ARTICLE

Synthesis and Ring-Opening (co)Polymerization of Lactones Derived from the Cotelomerization of Isoprene, Butadiene, and CO$_2$

Ryan J. Anderson,*[a] Takuya Akiyama [b] and Ian A. Tonks [a]

Herein, we report ring-opening polymerizations and copolymerizations of substituted δ-lactones derived from isoprene, butadiene, and CO$_2$. While the telomerization of CO$_2$ with butadiene to form a disubstituted δ-lactone is well-established, the similar telomerization of isoprene with CO$_2$—or cotelomerization of isoprene and butadiene with CO$_2$—have been less studied. Our initial efforts focused on identifying the factors that govern yield and selectivity in the cotelomerization of isoprene, butadiene, and CO$_2$. The most effective cotelomerization/hydrogenation reaction sequence was scaled-up, leading to mixtures of two isoprene-butadiene coupled lactones (3-ethyl-6-(prop-1-en-2-yl)tetrahydro-2H-pyran-2-one (**EtPeP**), and 3-ethyl-6-methyl-6-vinyltetrahydro-2H-pyran-2-one (**EtVMeP**) and the butadiene homocoupled lactone, 3-ethyl-6-vinyltetrahydro-2H-pyran-2-one (**EtVP**). The ratios of these three lactones varied depending on telomerization conditions and purification methods employed. Stepwise syntheses of pure **EtVMeP** and **EtPeP** via alternate routes were also carried out. The pure lactones as well as lactone mixtures were subjected to organocatalyzed ring-opening (co)polymerization (ROP) using triazabicyclodecene (TBD), yielding CO$_2$-based copolymers with molar masses (M_n) ranging from 5.5 to 12.7 kDa and narrow dispersities (Đ = 1.3). Increasing the proportion of **EtPeP** relative to **EtVP** led to a notable increase in the glass transition temperature (T_g) of the copolymers, reaching -20.5 °C. While **EtPeP** underwent successful ring-opening polymerization, reactions with **EtVMeP** resulted in termination of the polymerization owing to the formation of a non-nucleophilic tertiary alkoxide chain end. Thus, small amounts of **EtVMeP** can have a deleterious effect on copolymerizations of lactone mixtures derived from cotelomerization. These results motivate further development in the selective synthesis of **EtPeP** *via* cotelomerization of butadiene and isoprene with CO$_2$.

Introduction

The δ-lactone **EVP** (3-**e**thylidene-6-**v**inyl-tetrahydro-2H-**p**yran-2-one) derived from the telomerization of CO$_2$ and butadiene, has recently emerged as a powerful platform chemical for the synthesis of CO$_2$-derived and recyclable polyesters.[1] Since an initial report revealing that hydrogenation of **EVP** leads to facile ring-opening polymerization of the resultant lactones, significant advancements have been made to expand the **EVP** polymer platform, including alterations of the lactone structure,[2,3] copolymerizations with commercial monomers,[4–8] and post-polymerization modifications.[9,10]

δ-lactones derived from other 1,3-dienes such as isoprene have yet to be explored in ROP. Isoprene is typically sourced from petroleum for large-scale industrial applications,[11] but it is a biomolecule and there has been a significant effort in producing isoprene from bio-based feedstocks over the last few decades, making it an ideal candidate for sustainable polymer synthesis. [12,13]

While the telomerization of butadiene with CO$_2$ to **EVP** is well studied and has even been scaled to mini-plant level production,[14,15] similar telomerization of isoprene results in impractically low yields (<1%).[16] Alternately, the *co*telomerization of isoprene (or piperylene) with butadiene and CO$_2$ can result in significantly improved—and synthetically practical—yields of δ-lactones (Figure 1).[17,18] For example, Behr reported a Pd/P^{i}Pr$_3$-catalyzed cotelomerization of butadiene with various feed ratios of isoprene (Figure 1, inset),[17] leading to a mixture of **EVP** and two δ-lactones from isoprene/butadiene cotelomerization, 3-**e**thylidene-6-(**p**rop-1-**e**n-2-yl)tetrahydro-2H-**p**yran-2-one (**EPeP**) and 3-**e**thylidene-6-**me**thyl-6-**v**inyltetrahydro-2H-**p**yran-2-one (**EVMeP**). Chemoselectivity could be controlled by altering feed ratios, but

a. Department of Chemistry, University of Minnesota–Twin Cities, 207 Pleasant St SE, Minneapolis, Minnesota 55455, United States.
b. Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan.
c. Department of Chemistry, University of Minnesota–Twin Cities, 207 Pleasant St SE, Minneapolis, Minnesota 55455, United States.
† Footnotes relating to the title and/or authors should appear here.
Supplementary Information available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

