Sustainable Copolymer Synthesis from Carbon Dioxide and Butadiene

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CONSPECTUS: Carbon dioxide (CO_2) has long been recognized as an ideal C1 feedstock co-monomer for producing sustainable materials because it is renewable, abundant, and cost-effective. However, activating CO_2 presents a significant challenge because it is highly oxidized and stable. A CO_2/butadiene-derived δ-valerolactone (EVP), generated via palladium-catalyzed telomerization between CO_2 and butadiene, has emerged as an attractive intermediate for producing sustainable copolymers from CO_2 and butadiene. Owing to the presence of two active carbon-carbon double bonds and a lactone unit, EVP serves as a versatile intermediate for creating sustainable copolymers with CO_2 content of up to 29 wt% (33 mol%). In this Review, advances in the synthesis of copolymers from CO_2 and butadiene with divergent structures through various polymerization protocols has been summarized. Achievements made in homo- and co-polymerization of EVP or its derivatives are comprehensively reviewed, while the post-modification of the obtained copolymers to access new polymers are also discussed. Meanwhile, potential applications of the obtained copolymers are also discussed. The literature references were sorted into sections based on polymerization strategies and mechanisms, facilitating readers in gaining a comprehensive view of the present chemistry landscape and inspiring innovative approaches to synthesizing novel CO_2-derived copolymers.

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1. INTRODUCTION

Carbon dioxide (CO_2) serves as a stable and renewable C1 feedstock, and it is notably a pivotal component among greenhouse gases in the atmosphere. Its abundance and wide availability have directed a surge of attention towards the efficient transformation of CO_2 into value-added chemical compounds.[1-5] CO_2-based polymers have received continuous interests from academia and industry across a range of applications.[6-10] Nevertheless, activating CO_2 remains a substantial hurdle due to its high thermodynamic stability.[11] Consequently, polymerization reactions involving CO_2 commonly require the participation of high-energy comonomers to navigate the challenges posed by both thermodynamics and kinetics. In this context, the most explored transformation is the alternating copolymerization of CO_2 and epoxides, resulting in the formation of aliphatic polycarbonates.[12-21] Binucleophiles including diols,[22-26] amino alcohols,[27] diamines[28] and diynes,[29-31] are also able to copolymerize with CO_2 via polycondensation, producing corresponding polycarbonates, polyurethanes, polyureas, and polyesters, respectively. In addition to direct copolymerization with CO_2, significant focus has been directed towards the synthesis of copolymers using CO_2-derived comonomers through the process of ring-opening copolymerization (ROCOP).[6]

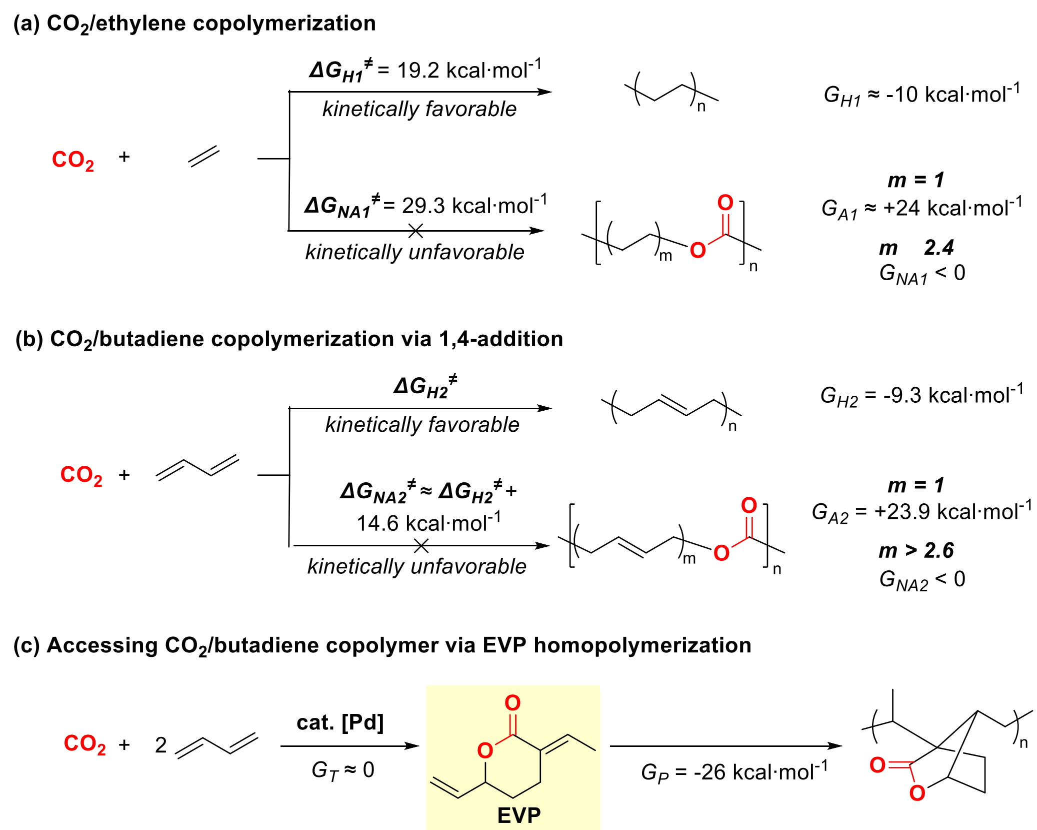
Polyolefins are highly important plastic materials, and produced in the largest volume among all polymer materials.[32-33] Aiming at accessing polyethylenes bearing in-chain degradable ester functionality, the copolymerization of CO_2 with ethylene has long been recognized as a significant but highly challenging transformation. Although copolymerization of CO_2 and olefins has caught continuous research interest, little success has been made in producing copolymers.[34-35] It is worth of noting that the homopolymerization of olefins proceeds smoothly even in supercritical CO_2.[36] There are examples for oligomerization of CO_2 with olefins such as dienes,[37] and vinyl ethers[38-40], although the obtained oligomers typically have low molecular weights. Most recently, efforts were taken to synthesize photodegradable nonalternating polyketones from CO_2 and ethylene using tandem electrocatalytic/photocatalytic CO_2 reduction and coordination/insertion copolymerization protocols.[41-42] Density function theory (DFT) calculations have shown that nonalternating CO_2/ethylene copolymerization is thermodynamically feasible with excess consecutive ethylene insertions.[43-44] Nevertheless, it is highly challenging to find an effective kinetically favorable pathway for chain propagation after CO_2 insertion. As a consequence, attempts to achieve the copolymerization of CO_2 and olefins generally result in olefin homopolymerization or alkyl carbonates.[43, 45]

In this Review, we demonstrate how the thermodynamic and kinetic problems of CO_2/olefin copolymerization can be circumvented by the use of 3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one (EVP), produced from palladium-catalyzed coupling between CO_2 and butadiene.[34-35, 46-48] Advances in the synthesis of copolymers from CO_2 and butadiene with divergent structures through various polymerization protocols has been summarized. Owing to its trifunctional reactivity, EVP serves as a versatile intermediate for creating sustainable copolymers with CO_2 content of up to 29 wt%. Achievements made in homo- and co-polymerization of EVP or its derivatives are comprehensively reviewed, while the post-modification of the obtained copolymers to access new polymers are also discussed. Potential applications of the obtained copolymers are also discussed. The literature references were sorted into sections based on polymerization strategies and mechanisms, facilitating readers in gaining a comprehensive view of the present chemistry landscape and inspiring innovative approaches to synthesizing novel CO_2-based copolymers.

