged behind short chains, so the short chains could catch up with the long chains which made the final polymer length converge. To further test this concept, a long chain and a short chain PLA (9.2 and 27.2 kg/mol) were first synthesized. Then, 1 equiv of lactide monomer was added to these two PLA chains to observe the difference of monomer consumption rate. As shown in Figure S6, the ROP of lactide initiated by long chain was indeed slower than that of short chain (k_{app} = 0.07 min^{-1} for the long chain and k_{app} = 0.24 min^{-1} for the short chain). The specific "random chain

scission, selective chain growth" property is the key to obtain narrower dispersity in "DE−RE polymerization".

After gaining a general understanding of the behavior of polylactide recovery, the influences of operating factors, such as time, catalyst loading, molecular weights of PLAs, etc., were further investigated. First, on the premise of the same conditions of depolymerization step, the molecular weights of final polymer were changed by adjusting the amount of monomer added in the repolymerization process (Table 1, entries 5 and 6). As the experimental results showed, adding 5 mmol of monomers increased the molecular weight to 1.5 times (26.1 kg/mol) that of the original or reduced it to half (8.8 kg/mol) when 1 mmol of lactide was employed for repolymerization. These experiments demonstrated that polymers with various molecular weights can be obtained by using this approach (Figure S7). In the meantime, the depolymerization time was also explored (Table 1, entries 7 and 8). Shortening the depolymerization time to 2 h, only part of the polymer degraded into short chain polymers (Figure S8). Then 1 mmol of rac-LA was supplemented for repolymerization; the GPC figure of the reclaimed polymer showed a bimodal trend (Table 1, entry 7, and Figure S9). It could be expounded that the addition of monomers was not
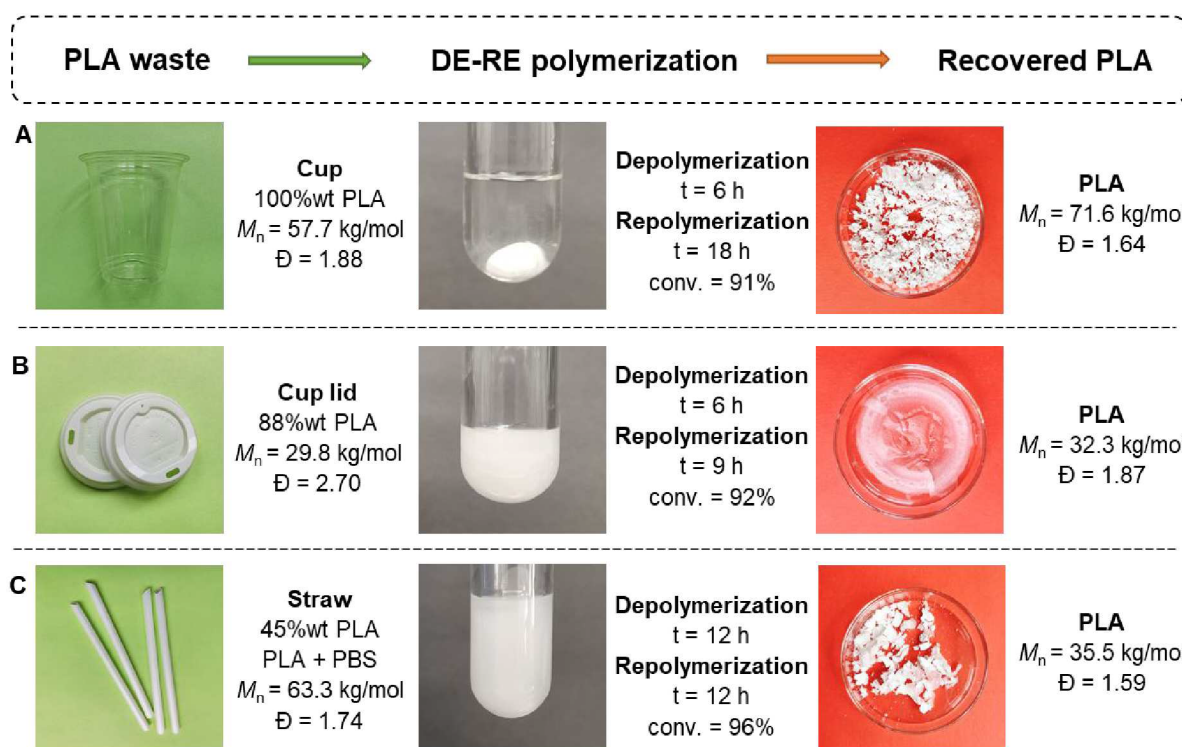
Figure 2. "DE−RE polymerization" strategy applied to different PLA wastes. Reaction conditions: 288 mg of PLA waste dissolved in 3 mL of DCM was employed. (A) Catalyzed by 5.2 mg (0.013 mmol) of Zn(HMDS)$_2$ with 20 μmol of MeOH, added 5 mmol of L-LA to repolymerization. (B) Catalyzed by 7.8 mg (0.020 mmol) of Zn(HMDS)$_2$ with 30 μmol of MeOH, added 2 mmol of L-LA to repolymerization. (C) Catalyzed by 7.8 mg (0.020 mmol) of Zn(HMDS)$_2$ with 30 μmol of MeOH, added 3 mmol of L-LA to repolymerization.

