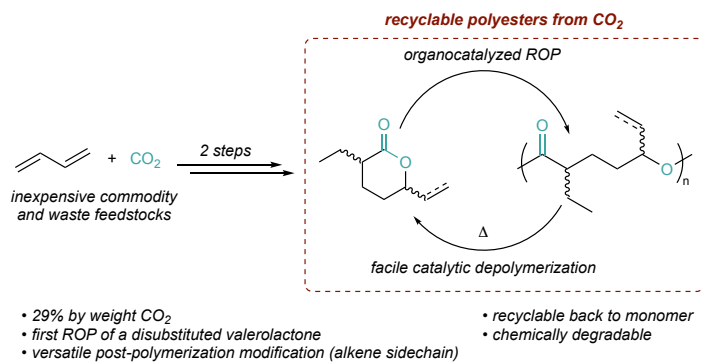


Tunable and Recyclable Polyesters from CO₂ and Butadiene

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Abstract

Carbon dioxide is inexpensive and abundant, and its prevalence as waste makes it attractive as a sustainable chemical feedstock. Although there are examples of copolymerizations of CO₂ with high-energy monomers, the direct copolymerization of CO₂ with olefins has not been reported. Herein, an alternate route to tunable, recyclable polyesters derived from CO₂ and butadiene *via* an intermediary lactone, 3-ethyl-6-vinyltetrahydro-2*H*-pyran-2-one, is described. Catalytic ring-opening polymerization of the lactone by 1,5,7-triazabicyclo[4.4.0]dec-5-ene yields polyesters with molar masses up to 13.6 kg/mol and pendent vinyl sidechains that can undergo post-polymerization functionalization. The polymer has a low ceiling temperature of 138 °C, allowing for facile chemical recycling. These results mark the first example of a well-defined polyester derived solely from CO₂ and olefins, expanding access to new feedstocks that were once considered unfeasible.



Introduction

Carbon dioxide is often considered an ideal sustainable polymer feedstock: inexpensive and abundant, and a significant industrial and energy sector waste product in need of sequestration.^{1–7} However, the thermodynamic stability of CO₂ renders polymerizations that directly incorporate CO₂ extremely challenging, requiring reaction with high-energy comonomers such as epoxides (resulting in polycarbonates).³ The direct copolymerization of CO₂ with inexpensive commodity alkenes to form aliphatic degradable polyesters is an attractive and potentially cost-competitive alternative to nondegradable petroleum-based plastics. However, aliphatic alkenes simply do not have enough energy to efficiently fix CO₂ on their own, represented by the fact that direct CO₂ and ethylene copolymerization is an as-of-yet unrealized reaction owing to the significant endothermicity (and kinetic challenges) of forming the 1:1 copolymer.⁸

Given the challenges of direct conversion of CO₂ into polyesters, alternate strategies involving CO₂ conversion to inexpensive polymerizable intermediates are critically

important. In this regard, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (**EVL**) is an ideal candidate for polyester synthesis. **EVL** can be synthesized via the high-yielding and efficient telomerization of butadiene with CO₂ (Figure 1, Top).^{9–15} Butadiene is also an economical platform chemical that can also be derived from biomass. Polyesters derived from the ring-opening of **EVL**-derived molecules are thus extremely attractive targets: they would have high CO₂ content, be constructed from commodity chemicals, and also have pendent alkene sidechains for rapid post-polymerization functionalization.