2. COMPUTATIONAL STUDIES OF THE COPOLYMERIZATION OF CO_2 AND OLEFINS

In 2006, Miller *et al.* studied the thermodynamics of CO_2/ethylene copolymerization using average bond dissociation energies, the Benson additivity method, and DFT calculations.[43] All the three calculation methods suggested that perfectly alternating CO_2/ethylene copolymerization is thermodynamically inaccessible at reasonable temperatures. According to the DFT calculations results, the Gibbs free energy for ethylene homopolymerization was determined to be -10 kcal·mol^{-1} (ΔG_{H1}), whereas the Gibbs free energy associated with CO_2 propagation was 24 kcal·mol^{-1} (ΔG_{A2}) (Scheme 1a). Nevertheless, when the molar ratio of ethylene/CO_2 exceeds 2.4, the copolymerization becomes possible owing to the energy release of C-C bond formation from sequential ethylene insertions. α-Diimine complexes were used as catalysts to test the feasibility of nonalternating CO_2/ethylene copolymerization at varied temperatures and pressures, and unfortunately none of the reactions showed CO_2 incorporation. The authors concluded that the key obstacle for ethylene/CO_2 copolymerization is the lack of an effective kinetically favorable pathway. In contrast to the problems of ethylene/CO_2 copolymerization, both the alternating and nonalternating copolymerization of ethylene/CO have been achieved and are well-understood.[49-50]

Scheme 1. Thermodynamic and Kinetic Analysis of CO_2/Olefin Copolymerizations



In a later DFT study by Müller *et al.*, palladium-catalyzed CO_2/ethylene copolymerization was compared with the corresponding CO/ethylene copolymerization and ethylene homopolymerization in order to identify suitable catalytic cycles and elementary steps for successful CO_2/ethylene copolymerization (Scheme 1a).[44] According to their computational results, alternating CO_2/ethylene copolymerization is both thermodynamically restricted and kinetically forbidden when palladium phosphine-sulfonate complexes are used as catalysts, confirming the results from Miller *et al*. While it is possible to propose a thermodynamically favorable closed catalytic cycle for the nonalternating copolymerization of ethylene and CO_2 (ethylene/CO_2 > 2.4), there are other pathways that hinder its successful execution. After incorporating three ethylene units before introducing a CO_2 molecule, the lowest Gibbs free activation barrier for CO_2 insertion is calculated as 29.3 kcal·mol^{-1} ($\Delta G_{NA1}^{\neq}$), which is in principle thermodynamically accessible for achieving a successful non-alternating copolymerization. However, this activation energy for copolymerization is still much higher than that of ethylene homopolymerization ($\Delta G_{H1}^{\neq}$ = 19.2 kcal·mol^{-1}). Additionally, a closer examination of potential termination steps revealed that the tendency for β-hydride elimination would also outcompete CO_2 insertion, and must be further reduced. As a result, there have no advancements in developing effective catalytic systems for the successful copolymerization of ethylene and CO_2.

EVP (also known as EVL), which is synthesized through a palladium-catalyzed telomerization between CO_2 and butadiene, has garnered significant attention as an intermediate for CO_2 utilization.[51-52] Continuous efforts have been dedicated to achieving high yields and selectivity in EVP synthesis since Inoue, Musco, and their colleagues first reported it in the 1970s.[53-62] Notably, Behr *et al.* demonstrated that EVP synthesis could be carried out with very low catalyst loadings with up to 95% selectivity over butadiene conversion and the recycling of palladium catalyst was possible.[63] Furthermore, Behr *et al.* have demonstrated the feasibility of scaling up the reaction to a large continuous miniplant.[63] Most recently, Dong and his colleagues achieved remarkable activity and selectivity in EVP synthesis, with TON/TOF values reaching up to 4540/568 h^{-1} and selectivity reaching up to 97%.[64] These significant advancements in synthesis have made EVP a practical intermediate for the production of materials derived from CO_2 and butadiene.

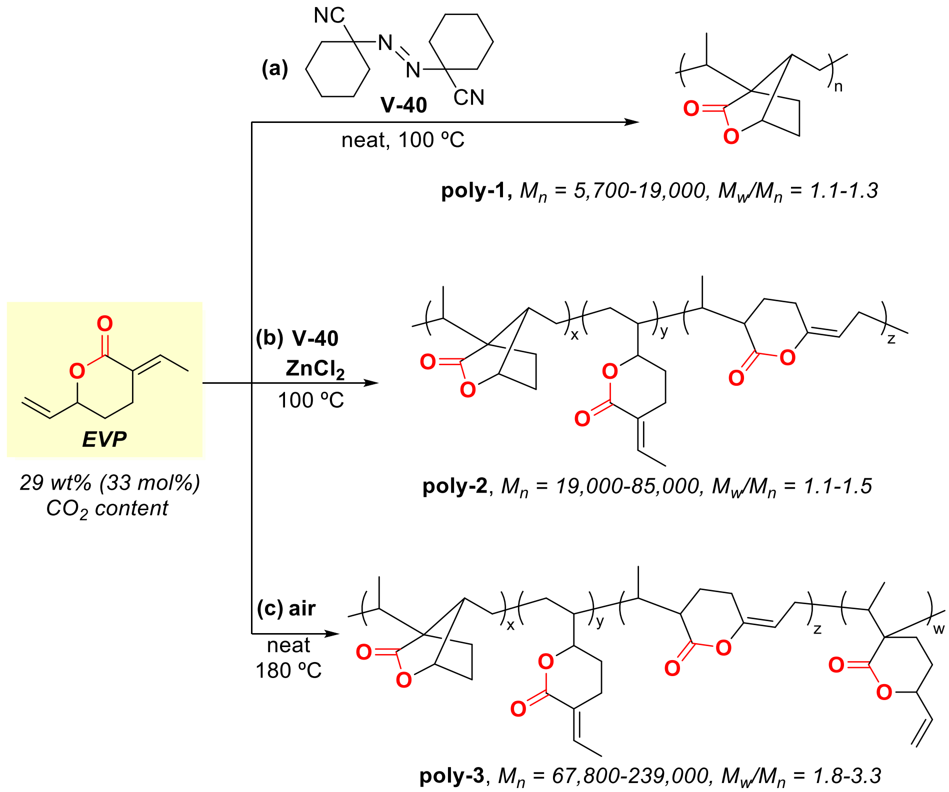
In 2014, Nozaki *et al.* conducted thermodynamic analysis on CO_2/butadiene copolymerization using DFT calculations (Scheme 1b and 1c),[65] comparing direct copolymerization through 1,4-addition of CO_2 to butadiene with reactions proceeding through the telomerization intermediate EVP. The Gibbs free energy associated with butadiene homopolymeization through 1,4-addition was determined to be -9.3 kcal·mol^{-1} (ΔG_{H2}) (Scheme 1b). In comparison, the Gibbs free energy associated with CO_2 propagation was 23.9 kcal·mol^{-1} (ΔG_{A2}). As seen in the discussion on CO_2/ethylene copolymerization mentioned above, an excess of butadiene insertion (butadiene/CO_2 > 2.6, ΔG_{NA2} < 0) plays a crucial role providing a thermodynamic driving force for the nonalternating copolymerization of butadiene and CO_2. However, the activation energy for CO_2 incorporation ($\Delta G_{NA2}^{\neq}$) is 14.6 kcal·mol^{-1} higher than that of butadiene insertion ($\Delta G_{H2}^{\neq}$), again suggesting unfavorable kinetics for nonalternating CO_2/butadiene copolymerization via 1,4-addition. In contrast, little to no change in Gibbs free energy was observed for EVP formation through telomerization of butadiene with CO_2 (ΔG_T) (Scheme 1c).[65] Further, EVP homopolymerization through cyclization to form a polymeric bicyclic lactone was found to be exothermic, with a value of -26.0 kcal·mol^{-1} (ΔG_P). Therefore, EVP can be effectively used as an intermediate for producing CO_2/butadiene copolymers.