combined **EPeP** and **EVMeP** yields remained around 5%. Nozaki subsequently reported a Pd/PPh₃-catalyzed cotelomerization of butadiene with isoprene (Figure 1, inset)[18] with improved yields (18%, TON = 45) and good (74%) chemoselectivity. Despite these advances, the yields of **EPeP** and **EVMeP** remain low compared to **EVP** synthesis[19] and control of the regioselectivity of cotelomerization is understudied, which motivates continued study into cotelomerization catalysis. Herein, we report an optimization study of the cotelomerization of isoprene, butadiene, and CO_2 along with scale-up and isolation of the δ-lactone mixtures. Once isolated, these δ-lactone mixtures can be hydrogenated to remove α,β-unsaturation, and the resultant hydrogenated δ-lactones can undergo organocatalyzed ring-opening (co)polymerization (Figure 1, bottom).
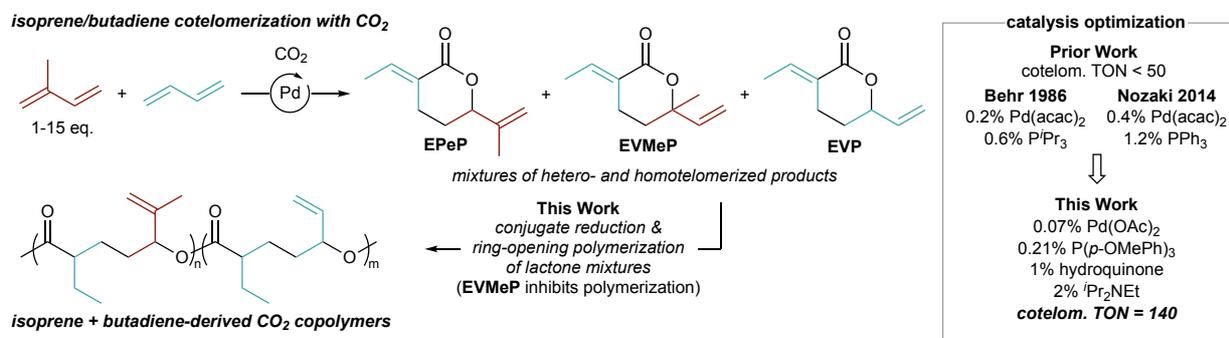

Figure 1. Landscape of the cotelomerization of isoprene with butadiene and CO_2, including catalyst development (inset) and lactone reduction/ring-opening polymerization (this work).

Results and Discussion

Initial reaction optimization focused on modifications of highly selective catalyst systems that have been reported for butadiene and CO_2 telomerization (Figure 2).[19,20] Reactions were screened using a high-pressure 6-well reactor (Figure S1) with each well containing an 8 mL glass vial. Through these studies, we identified a baseline "standard conditions" system composed of 0.04% Pd(OAc)₂ 0.12% P(*p*-OMePh)₃, 1% hydroquinone, and 2% ⁱPr₂NEt (DIPEA) at a 3:1 isoprene:butadiene feed ratio in MeCN, which yielded a mixture of **EPeP**, **EVMeP,** and **EVP** in a combined 31:69 ratio of **EPeP** and **EVMeP** relative to **EVP**. This system results in a 4.4% combined yield of **EPeP** and **EVMeP** (productive TON = 110).

Systematically examining deviations from the "standard conditions" reveals several trends in the cotelomerization reaction. First, electron rich triaryl phosphine ligands (*e.g.* P(*p*-OMePh)₃ and PPh₃) produce higher overall yields of **EPeP/EVMeP** relative to other ligand classes, although electron-deficient ligands (*e.g.* P(*p*-CF₃Ph)₃) provide better chemoselectivity toward cotelomerization. Using Pd(OAc)₂ as a Pd source results in higher overall yields and cotelomerization selectivity relative to PdCl₂, Pd(dba)₂, or even pre-formed diphosphine complexes. Deviation from the standard reaction temperature of 100 °C lowered both yield and cotelomerization selectivity. Selectivity plateaued with increasing CO_2 pressure, although at higher pressures the overall reaction yields were lower. The isoprene feed ratio had the largest impact on chemoselectivity and overall yield of **EPeP/EVMeP**, where using 6 equivalents of isoprene led to an overall 5.1% yield of cotelomerized products in a 42:58 ratio with **EVP**. Increasing to 10 equivalents of isoprene further increased the selectivity to 61:39, but at much lower overall yield.
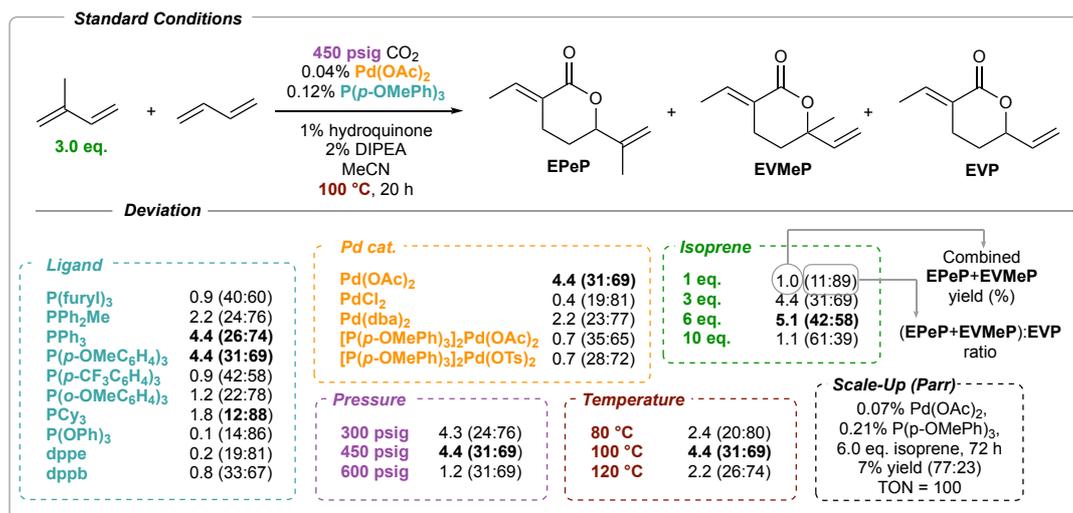
Figure 2. Systematic screening of phosphine ligands, Pd sources, isoprene equivalents, temperature, and pressure for isoprene cotelomerization. Yields determined by ^{1}H NMR spectroscopy against dimethylterepthalate standard, and reported against limiting reagent butadiene.

