Ring-Opening Copolymerizations of a CO_2-derived δ-Valerolactone with ε-Caprolactone and L-Lactide

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ABSTRACT: Ring-opening random, gradient, and block copolymerizations of the CO_2-derived δ-valerolactone 3-ethyl-6-vinyltetrahydro-2H-pyran-2-one (**EtVP**) with ε-caprolactone (**ε-CL**) and L-lactide (**LLA**) are reported. By employing both concurrent and sequential addition strategies, a variety of thermal and physical properties could be accessed. Concurrent copolymerization of **EtVP** with **ε-CL** yielded gradient copolymers with low glass transition temperatures, while block copolymerizations via sequential addition led to semi-crystalline materials regardless of monomer feed ratios. For **LLA** copolymerizations, glass transition temperatures increased with **LLA** incorporation regardless of addition method, but higher T_g values were observed in block copolymerizations from sequential addition. Tensile testing of a *poly*(**EtVP**-*b*-**LLA**) with molar ratio of 40:60 **EtVP**:**LLA** resulted in σ = 0.8 MPa, E = 5.6 MPa and 83% elongation at break. The chemical recyclability of **EtVP**-based copolymers was explored as an end-of-life option. Both **ε-CL** and **LLA** copolymers could be recycled, with block copolymers giving higher yields of recycled monomers than random copolymers.

Introduction

The disubstituted lactone, 3-ethylidene-6-vinyl-tetrahydro-2H-pyran-2-one (**EVP**) offers substantial promise as an inexpensive entry point into CO_2-derived materials because it can be selectively synthesized through efficient Pd-catalyzed telomerization of butadiene and CO_2.[1,2] Biodegradable and chemically recyclable **EVP**-derived polyesters can be accessed through the ring-opening polymerization (ROP) of either the semi- or fully-hydrogenated δ-valerolactone **EVP** derivatives, 3-ethyl-6-vinyltetrahydro-2H-pyran-2-one (**EtVP**) or 3,6-diethyltetrahydro-2*H*-pyran-2-one (**DEtP**).[3,4] However, *poly*(**EtVP**) and *poly*(**DEP**) are both amorphous polymers: although they may find use in flexible/ductile materials[5] or as adhesives,[4] there is significant interest in tuning the materials properties of these polymers in an effort to expand their applications.

Ring-opening copolymerization (ROCOP) of lactones has been well-demonstrated as a method for accessing polyesters with a wide array of thermal and mechanical properties.[6] ε-caprolactone (**ε-CL**) and L-lactide (**LLA**) are two of the most used and well-studied lactones for copolymer synthesis. *Poly*(ε-caprolactone) (**PCL**), which can be bioderived[7,8], has many biomedical applications due to its strong permeability, elasticity, and thermal properties.[9] More specifically, **PCL** is semi-crystalline with a melting point (T_m) of 59-64°C and a glass transition temperature (T_g) of -60 °C, which results in high toughness at human body temperatures.[10,11] **PCL** is also biodegradable, though it typically requires 2-3 years for complete degradation to occur in biological media.[12] Bulk **PCL** also exhibits low tensile strength (16-27 MPa) and elastic modulus (250-430 MPa).[13,14] On the other hand, *poly*(L-lactic acid) (**PLLA**) is an attractive bio-based[15] polymer with high tensile strength (28-50 MPa) and elastic modulus (1200-3250 MPa), though it suffers from poor toughness (2.0-6.0% elongation at break).[13,16–19] Due to these factors, copolymers of **PCL** and **PLLA** have been developed to address the weaknesses of the individual homopolymers.[19–22] While copolymer properties can be tuned through monomer feed ratios, molecular weights, and lactone choice, different copolymer microstructures (random, gradient, block copolymers) can also affect the overall thermal and mechanical properties. For example, **PLLA**-**PCL** random copolymers lack industrially relevant mechanical properties, as the randomization[19] of the structure results in a decrease in overall polymer crystallinity compared to the their block counterparts.[23] Comonomer reactivity ratios can be used to predict the type of copolymer (alternating, blocky, gradient or random) that will form under ROP conditions.[24,25]

