

# Isomerization Cationic Ring-Opening Polymerization of CO<sub>2</sub>-Based Disubstituted- $\delta$ -Valerolactone

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**ABSTRACT:** The challenging ring-opening homopolymerization of  $\alpha$ -ethylidene- $\delta$ -vinyl- $\delta$ -valerolactone (EVL), derived from CO<sub>2</sub> and 1,3-butadiene, has aroused extensive attention in consideration of economic efficiency and functionalization potential. Here, we achieve the first cationic ring-opening polymerization (CROP) of EVL, yielding well-defined polyester PEVL with number average molecular weight up to 12.8 kg/mol and low dispersity of 1.2. The obtained PEVL contains two kinds of structural units derived from EVL and three kinds of alkenyl groups, indicating an isomerization during propagation. The isomerization is necessary to the propagation, evidenced by density functional theory (DFT) calculation and unavailable CROP of the semi-hydrogenated EVL derivative without  $\delta$ -vinyl group ( $\alpha$ -ethylidene- $\delta$ -ethyl- $\delta$ -valerolactone). The fast intramolecular transfer reaction and slow initiation result in the cyclic topology fidelity of PEVL, providing the first example of quantitative formation of cyclic polyester in CROP. PEVL is degradable and recyclable, possessing a low glass transition temperature ( $T_g$ ) of -33.6 °C, while the product after modification with 1-octadecanethiol exhibits a melting point ( $T_m$ ) of 42.2 °C.

The utilization of carbon dioxide (CO<sub>2</sub>) to produce high-valued chemicals is attractive considering its practical advantages, such as abundance, economic efficiency and lack of toxicity. Due to the inherent inertness of CO<sub>2</sub>, its direct copolymerization with olefins to generate polymeric materials is promising but challenging.<sup>1,2</sup> An ingenious alternative method is the polymerization of intermediate  $\alpha$ -ethylidene- $\delta$ -vinyl- $\delta$ -valerolactone (EVL, also known as EVP, Figure S1-2), an unsaturated disubstituted  $\delta$ -valerolactone, which is efficiently prepared by telomerization of CO<sub>2</sub> and 1,3-butadiene.<sup>3,4</sup> Nozaki and co-workers firstly exploited EVL to produce undegradable functional polyolefins via radical<sup>2,5,6</sup> and coordinate<sup>7</sup> polymerizations of its C=C double bonds. Our group made use of its lactone ring to synthesize

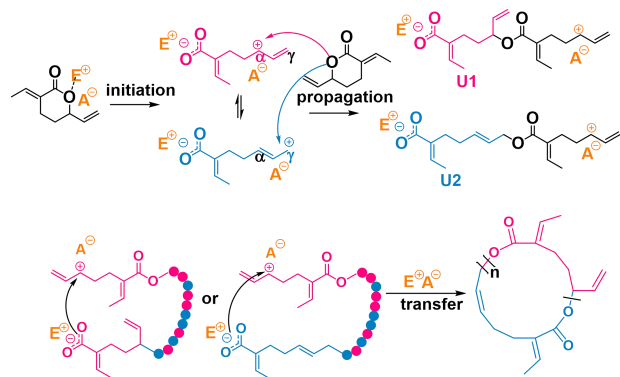
functionalizable polymer via reversible addition-fragmentation chain transfer,<sup>8</sup> “thiol-ene” click<sup>9,10</sup> and coordinate<sup>11</sup> polymerizations.

The first successful attempt to produce degradable polyester by ring-opening polymerization (ROP) of EVL was reported through cationic ring-opening copolymerization of EVL with  $\beta$ -butyrolactone catalyzed by scandium triflate (Sc(OTf)<sub>3</sub>).<sup>12</sup> Eagan and co-workers found that EVL underwent 1,4-conjugate addition and polymerization resulting in an ill-defined polyester with number average molecular weight ( $M_n$ ) up to 3.7 kg/mol catalyzed by the organic base 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).<sup>13</sup> They demonstrated that the conjugate addition was competitive with ROP of EVL preventing the synthesis of polyester with high molecular weight. We took advantages of the conjugate addition to activate EVL and provided a one-pot one-step “scrambling polymerizations” of EVL with  $\epsilon$ -caprolactone obtaining polyesters with controllable topologies.<sup>14</sup> Tonks', Lin's and our group deconjugated EVL via hydrogenation<sup>15,16</sup> and reversible Michael addition<sup>17</sup> to yield activated EVL derivatives and realized their controlled/living anionic ring-opening polymerization (AROP) to produce recyclable and functional polyesters. Li's and Lin's group suppressed the conjugate addition by decreasing polymerization temperature and used Lewis pair catalysts to realize the AROP of EVL yielding well-defined polyester with  $M_n$  up to 2.1 and 6.5 kg/mol respectively.<sup>18,19</sup>