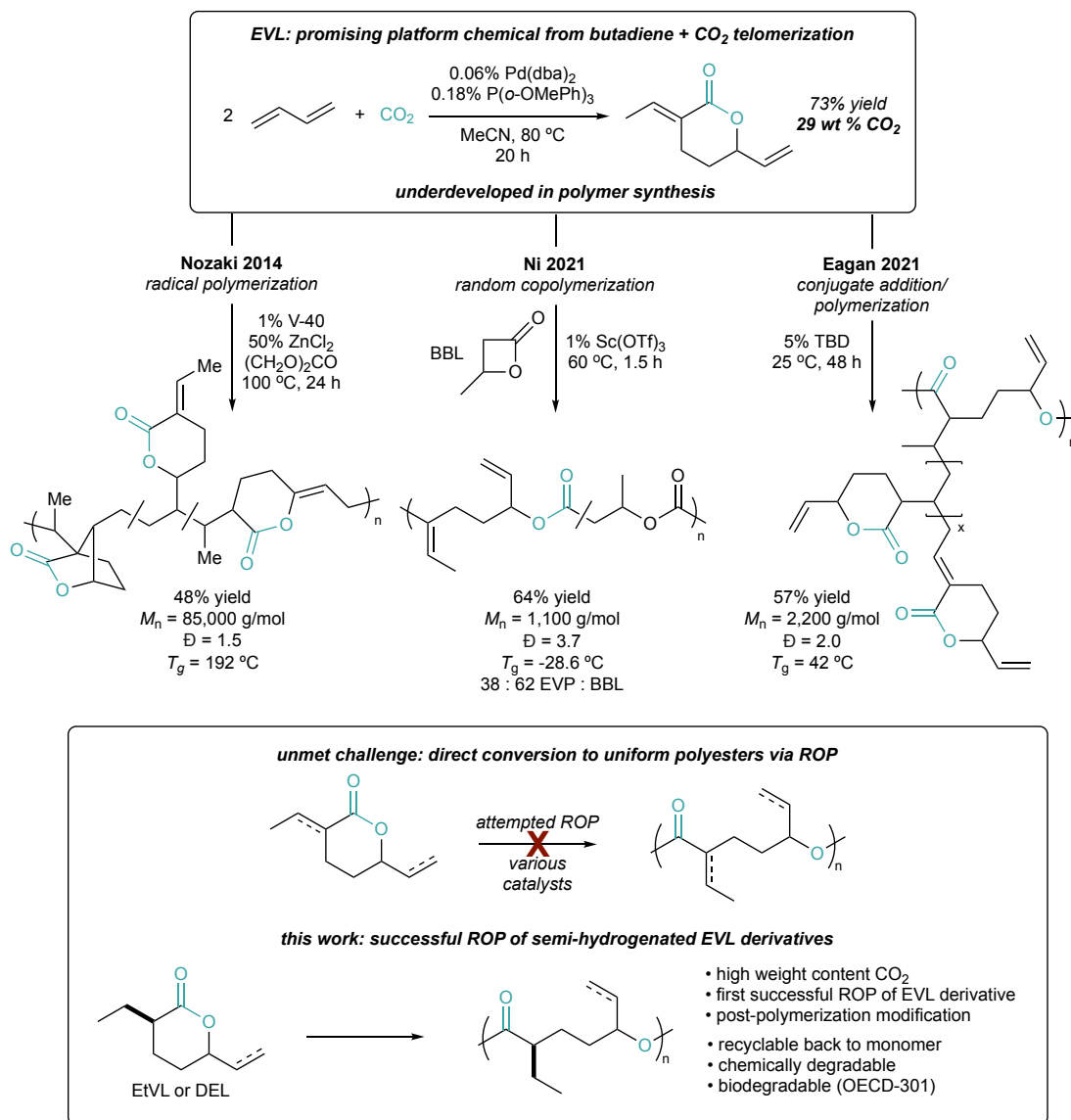


Figure 1. Overview of EVL synthesis and examples of its incorporation into polymers to date, plus the unmet challenge of polymerization of EVL derivatives.

Although significant work has been carried out by Behr and others into the use of **EVL** as a feedstock chemical, its direct use in polymerization reactions is quite limited.¹⁶ All prior attempts to directly ring-open polymerize (ROP) **EVL**, semi-hydrogenated 6-ethyl-3-ethylidenetetrahydro-2H-pyran-2-one (**EeTL**), and fully-hydrogenated 3,6-

diethyltetrahydro-2*H*-pyran-2-one (**DEL**) to their respective polyesters have been unsuccessful.¹⁷ In fact, an outstanding question in these prior studies is whether ROP of disubstituted δ -valerolactone derivatives is thermodynamically viable given the lack of ring strain and the deleterious impact of substitution from the Thorpe-Ingold effect.^{18–20}

Nonetheless, several landmark recent reports motivate continued study into this class of lactones in CO₂-derived polymer synthesis (Figure 1, Middle). For example, Nozaki demonstrated that **EVL** could undergo radical polymerization to form a random copolymer comprised of 29% CO₂ by mass.²¹ Lin later found that radical polymerization of **EVL** could be thermally initiated by O₂ in air, reaching molar masses up to 239 kg/mol.²² Ni has also demonstrated the random copolymerization of **EVL** with β -butyrolactone (BBL) via cationic ROP, albeit with low molar masses and broad dispersities.²³ Most recently, Eagan has reported that **EVL** can undergo a combination of vinylogous conjugate addition and polymerization to degradable macromolecules.²⁴

In the interest of further understanding the potential of CO₂-derived lactones to undergo ROP, we sought to re-investigate **EVL** polymerization with a specific focus on reduced **EVL** derivatives lacking α,β -unsaturation, envisioning that a limiting factor in successful ROP may be unwanted side reactions occurring as a result of the ester conjugation. Herein, we report the organocatalyzed ROP of the semi-hydrogenated 3-ethyl-6-vinyltetrahydro-2*H*-pyran-2-one (**EtVL**) to **poly(EtVL)** and fully hydrogenated 3,6-diethyl-tetrahydro-2*H*-pyran-2-one (**DEL**) to **poly(DEL)**, resulting in low-*T_g* and low-*T_c* polyesters that can be chemically recycled to monomer or degraded in dilute basic conditions. These polymers are the first examples of uniform polyester polymers derived from **EVL** and have a CO₂ weight content of 29%. Importantly, the 6-vinyl group of **EtVL** remains intact in the polymer, providing a facile handle for post-polymerization *via* simple alkene reactions.

Results and Discussion

EVL¹³ was selectively hydrogenated to **EtVL** (86% yield) *via* conjugate reduction of the α,β -unsaturated ester (Figure 1A).²⁵ Exhaustive hydrogenation of **EtVL** to **DEL** was then accomplished *via* reduction with *p*-TsNHNH₂ (77% yield). Although these reductions are convenient for academic lab-scale production of **EtVL** and **DEL**; larger scale reductions with more economically viable conditions (Mg⁰ and Pd/C + H₂, respectively) are also possible.^{26,27}