Given the successes in the synthesis of **PCL/PLLA** copolymers *via* ROCOP,[26] we hypothesized that **ε-CL** and **LLA** would be ideal candidates for copolymerization with **EtVP**. We envisioned a copolymer comprised of **EtVP** and **ε-CL** could be easily processable and potentially chemically recylable.[27] Alternately, in a **LLA/EtVP** copolymer the softness of *poly*(**EtVP**) could balance out the brittleness of **PLLA**, potentially yielding good mechanical strength and high toughness for biomedical applications.[28] In both cases, **EtVP** incorporation would promote enhanced biodegradation potential, recyclability, and provide the opportunity for post-polymerization modification through functionalization of the side chain vinyl groups.

No **EtVP**-based copolymers have been reported to date. However, there have been a few recent copolymer syntheses

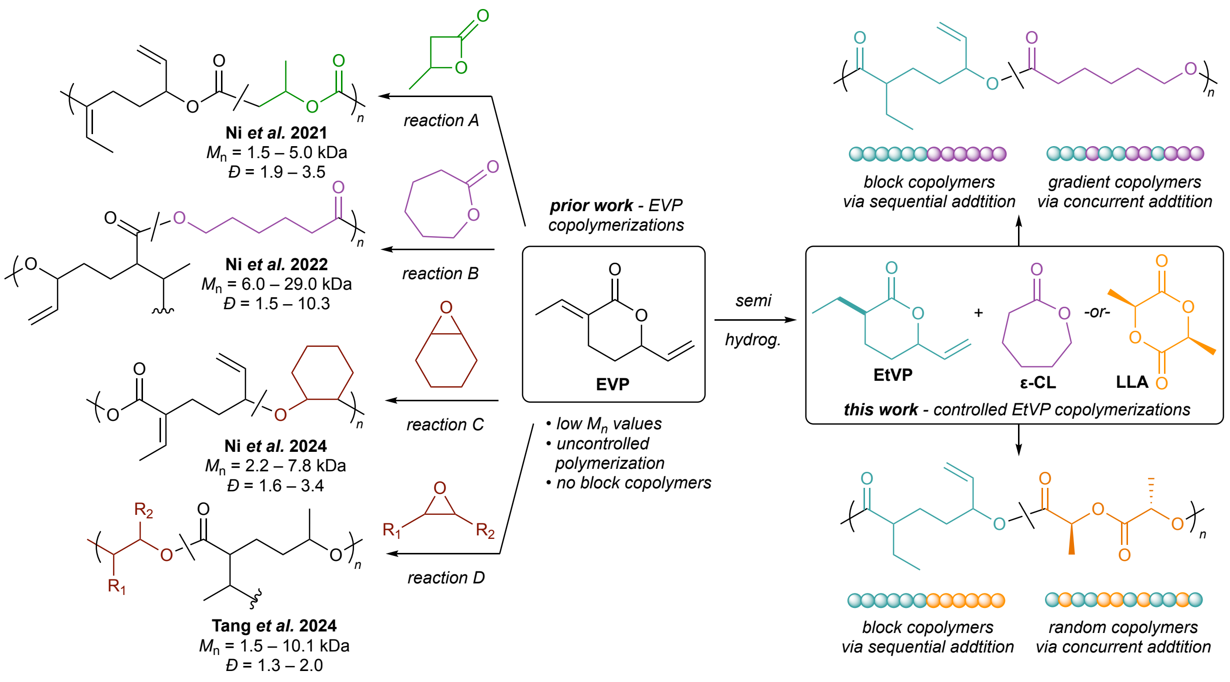


Figure 1. Left: previous reports of ring-opening copolymerizations with **EVP**. Right: controlled copolymerizations of **ε-CL** and **LLA** with **EtVP** can lead to various types of copolymer microstructure (this work).