It is obvious that the inherent  $\gamma$ -proton acidity of tiglate ester group in EVL disturbs its AROP,<sup>20,21</sup> while it is supported that its cationic ROP (CROP), which is not obliged to base, is more promising in homo-ROP of EVL in the absence of annoying conjugate addition side reaction.<sup>12,22</sup> Based on this hypothesis, we seek for strong cationic initiators to investigate the homo-ROP of EVL, to which less attention has been paid. Meerwein salts and triphenylcarbenium salts, regarded as robust cationic initiators have shown their excellent application in the ROP of thionolactone<sup>23</sup> and dioxolane<sup>24</sup>. Herein, we report

the first CROP of EVL initiated by commercial robust cationic initiators (*e.g.*,  $\text{Ph}_3\text{C}^+\text{PF}_6^-$ ) yielding well-defined cyclic polyester PEVL with  $M_n$  up to 12.8 kg/mol and low dispersity ( $\mathcal{D}$ ) of 1.2. Interestingly, an isomerization based on the  $\delta$ -vinyl group of EVL occurs during its ROP, producing polyester with EVL unit and isomerized EVL unit. By decreasing temperature from 10 to  $-30$  °C, the  $M_n$  of PEVL increases from 6.5 to 12.8 kg/mol. PEVL is degradable, recyclable and ready for post-polymerization functionalization by “thiol-ene” click reaction.

Guided by our hypothesis above, commercial cationic initiators are screened for the CROP of EVL at 0 °C in bulk (Table S1). Initiated by  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  (Entry 1 in Table S1), a moderate conversion (40.8% for 7 d, Figure S3) of EVL is achieved, and PEVL with  $M_n, \text{RI} = 6.0$  kg/mol or  $M_n, \text{MALS} = 7.1$  kg/mol (determined by size exclusion chromatography (SEC) with refractive index (RI) or multiangle light scattering (MALS) detectors, respectively) is prepared.



**Scheme 1.** The CROP of EVL initiated by  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  ( $\text{E}^+$  represents  $\text{Ph}_3\text{C}^+$ ,  $\text{A}^-$  represents  $\text{PF}_6^-$ ).

The obtained PEVL sample has been analyzed in detail by NMR spectra to conclude that an isomerization happens during the CROP of EVL (Scheme 1). In the  $^1\text{H}$  NMR spectrum (Figure 1A), the signal at 6.84-7.02 ppm ( $\text{H}_3$ ) is attributed to the proton of C=C double bond adjacent to carbonyl group, confirming that EVL undergoes a ring-opening process during polymerization rather than any reactions based on the conjugate C=C double bond. The methylene proton ( $\text{H}_{10}$ ) signal of isomerized EVL repeating unit (U2) is assigned to 4.55-4.67 ppm while the methine proton ( $\text{H}_9$ ) signal originated from EVL repeating unit (U1) at 5.30 ppm is overlapped with the methylene protons ( $\text{H}_6$ ) signal of vinyl group in U1 at 5.16-5.27 ppm. The signals at 5.57-5.85 ppm are ascribed to the methine protons ( $\text{H}_5, \text{H}_7, \text{H}_8$ ) of the isolated C=C double bonds. The U2 proportion in

PEVL calculated by the intensities of  $\text{H}_{10}$  versus  $\text{H}_3$  is 61% and the U1 proportion determined by the intensities of  $\text{H}_{5,6,9}$  versus  $\text{H}_3$  is 38%.

