Chemically recyclable polyesters from CO$_2$, H$_2$, and 1,3-butadiene

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GRAPHICAL ABSTRACT

PUBLIC SUMMARY

- CO$_2$-based recyclable polymers are promising in reducing CO$_2$ emission and pollution
- Disubstituted δ-lactone, a previously non-polymerizable monomer, was polymerized
- Complete monomer recovery was successfully achieved via chemical recycling process
- CO$_2$ constitutes 28% of the weight of newly designed chemically recyclable polymers
- The polymers show pressure-sensitive adhesive property comparable to commercial tapes
Chemically recyclable polyesters from CO$_2$, H$_2$, and 1,3-butadiene

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RESULTS

Methodology development for the synthesis of polyesters from CO$_2$, H$_2$, and 1,3-butadiene

As shown in Figure 1, a two-step palladium-catalyzed procedure was used to synthesize polyesters from CO$_2$, H$_2$, and 1,3-butadiene following the literature. The resultant polyester was a 63/37 diastereomeric mixture according to various NMR spectroscopic studies (Figures S1–S4). To generate polyesters, through ROP of CO$_2$, catalysts including tin(II)-ethylhexanoate (SnOct$_2$) and dibutyltin dilaurate (DBTDL) associated with benzyl alcohol (BnOH) were initially attempted at varied conditions ([HL]/[Cat.]/[BnOH] = 40/11 or 40/0.5/1 at different temperatures), but no polymer was obtained (Table S1, runs 1–4). Then diphenyl phosphite (DPP) was also employed, but no reaction was detected either (Table S1, runs 5–7, [HL]/[DPP]/[BnOH] = 30/11/1 at −25°C, 25°C, and 80°C in bulk for 24 h, respectively). Subsequently, organic bases, such as 1,8-diazabicyclo[5.4.0]undec-7-ene and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), were tested at a ratio of [HL]/[Cat.]/[BnOH] = 40/11/1 at 30°C for 96 h in tetrahydrofuran (THF) (Table S1, runs 8–13). Upon numerous experimental trials, we found that TBD/BnOH can catalyze the ROP of polyesters at room temperature in bulk or THF after 96 h, resulting in liquid polyesters with moderate conversion (Table S1, run 9. Conv. = 54%, M$_n$ = 6,010 g mol$^{-1}$, D = 1.14; run 10. Conv. = 57%, M$_n$ = 5,596 g mol$^{-1}$, D = 1.18, respectively).

Subsequently, we conjectured that increasing the basicity of the organocatalyst might promote the polymerization reactivity. Thus, three common phosphazene bases (PBs) in association with BnOH were investigated. For a 50/1 ratio of [HL]/[BnOH] with 1 mol % of Bu-P$_1$, (tert-butylkoiminodifumidamylphosphorane) or Bu-P$_2$ (1-tert-butyl-2,2,4,4,4-panetakis(dimethylamino)$_2$)2$^{,}$4-catenadi(phosphazene) at −25°C in THF ([HL]$_2$ = 5.3 M), no polymer was obtained for Bu-P$_2$ after 72 h (Table 1, run 1), whereas a 41% conversion was observed for Bu-P$_1$ after 120 h (Table 1, run 2, M$_n$ = 5,304 g mol$^{-1}$, D = 1.07). Encouragingly, the ROP process was dramatically improved when Bu-P$_4$ (1-tert-butyl-4,4,4-tris(dimethylamino)$_2$)-bis(tris(dimethylamino)$_2$)-phosphoranylide-naming$-$ (Table 1, run 3). Corresponding polyesters with M$_n$ = 19,880 g mol$^{-1}$ and moderate D = 1.90 was obtained. The difference in catalytic reactivity might be a consequence of the large basic differences among the three PBs$^{21}$ ($pK_a$ = 26.9, 33.5, and 42.7 in acetonitrile$^{22}$ for Bu-P$_1$, Bu-P$_2$, and Bu-P$_4$, respectively). Next, altering the Bu-P$_4$ loading from 2 mol % to 0.2 mol % led to a much more controlled polymerization (Table 1, runs 4–7). Particularly, polyHL$_2$ with M$_n$ = 9,154 g mol$^{-1}$ and a much narrower D = 1.09 was obtained when the Bu-P$_4$ loading was reduced to 0.2 mol % (Table 1, run 7), suggesting a living polymerization behavior. However, as the system was gradually diluted ([HL]$_2$ = 2.0, 1.6, and 1.3 M in THF), the ROP of polyesters became less controlled: the conversion and M$_n$ were significantly decreased, along with a broader D (Table 1, runs 8–10). Besides, elevating the reaction temperature from −25°C to 41°C also led to a less controlled polymerization (Table 1, runs 11–13). It should be emphasized that very careful drying of all reaction agents is a prerequisite for the success of the ROP methodology in our hands. In the
absence of drying, no polymerization was detected even using highly active catalysts, including PBs (Table S1, run 1, condition: [HL]/[Bu-P4]/[BnOH] = 40/1/0, [HL]₀ = 5.3 M in THF at −25 °C for 12 h).