with **EVP**.[29–34] For example, the Nozaki group reported radical alkene copolymerization of **EVP** with various commodity monomers.[29,30] ROCOP of **EVP** has also been explored since **EVP** is reticent to homopolymerize (Figure 1, left).[31–34] The Ni group has reported the use of β-butyrolactone (Figure 1, reaction A),[31] ε-CL (Figure 1, reaction B),[32] and cyclohexene oxide (Figure 1, reaction C)[33] as comonomers for the ROP of **EVP** to synthesize random copolymers; similarly, the Tang group has used propylene oxide (Figure 1, reaction D).[34] In all cases, low molar mass polymers with high dispersities were obtained, especially at high feed ratios of EVP. These limitations could be due to the α,β-unsaturated ester moiety of **EVP**, which generally impedes productive ring-opening and gives rise to deleterious Michael self-addition.[35] **EtVP** lacks this α,β-unsaturation and thus undergoes well-controlled ROP[3,5], so it is a good candidate for accessing more controlled copolymer microstructures *via* ROCOP. Herein, we report the copolymerization of **EtVP** with **ε-CL** and **LLA**. By altering when monomer addition occurs, copolymer microstructure can be controlled, leading to a broader range of thermal and physical properties (Figure 1, right).

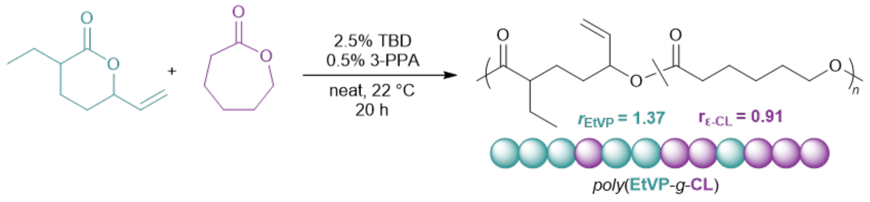
Results and Discussion

Initial copolymerization attempts with **ε-CL** were conducted with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)[36] and 3-phenyl-1-propanol (3-PPA) as an initiator (Table 1) under neat conditions, building on previous studies of TBD-catalyzed ring-opening polymerization of **EtVP.**[3] Across all feed ratios, high molar mass polymers (up to 54.0 kg/mol) could be achieved by employing 2.5 mol% TBD and 0.5% 3-PPA. At higher feed ratios of **EtVP** (Table 1, entries 4 and 5), lower molar masses are observed, which may be a result of increased undesirable TBD initiation.[3] Copolymer composition demonstrated good agreement with monomer feed ratios, indicating good control of the polymerization. T_g increased with the molar fraction of **EtVP**, from -60.5 at 19% **EtVP** in the polymer (Table 1, entry 2) to -33.1 °C at 100% **EtVP** (Table 1, entry 5) with values slightly lower than predicted by the Flory-Fox[37] equation (Figure S17). Melting points were observed when a high ratio of **ε-CL** (74%) was incorporated (Table 1, entry 2). Higher feed ratios of **ε-CL** also impacted the dispersity (*Đ*), increasing from 1.2 in pure *poly*(**EtVP**) (entry 5) to 1.7 in pure **PCL** (entry 1). This increase is most likely due to the propensity for **PCL** chain ends to undergo transesterification,[38] especially in the presence of TBD.[39] Transesterification can be minimized by employing shorter reaction times (Figure S19).

Kinetic studies were undertaken to further understand the reactivity of **EtVP** with **ε-CL** (Figure S18). The initial rate of polymerization was found to be 3.3 M h^{-1} at an **EtVP**:**ε-CL** molar ratio of 50:50, 5% TBD and 1% 3-PPA (Figure S18A). This is substantially faster than the homopolymerization of **EtVP** (1.44 M h^{-1}).[3] Reactivity ratios were determined by utilizing a simple non-terminal model (Figure S20).[24] It was found that $r_{\mathbf{EtVP}} = 1.37$ and $r_{\mathbf{\varepsilon\text{-}CL}} = 0.91$ when using a feed ratio of 40:60 **EtVP**:**ε-CL**, indicating the formation of a somewhat random copolymer with some gradient character. For reference, the reactivity ratios of monomers in the syntheses of *poly*(δ-valerolactone(VL)-*co*-**ε-CL**) and *poly*(**LLA**-*co*-**ε-CL**) gradient copolymers were found to be $r_{\mathrm{VL}} = 12.92$, $r_{\mathbf{LLA}} = 17.48$ and $r_{\mathbf{\varepsilon\text{-}CL}} = 0.10$.[24] A terminal model[25] was also explored, but no reasonable fit could be found for the obtained data set.