sufficient for short chain polymers growth to high molecular weight as the original polymer, although short chains in the system grew faster than long chains. This phenomenon further explained the conclusion that the chain propagation of repolymerization process was not uniform. However, the depolymerization time cannot be prolonged too much as well because the continuous reorganization of the polymer chains led to an excessively broad dispersity, which was also detrimental to subsequent chain growth (Table 1, entry 8, Đ = 1.48; Figures S10 and S11). In addition, with a view to raising the economic benefit, attempts with low catalyst to methanol loadings were also performed (Table 1, entries 9 and 10). With catalyst dosage as low as to 0.15 mol % relative to ester group, the reaction procedure could still be steadily advanced, which displayed high catalytic efficiency of this catalytic system. Most importantly, reducing the amount of methanol made the demand for monomer decrease upon repolymerization step, so as to improve practical application value. As shown in Table 1, entry 10, only 0.5 equiv of lactide was added to the reaction mixture, and a polymer with predicted molecular weight and narrow dispersity was still obtained. Furthermore, to extend the application scope, different kinds of PLAs were evaluated to this strategy (Table 1, entries 11−14). For example, the PLA sample (**b**) with 40.0 kg/mol molecular weight was depolymerized and then polymerized to the original chain length in an efficient and controllable manner (Table 1, entry 11, and Figures S12−S14). Besides, by use of this approach, the mixture of PLAs (**a** + **b**) with diverse molecular weight (17.8 and 40.0 kg/mol) could be leveled out and transformed into a single specific molecular weight (Table 1, entry 12, 30.1 kg/mol, Đ = 1.17); thus, the simultaneous treatment of various polylactide wastes

could be achieved (Figures S15 and S16). Aside from the above atactic PLA, the microstructures of recycled polymers were also surveyed after the fracture of isotactic PLLA (**c**) and the addition of L-LA (Table 1, entry 13). According to homo-decoupled ^{1}H NMR spectrum,[56] P_m greater than 0.99 was calculated, in which no undesired peaks were observed except for the *mmm* peak (Figure S17 and Figure 1D). Therefore, no epimerization occurred during the whole reaction.[57] Moreover, when the monomer applied in repolymerization was changed to the other chiral D-LA, the recovered polymer still had high regularity (P_m > 0.99), suggesting a block copolymer formed (Table 1, entry 13, and Figure 1D). In addition, the melting point (T_m) of the obtained polymer was exploited by differential scanning calorimetry (DSC). A higher T_m value of 210 °C was detected which revealed the formation of stereocomplexed PLA[58] (Figure 1E). The above evidence indicated that the transesterification side reaction could be neglected when the rapid chain growth was dominant in the process of repolymerization. Hence, copolymers with distinct composition might be obtained by altering the kind of repolymerized monomers. Besides, the strategy was also adopted without the use of solvents at 130 °C (Table 1, entry 15). Because of the increase of temperature, the reaction rate was obviously accelerated; thus, the PLA chain was cracked within 30 min (from 13.5 to 2.6 kg/mol). In the repolymerization progress, the short polymer chain was controlled to grow to the initial molecular weight (13.4 vs 13.5 kg/mol), which further showed the general applicability of this strategy.