From these observations, an extended reaction building off of the standard conditions was carried out in the 6-well reactor with 6 equivalents of isoprene and slightly higher catalyst loadings (0.07% Pd) and a 72 h reaction time (Figure 2, right). This reaction resulted in 10% **EPeP/EVMeP** yield (productive TON = 140). Increasing to 0.20% Pd resulted in a slightly higher yield (11.2%), but further increases led to lower overall yield (Table S4). These conditions (0.7% Pd) were then scaled from an 8 mL vial (5 mmol butadiene) all the way to a 1 L Parr reactor (340 mmol butadiene) with overhead stirring. Scaled-up reactions were run at 80 °C instead of 100 °C to decrease unwanted 5-membered lactone formation. Notably, improved selectivity (77:23 **EPeP/EVMeP:EVP**) was achieved during scaling, with a slight decrease in overall **EPeP/EVMeP** yield (7.0%). The total reaction volume as well as the temperature at which CO_2 was introduced had a profound impact on the overall **EPeP/EVMeP** yield (Table S5). This may be attributed due to a difference in mass transfer when going from an 8 mL vial with stir bar to a 1 L reactor with overhead stirring. Importantly, the TON with this catalyst system is much higher than previous reports,[18] and also produced higher selectivity for **EPeP** *vs* **EVMeP** (55:45 **EPeP:EVMeP** *vs* 20:80 **EPeP:EVMeP** reported by Nozaki[15]) which is important because **EVMeP** inhibits ring-opening polymerizations (*vide infra*). After each telomerization, excess unreacted isoprene can be recovered (up to 50% of the starting volume) and recycled for future runs with minimal impact on **EPeP/EVMeP** yield (Figure S10-11).