Next, block copolymerizations of **EtVP** and **ε-CL** were attempted, envisioning that the resultant diblock copolymers would be more crystalline. Employing a sequential monomer addition strategy, block copolymers [*poly*(**CL**-*b*-**EtVP**)] with varying amounts of **EtVP** incorporation were synthesized (Table 2). In the sequential addition reactions, the order of monomer addition as well as the presence of solvent had a significant impact on the copolymer synthesized (Table S3). It was found that initial polymerization of **ε-CL** to full conversion in concentrated toluene (8-9 M) followed

Table 1. Synthesis and properties of gradient copolymers from **EtVP** and **ε-CL**.

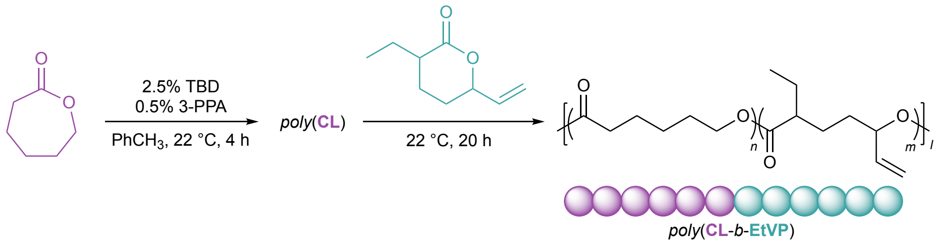


Entry	**EtVP/ε-CL** (mol/mol)[b]	Polymer **EtVP** (%)[c]	$M_{n,\mathrm{theo}}$ (kDa)	$M_{n,\mathrm{SEC}}$ (kDa)[d]	Đ	T_g, T_m (°C)
1	0/100	0	22.9	54.0	1.7	n.d.[e], 57.0

2	20/80	19	22.2	44.8	1.6	-60.5, 29.4
3	50/50	48	24.7	27.1	1.5	-50.8, none
4	80/20	74	26.4	23.7	1.2	-44.9, none
5	100/0	100	25.1	17.8	1.2	-33.1, none

[a]Reaction conditions: 2.5 mol% TBD, 0.5 mol% 3-PPA, neat, 22 °C, 20 h. [b]initial molar ratios. [c]calculated from ^{1}H NMR spectroscopy. [d]determined by THF SEC using polystyrene standards. [e]not determined.

Table 2. Synthesis and properties of block copolymers from **EtVP** and **ε-CL**.



Entry	**EtVP**/**ε-CL** (mol/mol)[b]	**EtVP** Conversion (%)[c]	Polymer **EtVP** (%)[c]	$M_{\mathrm{n,SEC}}$ (kDa)[d]	Đ	T_g, T_m (°C)
1	0/100	-	0	54.0	1.7	n.d.[e], 57.0
2	20/80	37	7	-	-	-
3	50/50	64	42	30.6	1.7	n.d.[e], 54.5
4	80/20	67	74	17.3	1.5	n.d.[e], 54.8
5	100/0	81	100	17.8	1.2	-33.1, none

[a]Reaction conditions: 2.5 mol% TBD, 0.5 mol% 3-PPA, 8-9 M toluene, 22 °C, 24 h. [b]initial molar ratios. [c]calculated from ^{1}H NMR spectroscopy. [d]determined by THF SEC using polystyrene standards. [e]not determined.

by subsequent chain extension through **EtVP** addition without pre-polymer purification resulted in the highest molar mass copolymers, and block copolymerizations under these conditions are reported in Table 2. Chain extension of purified *poly*(**EtVP**) was also explored and resulted in similar copolymers, but required more intensive purification steps and was less convenient (Figure S21). Molar masses and dispersities of *poly*(**CL**-*b*-**EtVP**) were similar to the gradient copolymers (Table 1) synthesized under identical feed ratios and catalyst/initiator loadings.

