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

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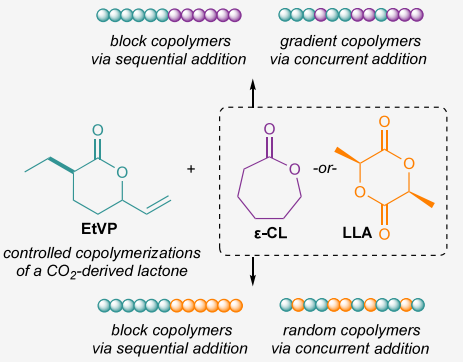
ABSTRACT: Ring-opening random, gradient, and block copolymerizations of CO_2-derived δ-valerolactone 3-ethyl-6-vinyltetrahydro-2*H*-pyran-2-one (EtVP) with ε-caprolactone (ε-CL) and L-lactide (LLA) are reported. By employing both concurrent and sequential addition strategies, we could access a variety of thermal and physical properties. Concurrent copolymerization of EtVP with ε-CL yielded gradient copolymers with low glass transition temperatures, while block copolymerizations via sequential addition led to semicrystalline materials regardless of monomer feed ratios. For LLA copolymerizations, glass transition temperatures increased with LLA incorporation regardless of the addition method, but higher T_g values were observed in block copolymerizations from sequential addition. Tensile testing of *poly*(EtVP-*b*-LLA) with a 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-2*H*-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 semihydrogenated or fully hydrogenated δ-valerolactone EVP derivatives, 3-ethyl-6-vinyltetrahydro-2*H*-pyran-2-one (EtVP) or 3,6-diethyltetrahydro-2*H*-pyran-2-one (DEtP).[3,4] However, *poly*(EtVP) and *poly*(DEtP) 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 material 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 semicrystalline 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 biobased[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, and 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 composed of EtVP and ε-

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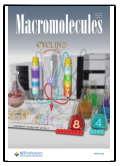

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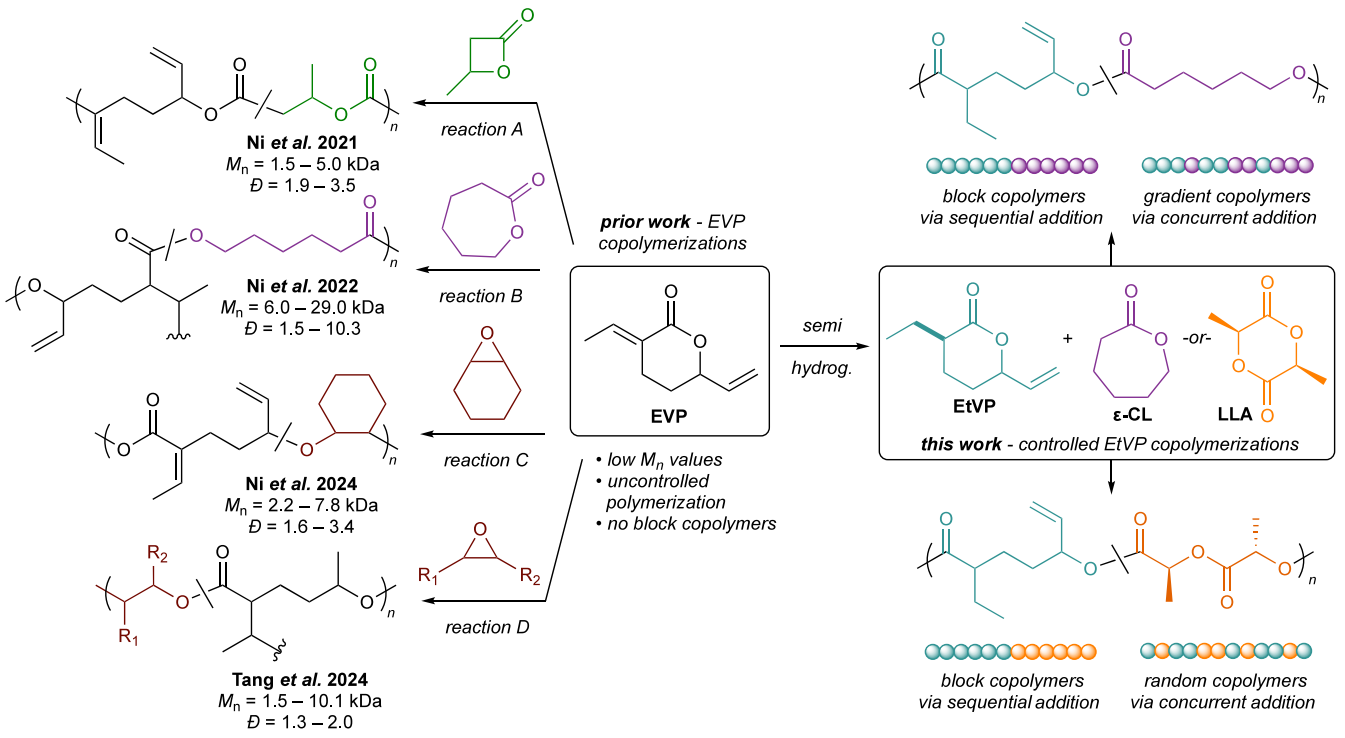
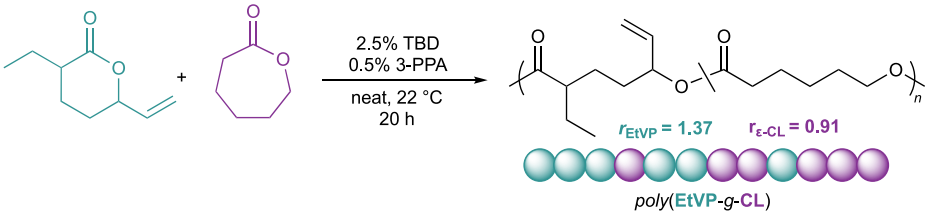