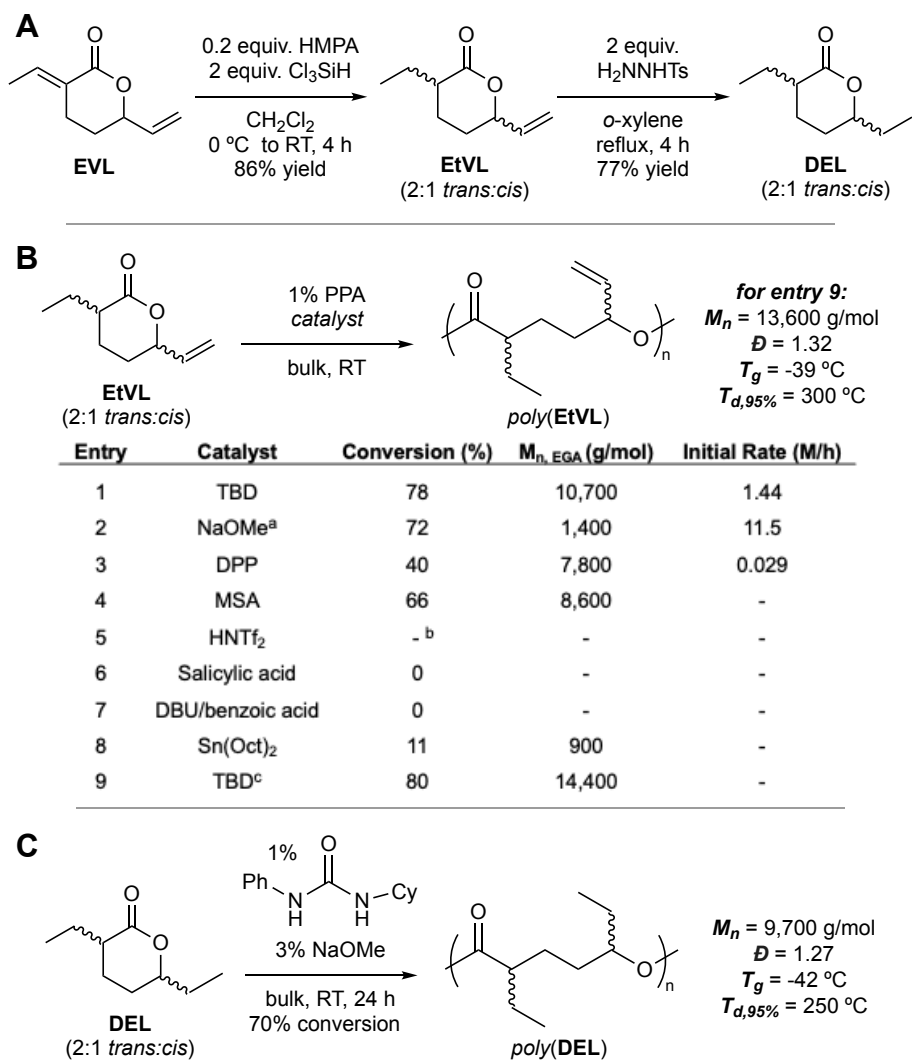


Figure 2. A: Synthesis of **EtVL** and **DEL**. B: optimization of bulk **EtVL** polymerization. Reaction conditions: 1% PPA initiator, 5% catalyst, 72 h. Conversion and M_n (end group analysis) determined by ^1H NMR. ^a10% NaOMe. ^bHNTf₂ led to some monomer decomposition. ^c0.5% PPA initiator. C: bulk **DEL** polymerization catalyzed by a urea organocatalyst.

Bulk-phase ROP of **EtVL** to **poly(EtVL)** was then examined using 1 mol% 3-phenylpropanol (PPA) initiator combined with a variety of well-established ROP catalyst systems (Figure 2B). Brønsted acid catalysts such as diphenyl phosphate (DPP) are efficient catalysts for well-controlled ROP of ϵ -caprolactone and δ -valerolactone.^{28,29} Bulk polymerization of **EtVL** with DPP was very slow, reaching only 40% conversion over 3 days. Kinetic analysis of the DPP-catalyzed **EtVL** polymerization revealed $k_{\text{obs}} = 0.029$ M/h, an order of magnitude slower (despite higher catalyst loading) than the rapid DPP-catalyzed polymerization of monosubstituted δ -hexalactone ($k_{\text{obs}} = 0.32$ M/h) and α -methylvalerolactone ($k_{\text{obs}} = 0.92$ M/h).¹⁸ Since both α - and δ -monosubstituted valerolactones undergo DPP-catalyzed ROP at slower rates than valerolactone ($k_{\text{obs}} =$

2.88 M/h), it stands to reason that an α,δ -disubstituted valerolactone like **EtVL** would polymerize even more slowly.

Base catalysts such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) have been broadly used for both lactide and lactone ROP. TBD, in particular, is one of the most active organocatalysts for ROP owing to its basicity and bifunctional mode of activation.^{30,31} Excitingly, ROP of bulk **EtVL** with TBD at room temperature led to 78% conversion and an M_n of 10,700 g/mol (measured by end-group analysis), and kinetic analysis revealed that the initial rate of polymerization was significantly faster ($k_{\text{obs}} = 1.4$ M/h) than the corresponding DPP-catalyzed polymerization.

A screen of additional catalysts was carried out (Figure 2B). NaOMe¹⁷ catalyzes very rapid polymerization, but required high loadings (10%) for productive ROP, limiting the overall molar mass. Strong acids resulted in lower conversions/molar masses (e.g. MSA³², 66% conv., $M_n = 8,600$ g/mol) or unproductive side reactions instead of polymerization (e.g. HNTf₂³³); DBU in combination with benzoic acid³⁴ or 1-cyclohexyl-3-phenylurea³⁵ did not polymerize **EtVL** at all. Other metal-based catalysts such as Sn(Oct)₂ require temperatures too close to the **poly(EtVL)** T_c and result in low conversion (*vide infra*).

Based on these results, TBD was determined to be the most effective ROP catalyst for **EtVL**. High molar mass **poly(EtVL)** (13.6 kg/mol, $\bar{D} = 1.36$) can be synthesized with 0.5% PPA initiator at room temperature (Figure 2B, entry 9). The glass transition temperature (T_g) of **poly(EtVL)** is -38.8 °C, making this potentially suitable as a soft block in thermoplastic elastomers.^{36,37} This value is approximately 10 °C higher than comparable monosubstituted δ -lactones (e.g. δ -hexalactone and δ -heptalactone¹⁸), most likely from impeded chain rotation from the additional substituent.