Across all cotelomerizations only 2 (**EPeP** and **EVMeP**) of the possible 4 heterocoupled regioisomers were observed. To elucidate the origins of this regioselectivity, we evaluated the energetics of CO_2 insertions by DFT calculations (Figure 3; CPCM (acetonitrile)-M06L/SDD for Pd and 6-311+G(d,p) for other atoms). **EPeP** and **EVMeP** necessarily form from CO_2 insertion into the butadiene side of the key Pd-diallyl species **INT-1** and **INT-2**, which form from oxidative cyclization with Pd^0. Alternately, CO_2 insertion into the isoprene side of these intermediates would lead to **PeVP** or **VMeVP**. **INT-2** is more stable than **INT-1** and is therefore set to 0.0 kcal/mol to evaluate the relative activation energies of the following CO_2 insertion steps. CO_2 insertion on the butadiene side of **INT-1** through **TS-A** leading to **EPeP** has the lowest transition state barrier ($\Delta G^\ddagger$ = 31.1 kcal/mol) among the four possible CO_2 insertions. CO_2 insertion into **INT-2** through **TS-B** leading to **EVMeP** ($\Delta G^\ddagger$ = 33.7 kcal/mol) is 2.6 kcal/mol higher in energy than **TS-A**, consistent with the fact that **EPeP** is the major regioisomer formed over **EVMeP**. CO_2 insertion into the isoprene side of **INT-2** leading to **VMeVP** ($\Delta G^\ddagger$ = 39.1 kcal/mol) is significantly higher than any other pathway. Interestingly, CO_2 insertion on the isoprene side of **INT-1** through **TS-C** leading to **PeVP** ($\Delta G^\ddagger$ = 31.7 kcal/mol) exhibits comparable activation energy to **TS-A**. While the high barrier for **TS-D** explains why **VMeVP** is not formed under catalytic conditions, the lower barrier for **TS-C** indicates that downstream intermediate and transition state energies or other CO2 insertion mechanisms[21] or the overall equilibrium speciation between **INT-1** and **INT-2** may also play a role in preventing **PeVP** formation. The ground state energies for the CO_2 inserted products (**INT-3A**, **INT-3B**, **INT-3C**, **INT-3D**) were also calculated but do not provide clear evidence for the absence of **PeVP** formation, although **INT-3C** is slightly higher in energy than **INT-3A** and **INT-3B** which may indicate greater potential for reversibility.
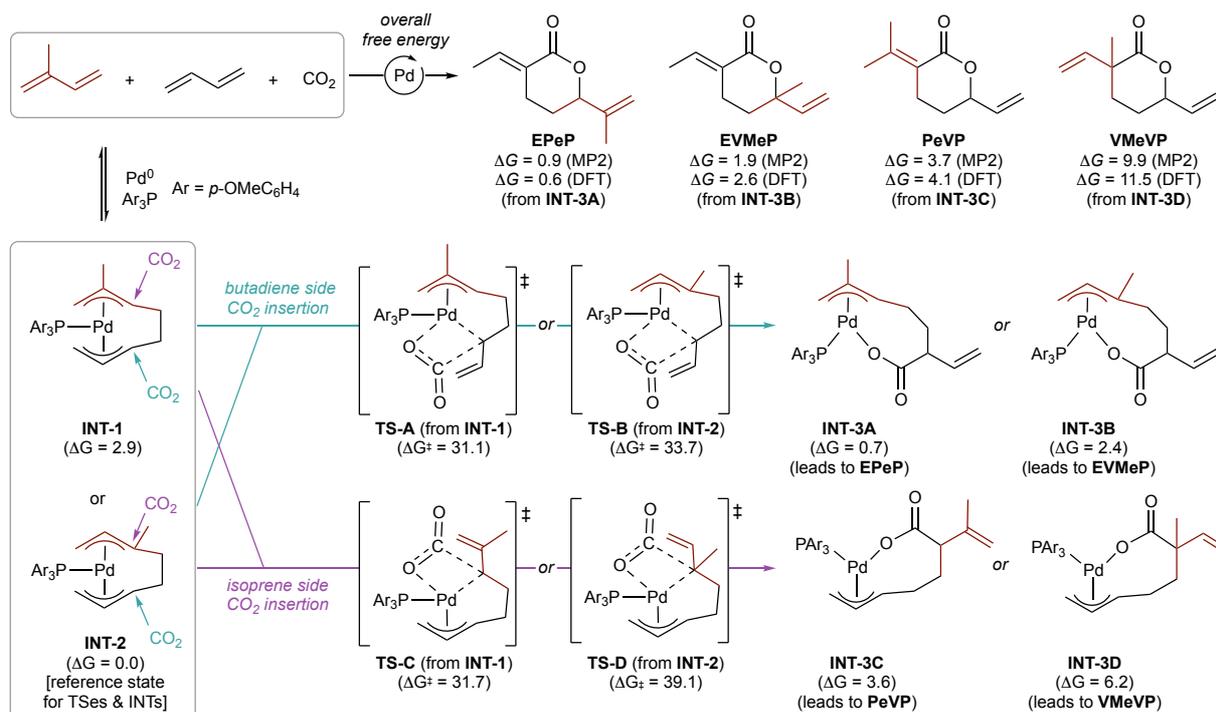
Figure 3. CO_2 insertions into **INT-1** or **INT-2** leading to four regioisomeric lactones. Calculated transition-state energies for CO_2 insertions (**TS-A**, **B**, **C**, and **D**) with respect to **INT-2** (CPCM (acetonitrile)-M06L/SDD (Pd)-6-311+G(d,p) (others) at 298.15 K level of theory) and energy changes from CO_2, butadiene, isoprene to δ-lactones (MP2: CPCM (acetonitrile)-MP2/cc-pVTZ at 298.15 K level of theory, DFT: CPCM (acetonitrile)-wB97XD/def2-QZVP at 298.15 K level of theory) are presented below each structures. $PAr_3 = (4-(OCH_3)C_6H_4)_3P$. All energies are denoted in kcal/mol.

We suspected that there may also be a thermodynamic limitation for the formation of **PeVP**, and thus *ΔG* for the cotelomerization of isoprene, butadiene and CO_2 to all 4 possible regioisomeric lactones were calculated using more sophisticated computational methods (Figure 3, top; MP2/cc-pVTZ and ωB97XD/def2-QZVP both with CPCM (acetonitrile) at 298.15K). In these computations, formation of **EPeP** and **EtVMeP** were calculated to be significantly lower in energy than **PeVP** and **VMeVP**. In fact, **PeVP** and **VMeVP** are significantly endergonic relative to starting materials (3.7 or 4.1 kcal/mol and 9.9 or 11.5 kcal/mol, respectively). The higher *ΔG* value for **PeVP** relative to **EPeP** and **EVMeP** can be ascribed to a steric repulsion between the carbonyl oxygen and the isoprene-derived methyl group; non-covalent interaction (NCI) analysis of **PeVP** displays a weakly repulsive isosurface between O1 and C4 (Figure 4). This repulsive interaction causes out-of-plane distortion around the α,β-unsaturated ester in **PeVP** as observed by O1-C1-C2-C3 dihedral angle (θ = 33.4º for **PeVP** *vs* θ = 13.5º for **EPeP**), which decreases the stabilization of conjugation. On the other hand, the lower stability of **VMeVP** is simply due to the lack of α,β-conjugation seen in the other three lactones. These thermodynamic considerations could also be a contributing factor for the low yields observed in isoprene homotelomerization.[16]
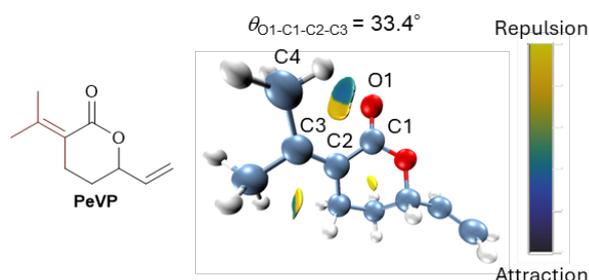
Figure 4. Non-covalent interaction (NCI) plot of **PeVP** (isovalue = 0.5, -0.04 < sign(I_2)r < 0.02).