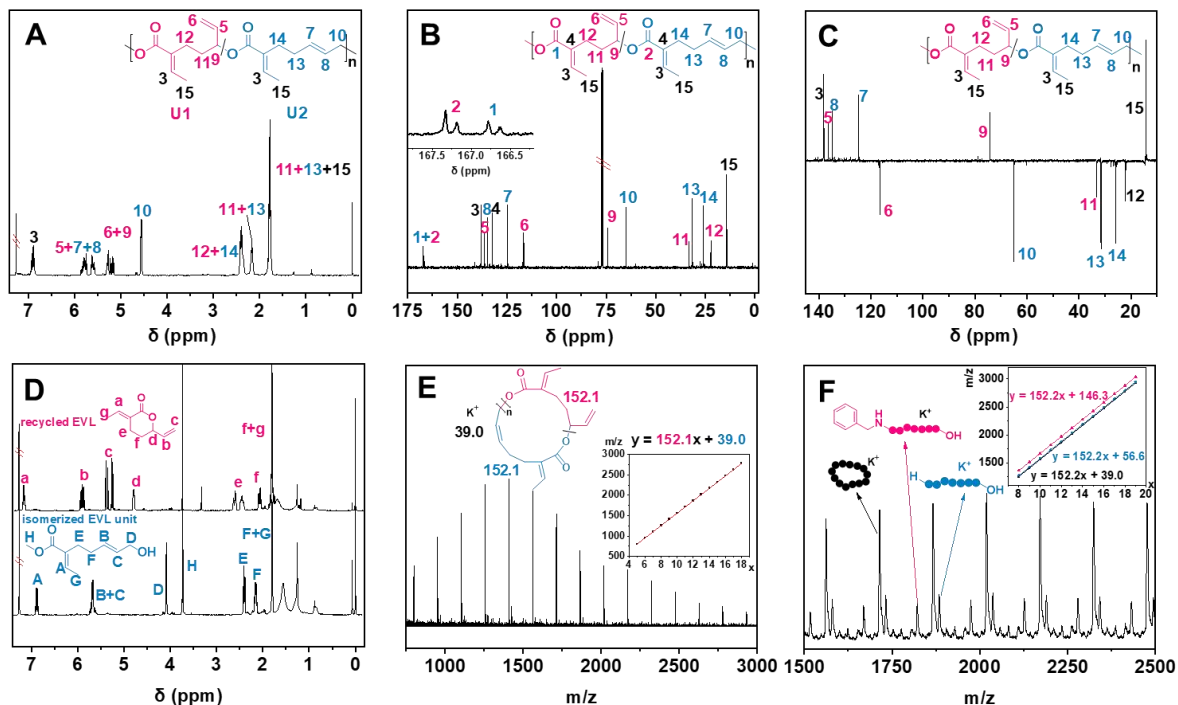
In the  $^{13}\text{C}$  NMR spectrum (Figure 1B), there are two kinds of signals of alkoxy carbon next to the carbonyl group ( $\text{C}_9$  at 74.26 ppm,  $\text{C}_{10}$  at 65.01 ppm) and two sets of carbonyl group signals ( $\text{C}_1$  adjacent to  $\text{C}_{10}$  at 166.63-166.79 ppm,  $\text{C}_2$  adjacent to  $\text{C}_9$  at 167.18-167.33 ppm), in good accordance with the two structural units (U1 and U2). The signals of C=C double bond of U2 in the backbone appear at 124.37 ppm ( $\text{C}_7$ ) and 134.86 ppm ( $\text{C}_8$ ). The DEPT 135 spectrum (Figure 1C) authenticates that  $\text{C}_{10}$  is a secondary carbon whose signal is inverted while  $\text{C}_{7-9}$  are tertiary ones with upright signals. The above assignments are affirmed by the coupling signals of  $\text{H}_9$ - $\text{C}_9$  and  $\text{H}_{10}$ - $\text{C}_{10}$  in the  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum (Figure S4) and those of  $\text{H}_5$ - $\text{C}_9$ ,  $\text{H}_6$ - $\text{C}_9$ ,  $\text{H}_7$ - $\text{C}_{10}$ , and  $\text{H}_8$ - $\text{C}_{10}$  in the  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum (Figure S5).

The alcoholysis of PEVL by methanol is carried out to confirm the existence of the structural unit U2. The methanolized U2 is separated by column chromatography and the proton signals of its isolated C=C double bond ( $\text{H}_B$  and  $\text{H}_C$ ) appear at 5.67 ppm (Figure 1D, bottom) which are totally different from those (5.91 and 5.09-5.28 ppm) of methanolized EVL (Figure S6). The structure is well confirmed by its  $^{13}\text{C}$  and  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectra (Figure S7-8). EVL is recovered from catalyst-free esterification of the methanolized U1 by removing the generated water (Figure 1D). The characterization of obtained polymer indicates the isomerization based on the  $\delta$ -vinyl group of EVL. The isomerization CROP endows the obtained polyester with three kinds of C=C double bonds, including a conjugated one, an isolated pendent alkenyl group and another one in the backbone.

In the Matrix-assisted laser desorption/ionization time-of-flight mass spectrum (MALDI-ToF MS), only one population is observed and the mass interval is 152.1 Da corresponding to the molar mass of EVL (Figure 1E). The observation of the molecular weight of polymer chain without any residues of initiators or terminators like methanol added during the work-up suggests the cyclic topology of PEVL. To further confirm the cyclic topology, the ammonolysis of PEVL is carefully conducted to obtain its linear analogue. As detected by MALDI-ToF MS, part of cyclic PEVL is broken by benzyl amine and water (Figure 1F). No shoulder of low molecular weight appears on the SEC curve and the  $M_n$  keeps constant (before: 6.8 kg/mol,  $\mathcal{D} = 1.4$ ; after: 7.2 kg/mol,  $\mathcal{D} = 1.4$ , Figure S9) thanks to the cyclic topology of the original PEVL. The topology fidelity of cyclic PEVL is further verified by the linear relationship of  $M_n$  to retention time

according to MALS-SEC test (Figure S10). Traditionally, cyclic structure is accessible via ring closing or ring expansion mechanisms. The former strategy requires extreme diluted condition<sup>25,26</sup> and the latter one includes ring-opening metathesis polymerization<sup>27</sup> and zwitterionic polymerization.<sup>28,29</sup> The formation of cyclic PEVL is similar to that in zwitterionic polymerization but

following the CROP mechanism (Scheme 1). The carboxylic group stabilized by  $\text{Ph}_3\text{C}^+$  is ready to attack the positive propagating chain end as intramolecular transfer reaction, to form cyclic PEVL and liberate a new initiator ( $\text{Ph}_3\text{C}^+\text{PF}_6^-$ ) for further initiation. To our best knowledge, it is the first time that cyclic polyester is synthesized via the CROP of lactone without any linear contaminants.