To verify the living polymerization behavior, the ROP of HL at a feed ratio of [HL]/[Bu-P4]/[BnOH] = 50/0.1/1 at −25 °C in THF was further investigated (Table S2). The polymerization kinetics data strongly support that the polymerization living: the monomer conversion grows linearly with the reaction time (Figure 2A); the ln[M]₀/[M] versus time plot showed a clear first-order kinetic characteristic relative to the monomer consumption [M] (Figure 2B); a linear correlation of the Mn of polyHL with the monomer conversion was observed, and the dispersity D of the obtained polyHL remained low (D ~ 1.1) during the chain propagation stage (Figure 2C).

In addition, the GPC curves for polyHL obtained at varied times were all confirmed to be unimodal (Figure 2D). In addition, the Mn of the resultant polymers increased linearly with increased [HL]/[BnOH] ratio, and the D of the polymers decreased, which further confirmed the living polymerization behavior (Table 1, runs 14 and 15).

Matrix-assisted laser desorption ionization time of flight mass spectrometer (MALDI-TOF MS) was carried out to interrogate the chain-end fidelity of the resultant polyHL produced at a feed ratio of [HL]/[Bu-P4]/[BnOH] = 25/0.1/1 at −25 °C in THF. The MS signals of polyHL (Table 1, run 14) showed only one group of molecular ion peaks with the same spacing of 156.1 g mol⁻¹ (Mₙ = n×156.1 + 131.5), which could be assigned to the linear-polyHL initiated by BnOH (Figure 3A). The NMR spectroscopies showed that both the methylene signal of BnO⁻ (δ 5.12 ppm) and methine signal (δ 3.49 ppm) next to the hydroxyl end group were observed in the ¹H NMR spectrum, and corresponding ¹³C NMR signals were also detected (Figures 3B and S5).

Inspired by the excellent chain-end fidelity of polyHL, telechelic polyHL catalyzed by Bu-P₄ and 1,4-benzenedimethanol (1,4-BDM) was obtained at a feed ratio of [HL]/[Bu-P₄]/[1,4-BDM] = 15/0.15/1. MALDI-TOF MS signals showed only one group of molecular ion peaks (Mₙ = n×156.1 + 161.1), which perfectly matched the expected telechelic polymer structure (Figure S6).

Mechanistic studies for the ROP of HL to polyHL

To investigate the possible mechanism in our system, ROPs at a feed ratio of [HL]/[BnOH] = 50/1 with varied loadings of Bu-P₄ (2, 1, 0.5, 0.4, and 0.2 mol %; Table 1, runs 3–7) were performed. Notably, the Mn of the polyHL produced increased significantly as the loading of Bu-P₄ increased, and the trends of bimodal distribution of the GPC traces have become more apparent as the Bu-P₄ loading increased, which might be due to the existence of other competitive initiation mechanisms (Figure S7). MALDI-TOF spectrum of low MW analogs catalyzed by 1 mol % of Bu-P₄ disclosed three sets of molecular ion peaks with the same MW spacing of 156 g mol⁻¹. The signals were assignable to BnOH end-capped, with no chain end, and water end-capped telechelic polyHL (Figure S8), respectively. As the Bu-P₄ loading increased to 2 mol % relative to HL, the major signal set changed from BnOH chain end to no chain end, and the observed MW increased significantly, and the signals of the oligomers initiated by residual water became negligible (Figure S9).

We next investigated the feasibility for PBs to directly catalyze the ROP of HL without the addition of any alcohol initiator. The ROP reactions were carried out at −25 °C in THF with 2 mol % of Bu-P₄, 2′-Bu-P₂, and 2′-Bu-P₄ (Table S3, run 1–3). After 12 h of reaction, no polymer was generated for 2′-Bu-P₂ and 2′-Bu-P₄. To our surprise, maximum conversion of 88% was achieved for 2′-Bu-P₄ after 12 h and a solid poly-HL sample with unexpected ultrahigh MW of Mₙ = 613.8 kg mol⁻¹ and moderate D = 1.45 was obtained (Table S3, run 3). Adjusting the concentrations of phosphazene base only had small effects on Mₙ and D of the polyHL samples (Table S3, runs 4–6).