With scale-up conditions for the cotelomerization reaction identified, pure δ-lactone mixtures with varying ratios of **EPeP:EVMeP:EVP** were isolated *via* vacuum distillation followed by column chromatography. Further column chromatography can be completed to remove more **EVP** and isolate predominantly **EPeP** or **EVMeP**, although complete removal was not pursued because the cost of chromatographic separation of the lactones would ultimately make such a process nonviable and impractical. The resultant lactone mixtures were then partially hydrogenated via conjugate reduction by Cl_3SiH and hexamethylphosphoramide (HMPA), resulting in mixtures of 3-**et**hyl-6-(**p**rop-1-

en-2-yl)tetrahydro-2*H*-**p**yran-2-one (**EtPeP**), 3-**et**hyl-6-**m**ethyl-6-**v**inyltetrahydro-2*H*-**p**yran-2-one (**EtVMeP**), and 3-**et**hyl-6-**v**inyltetrahydro-2*H*-**p**yran-2-one (**EtVP**) in various ratios according to the lactone starting feed ratio (Figure 5). Typically, 2-3 pure δ-lactone mixtures are isolated after column chromatography with varying molar ratios of **EtPeP** present (up to 93%) with an overall yield between 40 and 60%.
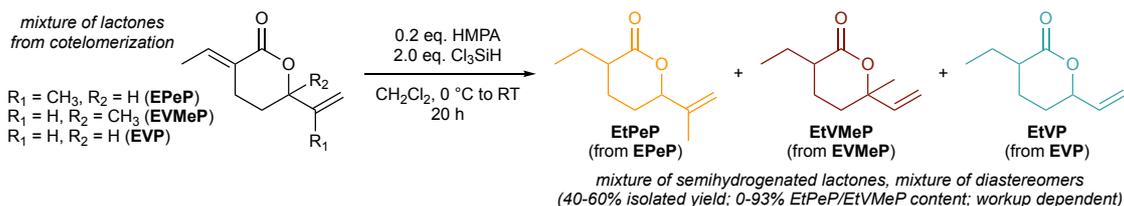
Figure 5. Selective-reduction of scaled-up cotelomerization products to mixtures of δ-lactones **EtPeP**, **EtVMeP**, and **EtVP**.

These lactone mixtures were then subjected to ring-opening polymerization using triazabicyclodecene (TBD) as a catalyst[22] and 3-phenyl-1-propanol (3-PPA) as an initiating alcohol (Table 1). In all cases, copolymers with a range of **EtPeP** incorporation were obtained (Table 1), with no significant incorporation of **EtVMeP** regardless of its ratio in the lactone feed. Thus, the isolated copolymers, *poly*(**EtVP**-*co*-**EtPeP**), have up to 93% **EtPeP** incorporation, in relatively good agreement with the initial molar ratios of **EtVP**:**EtPeP**. Using the Beckingham–Sanoja–Lynd (BSL) method,[23] the reactivity ratios of **EtVP** and **EtPeP** are $r_{EtVP} = 1.09$ and $r_{EtPeP} = 0.92$. These ratios indicate a near random copolymer with a small amount of gradient character. This behavior is somewhat expected as **EtVP** and **EtPeP** only differ by one methyl group on their sidechains, and both result in a secondary alkoxide upon ring-opening. Similar results were obtained in prior work with the copolymerization of **EtVP** and ε-caprolactone (**CL**) where the reactivity ratios were $r_{EtVP} = 1.37$ and $r_{CL} = 0.91$.[4]