3. DIRECT HOMOPOLYMERIZATION OF A CO_2/BUTADIENE-DERIVED LACTONE

3.1. Radical Polymerization

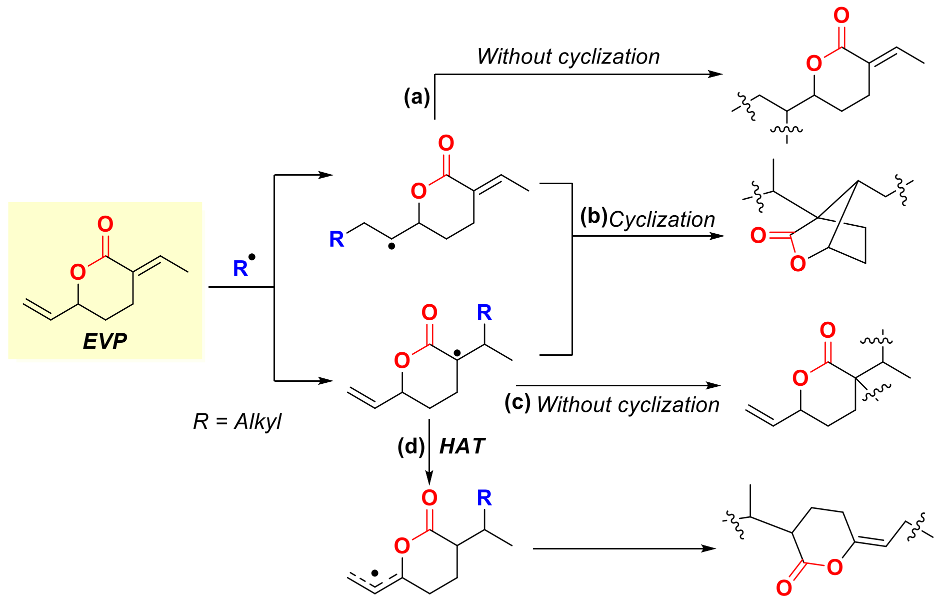
The homopolymerization of EVP was first explored by Dinjus *et al.*, where initial polymerization strategies using ring-opening polymerization, radial polymerization or cationic polymerization conditions failed to yield polymers.[66] The authors proposed that the limited reactivity of EVP might result from its structural resemblance to either a tiglate ester or an α-substituted allyl ester, both of which are known to display poor reactivity under typical polymerization conditions. Several decades later and after considerable effort, Nozaki and coworkers achieved the radical homopolymerization of EVP at 100 °C using typical radical initiators (Scheme 2a).[65] Heating of a neat mixture of EVP and 1,1'-azobis(cyclohexanecarbonitrile) (V-40) at 100°C for 24 hours, they were able to obtain polymeric material with a 22% yield (**poly-1**). The molecular weight and dispersity value of **poly-1** was determined to be M_n = 5,7 kg·mol^{-1} and M_w/M_n = 1.3 through size exclusion chromatography (SEC) analysis. When the polymerization was conducted in the presence of acetic acid, the molecular weight of **poly-1** increased to M_n = 19 kg·mol^{-1} with a narrow dispersity (M_w/M_n = 1.1). Based on ^{1}H and ^{13}C NMR spectroscopic analyses, the structure of **poly-1** exclusively exhibited repeating bicyclic lactone units, indicating that EVP homopolymerization occurred through the alternating copolymerization of its allylic ester and tiglate ester functional groups (Scheme 2a). Tiglate esters are typically considered unreactive in radical polymerization due to the steric hindrance between the radical chain-end and the adjacent monomer unit. In the case of radical homopolymerization of EVP, the challenge posed by steric hindrance for incorporating the tiglate ester unit was effectively overcome by alternatively incorporating the allylic ester unit. Scheme 2 outlines two plausible pathways for radical addition leading to the formation of the bicyclic lactone unit **α** (Scheme 3b). Both radical additions to the allylic ester moiety and the tiglate ester moiety can result in the formation of unit **α** through intramolecular radical cyclization. Previous studies have noted that Lewis acids can interact with the α,β-unsaturated ester group during radical polymerization.[67] By employing a combination of V-40 and $ZnCl_2$ in ethyl carbonate (EC) solvent, Nozaki *et al.* were able to further increase the molecular weight of the EVP homopolymer to M_n = 85 kg·mol^{-1} (M_w/M_n = 1.5) (Scheme 2b). The glass-transition temperature (T_g) of **poly-2** can reach as high as 192 °C under slightly modified polymerization conditions, suggesting the potential of such materials as a novel engineering plastic derived from sustainable raw feedstocks. In addition to the recurring bicyclic lactone units, they identified two distinct unsaturated lactone units, labeled as units **β** and **γ**, in the resulting **poly-2**. Based on the ^{1}H NMR spectroscopic analysis, the ratio of these three different units in **poly-2** was determined as **α:β:γ** = 3:5:2. Unit **β** is thought to originate from the radical chain propagation of EVP's allylic ester group without undergoing cyclization (Scheme 3a), while unit **γ** is likely formed through a hydrogen atom transfer (HAT) involving α-carbonyl radical intermediates during radical chain propagation (Scheme 3d). $ZnCl_2$ has been documented to expedite the polymerization of allylic acetate by potentially suppressing degradative chain transfer of the allylic acetate. Additionally, $ZnCl_2$ is believed to heighten the electrophilicity of α-carbonyl radicals through coordination, thereby accelerating the intramolecular hydrogen atom abstraction to generate allyl radicals. Consequently, units **β** and **γ** were observed alongside unit **α** during the homopolymerization of EVP in the presence of $ZnCl_2$.[67] Although calculations had suggested that the thermodynamic CO_2 content limit of direct CO_2/butadiene copolymerization via 1,4-addition is less than 28 mol% CO_2, this study showed that radical copolymerization of EVP can produce CO_2/butadiene copolymers with 33 mol% CO_2 incorporation.