Figure 1. Left: previous reports of ROP with EVP. Right: controlled copolymerizations of ε-CL and LLA with EtVP can lead to various types of copolymer microstructures (this work).

Table 1. Synthesis and Properties of Gradient Copolymers from EtVP and ε-CLP[a]



entry	EtVP/ε-CL (mol/mol)[b]	polymer EtVP (%)[c]	$M_{n,theo}$ (kDa)	$M_{n,SEC}$ (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.

CL could be easily processable and potentially chemically recyclable.[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 and recyclability and provide the opportunity for postpolymerization 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 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).

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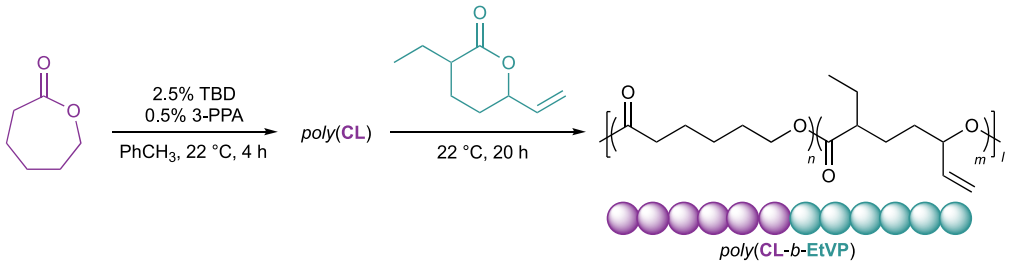
Table 2. Synthesis and Properties of Block Copolymers from EtVP and ε-CL[a]



entry	EtVP/ε-CL (mol/mol)[b]	EtVP conversion (%)[c]	polymer EtVP (%)[c]	$M_{n,SEC}$ (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.

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 ROP 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 those predicted by the Flory−Fox[37] equation (Figure S17). Melting points were observed when a high ε-CL (74%) ratio 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 nonterminal model (Figure S20).[24] It was found that r_{EtVP} = 1.37 and $r_{\varepsilon\text{-CL}}$ = 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_{VL} = 12.92, r_{LLA} = 17.48, and $r_{\varepsilon\text{-CL}}$ = 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, implying 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 the initial polymerization of ε-CL to full conversion in concentrated toluene (8−9 M) followed by subsequent chain extension through EtVP addition without prepolymer 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 those of the gradient copolymers (Table 1) synthesized under identical feed ratios and catalyst/initiator loadings.

The microstructures 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,

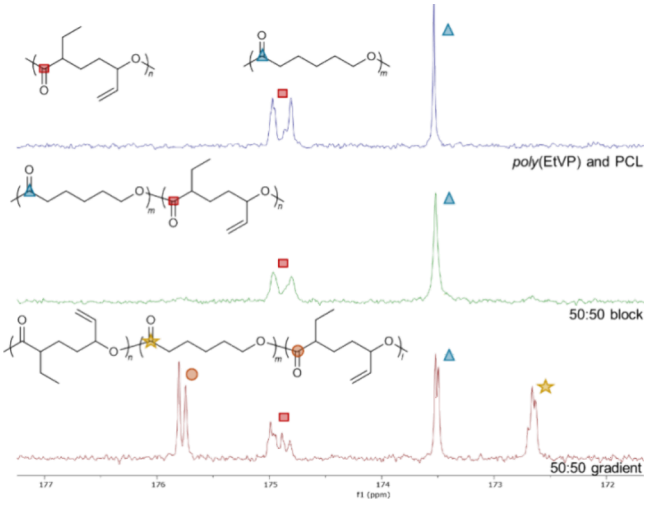


Figure 2. ^{13}C NMR of 50:50 *poly*(EtVP-*g*-CL) (bottom), 50:50 *poly*(CL-*b*-EtVP) (middle), and a mixture of *poly*(EtVP) and PCL (top).

