

## Degradable Polymer Structures from Carbon Dioxide and Butadiene

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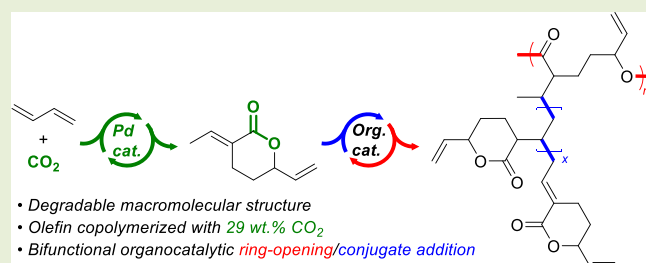


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Supporting Information

**ABSTRACT:** The utilization of carbon dioxide as a polymer feedstock is an ongoing challenge. This report describes the catalytic conversion of carbon dioxide and an olefin comonomer, 1,3-butadiene, into a polymer structure that arises from divergent propagation mechanisms. Disubstituted unsaturated  $\delta$ -valerolactone **1** (EVL) was homopolymerized by the bifunctional organocatalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) to produce a hydrolytically degradable polymer. Isolation and characterization of reaction intermediates using  $^1\text{H}$ ,  $^{13}\text{C}$ , COSY, HSQC, and MS techniques revealed a vinylogous 1,4-conjugate addition dimer forms in addition to polymeric materials. Polymer number-average molecular weights up to 3760 g/mol and glass transition temperatures in the range of 25–52 °C were measured by GPC and DSC, respectively. The polymer microstructure was characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , FTIR, MALDI-TOF MS, and ESI tandem MS/MS. The olefin/ $\text{CO}_2$ -derived materials depolymerized by hydrolysis at 80 °C in 1 M NaOH. This method and the observed chemical structures expand the materials and properties that can be obtained from carbon dioxide and olefin feedstocks.



The majority of thermoplastics are produced from olefin feedstocks such as ethylene, propylene, styrene, vinyl chloride, and 1,3-butadiene.<sup>1</sup> Polymerization of these monomers generates macromolecules containing thermodynamically favorable carbon–carbon backbones that resist hydrolysis and environmental degradation. The catalytic incorporation of carbon dioxide ( $\text{CO}_2$ ) into the chain theoretically affords a hydrolytically degradable polyester, but synthetically renders the alternating copolymerization reaction both thermodynamically and entropically unfavorable in practice.<sup>2–4</sup> Most syntheses of  $\text{CO}_2$ -based polymers rely on high-energy comonomers<sup>5</sup> such as oxiranes,<sup>6–10</sup> aziridines,<sup>11,12</sup> or alkynes.<sup>13–16</sup> Herein we report a degradable copolymer derived from the catalytic conversion of  $\text{CO}_2$  and the abundant olefin feedstock 1,3-butadiene (BD).

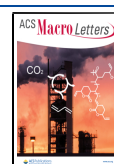
Inoue and Musco discovered coupling  $\text{CO}_2$  and BD with a phosphine-ligated palladium catalyst produces the unsaturated disubstituted delta-valerolactone 2-ethyliden-6-hepten-5-olide (**1**: EVL, Scheme 1a).<sup>17–19</sup> Behr further demonstrated the synthesis of **1** in a continuous reactor.<sup>20–28</sup> The homopolymerization of **1** was first described by Nozaki and co-workers to yield a poly(acrylate) structure (**2**, Scheme 1b) with high glass transition temperatures ( $T_g$ s) up to 192 °C.<sup>29–31</sup> Postpolymerization modification of the polylactone **2** results in reversible hydrolysis and aminolysis.<sup>30</sup> In addition to radical homopolymerization, the copolymerizations of EVL (**1**) with dithiols,<sup>32</sup> ethylene,<sup>33</sup> or methacroyl moieties<sup>34</sup> produce polysulfide, polyolefin, and polyacrylate repeating units, respectively.