Success with semi-hydrogenated **EtVL** led us to re-evaluate **DEL** and **EVL** as candidates for ROP. Conditions slightly modified from the **EtVL** ROP conditions (1% benzyl alcohol/5% TBD/-15 °C) led to only 18% conversion of **DEL** after two days. However, further exploration and optimization of catalysts and conditions led to the discovery that Waymouth's NaOMe/1-cyclohexyl-3-phenylurea catalyst system³⁸ is effective for **DEL** ROP, leading to 70% conversion after one day at room temperature ($M_n = 9.7$ kg/mol, $\bar{D} = 1.27$) (Figure 2C). Polymerization attempts of **EVL** with NaOMe resulted in similar conjugate addition/ROP competition as recently observed by Eagan.²⁴ The poor ROP behavior of **EVL** may be a reflection of the stability of the *s-cis* conformation of the α,β -unsaturated ester, which may disfavor ring-opening nucleophilic attack and promote unwanted conjugate addition reactivity.

van't Hoff analysis of TBD-catalyzed polymerization of **EtVL** revealed thermodynamic parameters of $\Delta H_p = -2.26 \pm 0.23$ kcal/mol and $\Delta S_p = -5.48 \pm 0.70$ cal/mol·K, resulting in a ceiling temperature (T_c) of 138 °C (Table 1). Similarly, van't Hoff analysis of 1-cyclohexyl-3-phenylurea-catalyzed polymerization of **DEL** revealed $\Delta H_p = -2.82 \pm 0.23$ kcal/mol and $\Delta S_p = -7.34 \pm 0.68$ cal/mol·K, resulting in a ceiling temperature (T_c) of 110 °C. These low T_c values open the possibility of facile chemical recycling (*vide infra*).

Comparison of these values to unsubstituted *poly*(δ -valerolactone) ($\Delta H_p = -2.92$ kcal/mol, $\Delta S_p = -2.27$ cal/mol \cdot K) and *poly*(δ -hexalactone) ($\Delta H_p = -3.3$ kcal/mol, $\Delta S_p = -5.5$ cal/mol \cdot K) reveals that the thermodynamics of **EtVL** and **DEL** polymerizations are surprisingly similar to *poly*(δ -hexalactone), likely owing to the fact that α -substitution has a limited impact on the entropy of polymerization of 6-membered lactones (Table 1).¹⁸ Importantly, the combined polymerization results of **EtVL** and **DEL** demonstrate that ROP of disubstituted valerolactones is thermodynamically feasible, although choice of the appropriate catalyst to engender kinetically-accessible polymerizations remains unpredictable.

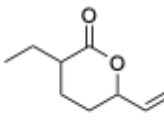
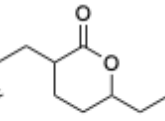
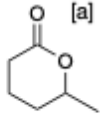
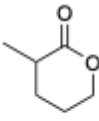
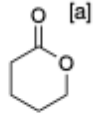
			 [a]	 [b]	 [a]
ΔH (kcal/mol)	-2.3	-2.8	-3.3	-3.1 (-3.1) ^c	-2.9
ΔS (cal/mol \cdot K)	-5.5	-7.3	-5.5	-3.7 (-8.1) ^c	-2.3
ΔG (kcal/mol) at 298 K	-0.6	-0.6	-1.7	-2.0 (-0.7) ^c	-2.2
T_c ($^{\circ}$ C)	138	110	322	540 (109) ^c	1018

Table 1. Comparison of the thermodynamics of polymerization of various substituted valerolactones (bulk conditions). ^adata from ref. 19. ^bdata from ref. 18. ^cdata calculated at 1 M.

Conjugate reduction of **EVL** to **EtVL** results in an approximate 2:1 ratio of the *trans* and *cis* diastereomers, consistent with the computationally predicted (B3LYP/6-31G*) thermodynamic equilibrium ratio ($\Delta G^{\circ} = 0.527$ kcal/mol). TBD-catalyzed polymerization of the 2:1 *trans:cis* diastereomeric mixture of **EtVL** results in the formation of a stereorandom polymer where the relative sidechain stereochemistry is indistinguishable by ¹H NMR, while remaining unconsumed **EtVL** monomer is still in a 2:1 *trans:cis* ratio (Figure 3, top). TBD-catalyzed polymerization of a diastereomerically-enriched 5.5:1 *trans:cis* sample of **EtVL** (Figure 3, bottom) resulted in a near-identical polymer to the 2:1 feedstock, and the remaining unconsumed **EtVL** was again found in a 2:1 *trans:cis* ratio by ¹H NMR analysis. Monitoring the polymerization over time revealed that the monomer was epimerized rapidly compared to polymerization, with the 2:1 *trans:cis* ratio being re-established within 20 minutes. Thus, **EtVL** undergoes rapid TBD-catalyzed α -epimerization under the polymerization conditions, and it stands to reason that the polymer itself would similarly undergo TBD-catalyzed epimerization. We are currently exploring the development of stereoretentive polymerization conditions to investigate the potential differential polymerization behavior and properties of each antipode.

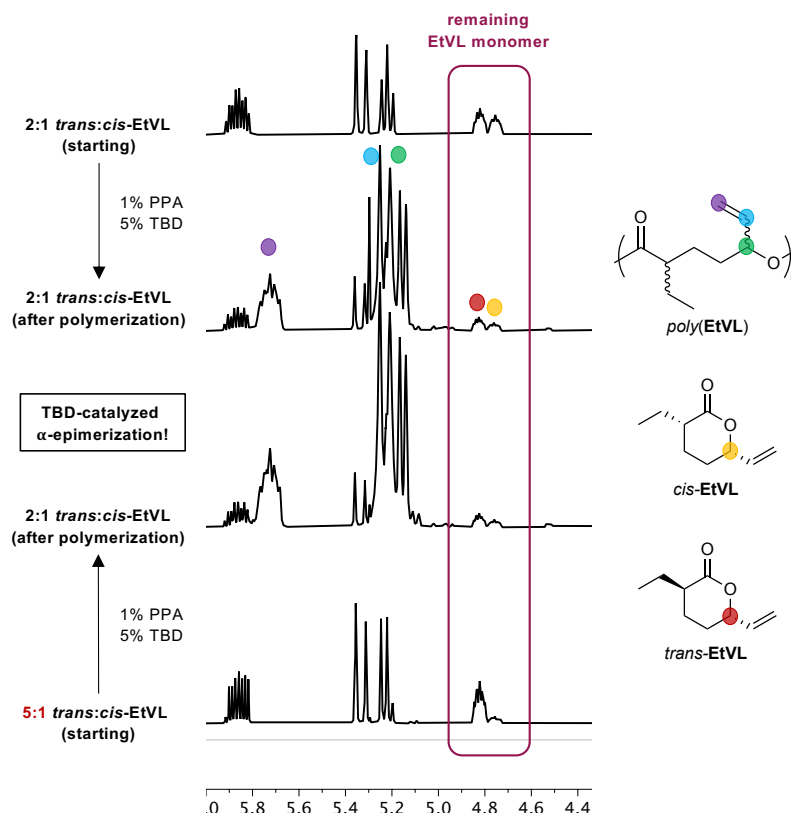


Figure 3. ^1H NMR spectra of TBD-catalyzed EtVL polymerizations demonstrating concurrent TBD-catalyzed *cis-trans* interconversion of EtVL via α -epimerization.