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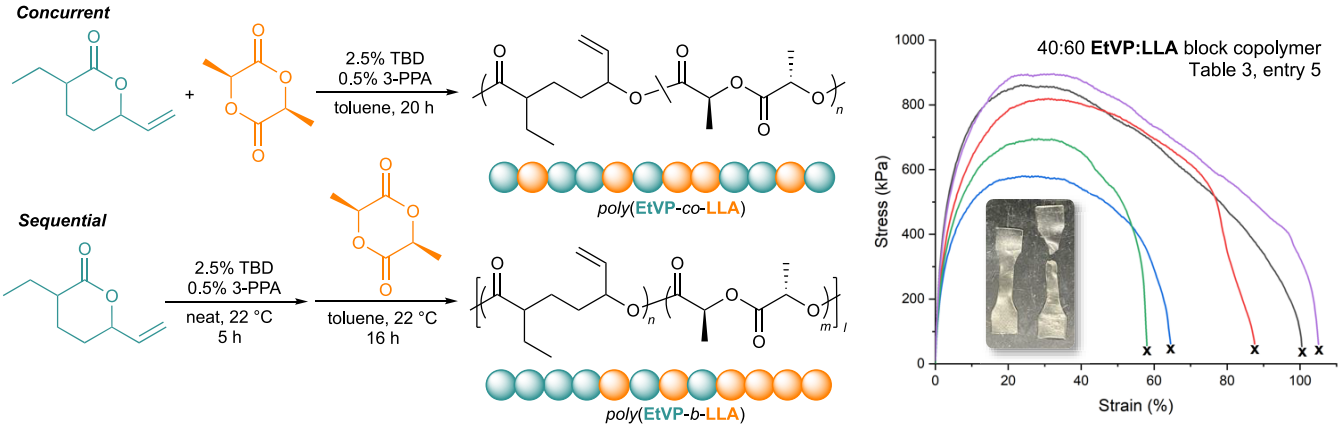
Table 3. Synthesis and Properties of EtVP and LLA Copolymers from Concurrent and Sequential Addition[a,b]



entry	addition	EtVP/LLA (mol/mol)[c]	EtVP conversion (%)[d]	polymer EtVP (%)[d]	$M_{n,SEC}$ (kDa)[e]	$Đ$	T_g (°C)
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]Inset graph: tensile testing of 40:60 EtVP:LLA block copolymer (five trials). [b]Reaction conditions: 2.5 mol % TBD, 0.5 mol % 3-PPA, 3.24 M toluene (respective to LLA), 22 °C, 25 h. [c]Initial molar ratios. [d]Calculated from ^{1}H NMR spectroscopy. [e]Determined by THF SEC using polystyrene standards. [f]Scaled up in 5.6 M THF (respective to LLA).

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 similar 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 (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% correspond to EtVP-ε-CL, 26.4% correspond to ε-CL-EtVP, and 26.5% correspond 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_{CL} = 3.0 and l_{EtVP} = 2.9 with R_{CL} = 0.62 and R_{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).

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 did (Table S5), which is the opposite of ε-CL block copolymerization. We attribute this difference primarily to solubility. Regardless of the feed strategy, the molar masses of the EtVP/LLA copolymers were lower than those of 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 the molar feed ratios. A broader range of molecular weights and dispersities was 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).

All copolymers synthesized were amorphous, even when LLA incorporation was 79% (Table 3, entry 4). However, the T_g values were significantly impacted by incorporation of LLA 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, entries 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

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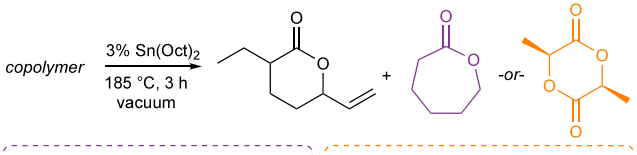
of EtVP incorporation, it is expected that blocky *poly*(EtVP-*b*-LLA) would have higher T_g values than the random of *poly*(EtVP-*co*-LLA) copolymers would based on comparison to PCL−PLLA copolymers.[41] The microstructure of 50:50 LLA copolymers was investigated via ^{13}C NMR spectroscopy (Figures 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 the 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 five samples were tested, 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 to 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) by employing the commonly used



	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.

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 a 35% combined yield of the two monomers, whereas *poly*(CL-*b*-EtVP) was recycled with a 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, the 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) suggest 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.

CONCLUSIONS

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 block, gradient, or random copolymers. ε-CL block copolymers resulted in semicrystalline 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 by 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

Data Availability Statement

All primary data files are available free of charge at 10.13020/cnxb-m954

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c00770.

Full experimental details and data (PDF)

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Author Contributions

R.J.A. and I.A.T. conceived 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.

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Notes

The authors declare the following competing financial interest(s): 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 ($LoopCO_2$) focused on commercialization of EtVP-based materials.

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