Although extensive advances in ring-opening polymerization (ROP) of lactones have been made,<sup>35–49</sup> no successful ring-opening homopolymerization of EVL (**1**) has been described. Recently, Ni and co-workers achieved the copolymerization of EVL (**1**) with the highly strained  $\beta$ -butyrolactone (**3**: BBL) to produce a polyester structure (**4**) with up to 50 mol % EVL incorporation and number-average molecular weights ( $M_n$ s) of 450 g/mol; lower EVL content (16 mol %) afforded higher  $M_n$ s of 1700 g/mol (Scheme 1c).<sup>37</sup> The resulting polyester structure is degradable under hydrolytic conditions. Regarding the homopolymerization of EVL via ring-opening mechanisms, Nozaki, Ni, Carpentier, and Guillaume have reported the lack of ROP reactivity for EVL and its hydrogenated derivatives (Scheme 1d).<sup>31,36,37</sup>

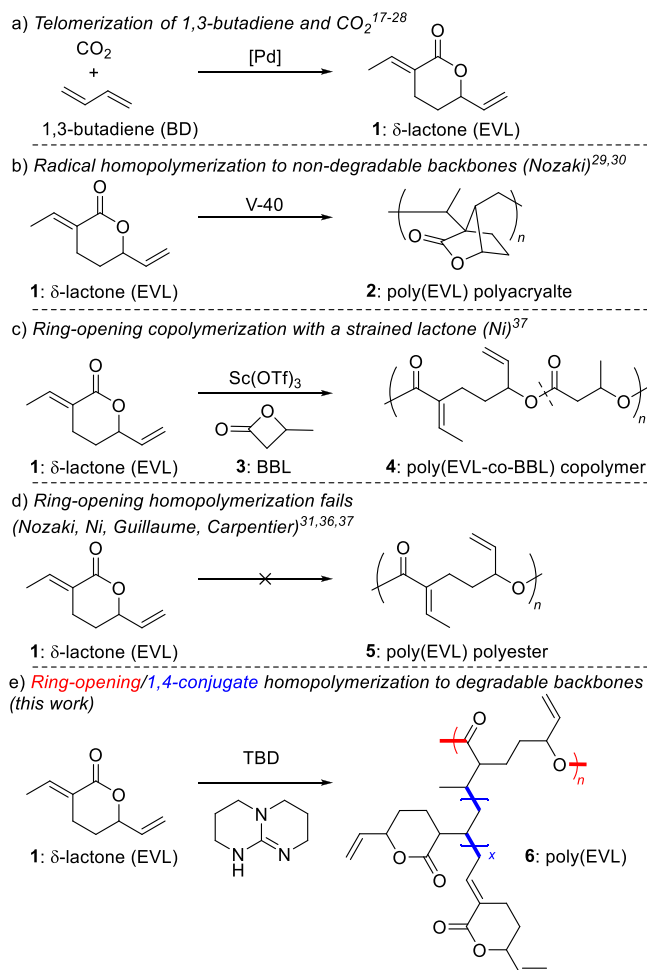
Herein, we report the bifunctional organic ROP catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)<sup>41–46</sup> produces degradable macromolecules from EVL (**1**), which we conclude arise from a combined vinylogous 1,4-conjugate addition/ring-opening polymerization reaction (Scheme 1e). This advance identifies previously unreported olefin-derived polymer structures that contain 29 wt %  $\text{CO}_2$  and are hydrolytically depolymerized.

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## Scheme 1. Synthesis and Polymerizations of EVL (1)