Next chemical recycling of **poly(EtVL)** to recover **EtVL** was explored, taking advantage of the low T_c of the polymer; chemical recyclability is an important feature when considering the overall sustainability of a material.^{39–41} Using a vacuum distillation apparatus, the isolated polymer was exposed to 3% $\text{Sn}(\text{Oct})_2$ at 165 °C, from which 84% pure monomer was obtained in less than 2 hours (Figure 4B). The Coates group recently reported poly(1,3-dioxolane) can similarly be chemically recycled *via* distillation.⁴² Further, the hydrolytic degradation potential of **poly(EtVL)** was determined by monitoring mass loss over time in basic (0.1 M NaOH) and acidic (0.1 M HCl) solutions at 50 °C and in 0.01 M phosphate-buffered saline solution (PBS) at 37 °C (Figure 4A). The polymer almost fully degraded in the basic solution over a period of 13 weeks, compared to only a loss of about 4% in both the HCl and PBS solutions in the same amount of time. Finally, biodegradation studies of this polymer in an aerobic environment using respirometry is currently ongoing. These studies demonstrate that a CO_2 -derived polyester such as **poly(EtVL)** has the potential for sustainable closed-loop recycling, while also being potentially degradable in the environment in instances where recycling is not possible.

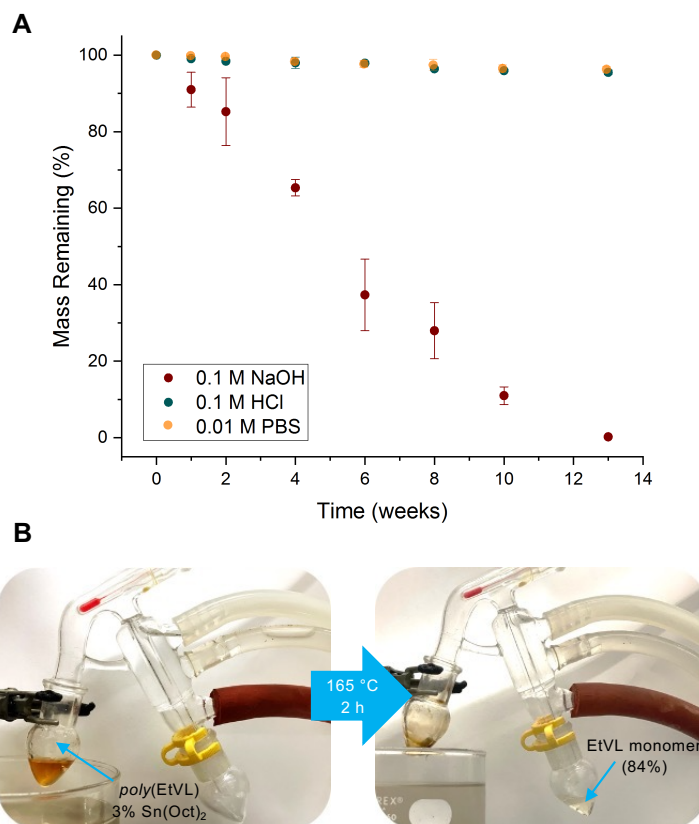


Figure 4. A. Hydrolytic degradation of **poly(EtVL)** under basic (red), acidic (blue), and buffered (orange) conditions. B. **poly(EtVL)** can be chemically recycled to **EtVL** via high-temperature catalytic depolymerization and distillation.

In addition to recyclability, another attractive feature of **poly(EtVL)** is the pendent alkene sidechain, which allows for facile post-polymerization modification *via* high-yielding and well-established alkene reaction chemistry. Prior examples of alkene functionalization in polyesters include Michael-type addition of thiols to side-chain appended acrylates in poly(γ -acryloyloxy- ϵ -caprolactone)⁴³ or backbone acrylates in poly(α -methylene- γ -butyrolactone)⁴⁴, as well as photoinitiated thiol-ene click reactions with poly(6-allyl- ϵ -caprolactone-co- ϵ -caprolactone).⁴⁵ Reactions with mercaptoacetic acid can tune polymer solubility⁴⁶, while protected cysteine provides a handle for peptide coupling.⁴⁵ Amine additions have also been applied to polymers like poly(dodecylitaconate)⁴⁷, and olefin metathesis has been demonstrated on poly(β -heptenolactone).⁴⁸

Figure 5 shows several proof-of-principle examples of the myriad simple and robust post-polymerization modifications available to **poly(EtVL)**. Butyl-3-mercaptopropionate was installed via radical thiol-ene reaction to **poly(EtVL)**, resulting in **poly(EtVL-BMP)** with 97.5% of vinyl sidechains converted by ¹H NMR and a decreased T_g of -57 °C (Figure 5A). Thiol-ene reaction of **poly(EtVL)** with 2-diethylaminoethane thiol resulted in 96.5% conversion to the amine-appended polymer, which could then undergo quaternization to cationic **poly(EtVL-NR₄)** *via* reaction with benzyl bromide (Figure 5B).