Scheme 2. Accessing CO_2/Butadiene Copolymers via Radical Homopolymerization of EVP



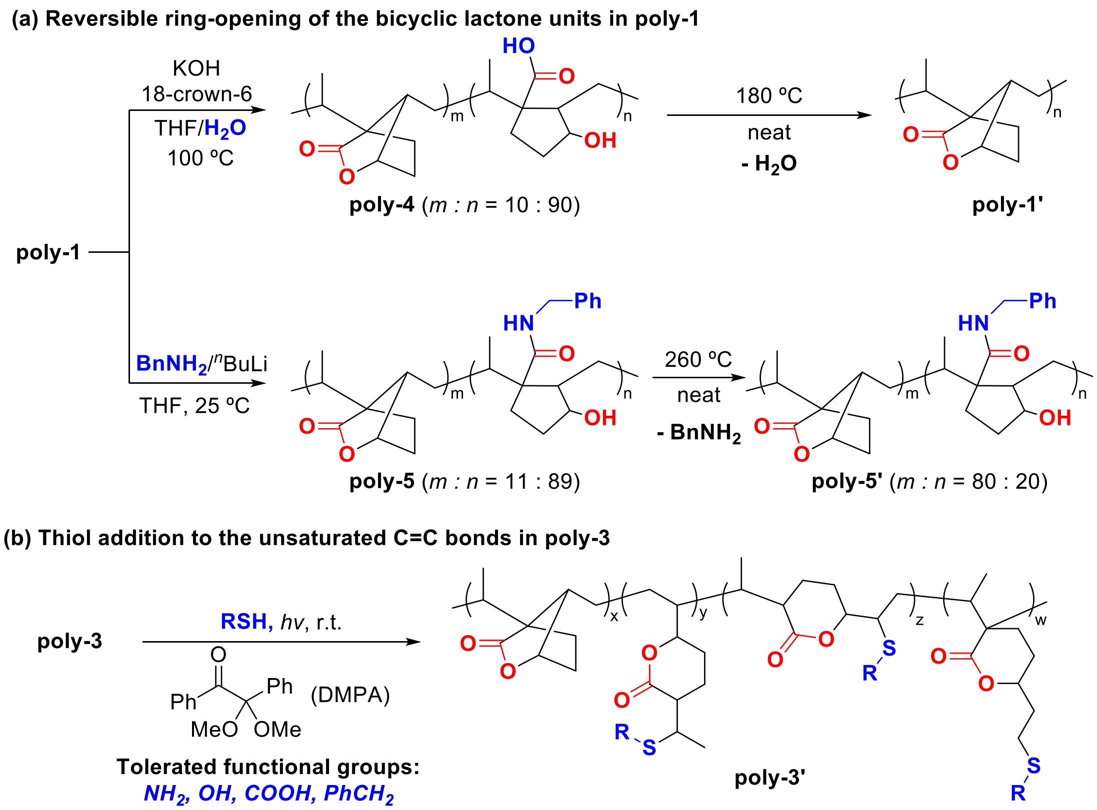
In 2017, Lin and colleagues reported a new method for polymerizing EVP using air as the radical initiator (Scheme 2c).[68] This method allowed for the production of polymers (**poly-3**) with a range of molecular weights (M_n = 67,800-239,000) and dispersity values (M_w/M_n = 1.8-3.3) by adjusting the reaction conditions. For example, full conversion of EVP was achieved at 180°C in 24 hours, without the need for additives or solvents. The resulting polymer had a M_n of 78.6 kg·mol^{-1} and a M_w/M_n of 3.3. Polymerization was also observed at temperatures as low as 60°C, yielding high molecular weight polymers with M_n = 216 kg·mol^{-1} and M_w/M_n=2.3. When the polymerization was carried out in the presence of about 0.26 equivalents of O_2 at 180°C, the M_n of **poly-3** increased further to 239 kg·mol^{-1} (M_w/M_n = 1.8). In addition to the previously observed repeating units (**α**, **β**, and **γ**), a new repeating unit (**δ**) was also formed from the direct insertion of the tiglate C=C into the backbone chain of the polymer (Scheme 3c). The ratio of these units was **α**:**β**:**γ**:**δ** =4:1.8:1.3:2.9. Notably, the presence of strong steric repulsions usually prevents the formation of unit **δ**. However, in this system, these repulsions were presumably absent due to the copolymerization of **δ** with other less sterically demanding units. In 2021, Lin and colleagues further demonstrated that the molecular weight of **poly-3** can be increased to 831 kg·mol^{-1} with a smaller dispersity value (M_w/M_n = 1.3) by adding polar solvents such as DMSO, DMA, DMF, and NMP.[69] The increased polarity in the polymerization media may reduce the solubility of O_2 and account for the improvement in molecular weight and dispersity value through limiting initiation.

Scheme 3. Proposed mechanism for the formation of different lactone units in **poly-1-3**.



Given that **poly-1** exclusively comprises strained bicyclic lactone units, efforts were taken to modify the copolymers through hydrolysis and aminolysis of the lactone units. By employing 10 equivalents of KOH and 1.0 equivalent of 18-crown-6 in a mixed tetrahydrofuran (THF)/H_2O solution, 90% of the bicyclic lactone units were hydrolyzed in **poly-1** after subjecting them to 100 °C for 72 hours, furnishing a new polymer bearing repeating *trans*-cyclopentan-1,2-diyl units (Scheme 3a, **poly-4**).[70] The carboxyl and hydroxy groups are situated in a *cis* configuration on the cyclopentane ring, which enabled the reversible dehydrative lactonization**.** Simply by heating **poly-4** to 180°C under neat conditions, full conversion of the *trans*-cyclopentan-1,2-diyl units to bicyclic lactone units were observed (Scheme 3a, **poly-1'**). It is important to highlight that the molecular weight and dispersity of the polymer remained constant during the reversible cycle of ring-opening hydrolysis and ring-closing dehydration. As a consequence of the dehydrative lactonization, two distinct reductions in weight were observed, occurring around 180 °C and 350 °C during thermogravimetric (TGA) analysis of **poly-4**. Nevertheless, both TGA and DSC (differential scanning calorimetry) analyses demonstrated that **poly-1'** displayed weight loss and glass transition behavior similar to that of **poly-1**. In addition to hydrolysis, aminolysis of **poly-1** was successfully achieved at room temperature using a mixture of benzylamine and ^{n}BuLi, resulting in the formation of **poly-5** with an 89% conversion of the bicyclic lactone units (Scheme 4a).[70] In comparison to the ring-closing process for hydrolyzed **poly-4**, a higher temperature (260 °C) was required for achieving partial ring-closing deamination of **poly-5** (Scheme 4a). The resulting **poly-5'** contained both bicyclic lactone and amide/alcohol units in an 8:2 ratio. TGA measurements of **poly-5** also displayed two distinct weight losses at approximately 260 °C and 350 °C. The weight loss at around 260 °C was attributed to ring-closing deamination. Like the reversible hydrolysis process, there was no observable alteration in molecular weight and dispersity value during the partial ring-opening aminolysis/ring-closing deamination process. Different from **poly-1**, there are unsaturated carbon-carbon double bonds in **poly-2** and **poly-3** (units **β-δ**), which provides an entry point for structure modification via thiol-ene addition. Lin and coworkers reported that post-modification of **poly-3** could be achieved by leveraging the abundant olefin groups present in the polymer structure.[68] Ten examples of different thiols, including cysteine and PEGylated dithiol, were introduced into **poly-3** through thiol-ene click reactions using 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator in $CHCl_3$ under UV light at room temperature for 24 h (Scheme 4b). The method is compatible with functional groups containing active protons, such as hydroxyl, amino, carboxyl and benzyl groups. The nonconjugated internal olefin of unit **γ** showed the highest reactivity toward most of the studied thiols.