The microstructure of the gradient and block copolymers can be differentiated by ^{13}C NMR spectroscopy (Figure 2). For the 50:50 *poly*(**CL**-*b*-**EtVP**) block copolymer (Figure 2, middle; from Table 2 Entry 3), two sets of resonances are present in the carbonyl region of the ^{13}C NMR spectrum at 174.9 and 173.5 ppm. These signals are consistent with long blocks of each monomer in the block copolymer, as a mixture of *poly*(**EtVP**) and **PCL** homopolymers (Figure 2, top) has identical chemical shift values for each polymer. In contrast, the random/gradient copolymer *poly*(**EtVP**-*g*-**CL**) (Figure 2, bottom; from Table 1 entry 3) exhibits two additional sets of resonances at 175.8 and 172.7 ppm corresponding to the heterosequences **EtVP-ε-CL** and **ε-CL-EtVP,** respectively. These heterosequence resonances were assigned by ^{1}H-^{13}C HMBC spectroscopy (Figure S11). The presence of **EtVP**-**EtVP** and **ε-CL**-**ε-CL** homosequences, as well as heterosequences and their ratios, further indicate that *poly*(**EtVP**-*g*-**CL**) is a gradient copolymer. Based on ^{13}C NMR carbonyl integrations, 21.4% correspond to **EtVP-EtVP**, 25.4% to **EtVP-ε-CL**, 26.4% to **ε-CL-EtVP** and 26.5% to **ε-CL-ε-CL** in the 50:50 gradient copolymer. The average length of monomer block (l) and degree of randomness (R) were also determined for the gradient copolymer using ^{13}C NMR spectroscopy.[40] It was found that $l_{\mathbf{CL}} = 3.0$ and $l_{\mathbf{EtVP}} = 2.9$ with $R_{\mathbf{CL}} = 0.62$ and $R_{\mathbf{EtVP}} = 0.76$; where $R = 1$ for a random copolymer and < 0.5 for a blocky copolymer. The thermal properties of the block copolymers were drastically impacted compared to the gradient copolymers. For example, in the case of 50:50 **EtVP**:**ε-CL**, a melting point of 54.5 °C was observed for the block copolymer (Table 2, entry 3), but no melting point was present for the gradient copolymer (Table 1, entry 3).

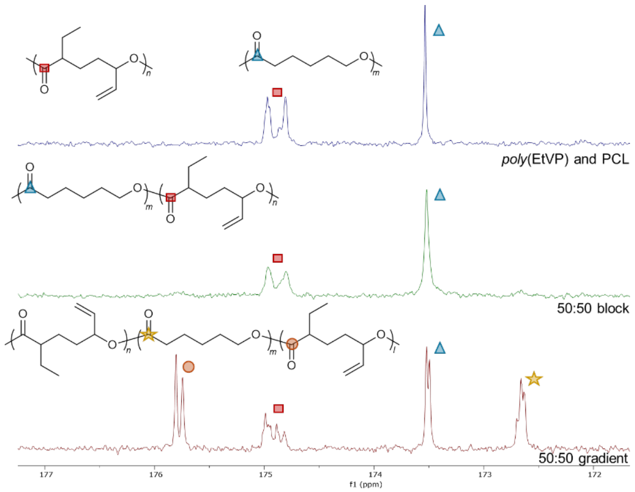
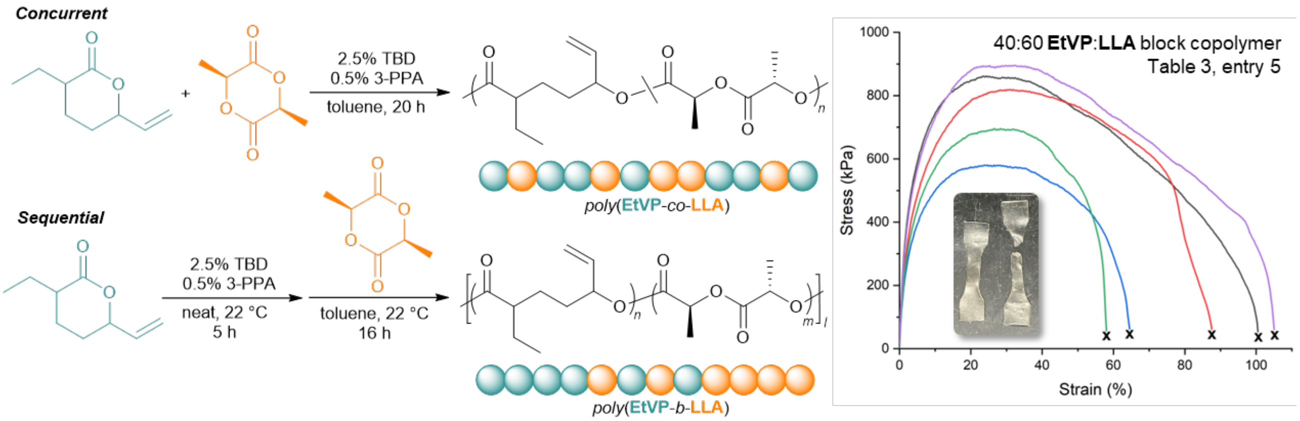