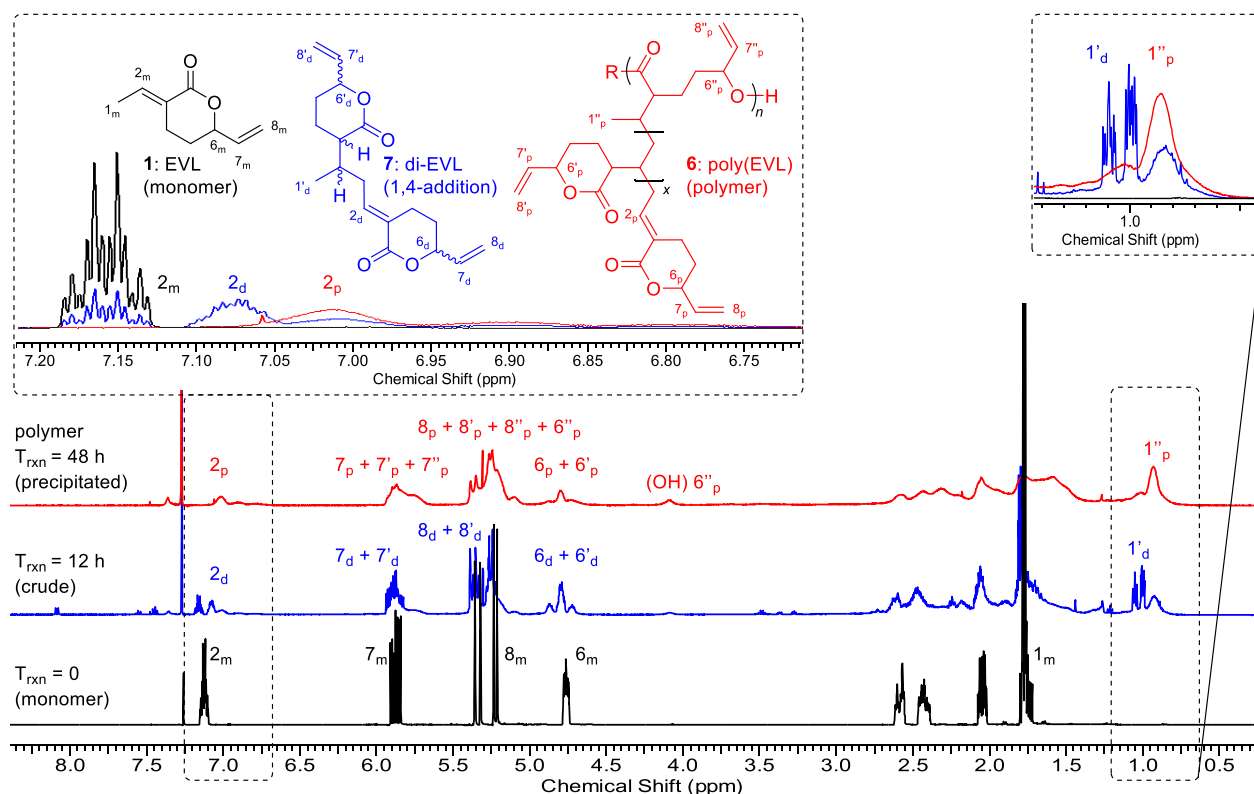
Initial screening of vacuum-distilled EVL (1) and several ring-opening polymerization catalysts<sup>36,39,40</sup> with and without solvents revealed a high-viscosity material was obtained when monomer, TBD, and benzyl alcohol initiator were combined in a molar ratio of 200:10:2, respectively, under solvent-free conditions (entry 2, Table 1). Precipitation in Et<sub>2</sub>O and gel-permeation chromatography (GPC) of the solids confirms polymeric material was formed with low  $M_n$  (2120 g/mol) and a dispersity ( $\bar{D}$ ) of 2.17, indicative of a nonliving polymerization. The <sup>1</sup>H NMR revealed that the reaction between EVL monomer (black trace, Figure 1) and TBD/BnOH produced a polymer microstructure (red trace, Figure 1) inconsistent with the expected ROP product 5. The 2-position  $\beta$ -H of the unsaturated lactone moiety of monomeric EVL (H-resonance 2<sub>m</sub>,  $\delta$  = 7.16 ppm) was observed in a 1:3 ratio with the 7-position vinyl C–H of the vinyl lactone in the polymer (H-resonance 7<sub>p</sub>,  $\delta$  = 5.87 ppm); a 1:1 ratio would be expected for ROP product 5. Additionally, both the <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figures S11–S13) of the polymer were inconsistent with those reported previously by Nozaki<sup>29,30</sup> or Ni.<sup>37</sup>

Crude <sup>1</sup>H NMR analysis of a reaction aliquot after 12 h (blue trace, Figure 1) indicated the formation of an intermediate compound during the course of the reaction. This molecule was isolated, purified by silica-gel column chromatography, and identified as dimeric lactone 7: di-EVL through a combination of MS and NMR experiments (<sup>1</sup>H, <sup>13</sup>C, COSY, HSQC, Figures S5–S10). Diagnostic resonances in the aliphatic region ( $\delta$  = 0.99–1.07 ppm, Figure 1) appear during the course of the reaction, indicating transformation of one of the acrylate moieties. The <sup>1</sup>H integration of the 2- and 7-positions in the dimer (i.e., 2<sub>d</sub>:7<sub>d</sub> + 7'<sub>d</sub>, Figures 1 and S5) are equal to 1:2 in the purified material, consistent with the di-EVL (7) assignment. Dimer 7 is generated as a mixture of eight diastereomers, as is evident in the <sup>13</sup>C NMR (Figures S6 and S7), which is due to the racemic starting material ( $\pm$ )-1 and