To test the controllability of the ROP of HL catalyzed by Bu-P₄ alone, kinetic experiments were performed at −25 °C in THF ([HL]/[Bu-P₄] = 50/1, [M]₀ = 4.0 M) (Figure S10; Table S4). The ln[M]₀/[M] versus time plot revealed that the monomer conversion achieved up to 63% in 4 h, then the polymerization rate tended to slow down and the conversion reached 84% in the subsequent 6–8 h (Figures S10A and S10B). Notably, the Mₙ of polyHL has a clear linear correlation with the monomer conversion throughout the polymerization process, but the dispersity D significantly broadened after half monomer conversion (Figure S10C). The GPC curves also exhibited a gradually emerging bimodal distribution, presumably due to inevitable transesterification reactions at higher monomer conversion (Figure S10D). These data indicated that relatively controlled ROP manners could be realized at which the reactions were quenched within the first 4 h.

MALDI-TOF spectrum for polyHL generated by 2′-Bu-P₄ alone only showed one set of mass peaks assignable to cyclic-polyHL mass peak (Figure S11). No characteristic signals of chain end could be seen in the ¹H and ¹³C NMR spectra either, further supporting the idea that the polymer obtained might have cyclic components (Figures S12 and S13). Notably, high abundance of water-initiated signals could only be detected by MALDI-TOF when the residual water was deliberately reserved in the ROP system (Figure S14).

The topologies of putative cyclic- and linear-polyHLs were further studied by intrinsically viscosity measurements. According to the Mark-Houwink plot (Figure S15), the ratio of [η]cyclic/[η]linear was estimated to be 0.79, which is slightly higher than the theoretically predicted value.¹⁵ This phenomenon might be attributed to the presence of minor linear-polyHL in the putative cyclic products. Besides, the Mark-Houwink exponent a values were 0.70 for cyclic-polyHL and 0.72 for linear-polyHL, suggesting that both polymers were random coils in THF solution.

Plausible chain initiation mechanisms for ROP of HL catalyzed by Bu-P₄/BnOH and 2′-Bu-P₄ alone were studied through NMR spectroscopy. Monitoring the stoichiometric reaction between Bu-P₄ and BnOH at RT in ¹H NMR exhibited the formation of complex [Bu-P₄H⁺••••OBn]. The disappearance of the hydroxyl proton signal at δ 0.92 ppm and chemical shift changes of Bu-P₄ and BnOH were also observed (Figure S16). In addition, in situ NMR tests were performed to gain further mechanistic evidence. By lowering the ratio of HL/BnOH to 1/1, the dominant product observed is consistent with the ring-opened intermediate generated in the initiation step (Figure 5, path 2, and Figure S17). In contrast, only a trace amount of BnO⁻ was observed (Figure S17). These results suggest that chain propagation is slower than the initiation step, thus leading to the accumulation of the initial intermediate with only one repeat unit. The disfavored ring-opening steps might be attributable to the increased steric hindrance surrounding the proposed propagating secondary alkoxides relative to the initiating primary BnO⁻.

Subsequently, the ability of Bu-P₄ to extract an acidic H from HL was also verified. HL and Bu-P₄ were mixed at ratios of 1/1, 2/1, 4/1, and 8/1, respectively, in a J-Yong tube with added toluene-d₈ at RT (no polymerization occurred under these conditions), and corresponding ¹H and ³¹P NMR spectra were taken after sufficient oscillations (Figures S18–S20). Characteristic signals of [Bu-P₄H⁺] (δ 7.92–8.07 ppm in ¹H NMR; δ 12.48 ppm and −23.64 ppm in ³¹P NMR) were clearly observed. However, as the HL/Bu-P₄ feed ratio increased, the intensity of the [Bu-P₄H⁺] signals increased slightly. Meanwhile, the characteristic signals of [Bu-P₄⁻] (δ 1.72, 2.70, and 2.72 ppm in ¹H NMR; δ 4.96 and −25.31 ppm in ³¹P NMR) remained unchanged; that is, Bu-P₄ could not be fully consumed even in the presence of a great excess of HL. These data clearly indicated that Bu-P₄ was only able to deprotonate a tiny portion of HL, which might account for the lack of direct correlation between Bu-P₄ concentration and the Mₙ of cyclic-polyHL produced in this system (vide supra).