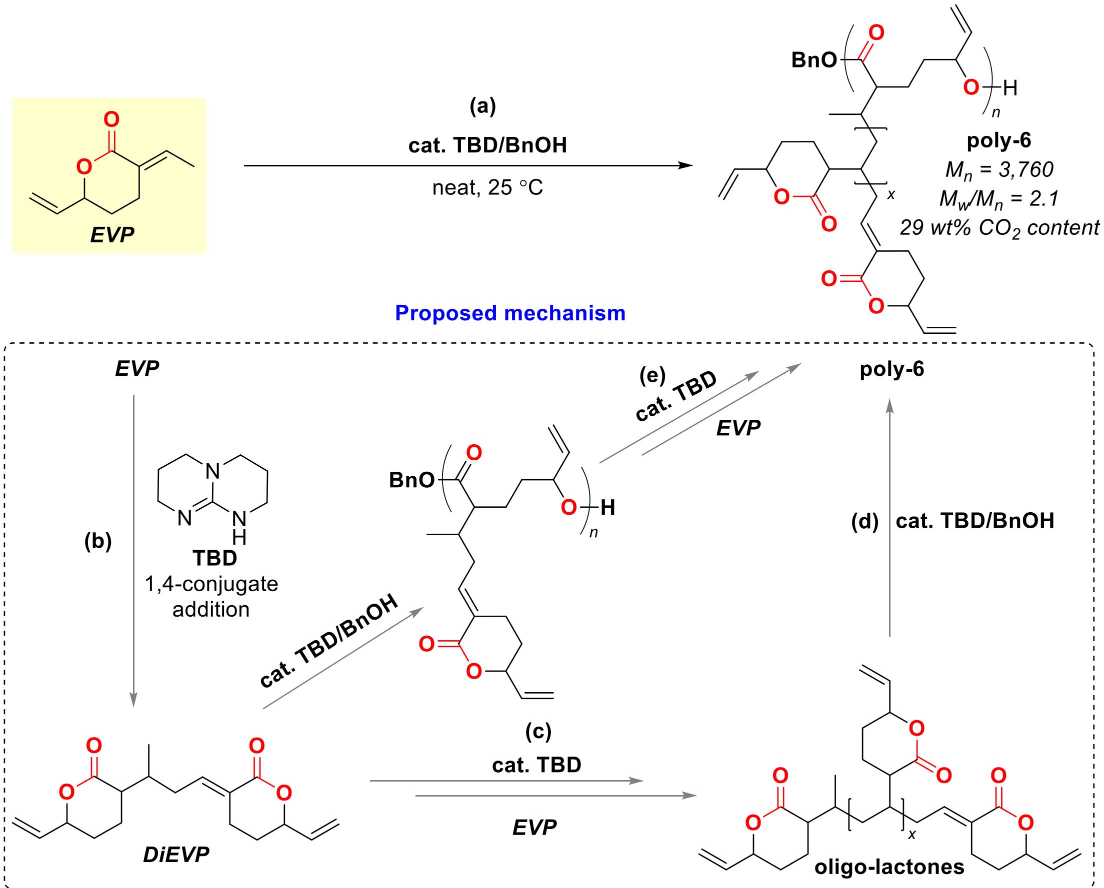
Scheme 4. Post-modifications of the Poly-1 and Poly-3



3.2. Conjugate Addition/Ring Opening Polymerization

In addition to its behavior as a bifunctional olefin monomer, EVP can also be regarded as a lactone monomer. Consequently, it is possible to consider synthesizing butadiene/CO_2 copolymers through the ROP of EVP. Substantial endeavors have been directed towards establishing optimal conditions for the ROP of EVP. While using EVP as an unsaturated monomer takes advantage of the enthalpic driving force of carbon-carbon bond formation, the ring-opening polymerization has a considerably less of a thermodynamic driving force. In fact, several earlier reports have described the inability to achieve ring-opening propagation of EVP under various conditions.[66, 71] The use of a bifunctional superbase catalyst TBD (1,5,7-Triazabicyclo[4.4.0]dec-5-ene), pioneered by Hedrick and Waymouth for ring-opening polymerization of lactones,[72] was investigated by Eagan and coworkers for its ability to promote EVP homopolymerization.[73] When EVP was reacted with 5 mol% TBD under neat conditions, low molar mass oligomers could be obtained with an M_n up to 3.8 kg·mol^{-1} by SEC (Scheme 5a, **poly-6**). Importantly however, the microstructures obtained consisted of a mixture of 1,4-conjugate adducts and ring-opened units, which could be characterized by tandem MS-MS, NMR spectroscopy, and degradation studies.

Scheme 5. Accessing CO_2/Butadiene Copolymers via Conjugate Addition/Ring-opening Homopolymerization of EVP