To confirm the DE−RE polymerization process, the polymers after depolymerization and repolymerization were analyzed by ^{1}H NMR and MALDI-TOF (Figures S18 and
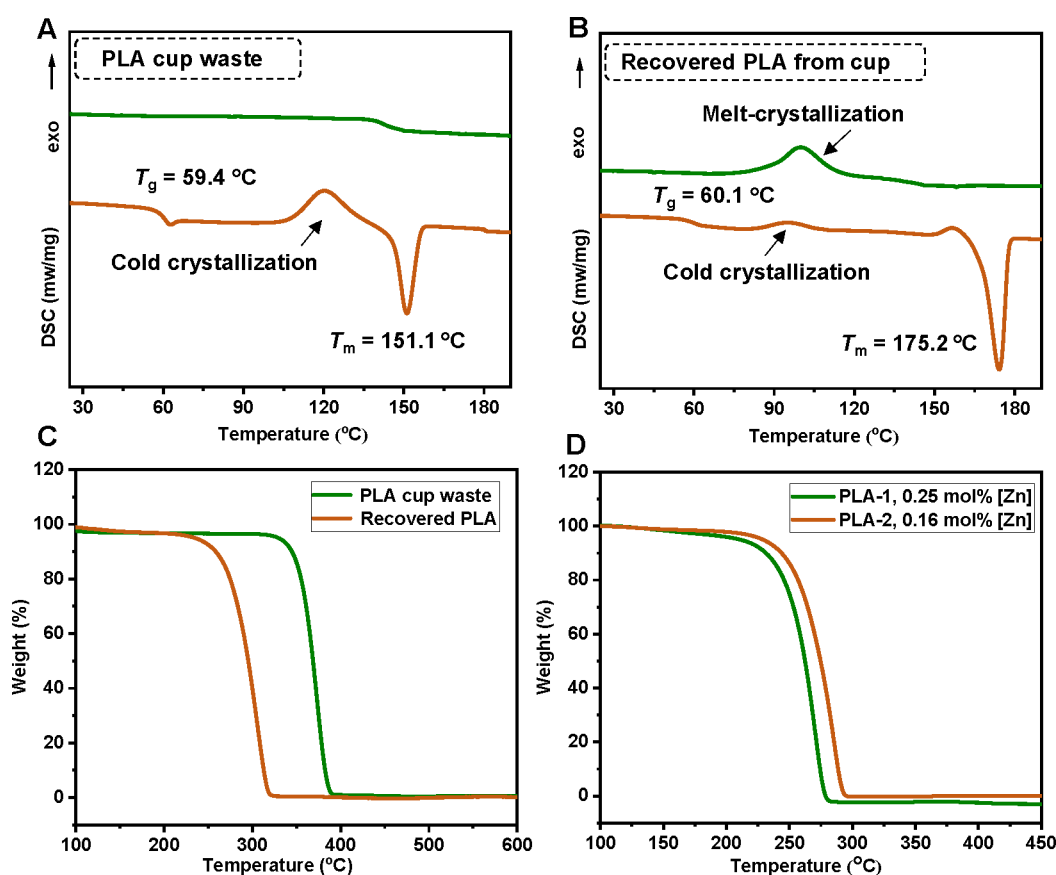
Figure 3. Properties of polymerization after the "DE−RE polymerization" strategy. (A) DSC curves of PLA cup waste after cooling at 20 °C/min (green) and second heating scan at 10 °C/min (orange). (B) DSC curves of recovered PLA from cup waste. (C) TGA analysis of the recovered PLA from cup waste. (D) TGA analysis of the PLA with different metallic zinc contents. PLA-1, $[M]/[Zn]/[OH]$ = 400/1/4, 0.25 mol % $[Zn]$, M_n = 16.6 kg/mol, $Đ$ = 1.10. PLA-2, $[M]/[Zn]/[OH]$ = 600/1/6, 0.16 mol % $[Zn]$, M_n = 15.6 kg/mol, $Đ$ = 1.10.