**Table 1.** Copolymerization and results of **EtVP**, **EtPeP** and **EtVMeP** at varying molar ratios.
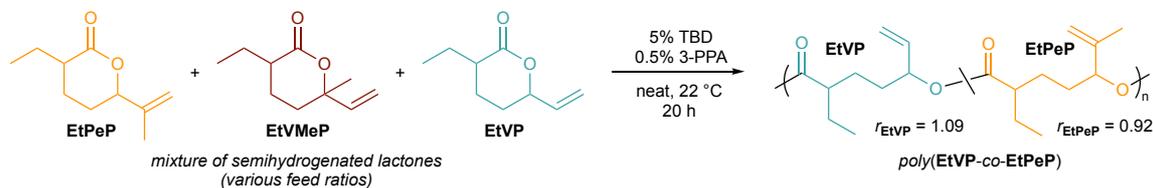
Entry	EtPeP/EtVMeP/EtVP feed ratio (%)[b]	Polymer EtPeP (%)[c]	EtPeP Conversion (%)[c]	Total Conversion (%)[c]	M_n (kDa)[d]	Đ	T_g (°C)
1	**0**/0/100	0	-	80	13.6	1.3	-39.2
2	**19**/6/75	20	76	72	12.7	1.4	-35.5
3	**29**/6/65	32	71	71	9.5	1.2	-33.0
4	**40**/4/56	42	67	70	8.9	1.4	-28.6
5	**52**/7/41	56	70	65	7.4	1.2	-28.1
6	**71**/10/19	76	57	56	5.5	1.3	-27.5
7	**79**/14/7	93	56	51	7.4	1.4	-23.2
8[e]	**100**/0/0	100	77	77	10.2	1.2	-20.5
9[e,f]	**0**/50/50	-	-	62	0.8	1.6	-
10[e,f]	**0**/100/0	-	-	<1	-	-	-

[a]Reaction conditions: 5.0 mol% TBD, 0.5 mol% 3-PPA(3-pheny, 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]from stepwise synthesis (Figure 6). [f]5% 3-PPA

When the **EtPeP** content was low in the feed (*e.g.* 19%, Table 1, Entry 2), the total monomer conversion and resulting molar mass rivalled that of **EtVP** homopolymerization under the same conditions (Table 1, Entry 1). Increasing **EtPeP** incorporation resulted in a decrease in total

monomer conversion and polymer molar masses. This is most likely due to the added entropic penalty[24] from the propenyl group (calculated steric A-value = 2.9) relative to a vinyl group (A-value = 1.8) (Figure S50-51) along with the potential for residual **EtVMeP** to inhibit polymerization (*vide infra*). Moderate molar masses (5.5-12.7 kDa) and narrow dispersities (1.2-1.4) were observed in all cases. Higher molar mass *poly*(**EtVP**-*co*-**EtPeP**) (17.9 kDa, 48% **EtPeP** incorporation) could be obtained when employing a Waymouth-type urea catalyst,[25] but resulted in a much higher *Đ* of 1.9 (Figure S20). The glass transition temperature (T_g) increased with increasing **EtPeP** content, going from -35.5 °C at 20% **EtPeP** incorporation to -23.2 °C at 93% **EtPeP** incorporation, potentially due to decreased in-chain rotation relative to *poly*(**EtVP**).

Practical separation of **EtPeP** and **EtVMeP** mixtures on a large-scale is currently not possible. Nonetheless, to explore the homopolymerization reactivity behaviour of these lactones, pure **EtPeP** and **EtVMeP** were independently synthesized following multi-step syntheses (Figure 6). **EtVMeP** was synthesized by vinylation of ethyl 5-oxohexanoate with vinyl magnesium bromide leading to an intermediary lactone, 6-methyl-6-vinyltetrahydro-2*H*-pyran-2-one (**VMeP**). α-alkylation of **VMeP** to **EtVMeP** was then accomplished through enolization with LiHMDS and addition of EtI as the electrophile in an overall yield of 8% across two steps. Next, **EtPeP** was synthesized through a three-step process. First, glutardialdehyde was reacted with isopropenyl magnesium bromide to give cyclized intermediary alcohol which was then oxidized to **PeP** using pyridinium chlorochromate (PCC). **EtPeP** was then isolated in 2% overall yield after α-alkylation.
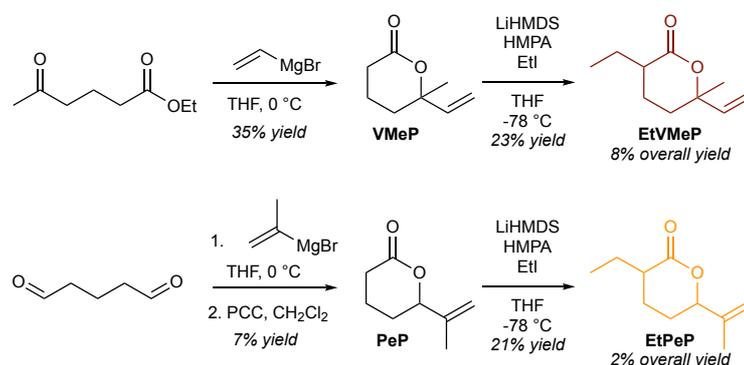
Figure 6. Stepwise synthesis of **EtVMeP** and **EtPeP**.