**Figure 1.** (A)  $^1\text{H}$ , (B)  $^{13}\text{C}$  and (C) DEPT 135 NMR ( $\text{CDCl}_3$ ) spectra of PEVL obtained from Entry 1 in Table 1; (D)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of recycled EVL and methanolized U2 from the alcoholysis of PEVL; (E) MALDI-ToF MS of cyclic PEVL; (F) MALDI-ToF MS of linear PEVL from ammonolysis of cyclic one.

Accordingly, the CROP of EVL is investigated in detail using  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  as initiator. The results are summarized in Table 1. When polymerization temperature increases from 0 to 40 °C, the bulk of polymerization is gelled after 1 day and the conversion of EVL reaches 74.2% (Entry 2 in Table 1). However, NMR analysis (Figure S11-13) of the obtained polymer with decreased  $M_n$  of 1.3 kg/mol indicates a hybrid polymerization of EVL (CROP and addition polymerization of its  $\delta$ -vinyl group) at 40 °C. Additionally, the yield of polymer is reduced to 37.6% after precipitation in hexane. In the hexane soluble fraction, an isomer of EVL, (*E*)-2-ethylidene-5-heptene-4-olide (EHO) is separated and characterized (Figure S14-15), explaining the mismatch between conversion and yield. EHO has been reported as a by-product in the synthesis of EVL.<sup>3,30</sup> Decreasing polymerization temperature significantly suppresses the side reaction forming EHO and switches hybrid polymerization into CROP.

As the temperature decreases from 10 to -30 °C, the  $M_n$  of PEVL increases from 6.5 to 12.8 kg/mol (Entries 1, 3-6 in Table 1, Figure S16). Solvents no mattering their polarity are all adverse to the  $\text{Ph}_3\text{C}^+\text{PF}_6^-$ -initiated CROP of EVL (Table S2). Only in dioxane (Entry 4 in Table S2), PEVL with a significantly lower yield (11.9%) than those in bulk (31.5%) is obtained. Increasing the feed ratio of cationic initiators results in higher conversion of EVL, but the  $M_n$ s and  $\bar{D}$ s are constant indicating a non-living polymerization characteristic (Entry 1, 7, 8 in Table 1).

A kinetic study of CROP of EVL is conducted at 0 °C. A linear relationship between  $\ln([M]_0/[M])$  and polymerization time is observed, confirming a first-order kinetics (Figure S17). As polymerization process progresses, the conversion of EVL increases while the  $M_n$ s and  $\bar{D}$ s are changeless. Specially, the U2 proportion in PEVL has no significant alteration during the polymerization process (59-61%, Entries

1, 9-14), indicating a random distribution of U1 and U2 in PEVL. The characteristics of the CROP of EVL are quite similar with those of the traditional radical polymerization, which are “slow initiation, fast propagation and easy transfer/termination”. The concentration of active propagating chains can be considered as constant, resulting in the first-ordered kinetic of EVL.

To reveal the polymerization mechanism, the hexane-soluble fraction of CROP of EVL at 0 °C is investigated and another five-membered lactone, (*E*)-3-ethylidene-5-(3,3,3-triphenylprop-1-en-1-yl)dihydrofuran-2(3H)-one (EtPPL), is isolated. The structure of EtPPL, which is exactly a trityl-attached EHO, is characterized by NMR spectrometry and electrospray ionization mass spectrometry (ESI-MS) (Figure S18-23). EtPPL is generated by the side

reaction between the  $\delta$ -vinyl group of EVL and trityl (Scheme S1), which is confirmed by density functional theory (DFT) calculation (Figure S24). The exocyclic carbenium (intermediate S-1 in Scheme S1), generated by the attack of  $\delta$ -vinyl group of EVL to trityl, undergoes [1,3]-H shifts to form an intra-ring carbenium (S-2 in Scheme S1) and the calculated Gibbs free energy barrier ( $\Delta G^\ddagger$ ) is low (9.0 kcal/mol). Then the carbon-oxygen bond shifts to the endocyclic carbenium through an oxonium intermediate (S-3 in Scheme S1) with  $\Delta G^\ddagger$  of 7.0 kcal/mol, generating a five-membered lactone with an exocyclic carbenium (S-4, Scheme S1). The shrinkage of ring size from six to five is exothermic with  $\Delta G$  of -3.9 kcal/mol. The  $\beta$ -proton elimination of species S-4 generate EtPPL and  $H^+PF_6^-$ . The later one catalyzes the isomerization of EVL into EHO at 40 °C.