S19). After depolymerization by adding 2 times the amount of methanol respect to the polymer chain, it was obvious in ^{1}H NMR that the ratio of the characteristic peak of methanol chain end to the initial benzyl alcohol chain end was 2:1, which was consistent with the design of cutting the polymer into three segments. When monomers were added during repolymerization, the ratio of methanol chain end to the benzyl alcohol chain end remained unchanged in the final polymer. Meanwhile, the polymers after depolymerization and repolymerization were also analyzed by MALDI-TOF (Figure S19). It could be observed that the molecular weight of the polymer changed significantly after depolymerization, which further indicated that the polymer chain was cut off completely due to the transesterification reaction of methanol. During repolymerization, an overall increase in the molecular weight of the polymers was observed, which showed that PLA was not formed by the homopolymerization of newly added LA that initiated by MeOH residue but originated from depolymerization short-chain PLA.

In addition, to further illustrate the versatility of the $Zn(HMDS)_2$, ring-opening polymerization of lactide by using PLA polymer as a macroinitiator was performed (Table 1, entry 16). The experimental results showed that lactide monomer was transformed into PLA chains. GPC traces demonstrated that the subsequent polymer showed a single peak, and its molecular weight was twice that of the initial polymer (Figure S21). Moreover, the chain extension was also achieved (Table S2 and Figure S22). This evidence proved

that the ring-opening polymerization of lactide was initiated on the basis of the original polymer chain, which demonstrated the ability of $Zn(HMDS)_2$ to catalyze polymer chain growth robustly. However, this direct repolymerization by using polymer as a macroinitiator is only applicable to polymers with well-defined hydroxyl chain ends, which reflects the universality of the "DE−RE polymerization" strategy.

"DE−RE Polymerization" Strategy of Commercial PLA Products. Through the above research, the "DE−RE polymerization" strategy was proved to be a useful tactics by exploring various kinds of PLA synthesized in the laboratory. Furthermore, to improve the practical application value, experiments were performed to apply this methodology on a variety of commercially available products containing PLA. For commercial PLAs, these products underwent melting, hot forming, and other processes. Therefore, with such a small amount of catalyst and the addition of methanol, the DE−RE polymerization reaction time required was much longer.