Figure 2. ^{13}C NMR of 50:50 *poly*(**EtVP**-*g*-**CL**) (bottom), 50:50 *poly*(**CL**-*b*-**EtVP**) (middle) and a mixture of *poly*(**EtVP**) and **PCL** (top).

Encouraged by the ability to synthesize gradient and block copolymers with **ε-CL**, copolymerizations of **EtVP** with **LLA** were next explored (Table 3). **LLA** is not very soluble in **EtVP**, and as a result reactions were carried out with toluene as the solvent. Reactions were run as concentrated as possible owing to the low T_c of **EtVP**. Here, both concurrent polymerizations as well as sequential additions for block copolymer synthesis were attempted. For **LLA**, polymerization of **EtVP** followed by

LLA yielded better results than the reverse order (Table S5), which is opposite of **ε-CL** block copolymerization. We attribute this difference primarily to solubility. Regardless of the feed strategy, molar masses of the **EtVP/LLA** copolymers were lower than the **EtVP/ε-CL** copolymers. For concurrent addition (random) copolymers, *poly*(**EtVP**-*co*-**LLA**), a feed ratio of 50:50 EtVP:LLA resulted in the highest molar mass copolymer (Table 3, entry 2), and no clear molar mass trend was observed with molar feed ratios. A broader range of molecular weights and dispersities were found for the block copolymers, *poly*(**EtVP**-*b*-**LLA**) (Table 3, entries 4-7), compared to the random copolymers. For example, a maximum M_n of 27.3 kg/mol and a $Đ$ = 1.5 was obtained with 21% **EtVP** incorporation in *poly*(**EtVP**-*b*-**LLA**) (Table 3, entry 4).

Table 3. Synthesis and properties of **EtVP** and **LLA** copolymers from concurrent and sequential addition. Inset graph: tensile testing of 40:60 **EtVP**:**LLA** block copolymer (5 trials).



Entry	Addition	EtVP/LLA (mol/mol)[b]	EtVP Conversion (%)[c]	Polymer EtVP (%)[c]	$M_{n,SEC}$ (kDa)[d]	Đ	T_g (°C)[e]
1	concurrent	20/80	74	23	13.7	1.6	30.0
2	concurrent	50/50	75	49	18.6	1.5	5.0
3	concurrent	80/20	69	77	15.6	1.9	-16.8
4	sequential	20/80	99	21	27.3	1.5	40.8
5	sequential	40/60[f]	90	41	18.8	1.5	-26.7, 35.4
6	sequential	50/50	89	55	16.7	1.4	-25.6, 30.5
7	sequential	80/20	88	84	23.9	2.5	-22.9