**Table 1. Cationic Ring-opening Polymerization of EVL initiated by  $Ph_3C^+PF_6^-$ .<sup>a</sup>**

Entry	[M] <sub>0</sub> /[I] <sub>0</sub>	T/°C	Time(d)	Conv.(%) <sup>b</sup>	Yield(%)	U2(%) <sup>c</sup>	<i>M<sub>n</sub></i> (kg/mol) <sup>d</sup>	$\bar{D}$ <sup>d</sup>
1	50	0	7	40.8	31.5	61	7.1	1.4
2	50	40	1	74.2	37.6	63 <sup>e</sup>	1.3 <sup>f</sup>	1.6 <sup>f</sup>
3	50	10	7	50.0	38.9	58	6.5	1.2
4	50	-10	15	31.1	29.6	59	10.7	1.4
5	50	-20	15	24.1	24.3	59	12.8	1.4
6	50	-30	15	17.0	15.1	57	12.8	1.2
7	25	0	7	56.8	28.4	60	6.8	1.4
8	100	0	7	34.7	20.6	59	6.8	1.3
9	50	0	1.5	11.4	9.1	61	9.7	1.2
10	50	0	2	15.1	11.9	60	8.1	1.3
11	50	0	2.5	20.2	15.7	60	8.3	1.3
12	50	0	4	28.4	19.7	61	6.6	1.5
13	50	0	5	31.9	23.7	61	6.8	1.5
14	50	0	6	35.7	27.3	59	7.0	1.4

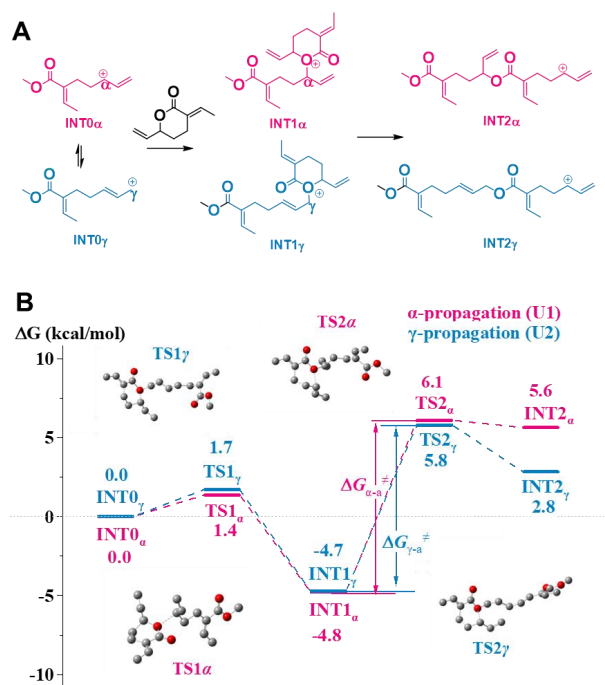
<sup>a</sup> Polymerizations are conducted in bulk. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy of the polymerization mixture. <sup>c</sup> The molar ratio of isomerized EVL unit (U2) in PEVL determined by <sup>1</sup>H NMR spectroscopy of the obtained PEVL. <sup>d</sup> Determined by SEC equipped with multi angle light scattering detector. <sup>e</sup> The obtained polymer is hybrid with polyester and polyolefin (Figure S11), which is not polyester PEVL. The U2 portion versus (U1+U2) portion is 63%. <sup>f</sup> Determined by SEC equipped with refractive index detector because of its different structure from PEVL.

To demonstrate the necessity of isomerization to CROP, the semi-hydrogenated EVL derivative,  $\alpha$ -ethylidene- $\delta$ -ethyl- $\delta$ -valerolactone (EEL, Figure S25-27), is prepared for CROP initiated by  $Ph_3C^+PF_6^-$ . It turns out that the homo-polymerization of EEL initiated by  $Ph_3C^+PF_6^-$  at 0 °C for 7 d yields no polymer (Entry 1 in Table S3). The copolymerization of EVL with EEL results in trace polymer (Entry 2 in Table S3). In the <sup>1</sup>H NMR spectrum of the polymer

(Figure S28), the intensity ratio of signals at 4.51-5.95 ppm (H<sub>2-7</sub>) versus those at 6.86-7.02 ppm (H<sub>1</sub>) is 4.0, which confirms only PEVL from CROP is obtained without EEL unit. Otherwise, the intensity ratio should be lower than 4.0 due to the absence of vinyl group in EEL. In addition, no signals near 1.00 ppm are observed, to which the methyl proton of EEL unit should be assigned. Furthermore, only one population with 152.1 Da mass interval is detected

by the MALDI-ToF MS (Figure S29), confirming no incorporation of EEL. The results indicate that the resonance of the vinyl group with the carbenium propagating chain end is essential to the CROP of EVL (Scheme 1) and CROP fails when the  $\delta$ -vinyl group is absent (EEL).

DFT calculation provides further insight in the isomerization CROP of EVL (Figure 2). The ester group of EVL cooperates with the carbenium  $E^+$  ( $Ph_3C^+$ ) and EVL ring-opens to generate an active carbenium (Scheme 1) stabilized by as well as resonated with the neighboring vinyl group. The next EVL monomer comes to be attacked by the carbenium at  $\alpha$ - or  $\gamma$ -position (*i.e.*  $\alpha$ - or  $\gamma$ -propagation, Figure 2A), followed by the ring-opening of the coming EVL. In  $\gamma$ -propagation, the vinyl group rearranges generating ethylene on backbone and EVL is inserted into the polymer in an isomerized structure (U2). According to DFT calculation, the Gibbs free energy profiles of  $\alpha$ - and  $\gamma$ -propagation to form different units (U1 and U2) are demonstrated (Figure 2B). The propagations include two transition steps consisting of cationic addition and cleavage of alkoxy bonds. In cationic addition, alkoxy oxygen on EVL is attacked by active carbenium (INT0 $_{\alpha}$  and INT0 $_{\gamma}$ ) to give stable species (INT1 $_{\alpha}$  and INT1 $_{\gamma}$ ) travelled by TS1 $_{\alpha}$  and TS1 $_{\gamma}$ . The new allyl cations (INT2 $_{\alpha}$  and INT2 $_{\gamma}$ ) are formed via cleavage of alkoxy bond as a typical cationic polymerization process.