First of all, the PLA cold drink cup was explored as trial run, which was transparent and contained almost no other impurities except the main body of polylactide (Figure 2A). The cup was shredded into a square of 0.5 mm in length and then directly entered the experimental procedure without any further postprocessing such as drying, purification, and so on. The result showed that after the depolymerization process methanol could also enter into the polymer chain through transesterification in the presence of 0.35 mol % $Zn(HMDS)_2$. The addition of L-LA monomer was followed by repolyme-
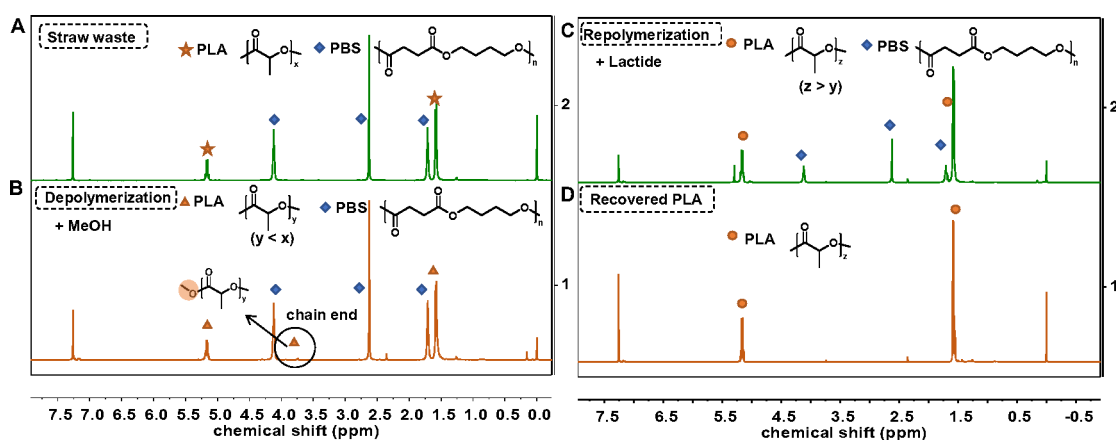
Figure 4. ^{1}H NMR (CDCl$_3$, 400 MHz) analysis of straw material before and after the "DE−RE polymerization" strategy. (A) Original straw material. (B) After 12 h of depolymerization catalyzed by 7.8 mg (0.020 mmol) of Zn(HMDS)$_2$ with 30 μmol of MeOH. (C) After adding 2 mmol of lactide and repolymerizing for 12 h. (D) Recovered PLA after "DE−RE polymerization" strategy of straw material.

rization to form a new polymer chain, which showed a molecular weight of 71.6 kg/mol as well as a dispersity of 1.64 (Figures S23 and S24). The dispersity of the polymer itself is relatively broad, so we did not try to obtain narrow dispersity polymer deliberately. Noticeably, the thermal properties of newly generated PLA were evaluated through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). As shown in Figures 3A and 3B, the polymers were first programmed heated to 220 °C (10 °C/min) and then cooled to 0 °C (20 °C/min). For the recovered PLA, a distinct melt-crystallization peak was observed during cooling. The melt-crystallization peak was not observed for the PLA cup materials, indicating that this polymer did not crystallize but cooled in an amorphous state, while a cold crystallization peak appearing after the segment regained its mobility during the secondary heating. Besides, on the second heating scans, the newly formed PLA exhibited a high T_m (175 °C), which illustrated that the recycling PLA had good crystallization ability. In addition, the thermostabilities of polymers were examined by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min (Figure 3C and Figure S25). According to TGA and DTG curves, the weight loss of recovered PLA started at 260 °C, and the maximum decomposition temperature T_{max} was 303 °C. However, for the PLA cup, the beginning of degradation at about 340 °C and T_{max} was 368 °C. These results revealed that the decomposition pathways of the two polymers may be different on account of the residue of metal zinc may promote the degradation of PLA.[59] To demonstrate the effect of metallic zinc on thermal stability, PLA with different metallic zinc contents was synthesized (0.25 mol % vs 0.16 mol %). The TGA results show a decrease in the maximum decomposition temperature T_{max} with increasing zinc catalyst content (267 °C vs 282 °C), which indicated that the thermal stability of the PLA was significantly affected by metallic zinc (Figure 3D and Figure S26).

It is often the case that commercially available polylactides contained a few other compounds to modify some of their macroscopic properties, giving them a broader range of applications.[60,61] The "DE−RE polymerization" strategy was directly implemented after fragmentation of this cup lid (containing 88 wt % PLA) without any other treatment (Figure 2B). After depolymerization, insoluble impurities were removed by filtration to obtain pure PLA for analysis. By controlling the amount of LA added in the repolymerization

step, a molecular weight equivalent to that of the initial polymer was obtained. Notably, the initial polymer had a broad dispersity (Đ = 2.70), but a significantly narrower dispersity of the recovered PLA was observed (Đ = 1.87). This result once again manifested the characteristics of the polymerization catalyzed by Zn(HMDS)$_2$; the difference in the rate of long versus short chain growth makes the polymer chains more homogeneous. Moreover, the reaction proceeded smoothly despite the interference of existing impurities, showing the robustness of this catalytic system.