We targeted this modification since polymers containing quaternized amine sidechains have been shown to afford antimicrobial properties.^{46,49} Next, crosslinked polymers of **poly(EtVL)** were synthesized using various molar ratios of a multi-mercapto coupling agent, trimethylolpropane tris(3-mercaptopropionate) (TMPT). Crosslinking with 10%, 6%, or 3% TMPT resulted in materials that were more solid than the homopolymer and were slightly sticky, with gel fractions of 75.5%, 57.9%, and 15% and swelling ratios of 26.9%, 20%, and 4.4%, respectively (Figure 5C). Crosslinked materials are used in many different contexts such as coatings, foams, adhesives, and hydrogels; however, the use of aliphatic polyesters for these materials is less common, and most are instead employed as elastomers.^{50–52} Finally, diblock copolymers^{53,54} of **poly(EtVL)** and *L*-lactide can be synthesized *via* chain extension of a 9 kg/mol sample using DBU as a catalyst ($M_n = 13.9$ kg/mol, $\bar{D} = 1.42$) (Figure 5D). Overall, these post-polymerization modifications demonstrate that the utility of **EtVL**-based materials extends beyond simply its high CO₂ content.

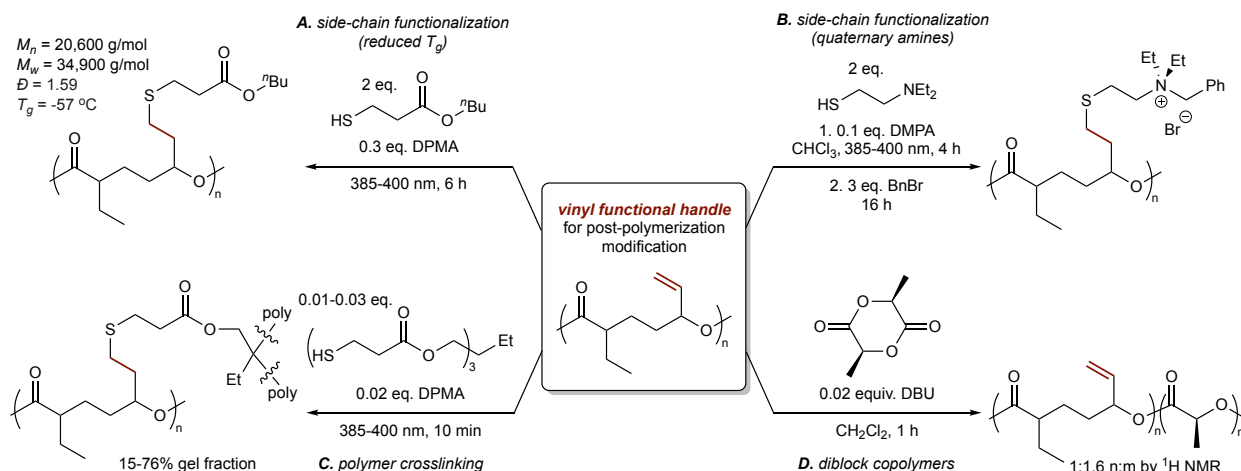


Figure 5. Post-polymerization modification of **poly(EtVL)**.

In conclusion, conjugate reduction of **EVL** to remove α,β -unsaturation unlocks access to well-defined recyclable and biodegradable polyesters with high CO₂ content from commodity (butadiene) and waste (CO₂) feedstocks. This work represents the first example of a polyester homopolymer derived from CO₂ and an olefin feedstock, addressing a longstanding challenge in polymer synthesis. The resulting polymers also contain pendent alkene sidechains, which broadens the potential application of CO₂-derived polyesters through facile post-polymerization functionalization.

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Conflicts of Interest

I.A.T. and R.M.R. are co-inventors on a provisional US patent based on this work.

Supporting Information Available

Full experimental details and analytical data, as well as computational details for *cis*- and *trans*-EtVL (.pdf)

References

- (1) Omae, I. Recent Developments in Carbon Dioxide Utilization for the Production of Organic Chemicals. *Coord. Chem. Rev.* **2012**, *256*, 1384–1405.
- (2) Sakakura, T.; Choi, J. C.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107*, 2365–2387.
- (3) Grignard, B.; Gennen, S.; Jérôme, C.; Kleij, A. W.; Detrembleur, C. Advances in the Use of CO₂ as a Renewable Feedstock for the Synthesis of Polymers. *Chem. Soc. Rev.* **2019**, *48*, 4466–4514.
- (4) Artz, J.; Müller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternberg, A.; Bardow, A.; Leitner, W. Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment. *Chem. Rev.* **2018**, *118*, 434–504.
- (5) Dabral, S.; Schaub, T. The Use of Carbon Dioxide (CO₂) as a Building Block in Organic Synthesis from an Industrial Perspective. *Adv. Synth. Catal.* **2019**, *361*, 223–246.
- (6) Khoo, R. S. H.; Luo, H.-K.; Braunstein, P.; Hor, T. S. A. Transformation of CO₂ to Value-Added Materials. *J. Mol. Eng. Mater.* **2015**, *03*, 1540007.
- (7) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable Polymers from Renewable Resources. *Nature* **2016**, *540*, 354–362.
- (8) Price, C. J.; Jesse, B.; Reich, E.; Miller, S. A. Thermodynamic and Kinetic Considerations in the Copolymerization of Ethylene and Carbon Dioxide. *Macromolecules* **2006**, *39*, 2751–2756.
- (9) Musco, A.; Perego, C.; Tartari, V. Telomerization Reactions of Butadiene and CO₂ Catalyzed by Phosphine Pd(0) Complexes: (E)-2-Ethylidenehept-5-ene and Octadienyl Esters of 2-Ethylidenehepta-4,6-dienoic Acid. **1978**, *28*, 147–148.
- (10) Inoue, Y.; Sasaki, Y.; Hashimoto, H. Incorporation of CO₂ in Butadiene Dimerization Catalyzed by Palladium Complexes. Formation of 2-Ethylidene-5-Hept-4-ene. *Bulletin of the Chemical Society of Japan*. 1978, 2375–2378.
- (11) Braunstein, P.; Matt, D.; Nobel, D. Carbon Dioxide Activation and Catalytic Lactone Synthesis by Telomerization of Butadiene and CO₂. *J. Am. Chem. Soc.* **1988**, *110*, 3207–3212.
- (12) Behr, A.; Juszak, K. D. Palladium-Catalyzed Reaction of Butadiene and Carbon Dioxide. *J. Organomet. Chem.* **1983**, *255*, 263–268.
- (13) Sharif, M.; Jackstell, R.; Dastgir, S.; Al-Shihi, B.; Beller, M. Efficient and Selective Palladium-Catalyzed Telomerization of 1,3-Butadiene with Carbon Dioxide. *ChemCatChem* **2017**, *9*, 542–546.
- (14) Balbino, J. M.; Dupont, J.; Bayón, J. C. Telomerization of 1,3-Butadiene with