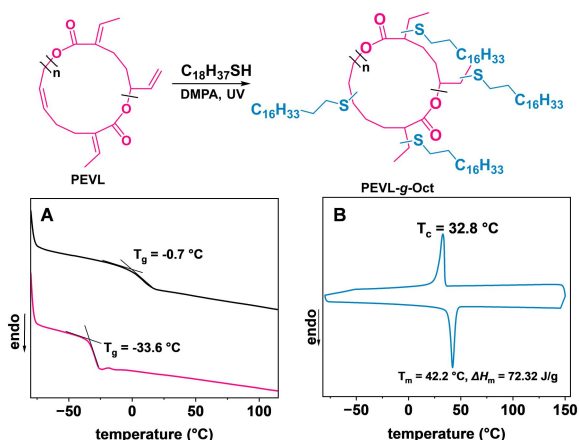


**Figure 2.** DFT calculated reactions of  $\alpha$ -propagation (rose) and  $\gamma$ -propagation (blue) in propagation using M06-2X/6-31+G(d,p) method with 3D structures.

The results confirm that both of the rate determined steps of  $\alpha$ - and  $\gamma$ -propagation are the cleavage of alkoxy bond (TS2 $_{\alpha}$  and TS2 $_{\gamma}$ ). The energy barrier  $\Delta G_{\gamma-\alpha}^{\ddagger}$  of 10.5 kcal/mol is slightly lower than  $\Delta G_{\alpha-\gamma}^{\ddagger}$  of 10.9 kcal/mol and the  $\Delta G$  (2.8 kcal/mol) of  $\gamma$ -propagation is also lower than that (5.6 kcal/mol) of  $\alpha$ -propagation, indicating that the  $\gamma$ -propagation is both kinetically and thermodynamically favored over  $\alpha$ -propagation. According to the RRKM theory,<sup>31</sup> the proportion of  $\gamma$ -propagation is about 63% (Equation S1), in accordance with the experimental results that the U2 portion in the obtained PEVL is 59-61%. It is worthy of noticing that the energy barrier of the side reaction of vinyl group and carbenium ( $\Delta G_{re}^{\ddagger} = 16.0$  kcal/mol) is higher than those of  $\alpha$ - and  $\gamma$ -propagation, implying that the main reaction is CROP of EVL rather than the formation of EtPPL byproduct.

The yielded PEVL exhibits great thermal stability with decomposition temperature at 5% mass loss ( $T_{d,5\%}$ ) of 279 °C (Figure S30). The glass transition temperature ( $T_g$ ) of cyclic PEVL is barely dependent on its  $M_n$  (-33.6 °C for  $M_n = 7.1$  kg/mol and -33.1 °C for  $M_n = 12.8$  kg/mol, Figure 3A). On the contrary, the obtained polymer from polymerization of EVL at 40 °C possesses a  $T_g$  of 0.7 °C (Figure S31) as the result of hybrid polymer backbone.

The intact C=C double bonds in PEVL is ready for post-polymerization functionalization. PEVL ( $M_{n, RI} = 9.3$  kg/mol) is modified with 1-octadecanethiol by “thiol-ene” click reaction, obtaining PEVL-*g*-Oct ( $M_{n, RI} = 17.9$  kg/mol) with an 82.5% modification ratio of C=C double bond (Figure S32-33). The introduction of crystalline octadecyl side group endows PEVL with a melting point ( $T_m$ ) of 42.2 °C and crystallization temperature ( $T_c$ ) of 32.8 °C (Figure 3B), different from those of free 1-octadecanethiol (Figure S34).



**Figure 3.** DSC curves of PEVL with different  $M_n$  (A) and PEVL-*g*-Oct (B).

In conclusion, the ring-opening homo-polymerization of  $\alpha$ -ethylidene- $\delta$ -vinyl- $\delta$ -valerolactone (EVL), a difunctional lactone derived from CO<sub>2</sub> and 1,3-butadiene, is realized via isomerization CROP initiated by robust cationic initiators (e.g., Ph<sub>3</sub>C<sup>+</sup>PF<sub>6</sub><sup>-</sup>). The obtained cyclic polyester PEVL is carefully characterized to bear two structural units derived from EVL and three kinds of alkenyl groups (an ethylidene and a vinyl group in the side chain and a C=C double bond in the main chain). It is the first example of quantitative formation of cyclic polymer in CROP of lactone. The  $\delta$ -vinyl group is proved to play a key role in the polymerization, promoting the propagation and leading to the isomerization. The  $M_n$  of PEVL is tunable from 6.5 to 12.8 kg/mol by adjusting polymerization temperature, holding low dispersity ( $\bar{D} = 1.2$ -1.4). PEVL composed of 29 wt% CO<sub>2</sub> is not only degradable and recyclable, but also ready for functionalization. Modification with 1-octadecanethiol renders the amorphous PEVL ( $T_g = -33.6$  °C) with a melting temperature ( $T_m = 42.2$  °C).