Density functional theory (DFT) calculations indicate that deprotonation of the acidic HL monomer at the α position to generate the [α-C=O-C(O)-R]-(Table S13,
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Physical properties of polyHL

The presence of water impurity can presumably interfere with the above-mentioned process. HL with approximately 100 ppm water was prepared for the ROP with Bu-P₄/BnOH at a ratio of [HL]/[Bu-P₄]/[BnOH] = 100/1/1 at −25°C for 12 h. This solution was 5.3 M in THF (Table S12, run 2). Intriguingly, the HL conversion dramatically dropped to 21%, and the polyHL produced had a lower MW of Mₘ = 17,938 g mol⁻¹ with a greatly broadening dispersity of D = 2.258.

Physical properties of polyHL

We next investigated the physical properties of polyHL. The thermosensitivity of polyHL produced by Bu-P₄ and Bu-P₄/BnOH systems were also analyzed through thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both the linear- and cyclic-polyHL exhibited high thermal stability (Tₘ > 325°C). The TGA and derivative thermogravimetry (DTG) curves of cyclic-product showed Tₘ = 323.2°C and Tₘ = 367.3°C (Figure S23), which were 6°C and 12°C higher than those of the linear polymer with a similar MW (Figure S24). These results are consistent with conclusions from another study that the thermal stability of cyclic polymers are generally higher than that of their linear analogs.  

Figure S21). The free energy for the formation of α-H abstracted acylated anion is 26.5 kcal mol⁻¹ less than that of the formation of δ-H abstracted alkyl anion in THF. We also performed quantum-mechanical calculations to evaluate the Gibbs free energy for proton abstraction from BnOH, HL, and H₂O by Bu-P₄ (see supplemental information and Figure S22). The Gibbs free energy for the deprotonations follows the order of BnOH (3.9 kcal mol⁻¹) < HL (5.7 kcal mol⁻¹) < H₂O (9.3 kcal mol⁻¹). Such order suggests that BnO⁻ is the most readily generated active initiating species, while deprotonation of HL is slightly disfavored.

The feasibility of BnO⁻ being the active initiating species was further supported by the observation that alkali metal alkoxydes, such as KOMe, NaOMe, KOEt, NaOEt, KOBu, and NaOBU, could also initiate the ROP of HL at −25°C, giving solid polyHL with a MW of up to 475.7 kg mol⁻¹ and narrow dispersity D (see in Table S5). It is also worth mentioning that the ROPs initiated by alkali metal alcohols were less rapid compared with Bu-P₄ catalyst, which might be attributed to the observed poor solubility of the alkali metal alkoxydes in the reactant mixture.

Table 1. Results of ROP of HL by phosphazene bases/BnOH systems

| Run  | HL/Catalyst/BnOH | Catalyst | Temp. (°C) | Time (h) | [HL]₀ (mol L⁻¹) | Conv. (%) | Mₘ(cal) (g mol⁻¹) | Mₘ(exp) (g mol⁻¹) | D² |
|------|-----------------|----------|------------|----------|----------------|-----------|-----------------|-----------------|----|
| 1    | 50/0.5/1        | Bu-P₁    | −25        | 72       | 5.3            | ND        | −               | −               | −  |
| 2    | 50/0.5/1        | Bu-P₂    | −25        | 120      | 5.3            | 41        | 3,308           | 5,304           | 1.07 |
| 3    | 50/0.5/1        | Bu-P₃    | −25        | 12       | 5.3            | 87        | 6,899           | 19,880          | 1.90 |
| 4    | 50/1/1          | Bu-P₄    | −25        | 12       | 5.3            | 88        | 6,977           | 18,921          | 1.69 |
| 5    | 50/0.25/1       | Bu-P₄    | −25        | 12       | 5.3            | 88        | 6,977           | 13,116          | 1.35 |
| 6    | 50/0.2/1        | Bu-P₄    | −25        | 12       | 5.3            | 88        | 6,977           | 12,885          | 1.23 |
| 7    | 50/0.1/1        | Bu-P₄    | −25        | 8        | 5.3            | 88        | 6,977           | 9,154           | 1.09 |
| 8    | 50/0.1/1        | Bu-P₄    | −25        | 12       | 2.0            | 67        | 5,338           | 6,888           | 1.74 |
| 9    | 50/0.1/1        | Bu-P₄    | −25        | 12       | 1.6            | 58        | 4,635           | 6,834           | 1.39 |
| 10   | 50/0.1/1        | Bu-P₄    | −25        | 12       | 1.3            | 37        | 2,996           | 4,678           | 1.60 |
| 11   | 50/0.1/1        | Bu-P₄    | −9         | 12       | 5.3            | 82        | 6,509           | 10,290          | 1.64 |
| 12   | 50/0.1/1        | Bu-P₄    | 28         | 12       | 5.3            | 65        | 5,182           | 5,726           | 2.29 |
| 13   | 50/0.1/1        | Bu-P₄    | 41         | 12       | 5.3            | 52        | 4,167           | 5,479           | 2.18 |
| 14   | 25/0.1/1        | Bu-P₄    | −25        | 12       | 5.3            | 87        | 3,504           | 4,127           | 1.11 |
| 15   | 100/0.2/1       | Bu-P₄    | −25        | 12       | 5.3            | 88        | 13,846          | 19,601          | 1.08 |