- Carbon Dioxide: A Highly Efficient Process for δ -Lactone Generation. *ChemCatChem* **2018**, *10*, 206–210.
- (15) Song, J.; Feng, X.; Yamamoto, Y.; Almansour, A. I.; Arumugam, N.; Kumar, R. S.; Bao, M. Selective Synthesis of δ -Lactone via Palladium Nanoparticles-Catalyzed Telomerization of CO₂ with 1,3-Butadiene. *Tetrahedron Lett.* **2016**, *57*, 3163–3166.
 - (16) Behr, A.; Henze, G. Use of Carbon Dioxide in Chemical Syntheses via a Lactone Intermediate. *Green Chem.* **2011**, *13*, 25–39.
 - (17) Hardouin Duparc, V.; Shakaroun, R. M.; Slawinski, M.; Carpentier, J. F.; Guillaume, S. M. Ring-Opening (Co)Polymerization of Six-Membered Substituted δ -Valerolactones with Alkali Metal Alkoxides. *Eur. Polym. J.* **2020**, *134*, 109858.
 - (18) Schneiderman, D. K.; Hillmyer, M. A. Aliphatic Polyester Block Polymer Design. *Macromolecules* **2016**, *49*, 2419–2428.
 - (19) Olsén, P.; Odelius, K.; Albertsson, A. C. Thermodynamic Presynthetic Considerations for Ring-Opening Polymerization. *Biomacromolecules* **2016**, *17*, 699–709.
 - (20) Wheeler, O. H.; Granell, E. E. Solvolysis of Substituted γ -butyrolactones and δ -Valerolactones. 1964, *701*, 1959–1961.
 - (21) Nakano, R.; Ito, S.; Nozaki, K. Copolymerization of Carbon Dioxide and Butadiene via a Lactone Intermediate. *Nat. Chem.* **2014**, *6*, 325–331.
 - (22) Liu, M.; Sun, Y.; Liang, Y.; Lin, B. L. Highly Efficient Synthesis of Functionalizable Polymers from a CO₂/1,3-Butadiene-Derived Lactone. *ACS Macro Lett.* **2017**, *6*, 1373–1378.
 - (23) Yue, S.; Bai, T.; Xu, S.; Shen, T.; Ling, J.; Ni, X. Ring-Opening Polymerization of CO₂-Based Disubstituted δ -Valerolactone toward Sustainable Functional Polyesters. **2021**.
 - (24) Espinosa, L. D. G.; Williams-pavlangos, K.; Turney, K. M.; Wesdemiotis, C.; Eagan, J. M. Degradable Polymer Structures from Carbon Dioxide and Butadiene. **2021**.
 - (25) Sugiura, M.; Sato, N.; Kotani, S.; Nakajima, M. Lewis Base-Catalyzed Conjugate Reduction and Reductive Aldol Reaction of α,β -Unsaturated Ketones Using Trichlorosilane. *Chem. Commun.* **2008**, *2*, 4309–4311.
 - (26) Behr, A.; Brehme, V. A. Bimetallic-Catalyzed Reduction of Carboxylic Acids and Lactones to Alcohols and Diols. *Adv. Synth. Catal.* **2002**, *344*, 525–532.
 - (27) Hudlicky, T.; Sinai-Zingde, G.; Natchus, M. G. Selective Reduction of α,β -Unsaturated Esters in the Presence of Olefins. *Tetrahedron Lett.* **1987**, *28*, 5287–5290.
 - (28) Makiguchi, K.; Satoh, T.; Kakuchi, T. Diphenyl Phosphate as an Efficient Cationic Organocatalyst for Controlled/Living Ring-Opening Polymerization of δ -Valerolactone and ϵ -Caprolactone. *Macromolecules* **2011**, *44*, 1999–2005.
 - (29) Delcroix, D.; Couffin, A.; Susperregui, N.; Navarro, C.; Maron, L.; Martin-Vaca, B.; Bourissou, D. Phosphoric and Phosphoramidic Acids as Bifunctional Catalysts for the Ring-Opening Polymerization of ϵ -Caprolactone: A Combined Experimental and Theoretical Study. *Polym. Chem.* **2011**, *2*, 2249–2256.