## ASSOCIATED CONTENT

### Supporting Information.

Experimental details, materials, measurements, characterization of monomer and polymers, calculation details, NMR spectra, MALDI-ToF MS, SEC and DSC data. (PDF)

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## REFERENCES

- (1) Price, C. J.; Reich, B. J. E.; Miller, S. A. Thermodynamic and Kinetic Considerations in the Copolymerization of Ethylene and Carbon Dioxide. *Macromolecules* **2006**, *39* (8), 2751–2756.
- (2) Nakano, R.; Ito, S.; Nozaki, K. Copolymerization of Carbon Dioxide and Butadiene via a Lactone Intermediate. *Nat. Chem.* **2014**, *6* (4), 325–331.
- (3) Behr, A.; Henze, G. Use of Carbon Dioxide in Chemical Syntheses via a Lactone Intermediate. *Green Chem.* **2011**, *13* (1), 25–39.
- (4) Wang, J.; Feng, X.; Song, J.; Gao, Z.; Wang, W.-H.; Bao, M. The Ultrasmall Palladium Nanoparticles Catalyzed Telomerization of CO<sub>2</sub> with 1,3-Butadiene at Room Temperature: Selective Synthesis of  $\delta$ -Lactone. *ChemistrySelect* **2020**, *5* (30), 9404–9408.
- (5) Moon, S.; Masada, K.; Nozaki, K. Reversible Polymer-Chain Modification: Ring-Opening and Closing of Polylactone. *J. Am. Chem. Soc.* **2019**, *141* (28), 10938–10942.
- (6) Hill, M. R.; Tang, S.; Masada, K.; Hirooka, Y.; Nozaki, K. Incorporation of CO<sub>2</sub>-Derived Bicyclic Lactone into Conventional Vinyl Polymers. *Macromolecules* **2022**, *55* (8), 3311–3316.
- (7) Tang, S.; Zhao, Y.; Nozaki, K. Accessing Divergent Main-Chain-Functionalized Polyethylenes via Copolymerization of Ethylene with a CO<sub>2</sub>/Butadiene-Derived Lactone. *J. Am. Chem. Soc.* **2021**, *143* (43), 17953–17957.
- (8) Chen, L.; Li, Y.; Yue, S.; Ling, J.; Ni, X.; Shen, Z. Chemoselective RAFT Polymerization of a Trivinyl Monomer Derived from Carbon Dioxide and 1,3-Butadiene: From Linear to Hyperbranched. *Macromolecules* **2017**, *50* (24), 9598–9606.
- (9) Chen, L.; Ling, J.; Ni, X.; Shen, Z. Synthesis and Properties of Networks Based on Thiol-Ene Chemistry Using a CO<sub>2</sub>-Based  $\delta$ -Lactone. *Macromol. Rapid Commun.* **2018**, *39* (23), 1800395.
- (10) Song, J.; Chen, K.; Feng, Y.; Ni, X.; Ling, J. One-Pot Orthogonal Thiol-Ene Click Polymerization and Ring-Opening Grafting Reaction of CO<sub>2</sub>-Based Disubstituted  $\delta$ -Valerolactone. *J. Polym. Sci.* **2022**, *60* (15), 2352–2361.
- (11) Zhang, Y.; Xia, J.; Song, J.; Zhang, J.; Ni, X.; Jian, Z. Combination of Ethylene, 1,3-Butadiene, and Carbon Dioxide into Ester-Functionalized Polyethylenes via Palladium-Catalyzed Coupling and Insertion Polymerization. *Macromolecules* **2019**, *52* (6), 2504–2512.
- (12) Yue, S.; Bai, T.; Xu, S.; Shen, T.; Ling, J.; Ni, X. Ring-Opening Polymerization of CO<sub>2</sub>-Based Disubstituted  $\delta$ -Valerolactone toward Sustainable Functional Polyesters. *ACS Macro Lett.* **2021**, *10* (8), 1055–1060.
- (13) Garcia Espinosa, L. D.; Williams-Pavlantos, K.; Turney, K. M.; Wesdemiotis, C.; Eagan, J. M. Degradable Polymer Structures from Carbon Dioxide and Butadiene. *ACS Macro Lett.* **2021**, *10* (10), 1254–1259.
- (14) Chen, K.; Zhu, Z.; Bai, T.; Mei, Y.; Shen, T.; Ling, J.; Ni, X. A Topology-Defined Polyester Elastomer from CO<sub>2</sub> and 1,3-Butadiene: A One-Pot-One-Step “Scrambling Polymerizations” Strategy. *Angew. Chem. Int. Ed.* **2022**, *61* (46), e202213028.
- (15) Rapagnani, R. M.; Dunscomb, R. J.; Fresh, A. A.; Tonks, I. A. Tunable and Recyclable Polyesters from CO<sub>2</sub> and Butadiene. *Nat. Chem.* **2022**, *14*, 877–883.
- (16) Lou, Y.; Xu, L.; Gan, N.; Sun, Y.; Lin, B.-L. Chemically Recyclable Polyesters from CO<sub>2</sub>, H<sub>2</sub>, and 1,3-Butadiene. *The Innovation* **2022**, *3* (2), 100216.
- (17) Zhang, Z.; Shen, T.; Chen, K.; Zeng, J.; Mei, Y.; Ling, J.; Ni, X. Polyester Platform with High Refractive Indices and Closed-Loop Recyclability from CO<sub>2</sub>, 1,3-Butadiene, and Thiols. *ACS Macro Lett.* **2024**, *13* (6), 741–746.
- (18) Xu, J.; Niu, Y.; Lin, B.-L. Monomer-Recyclable Polyester from CO<sub>2</sub> and 1,3-Butadiene. *Macromol. Rapid Commun.* **2024**, *45* (15), 2400163.
- (19) Zhang, J.; Jiang, L.; Liu, S.; Shen, J.; Braunstein, P.; Shen, Y.; Kang, X.; Li, Z. Bifunctional and Recyclable Polyesters by Chemoselective Ring-Opening Polymerization of a  $\delta$ -Lactone Derived from CO<sub>2</sub> and Butadiene. **2024**. <https://doi.org/10.26434/chemrxiv-2024-0p221>.