Next, the depolymerization of the opaque straw was also performed under standard conditions (Figure 2C). This straw was formed by mixing PLA with poly(butylene succinate) (PBS) as detected by ^{1}H NMR in CDCl$_3$ (Figure 4A). When dichloromethane was adopted as the reaction solvent, both PLA and PBS materials dissolved well. After the addition of methanol and reaction with Zn(HMDS)$_2$ at room temperature for 12 h, ^{1}H NMR revealed that the characteristic peak of chain end initiated by methanol appeared in the polymer, but there were no peaks of PBS intercalated by MeOH (Figure 4B). This appearance illustrated that under such mild conditions the catalyst exhibited selectivity for catalyzing the ester group scission of PLA without contributing to PBS. The reason selective chain scissions could be achieved was that polymers have different structures and therefore different degradation rates. For further verification, the methanolysis reactions of these two polyesters were contrasted. As shown in Table S3, PLA had rapid degradation ability and could be completely converted into methyl lactate at room temperature within 2 h. In contrast, the degradation rate of PBS was very slow, and an extension of time (96 h, 71% conversion) was required. Then the repolymerization process proceeded; 3 mmol of LA underwent ring-opening polymerization smoothly so that the chain length of PLA increased and the integral area of the characteristic peaks of PLA increased (Figure 4C). The above experimental phenomena indicated that although the carbonyl group in PBS might also coordinate to the zinc, its presence neither significantly inhibited the alcoholysis or polymerization process. Finally, after the end of repolymerization, taking advantage of the differences in the solubility between PLA and PBS in toluene, separation of the two types of polymers was achieved, and thus pure PLA was recovered (Figure 4D).

The above experimental results confirmed that the "DE−RE polymerization" strategy can be applied to commercially

available PLA products. Compared with the chemical recycling of PLA to lactide monomer strategy, this strategy has the following advantages. First, the DE−RE polymerization conditions are milder and can be performed at room temperature and atmospheric pressure. Second, there are fewer side reactions in the DE−RE polymerization process. Third, this DE−RE polymerization strategy improves the recycling efficiency (polymer to polymer vs polymer to monomer) of PLA waste. In this strategy, new polymers with different architectures are synthesized from end-of-life PLA to reduce the raw material consumption for completely reproducing PLA. However, this new strategy does not achieve a complete closed-loop chemical recycling due to a certain amount of new monomers need to be added. It represents a promising concept for further development, not only for chemical recovery but also for polymer modification and synthesis. In terms of maximizing the reuse of PLA waste, a combination of the two strategies is probably the best option.

■ CONCLUSIONS

In summary, a "polymer to polymer" chemical recycling "DE−RE polymerization" strategy of PLA plastics waste was achieved under mild conditions. Utilizing transesterification catalyzed by Zn(HMDS)$_2$ with methanol participation, the PLA polymer chain could be controllably cleaved to a certain molecular weight, at which point the polymer possessed chain growth activity. Afterward, chain expansion occurred after monomer supplement in the process of repolymerization. The difference in chain propagation rates of repolymerization made the recovered polymer chain length tend to be uniform. Different types of commercial PLA plastics, varying in molecular weight and dispersity, are suitable for this strategy. In this strategy, new polymers are synthesized on the basis of end-of-life PLA, which will reduce the burden of raw materials for completely resynthesizing PLA. Although this new research did not achieve complete closed-loop chemical recycling, it represents a promising concept, not just for chemical recycling, which can be further developed in the field of polymer modification and synthesis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c02085.

> Materials and instruments, depolymerization−repolymerization procedure and data, NMR spectra (PDF)

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Author Contributions

G.X. and Q. W. conceived the idea and designed the experiments. R.Y. performed the experiments, and G.X. analyzed the data. G.X., R.Y., and Q.W. cowrote the manuscript, and all authors participated in data analysis and discussions and read and edited the manuscript. Q.W. directed the project.

Notes

The authors declare no competing financial interest.

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