Conditions: HL = 0.104 g, (0.67 mmol) in THF; HL were added to a Bu-P₄/BnOH mixture.

*Monomer conversion were measured by ¹H NMR.

Mₘ(cal) = ([HL]/[BnOH]) × C(0) × Mₘ(cal) + Mₘ(BnOH).

Mₘ and D were determined by GPC at 40°C in THF relative to PMMA standards.
linear one. Glass slides were utilized as the rigid substrate, and a sheet of A4 paper (15 x 2.6 cm) was used as the face substrate (Figure 4A). The polyHL samples were evenly coated on the glass slides by using a coating blade. Cross-sectional scanning electron microscope (SEM) showed that the thin film had a fair uniform thickness of 36.9 ± 1.2 μm (Figure 4B). The test was performed at 25°C on an Instron 5966 universal testing instrument at 180° peel angle at a rate of 10 mm min⁻¹. To our delight, polyHL 319, polyHL 562, and polyHL 160 (the numbers refer to the sample with an Mn of 319, 562, and 160 kg mol⁻¹, respectively) exhibited adhesion with peel strength of 3.8 ± 0.12, 3.5 ± 0.20, and 1.5 ± 0.65 N cm⁻¹, respectively (Figure 4C; Table S6). The peel strength of polyHL 319 and polyHL 562 were relatively higher than those of commercialized 3M Scotch tapes tested under the same test conditions (3M 665, 2.4 ± 0.009 N cm⁻¹; 3M 810, 1.9 ± 0.031 N cm⁻¹) and vinyl electrical tape (3M 1,600, 0.8 ± 0.17 N cm⁻¹). PolyHL 160 exhibited a peel strength of 1.5 ± 0.65 N cm⁻¹, comparable with that of the 3M 810 Scotch tape. In addition, a high MW polymer sample (Mn = 613.8 kg mol⁻¹, D = 1.45, Table S3, run 3) was solvent-cast into a PTFE mold to form a transparent and colorless polymer film with good flexibility and viscoelasticity (Figure 4D).

Development of methodology for chemical recycling of polyHL to HL

Van’t Hoff analysis was performed to calculate the thermodynamic parameters of the polymerization (Figures S27 and S28; Tables S7–S9). According to Dainton’s equation, the change in enthalpy (ΔH°) and entropy (ΔS°) were calculated to be -1312 kJ mol⁻¹ and -49.09 J mol⁻¹ K⁻¹, respectively, which further gave a Tc of -6°C in THF at [HL]₀ = 1.0 mol L⁻¹.