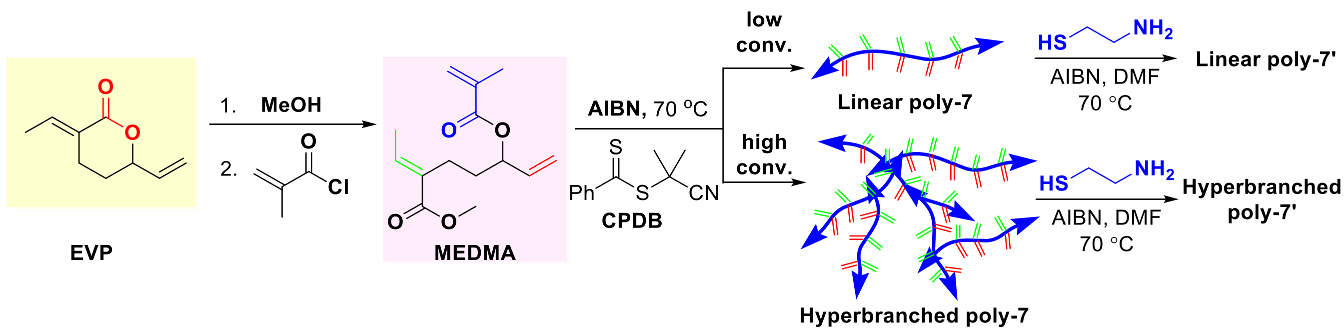
A polymerization mechanism for the TBD-catalyzed homopolymerization of EVP involving combined conjugate addition and ring-opening homopolymerization of EVP was proposed. The proposed pathway initiates with TBD serving as a base to deprotonate EVP, resulting in the formation of a nucleophilic dienolate. This dienolate then undergoes a 1,4-conjugate addition to an electrophilic EVP. At low reaction conversions, it is possible to isolate EVP dimer (Scheme 5b, DiEVP). However, if the reaction is allowed to continue, it leads to the propagation of oligomeric lactones (Scheme 5c). Notably, this 1,4-addition pathway generates one or more saturated lactone moieties, which become activated for ring-opening polymerization when initiated by TBD or an alcohol initiator (Scheme 5d and 5e). Based on tandem mass spectrometry mass spectrometry (MS-MS) studies and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis, it was observed that ring-opened dimer fragments are incorporated into higher 1,4-oligomers. This suggests that both the conjugate addition and ring-opening pathways occur simultaneously. The resulting products display reactivity consistent with polyester moieties and can undergo chemical degradation under saponification conditions to form hydroxyacids. Ring-opening homopolymerization of EVP remains a challenging task due to the complex mixture of both 1,4-addition and ring-opening mechanisms, as well as the overall low molar masses.

4. HOMOPOLYMERIZATION OF CO_2/BUTADIENE-DERIVED LACTONE DERIVATIVES

4.1. Radical Polymerization

In order to improve the reactivity of EVP in radical polymerization, Ni *et al.* developed a method wherein EVP undergoes alcoholysis with methanol, followed by esterification with methacryloyl chloride, resulting in the formation of methyl-2-ethylidene-5-hydroxyhept-6-enoate methacrylate (MEDMA). Utilizing azobisisobutyronitrile (AIBN) as an initiator and 2-cyanoprop-2-yl-dithiobenzoate (CPDB) as a chain transfer agent (CTA), chemoselective reversible addition-fragmentation chain transfer (RAFT) homopolymerization of MEDMA was achieved (Scheme 6). Beginning with an initial [MEDMA]/[CTA] ratio of 60/1, the RAFT polymerization initially targeted the methacrylate moiety, affording linear **poly-7** with unimodal molecular weights and narrow dispersity. As the MEDMA conversion increased, the tiglate moiety also participated in polymerization, acting as a branching point and generating hyperbranched **poly-7** with M_w determined as 313 kg·mol^{-1} by size-exclusion chromatography coupled to multi-angle light scattering (SEC-MALS) analysis. The dispersity value increased from 1.70 to 4.83 during polymerization along with increasing MEDMA conversion. The pendent vinyl groups of both linear and hyperbranched **poly-7**s were easily modified by thiol-ene click reaction with 2-aminoethanethiol. The amino functionalized polymer (**poly-7'**) can exhibit pH-sensitive behavior. Moreover, **poly-7'** also self-assembled in water to form micelles with thin hydrophilic shells for hyperbranched **poly-7'** and small hydrophobic domains for linear **poly-7'**.

Scheme 6. Synthesis and Topology Control of CO_2/Butadiene Copolymers via Methacryloylic EVP Radical Polymerization

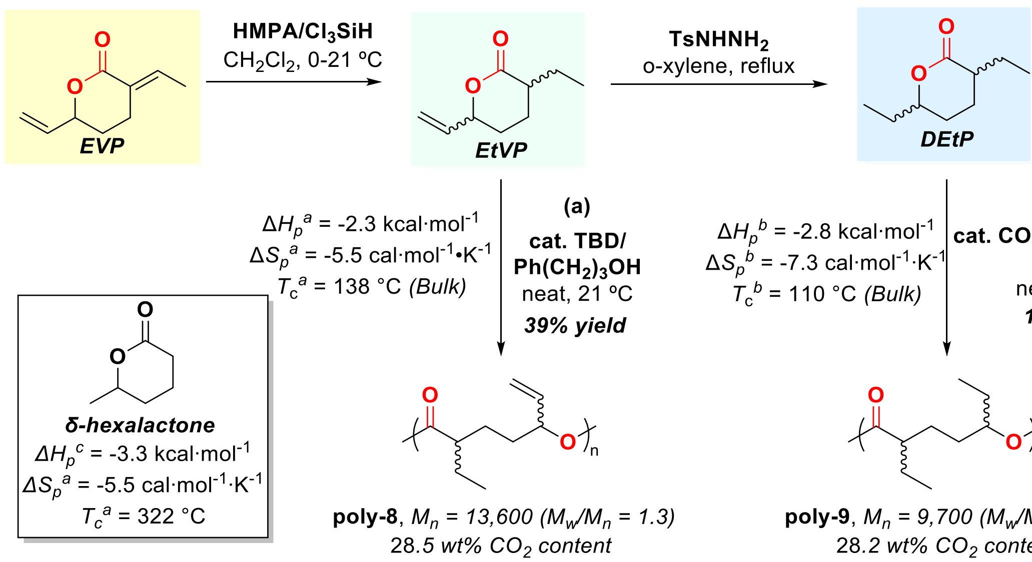


4.2. Ring-opening polymerization

The poor reactivity of EVP toward ring-opening polymerization could be attributable to two main obstacles. First, the α-ethylidene group or the δ-vinyl group may provide steric hindrance against ring opening, in particular in the context of a propagating secondary alkoxide from the lactone δ-substitution. Second, the conjugated olefin is a typical Michael acceptor that may react with potential chain-end alkoxides to terminate chain-propagating processes in anionic ROPs, similar to that observed by Eagan.[73] In fact, although ring-opening homopolymerizations of six-membered lactones with 0 to 1 substituents on the ring have been well known, early efforts for ROP of the disubstituted counterpart failed.[71, 74] Model studies of the thermodynamics of ring-opening polymerization of various EVP derivatives by Hoye suggest that ROP of EVP and its derivatives should be thermodynamically feasible; further indicating that the challenges of EVP ROP may mostly be a consequence of the kinetics of competitive Michael addition.[75] The question of Michael addition can be overcome through hydrogenation of the conjugated olefin to produce one of two new disubstituted six-membered lactones, fully-hydrogenated 3,6-diethyltetrahydro-2H-pyran-2-one (DEtP) and partially-hydrogenated 3-ethyl-6-vinyltetrahydro-2H-pyran-2-one (EtVP) (Scheme 7).