- (20) Rapagnani, R. M.; Tonks, I. A. 3-Ethyl-6-Vinyltetrahydro-2H-Pyran-2-One (EVP): A Versatile CO<sub>2</sub>-Derived Lactone Platform for Polymer Synthesis. *Chem. Commun.* **2022**, 58 (69), 9586–9593.
- (21) Chen, K.; Mei, Y.; Zhang, Z.; Ling, J.; Ni, X. How to Open the Ring of a Di-Ene-Substituted- $\delta$ -Valerolactone: From Carbon Dioxide and 1,3-Butadiene to Functional Polyesters. *ChemPlusChem* **2023**, 88 (3), e202300022.
- (22) Wang, Z.; Zheng, W.; Yue, S.; Chen, K.; Ling, J.; Ni, X. Random Terpolymer of Carbon Dioxide, Butadiene and Epoxides: Synthesis, Functionalization and Degradability. *Chin. J. Chem.* **2024**, 42 (14), 1630–1636.
- (23) Xia, Y.; Yuan, P.; Zhang, Y.; Sun, Y.; Hong, M. Converting Non-Strained  $\gamma$ -Valerolactone and Derivatives into Sustainable Polythioesters via Isomerization-Driven Cationic Ring-Opening Polymerization of Thionolactone Intermediate. *Angew. Chem. Int. Ed.* **2023**, 62 (14), e202217812.
- (24) Hester, H. G.; Abel, B. A.; Coates, G. W. Ultra-High-Molecular-Weight Poly(Dioxolane): Enhancing the Mechanical Performance of a Chemically Recyclable Polymer. *J. Am. Chem. Soc.* **2023**, 145 (16), 8800–8804.
- (25) Schappacher, M.; Deffieux, A. Synthesis of Macrocyclic Copolymer Brushes and Their Self-Assembly into Supramolecular Tubes. *Science* **2008**, 319 (5869), 1512–1515.
- (26) Laurent, B. A.; Grayson, S. M. An Efficient Route to Well-Defined Macrocyclic Polymers via “Click” Cyclization. *J. Am. Chem. Soc.* **2006**, 128 (13), 4238–4239.
- (27) Boydston, A. J.; Xia, Y.; Kornfield, J. A.; Gorodetskaya, I. A.; Grubbs, R. H. Cyclic Ruthenium-Alkylidene Catalysts for Ring-Expansion Metathesis Polymerization. *J. Am. Chem. Soc.* **2008**, 130 (38), 12775–12782.
- (28) Brown, H. A.; Waymouth, R. M. Zwitterionic Ring-Opening Polymerization for the Synthesis of High Molecular Weight Cyclic Polymers. *Acc. Chem. Res.* **2013**, 46 (11), 2585–2596.
- (29) Piedra-Arroni, E.; Ladavière, C.; Amgoune, A.; Bourissou, D. Ring-Opening Polymerization with Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-Based Lewis Pairs: Original and Efficient Approach to Cyclic Polyesters. *J. Am. Chem. Soc.* **2013**, 135 (36), 13306–13309.
- (30) Braunstein, Pierre.; Matt, Dominique.; Nobel, Dominique. Carbon Dioxide Activation and Catalytic Lactone Synthesis by Telomerization of Butadiene and Carbon Dioxide. *J. Am. Chem. Soc.* **1988**, 110 (10), 3207–3212.
- (31) Marcus, R. A.; Rice, O. K. The Kinetics of the Recombination of Methyl Radicals and Iodine Atoms. *J. Phys. Chem.* **1951**, 55 (6), 894–908.