With the pure lactones in hand, polymerization studies were then attempted. Under standard polymerization conditions, polymerization of pure **EtPeP** led to 77% monomer conversion and isolated *poly*(**EtPeP**) with M_n = 10.2 kDa, *Đ* = 1.2, and T_g = -20.5 °C, in line with trends expected from the copolymerizations (Table 1 Entry 8). All attempts at homopolymerization of **EtVMeP** resulted in no clear propagation (Table 1 Entry 9). Given this result, we next studied the potential inhibitory effect of **EtVMeP** on copolymerizations, by attempting copolymerization of a 50:50 mixture of **EtVP** and **EtVMeP** (Table 1 Entry 9). In this instance, polymerization resulted in only 54% **EtVP** conversion (as opposed ~80% in homopolymerization, *e.g.* Table 1 Entry 1), and only single incorporations of **EtVMeP** were observed in polymer chains by MALDI-TOF analysis, indicating that **EtVMeP** likely terminates polymerization upon incorporation as a chain end (Figure 7). Together, these results suggest that **EtVMeP** can undergo ring-opening, but the resulting tertiary alkoxide is unlikely to propagate (Figure 6, right). End-capping of *poly*(**EtVP**-*co*-**EtPeP**) (Table 1, entry 5) with trifluoroacetic anhydride revealed **EtPeP**, **EtVMeP** and **EtVP** chain ends (Figure S48-49), indicating a mixture of active and inactive chain ends that provides further evidence for the lower conversions with higher loadings of **EtVMeP**.
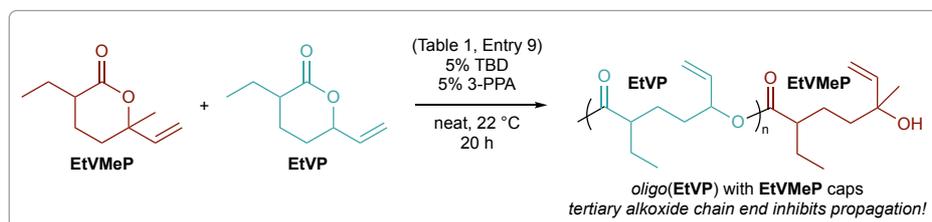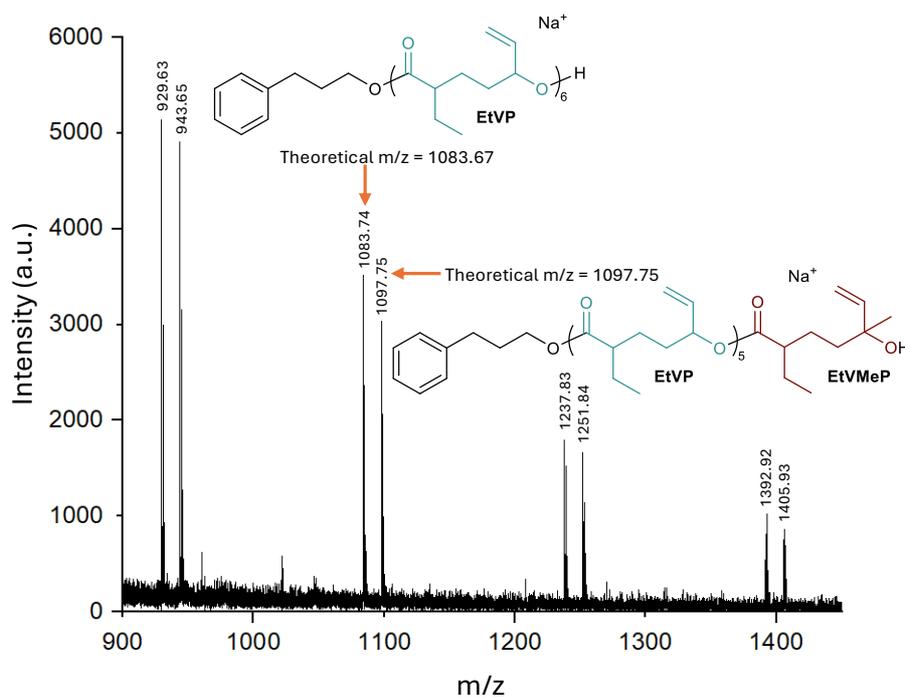
Figure 7. MALDI-TOF spectrum of the attempted copolymerization of **EtVMeP** with **EtVP** (Table 1 Entry 9) revealing **EtVMeP** end-capping that terminates polymerization.

Conclusions

This study highlights strategies for influencing selectivity in the cotelomerization of 1,3-dienes such as isoprene with CO_2, which could be valuable for future studies related to isoprene homotelomerization. Depending on the catalyst system and purification methods used, mixtures of δ-lactones with varying ratios of isoprene-derived monomers were obtained, where electron-rich, aryl monophosphines typically deliver higher yields and selectivities toward cotelomerization. These lactone mixtures can be selectively reduced via conjugate reduction, and the reduced lactone mixtures undergo organocatalyzed ring-opening polymerization to polyesters. However, one of the lactones (**EtVMeP**) hinders polymer reactivity, which results from the formation of an unreactive tertiary alkoxide that terminates propagation. This further demonstrates the need for the development of not only high yielding but highly regioselective catalyst systems for isoprene hetero- and homotelomerization with CO_2.

Author contributions

R.J.A. and I.A.T. conceived the work. R.J.A. executed the experimental plan and analyzed the data. T.A. executed and analyzed all the computational 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

The authors declare the following competing financial interest(s): I.A.T. is co-inventor on a patent describing the composition of matter of poly(EtVP) and related CO_2-derived polymers, and is the co-founder and CSO of LoopCO2, a company focused on commercialization of CO_2-derived materials.