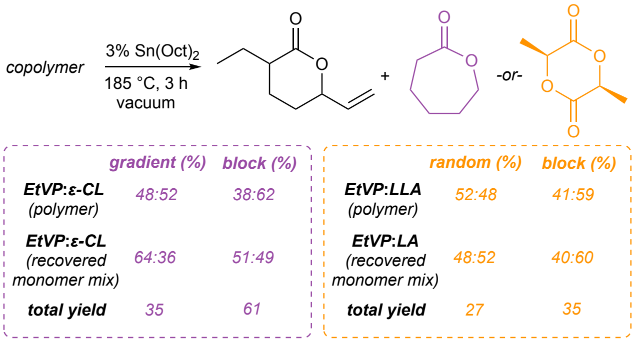
[a]Reaction conditions: 2.5 mol% TBD, 0.5 mol% 3-PPA, 3.24 M toluene (respective to **LLA**), 22 °C, 25 h. [b]initial molar ratios. [c]calculated from ^{1}H NMR spectroscopy. [d]determined by THF SEC using polystyrene standards. [f]scaled-up in 5.6 M THF (respective to **LLA**).

All copolymers synthesized were amorphous, even when **LLA** incorporation was 79% (Table 3, entry 4). However, the T_g values were significantly impacted by **LLA** incorporation in both the random and block copolymers. For example, the T_g values of *poly*(**EtVP**-*co*-**LLA**) spanned from -16.8 °C with 77% **EtVP** incorporation to 30.0 °C with 23% **EtVP** incorporation (Table 3, entries 1-3). A similar trend can be seen in *poly*(**ε-CL**-*co*-**LLA**), where T_g increased from -23 to 19 °C when the molar fraction of **ε-CL** decreased from 46% to 18%.[20] The T_g of the *poly*(**EtVP**-*b*-**LLA**) block copolymers increased from -22.9 to 40.8 °C when increasing from 16% to 79% **LLA** incorporation (Table 3, entries 4-7). Interestingly, when **EtVP** incorporation was 41 and 55% (Table 3, entry 5 and 6), two T_g values were observed suggesting some immiscibility. While it is hard to directly compare T_g values of the two copolymer types due to a difference in the degrees of **EtVP** incorporation, it is expected that blocky *poly*(**EtVP**-*b*-**LLA**) would have higher T_g values than the random of *poly*(**EtVP**-*co*-**LLA**) copolymers based on comparison to **PCL**-**PLLA** copolymers[41]. The microstructure of 50:50 LLA copolymers was investigated *via* ^{13}C NMR spectroscopy (Figure S39 and S52). Resonances consistent with **EtVP**-**LLA** and **LLA**-**EtVP** heterosequences were the most predominant in *poly*(**EtVP**-*co*-**LLA**), although trace homosequences could be observed. This could provide evidence for a random copolymer when employing concurrent addition with **EtVP**-**LLA**, although reactivity ratios could not be established because of signal overlap between **EtVP** and **LLA**. For *poly*(**EtVP**-*b*-**LLA**), trace heterosequences were observed which can be explained by the increase in **EtVP** conversion after the addition of **LLA**.

Next, mechanical testing of the **LLA** copolymers was undertaken. Initially *poly*(**EtVP**-*co*-**LLA**) with a molar ratio of 50:50 was used for tensile testing (Figure S61). While this polymer exhibited excellent elasticity, its tensile strength was too low (< 15 kPa) for accurate measurement. *Poly*(**EtVP**-*b*-**LLA**) with 40% **EtVP** (Table 3, entry 5) was then investigated. After testing five samples, the average tensile strength was found to be 0.8 MPa with an elastic modulus of 5.6 MPa and an 83% elongation at break (Table 3 inset graph, right). Ni observed similar values for their *poly*(**CL**-*co*-**EVP**) network when employing a 50:50 molar ratio which exhibited a tensile strength of 1 mPa and 150% elongation at break.[32] Compared to bulk **PLLA**, elongation has significantly improved from 2.0-6.0%, however the tensile strength is much lower than 28-50 MPa.[17] **PLLA**-**PCL** copolymers exhibit excellent strength and elongation (up to 800%)[21] , however multiblocks[21], stereocomplexes[42–45], or blends[46–48] are typically employed.