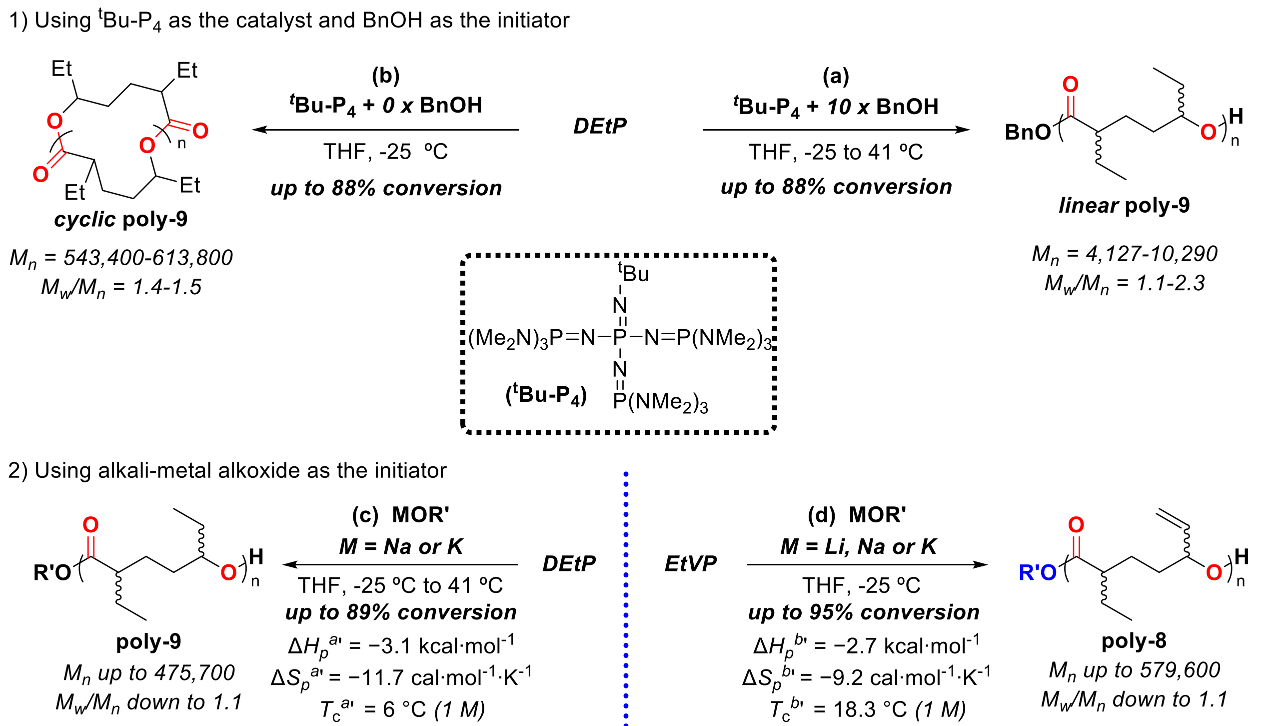
In 2022, Tonks and coworkers reported on the successful homopolymerization of an EVP derivative by ring-opening polymerization, using both EtVP and DEtP as substrates.[76] Using 3-phenylpropanol (PPA) as initiator, TBD was found to be an active catalyst for the ROP of neat EtVP, furnishing degradable polyesters (**poly-8**) with up to 13.6 kg·mol^{-1} molecular weight (M_w/M_n = 1.32) (Scheme 7a). The polymerization demonstrated good linear correlation between molecular weight and monomer conversion. The major peaks in the MALDI-TOF MS spectra corresponds to poly(EtVP) initiated by PPA with a proton chain end. Meanwhile, minor peaks were detected in the MS spectra of the obtained polymers which were assigned to the chains initiated by water or the TBD catalyst. A low glass transition temperature (-39 °C) was determined for **poly-8**, which may potentially serve as a soft block in thermoplastic elastomers. The ROP of DEtP was also observed but with a low conversion (46%) using similar conditions for the ROP of EtVP. An increased conversion (74%) of DEtP to **poly-9** (M_n=9.7 kg mol^{-1}, M_w/M_n = 1.27) was obtained when NaOMe/1-cyclohexyl-3-phenylurea[77] was applied as catalyst (Scheme 7b). Comparing with **poly-8**, a slightly lower glass transition temperature was determined for **poly-9** (-42 °C). The thermodynamic parameters of polymerization of EtVP (ΔH_p^a = -2.3 kcal·mol^{-1} and ΔS_p^a = -5.5 cal·mol^{-1}·K^{-1}) and DEtP (ΔH_p^b = -2.8 kcal·mol^{-1} and ΔS_p^b = -7.3 cal·mol^{-1}·K^{-1}) indicate that ROP of these disubstituted valerolactones is thermodynamically feasible at room temperature in the bulk, and that **poly-8** (T_c^a = 138 °C) and **poly-9** (T_c^b = 110 °C) have low ceiling temperatures (T_c) compared to δ-hexalactone (ΔH_p^c = -3.3 kcal·mol^{-1}, ΔS_p^c =-5.5 cal·mol^{-1}·K^{-1}, T_c^c = 322 °C), suggesting that they may be good candidates for chemical recycling (Scheme 7).