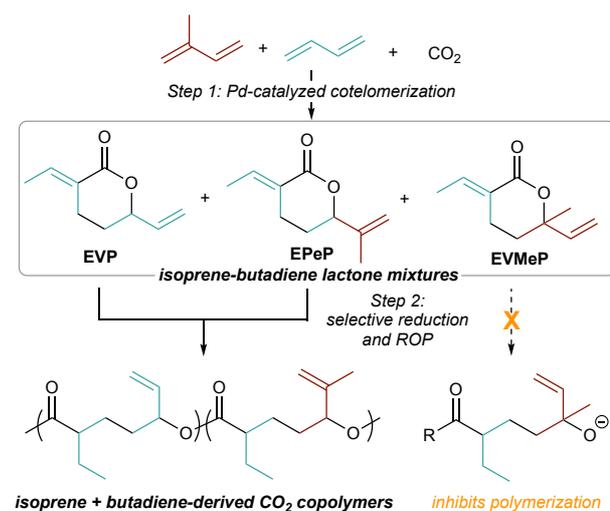## Data availability

A data availability statement (DAS) is required to be submitted alongside all articles. Please read our full guidance on data availability statements for more details and examples of suitable statements you can use.

Acknowledgements

TOC Image

References

1   R. M. Rapagnani, R. J. Dunscomb, A. A. Fresh and I. A. Tonks, *Nat. Chem.*, 2022, **14**, 1–7.

2   Z. Zhang, T. Shen, K. Chen, J. Zeng, Y. Mei, J. Ling and X. Ni, *ACS Macro Lett.*, 2024, **13**, 741–746.

3   J. Xu, Y. Niu and B. L. Lin, *Polym. Chem.*, 2025, **16**, 82–89.

4   R. J. Anderson, R. L. Fine, R. M. Rapagnani and I. A. Tonks, *Macromolecules*, 2024, **57**, 6248–6254.

5   S. Yue, T. Bai, S. Xu, T. Shen, J. Ling and X. Ni, *ACS Macro Lett.*, 2021, **10**, 1055–1060.

6   K. Chen, Z. Zhu, T. Bai, Y. Mei, T. Shen, J. Ling and X. Ni, *Angew. Chemie - Int. Ed.*, 2022, **61**, e202213028.

7   Y. Zhao, X. Zhang, Z. Li, Z. Li and S. Tang, *ACS Macro Lett.*, 2024, **13**, 315–321.

8   Z. Wang, W. Zheng, S. Yue, K. Chen, J. Ling and X. Ni, *Chinese J. Chem.*, 2024, **42**, 1630–1636.

9   Y. Lou, J. Xu, L. Xu, Z. Chen and B. L. Lin, *Macromol. Rapid Commun.*, 2022, **43**, 1–8.

10   R. A. J. Ditzler, R. M. Rapagnani, N. K. Berney, R. F. Koby, E. C. Krist, B. J. Kruse, H. D. Fokwa, I. A. Tonks and A. V. Zhukhovitskiy, *J. Am. Chem. Soc.*, 2024, **146**, 15286–15292.

11   T. D. Sharkey, 1996, **9327**, 74–78.

12   G. M. Whited, F. J. Feher, D. a Benko and a Marguerite, *Ind. Biotechnol.*, 2010, **6**, 152–163.

13   J. Isar, D. Jain, H. Joshi, S. Dhoot and V. Rangaswamy, *World J. Microbiol. Biotechnol.*, 2022, **38**, 1–12.

14   A. Behr, M. Becker, T. Beckmann, L. Johnen, J. Leschinski and S. Reyer, *Angew. Chemie - Int. Ed.*, 2009, **48**, 3598–3614.

15   A. Behr and M. Heite, *Chem. Eng. Technol.*, 2000, **23**, 952–955.

16   E. Dinjus and W. Leitner, *Appl. Organomet. Chem.*, 1995, **9**, 43–50.

17   A. Behr, R. He, K. -D Juszak, C. Krüger and Y. -H Tsay, *Chem. Ber.*, 1986, **119**, 991–1015.

18   R. Nakano, S. Ito and K. Nozaki, *Nat. Chem.*, 2014, **6**, 325–331.

19   M. Sharif, R. Jackstell, S. Dastgir, B. Al-Shihi and M. Beller, *ChemCatChem*, 2017, **9**, 542–546.

20   J. M. Balbino, J. Dupont and J. C. Bayón, *ChemCatChem*, 2018, **10**, 206–210.

21   J. Wu, J. C. Green, N. Hazari, D. P. Hruszkewycz, C. D. Incarvito and T. J. Schmeier, *Organometallics*, 2010, **29**, 6369–6376.

22   A. P. Dove, *ACS Macro Lett.*, 2012, **1**, 1409–1412.

23   B. S. Beckingham, G. E. Sanoja and N. A. Lynd, *Macromolecules*, 2015, **48**, 6922–6930.

24   D. K. Schneiderman and M. A. Hillmyer, *Macromolecules*, 2016, **49**, 2419–2428.

25   B. Lin and R. M. Waymouth, *J. Am. Chem. Soc.*, 2017, **139**, 1645–1652.