Table 1. Results of TBD-Catalyzed Polymerization of EVL (1)<sup>a</sup>

| entry (#) | TBD (mmol) | BnOH (mmol) | [M] <sub>0</sub> /[TBD] <sub>0</sub> /[BnOH] <sub>0</sub> (mol equiv) | yield of 6 (%) | $M_n^b$ (GPC; g/mol) | $M_w^b$ (GPC; g/mol) | $\bar{D}^b$ ( $M_w/M_n$ ) | $T_g^c$ (°C) |
|-----------|------------|-------------|-----------------------------------------------------------------------|----------------|----------------------|----------------------|---------------------------|--------------|
| 1         | 0.20       | 0.10        | 200:4:2                                                               | 15             | 3760                 | 7930                 | 2.11                      | 33           |
| 2         | 0.50       | 0.10        | 200:10:2                                                              | 40             | 2120                 | 4600                 | 2.17                      | 49           |
| 3         | 0.50       | 0.25        | 200:10:5                                                              | 22             | 2120                 | 5050                 | 2.38                      | 25           |
| 4         | 0.50       | 0.50        | 200:10:10                                                             | 19             | 2100                 | 4240                 | 2.05                      | 38           |
| 5         | 1.00       | 0.25        | 200:20:5                                                              | 45             | 1810                 | 3830                 | 2.12                      | 40           |
| 6         | 1.00       | 0.50        | 200:20:10                                                             | 36             | 1350                 | 2600                 | 1.93                      | 38           |
| 7         | 0.20       |             | 200:4:0                                                               | 36             | 3490                 | 8950                 | 2.56                      | 37           |
| 8         | 0.50       |             | 200:10:0                                                              | 57             | 2220                 | 4510                 | 2.04                      | 42           |
| 9         | 1.00       |             | 200:20:0                                                              | 42             | 1710                 | 5150                 | 3.01                      | 52           |

<sup>a</sup>Reagents and conditions: 10 mmol EVL (1), TBD, BnOH (entries 1–6), neat, 25 °C, 48 h; precipitated in Et<sub>2</sub>O (250 mL) twice. <sup>b</sup>Determined with gel-permeation chromatography (GPC) in THF relative to polystyrene standards. <sup>c</sup>Determined with differential scanning calorimetry (DSC) using midpoint half height analysis values of the second heating cycle from –50 to 150 °C.

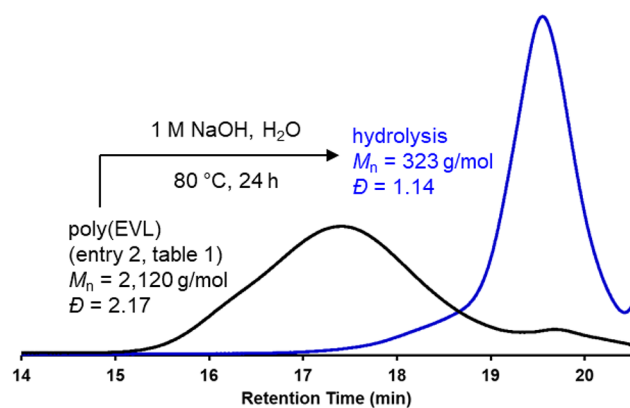


**Figure 1.**  $^1\text{H}$  NMR analysis of monomer (black), crude polymerization aliquot (blue), and precipitated polymer (red); 500 MHz,  $\text{CDCl}_3$ .

lack of stereoselectivity in the dimerization. Exclusive formation of the (*E*)-alkene is observed in the unsaturated lactone moiety. We propose di-EVL is formed by a formal vinylogous 1,4-conjugate Michael addition of one TBD-activated dienolate of EVL to the  $\alpha,\beta$ -unsaturated carbonyl of a second EVL molecule (Figure S14).

Having identified the vinylogous Michael reactivity of EVL with the bifunctional organocatalyst, the 1:3 ratio of  $\beta$ -H resonance/vinyl lactone moiety (i.e., 2-position/7-position) observed in the polymer  $^1\text{H}$  NMR spectrum could be rationalized as concomitant ring-opening ( $n$  repeat units) and conjugate addition propagation ( $x$  repeat units; **6**, Figure 1). Within the ROP units is a distribution of  $x$  integers and  $x$  can equal 0 (as in **7**: di-EVL), but the average distribution throughout the material is  $x_{\text{avg}} = 1$ , a conclusion we reach based on the above  $^1\text{H}$  NMR integrations. Based on Ni's copolymerization assignments,<sup>37</sup> we observed no ROP of EVL without conjugate addition (i.e., microstructure **5**, Scheme 1 was not observed). We have no evidence at this time excluding ring-opening of the conjugate addition lactones (i.e.,  $x$  units), but all materials behaved as soluble thermoplastics, indicating minimal cross-linking (Figure S23).