Finally, the chemical recyclability of **EtVP**-based copolymers was explored (Figure 3) employing the commonly used catalyst, tin(II) 2-ethylhexanoate $(SnOct)_2$. Chemical recycling has been demonstrated for *poly*(**EtVP**)[3,5], **PCL**[27,49], **PLLA**[50,51], and many CO_2-based polymers[52–54] making it a potentially viable end-of-life option for these copolymers. *Poly*(**EtVP**-*g*-**CL**) with

48% **EtVP** could be recycled at 185 °C under vacuum with 35% combined yield of the two monomers, whereas *poly*(**CL**-*b*-**EtVP**) was recycled with 61% combined yield of the two monomers. More **EtVP** was recovered relative to **ε-CL** in both cases (64% and 51% for gradient and block, respectively). The residual material for both copolymers was primarily unreacted **PCL** with some *poly*(**EtVP**) still present (Table S6). **LLA** copolymers resulted in lower recyclability, with only 27% yield for *poly*(**EtVP**-*co*-**LLA**) and 35% yield for *poly*(**EtVP**-*b*-**LLA**). In this case, residual material was a mixture of decomposition or cross-linked products (Figure S62). A mixture of **LLA** and meso-lactide was recovered with **EtVP**. End-capped *poly*(**CL**-*b*-**EtVP**) was synthesized and recycled under our standard conditions. The decreased monomer recovery (28%) and low dispersity of the residual polymer (Figure S63) suggests a domino-type unzipping mechanism which may explain the increase in recyclability from gradient to block **CL** copolymers. Overall, monomer recovery of the copolymer systems is significantly lower than *poly*(**EtVP**) and **PCL** homopolymers (Table S6, 85% and 78% recovery, respectively), but much higher than bulk **PLLA** (4% recovery). Nonetheless, these results show the potential for chemical recycling of **EtVP**-based copolymers although a different catalyst system[27,49–51] may be required for higher monomer recovery/selectivity.



	gradient (%)	*block (%)*
EtVP:ε-CL *(polymer)*	*48:52*	*38:62*
EtVP:ε-CL *(recovered monomer mix)*	*64:36*	*51:49*
total yield	*35*	*61*

	random (%)	*block (%)*
EtVP:LLA *(polymer)*	*52:48*	*41:59*
EtVP:LA *(recovered monomer mix)*	*48:52*	*40:60*
total yield	*27*	*35*

Figure 3. Chemical recycling of **EtVP** based copolymers employing Sn(Oct)$_2$ as a depolymerization catalyst.

Conclusion

This work has expanded the synthetic polymer chemistry of the CO$_2$-derived lactone **EtVP** through ring-opening copolymerizations with **ε-CL** and **LLA**. Polymer properties and microstructures could be tuned through concurrent and sequential copolymerization strategies, which led to the formation of either block, gradient, or random copolymers. **ε-CL** block copolymers resulted in semi-crystalline polymers regardless of the molar ratio employed. For **LLA**, copolymers remained amorphous, and mechanical testing showed improved elasticity relative to **PLLA**. Furthermore, **ε-CL** and **LLA** copolymers could be chemically recycled back to monomer utilizing Sn(Oct)$_2$. While this work lays the foundation for **EtVP**-based copolymers, investigation into triblocks and other end-of-life options may further improve the potential applications of these CO$_2$-based (co)polymers.

ASSOCIATED CONTENT

Supporting Information

Full experimental details and data (.pdf)

The Supporting Information is available free of charge on the ACS Publications website.

Data Availability Statement. All primary data files are available free of charge at https://doi.org/10.13020/cnxb-m954

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Author Contributions

R.J.A. and I.A.T. conceived of the work. R.J.A., R.L.F., and R.M.R. executed the experimental plan and analyzed the data. I.A.T. supervised the work. R.J.A. wrote the initial manuscript draft which was then edited through contributions of all the authors. All authors have given approval to the final version of the manuscript.

Conflicts of Interest

I.A.T. and R.M.R. are co-inventors on a patent describing the composition of matter of EtVP, and I.A.T. is the co-founder of a start-up company (LoopCO2) focused on commercialization of EtVP-based materials.

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