To test the chemical recyclability, cyclic-polyHL with Mn in the range of 300–400 kg mol⁻¹ were employed. Initially, several trifluoromethanesulfonyl metal salts, including Ag(CF₃SO₂)₂, Cu(CF₃SO₂)₂, Fe(CF₃SO₂)₃, Sc(CF₃SO₂)₃, and Y(CF₃SO₂)₃ were employed to catalyze the depolymerization of polyHL in a sealed tube toluene ([HL]₀ = 0.5 M) at 120°C for 24 h (Table S10, runs 1–5). However, only Fe(CF₃SO₂)₃ and Sc(CF₃SO₂)₃ gave 53% and 27% recovery of HL monomer, respectively (Table S10, runs 3 and 4). FeCl₃, Fe(acac)₃, SnOct₂, DBTDL, and Bu₃P gave no obvious reactivity even at a higher temperature of 150°C in mesitylene for 12 h (Table S10, runs 6–10). We next examined ZnCl₂ in toluene at 130°C, 140°C, and 150°C for 12 h, respectively, and found that the monomer conversion increased with an elevated temperature (Table S10, runs 11–13, 31%, 39%, and 54%, respectively). Particularly, when employing more polar 1,2-dichlorobenzene (o-DCB) at 150°C and 160°C, the monomer recovery significantly increased to 91% and 100%, respectively (Table S10, runs 14 and 15), thus achieving a complete chemical recycling procedure by zinc chloride catalyst.
remained constant over 12 h (Table S11, runs 6 and 7), indicating a much more rapid depolymerization process. When the system was diluted to 0.1 M at 80°C, 93% recovery of HL monomer was achieved in 3 h (Table S11, run 8), and 100% recovery was achieved in 12 h (Figure S29; Table S11, run 9). Finally, the validity of our catalytic method to chemically recycle linear-polylHL was confirmed with ZnCl₂, giving 100% recovery of HL in o-DCB at 160°C in 12 h (Figure S30).

**DISCUSSION**

Our mechanistic studies may rationalize why HL was observed to be non-polymerizable previously. Firstly, for the initiation step, our data support a multiple competitive initiating mechanism (Figure 5), including (path 1) direct abstraction of the proton from the C-H bond vicinal to the carbonyl group of HL (the most acidic proton in the lactone, Figure S21) to generate highly reactive species, (path 2) hydroxyl deprotonation of alcohols to form alkoxides, and (path 3) deprotonation of residual water to form hydroxide. Compared with lactones without a substituent at the carbon vicinal to the carbonyl group, the ethyl substituent at the same carbon lowers the acidity of the C-H bond and also sterically hinders the approach of bulky bases, especially Bu₃P or, thus disfavoring the polymerization process through path 1. Secondly, for the subsequent nucleophilic ring-opening step, both ethyl substituents are vicinal to the ester group, which sterically hinders the approach to the ester by any nucleophiles, thus increasing corresponding activation barriers no matter which initiating mechanism leads to the ring-opening nucleophile. The experimentally measured thermodynamic data for ROP of HL also clearly indicated that the two ethyl substituents of HL greatly increase the entropic penalty compared with non-mono-substituted 4-lactones, thus resulting in significantly less thermodynamically favorable polymerization than the less-substituted counterparts (Table S9). Therefore, the ROPs of HL are both thermodynamically and kinetically challenging, requiring judiciously selected reaction conditions to allow for polymerization, including sub-zero temperatures, prolonged reaction times, and highly concentrated conditions (vide supra).

Our work subsequently showed that the polymerization of HL is highly sensitive to water impurity in the reaction system. In essence, the H₂O-initiated oligomers contain a carboxylic acid end group, which should have a strong tendency to quench the active alkoxide species for the chain propagation process and form dormant species featured by a terminal carboxylate anion (Figure 5, path 3). Potassium benzoate and cesium formate were tested as potential ROP initiators under our optimized conditions (Table S12, run 3 and 4, 7, T = 25°C, t = 24 h, [HL]₀ = 5.0 M in THF). At elevated temperature T = 30°C, potassium acetate (KOAç) was also employed at a ratio of [HL]/[KOAç]/[BnOH] = 50/1/1 and 50/1/0 (Table S12, runs 5 and 6). However, no HL conversion was detected for all three species. These observations confirm that carboxylate is a dormant species. As such, rigorous drying is the key to the present success of ROP of HL, or the formation of carboxylate would inhibit the reaction.

**CONCLUSION**

In conclusion, we have developed the first methodology to polymerize six-membered lactone with two substituents vicinal to the ester group, which enables the first synthesis of chemically recyclable solid polyesters with a high CO₂ content, high MW, and promising adhesive properties comparable with commercial counterparts by only using CO₂ and bulk chemicals as the starting materials. This work provides a brand-new avenue to potential large-scale utilization of CO₂ as a main chemical feedstock, while the chemical recyclability may allow for fixation of CO₂ in solid polymeric materials over a long period of time.

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AUTHOR CONTRIBUTIONS

B.L. conceived the project and analyzed the data. Y.L. performed experiments, analyzed the data, and drafted the manuscript. L.X. conducted the DFT calculations and wrote sections of the manuscript. N.G. and Y.-S. performed part of the syntheses of the monomer and samples. All authors discussed the experimental and theoretical results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

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