Mass spectrometry (MS) studies were conducted on the isolated polymer, including tandem MS/MS (Figure 2) and MALDI-TOF MS (Figure S15). MALDI-TOF MS analysis of poly(EVL) (**6**; entry 2, Table 1) corroborates the macromolecule formation ( $M_n = 1080$  g/mol,  $\bar{D} = 1.17$ ). The discrepancy between MALDI-TOF and GPC analysis is attributed to the larger radius of gyration for poly(EVL) (**6**) relative to the PS standards in GPC. The MALDI-TOF MS exhibits a polymeric distribution with an average repeat mass of a single EVL unit (152.02 g/mol) rather than increments of di-EVL. This distribution suggests conjugate addition is



**Figure 2.** GPC analysis of poly(EVL) and the crude degradation product after hydrolysis in 1 M NaOH at 80 °C.

competitive with ring-opening polymerization and P(EVL) is not formed via conjugate addition to di-EVL and subsequent ROP of di-EVL, alone. This was further corroborated by low rates of polymerization and conversion when di-EVL was subjected to polymerization conditions. Of note, the MALDI molar mass distribution ( $152.08n + 140.12$  g/mol) is observed with a TBD end-group (140.12 g/mol) at the  $\alpha$  end and a hydrogen atom as the  $\omega$  end group. Repeating the polymerization under identical conditions, but excluding BnOH (entry 8, Table 1), also produced polymeric material ( $M_n = 2220$  g/mol,  $\bar{D} = 2.04$  by GPC). We conclude that TBD is a catalyst for conjugate addition as well as both the initiator and the mediator in the ring-opening propagation via an acyl ammonium intermediate, similar to a previous zwitterionic polymerization of lactones.<sup>48–50</sup>

To better understand the microstructure of the polymers, tandem ESI MS/MS was performed on entry 2 in which the ion fragment 900.5360  $m/z$  was sequentially fragmented (Figure S16). The observed loss of 322 g/mol is consistent with carbo-alkoxy elimination in the polyester backbone of the dimeric ROP repeat unit where  $x = 0$ . Consecutive fragments of 152 g/mol are assigned to the loss of conjugate addition repeat units ( $x$ ) via retro-Michael pathways.

The effects of monomer/catalyst/initiator ratios on molecular weight and thermal properties are reported in Table 1. Increasing TBD/monomer from 1:50 to 1:20 afforded higher yields of polymer (entries 1 and 2). Increasing BnOH/monomer from 1:100 to 1:20 with a constant TBD/monomer loading of 1:20 resulted in negligible changes in the molecular weight (entries 2–4), but a significant decrease in yield. This observation is consistent with TBD-acyl intermediates as the active species in a noncontrolled propagation mechanism, a moiety which is deactivated by BnOH addition. In the absence of BnOH, increasing TBD/monomer ratios from 1:50 to 1:10 (entries 7–9) decreased  $M_n$  from 3490 to 1710 g/mol. The glass transition temperature ( $T_g$ ) of poly(EVL) ranged from 25–52 °C and was not well-correlated with molecular weight.

Interestingly, in some samples the two variables were inversely related (entries 7–9). We hypothesize the conjugate addition and ring-opening mechanisms produce microstructures with different thermal properties.

Chemical degradation of the polymer product ( $M_n = 2120$  g/mol, entry 2, Table 1) was studied under hydrolytic conditions (Figure 2). A sample of poly(EVL) was heated in basic water (1 M NaOH, 80 °C) for 24 h, acidified with 1 M HCl, and extracted with EtOAc. The resulting crude products were absent of polymeric species by GPC analysis (Figure 2). Comparing the  $^1\text{H}$  NMR of P(EVL) and EVL hydrolysis revealed the hydroxyacid is the major degradation product for both materials (Figure S22).

In conclusion, the catalytic telomerization of 1,3-butadiene with  $\text{CO}_2$  produces lactone **1** (EVL), which is capable of undergoing vinylogous 1,4-conjugate addition to form dimer **7** (di-EVL) and polymerization to degradable macromolecules (**6**). The effects of catalyst and initiator were investigated, revealing that the polymerization does not proceed by a controlled chain-growth mechanism and produces amorphous polymers with  $T_g$ s between 25 and 52 °C. Further investigations into the mechanisms of propagation and depolymerization will be described separately. The findings reported herein indicate the modular reactivity of unsaturated lactone (**1**) and expands the molecular structures that can be accessed through the catalytic activation of  $\text{CO}_2$  and olefins.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.1c00523>.

Detailed experimental procedures for monomer synthesis, polymerizations, and characterization data (1D and 2D NMR, GPC, DSC, TGA, IR, MALDI-MS, and tandem MS<sup>2</sup>) (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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### Notes

The authors declare no competing financial interest.

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