- (30) Dove, A. P. Organic Catalysis for Ring-Opening Polymerization. *ACS Macro Lett.* **2012**, *1*, 1409–1412.
- (31) Thomas, C.; Bibal, B. Hydrogen-Bonding Organocatalysts for Ring-Opening Polymerization. *Green Chem.* **2014**, *16*, 1687–1699.
- (32) Gazeau-Bureau, S.; Delcroix, D.; Martín-Vaca, B.; Bourissou, D.; Navarro, C.; Magnet, S. Organo-Catalyzed ROP of ϵ -Caprolactone: Methanesulfonic Acid Competes with Trifluoromethanesulfonic Acid. *Macromolecules* **2008**, *41*, 3782–3784.
- (33) Makiguchi, K.; Kikuchi, S.; Satoh, T.; Kakuchi, T. Synthesis of Block and End-Functionalized Polyesters by Triflimide-Catalyzed Ring-Opening Polymerization of ϵ -Caprolactone, 1,5-Dioxepan-2-One, and Rac-Lactide. *J. Polym. Sci. Part A Polym. Chem.* **2013**, *51*, 2455–2463.
- (34) Coady, D. J.; Fukushima, K.; Horn, H. W.; Rice, J. E.; Hedrick, J. L. Catalytic Insights into Acid/Base Conjugates: Highly Selective Bifunctional Catalysts for the Ring-Opening Polymerization of Lactide. *Chem. Commun.* **2011**, *47*, 3105–3107.
- (35) Lin, B.; Waymouth, R. M. Organic Ring-Opening Polymerization Catalysts: Reactivity Control by Balancing Acidity. *Macromolecules* **2018**, *51*, 2932–2938.
- (36) Whelan, D. Thermoplastic Elastomers. *Brydson's Plast. Mater. Eighth Ed.* **2017**, No. 4, 653–703.
- (37) Wanamaker, C. L.; O'Leary, L. E.; Lynd, N. A.; Hillmeyer, M. A.; Tolman, W. B. Renewable-Resource Thermoplastic Elastomers Based on Polylactide and Polymenthide. *Biomacromolecules* **2007**, *8*, 3634–3640.
- (38) Lin, B.; Waymouth, R. M. Urea Anions: Simple, Fast, and Selective Catalysts for Ring-Opening Polymerizations. *J. Am. Chem. Soc.* **2017**, *139*, 1645–1652.
- (39) Hong, M.; Chen, E. Y. X. Future Directions for Sustainable Polymers. *Trends Chem.* **2019**, *1*, 148–151.
- (40) Tang, X.; Chen, E. Y. X. Toward Infinitely Recyclable Plastics Derived from Renewable Cyclic Esters. *Chem* **2019**, *5*, 284–312.
- (41) Fagnani, D. E.; Tami, J. L.; Copley, G.; Clemons, M. N.; Getzler, Y. D. Y. L.; McNeil, A. J. 100th Anniversary of Macromolecular Science Viewpoint: Redefining Sustainable Polymers. *ACS Macro Lett.* **2021**, *10*, 41–53.
- (42) Abel, B. A.; Snyder, R. L.; Coates, G. W. Chemically Recyclable Thermoplastics from Reversible-Deactivation Polymerization of Cyclic Acetals. *Science (80-.).* **2021**, *789*, 783–789.
- (43) Rieger, J.; Van Butsele, K.; Lecomte, P.; Detrembleur, C.; Jérôme, R.; Jérôme, C. Versatile Functionalization and Grafting of Poly(ϵ -Caprolactone) by Michael-Type Addition. **2004**.
- (44) Tang, X.; Hong, M.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y. X. The Quest for Converting Biorenewable Bifunctional α -Methylene- γ -Butyrolactone into Degradable and Recyclable Polyester: Controlling Vinyl-Addition/Ring-Opening/Cross-Linking Pathways. *J. Am. Chem. Soc.* **2016**, *138*, 14326–14337.
- (45) Campos, L. M.; Killips, K. L.; Sakai, R.; Paulusse, J. M. J.; Dameron, D.; Drockenmuller, E.; Messmore, B. W.; Hawker, C. J. Development of Thermal and

- Photochemical Strategies for Thiol-Ene Click Polymer Functionalization. *Macromolecules* **2008**, *41*, 7063–7070.
- (46) Hauenstein, O.; Agarwal, S.; Greiner, A. Bio-Based Polycarbonate as Synthetic Toolbox. *Nat. Commun.* **2016**, *7*, 1–7.
 - (47) Chanda, S.; Ramakrishnan, S. Poly(Alkylene Itaconate)s – an Interesting Class of Polyesters with Periodically Located Exo-Chain Double Bonds Susceptible to Michael Addition. *Polym. Chem.* **2015**, *6*, 2108.
 - (48) Ohsawa, S.; Morino, K.; Sudo, A.; Endo, T. Synthesis of a Reactive Polyester Bearing α,β -Unsaturated Ketone Groups by Anionic Alternating Copolymerization of Epoxide and Bicyclic Bis(γ -Butyrolactone) Bearing Isopropenyl Group. **2011**, *44*, 1814–1820.
 - (49) Huang, K. S.; Yang, C. H.; Huang, S. L.; Chen, C. Y.; Lu, Y. Y.; Lin, Y. S. Recent Advances in Antimicrobial Polymers: A Mini-Review. *Int. J. Mol. Sci.* **2016**, *17*.
 - (50) Şucu, T.; Shaver, M. P. Inherently Degradable Cross-Linked Polyesters and Polycarbonates: Resins to Be Cheerful. *Polym. Chem* **2020**, *11*, 6397.
 - (51) Brutman, J. P.; De Hoe, G. X.; Schneiderman, D. K.; Le, T. N.; Hillmyer, M. A. Renewable, Degradable, and Chemically Recyclable Cross-Linked Elastomers. *Ind. Eng. Chem. Res.* **2016**, *55*, 11097–11106.
 - (52) Robert, T.; Friebel, S. Itaconic Acid-a Versatile Building Block for Renewable Polyesters with Enhanced Functionality. *Green Chem.* **2016**, *18*.
 - (53) Anderson, K. S.; Schreck, K. M.; Hillmyer, M. A. Toughening Polylactide. *Polym. Rev.* **2008**, *48*, 85–108.
 - (54) C. Jacobs, Ph. Dubois, R. Jerome, P. T. Macromolecular Engineering of Polylactones and Polylactides. 5. Synthesis and Characterization of Diblock Copolymers Based on Poly- ϵ -Caprolactone and Poly(L,L or D,L)Lactide by Aluminum Alkoxides. **1991**, *24*.