Scheme 7. Ring-opening Polymerization of Hydrogenated EVP Derivates



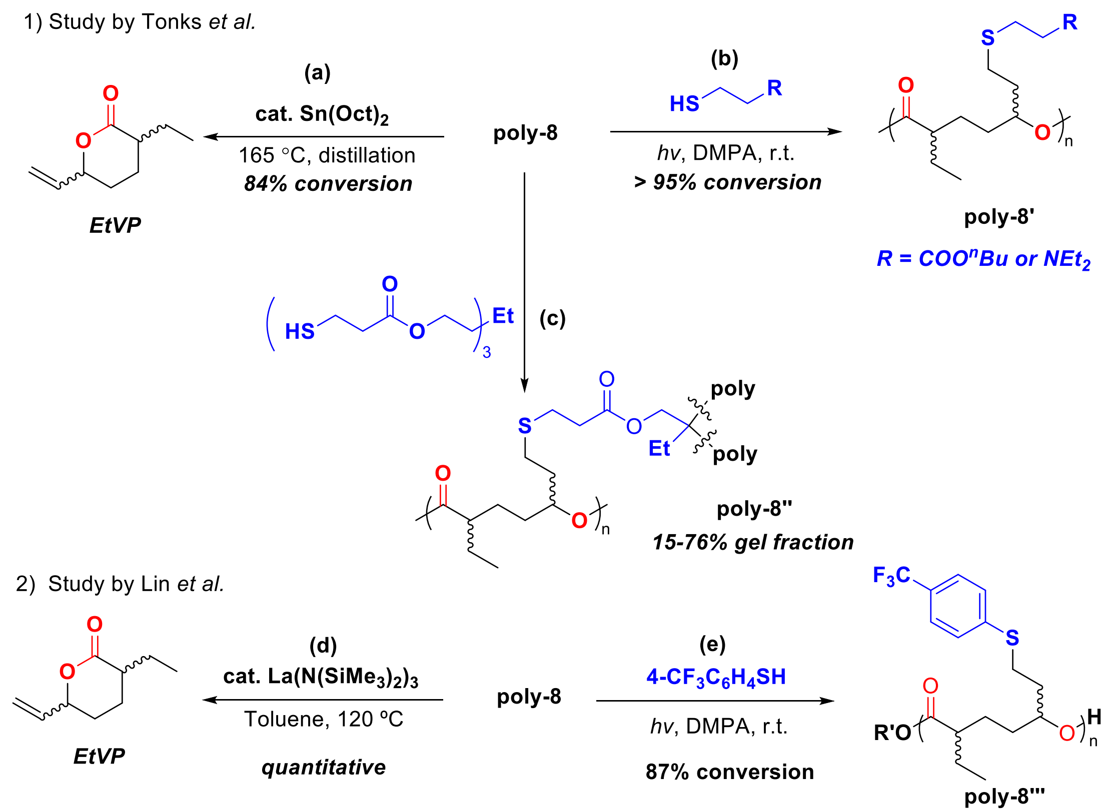
Simultaneously, Lin and coworkers reported highly efficient ROPs of DEtP in THF at -25 °C (Scheme 8a).[78] They found that high purity and dryness are crucial to the successful ROP of DEtP. Using ^{t}Bu-P$_4$ [1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene)] as the catalyst and benzyl alcohol (BnOH) as the initiator, chemically recyclable polyesters (**poly-9**) with good molecular weights and low polydispersities were successfully obtained. Subzero reaction temperature (-25 °C) was found to be beneficial for achieving a controlled polymerization, which is an effect of the increased entropic penalty associated with conducting the polymerization in THF solvent instead of that in the bulk. Up to 88% conversion of DEtP to **poly-9** with high molecular weight can be achieved. The ratio of initiator to catalyst, *i.e.* BnOH to ^{t}Bu-P$_4$, was found to significantly impact the ROP behavior of DEtP (Scheme 8a and 8b). With 10 equiv of BnOH to ^{t}Bu-P$_4$, living ring-opening polymerization of DEtP to form linear **poly-9** (M_n up to 10.3 kg·mol^{-1}; M_w/M_n down to 1.1) was observed by MALDI-TOF MS and NMR spectroscopy (Scheme 8a). In contrast, cyclic **poly-9** (M_n up to 614 kg·mol^{-1}; M_w/M_n down to 1.4) became the only product detected by MALDI-TOF MS and NMR spectroscopy if no BnOH initiator was added (Scheme 8b). A similar dependence of the formation of cyclic products on the ratio of BnOH to trisaminophosphine ylide, a catalyst reminiscent of phosphazene, was later reported for ROP of cyclic oligosiloxanes.[79] The observation of cyclic **poly-9** as the only product for the initiator-free ROP suggests a special mechanism in which back biting occurred selectively from a propagating chain tail to the chain head. Glass-transition temperatures for both linear **poly-9** and cyclic **poly-9** are determined around -30 °C. Linear **poly-9** diol that may be used as the soft block in polyurethanes was synthesized. Successful ROP of DEtP leading to solid **poly-9** (M_n up to 476 kg·mol^{-1}; M_w/M_n down to 1.1) can also be achieved with up to 89 mol% conversion by using cheap alkali-metal alkoxides as the initiator (Scheme 8c). No catalyst is needed for this ROP protocol. Both sodium and potassium alkoxides showed high activities, while no activity was observed for lithium alkoxides. In a follow up study, Lin and coworkers further found that the ROP behaviors of EtVP are only slightly different from those of DEtP, except that lithium alkoxide is also an active initiator for EtVP (Scheme 8d, **poly-8**).[80] Such difference might be attributable to the different solubilities of lithium alkoxide in EtVP and DEtP, as suggested by the significant impact onto the ROP of EtVP by the addition of crown ether. For KOMe-initiated ROP of EtVP, higher conversion (up to 95%) and molecular weights (M_n up to 580 kg·mol^{-1}, M_w/M_n down to 1.1) were observed than those using ^{t}BuP$_4$. The changes in ROP enthalpy and entropy were measured to be −2.7 kcal·mol^{-1} and −9.2 cal·mol^{-1}K^{-1} for EtVP, while for DEtP, they were −3.1 cal·mol^{-1} and −11.7 cal·mol^{-1}K^{-1}. Comparing to the calculated results under bulk conditions by Tonks *et al.*,[76] significantly lower ceiling temperatures were determined for both **poly-8** ($T_c^{a'}$ = 18.3 °C)[80] and **poly-9** ($T_c^{a'}$ = 6 °C)[78] at a starting monomer concentration of 1 M. In a series of peeling experiments, the adhering strength of high molecular weight **poly-9** was found to be comparable to or even stronger than commercial 3M tape.[78]

Scheme 8. Accessing Cyclic/Linear Polyesters via Ring-opening Polymerizations of Hydrogenated EVP Derivates



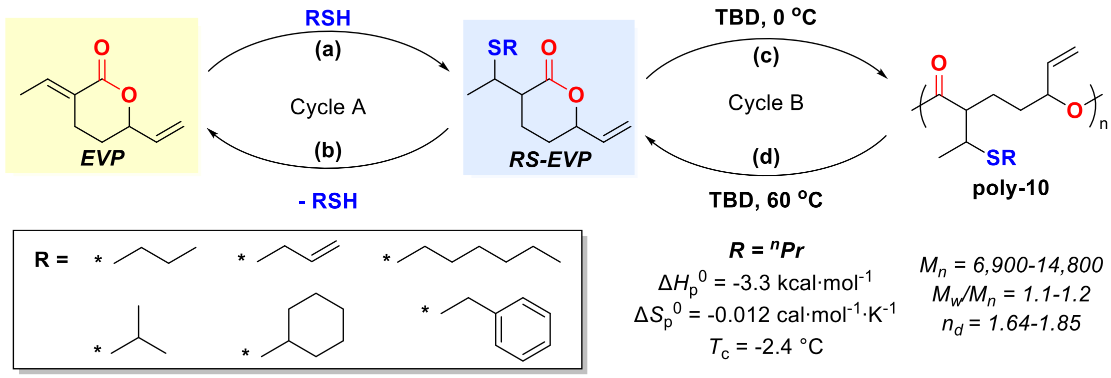
Chemical recycling and post-modification of the polyesters were also independently demonstrated by the Tonks group[76] and the Lin group[78, 80]. Taking advantage of its low ceiling temperature (T_c = 138 °C), chemical recycling of **poly-8** was successfully achieved by Tonks *et al.* through distillation with 84% yield in the presence of tin(II) 2-ethylhexanoate (Sn(Oct)$_2$) at 165 °C (Scheme 9a).[76] Moreover, **poly-8** undergoes full degradation in basic solution (0.1 M NaOH), and naturally degrades in aerobic aqueous environments according to the OECD-301B protocol. Different from the study by Tonks where recycling of the polymer was done neat, the group of Lin demonstrated the chemical recycling study using La(N(SiMe$_3$)$_2$)$_3$ as the catalyst in toluene solution.[80] A complete monomer recycling was achieved at 80 °C for **poly-9**,[78] while 120 °C was needed for **poly-8**[80] (Scheme 9d), which is consistent with the relative magnitude of their ceiling temperatures. Significantly, the 6-vinyl group in EtVP remains unaltered within the polymer structure of **poly-8**, offering a convenient means for subsequent modifications through straightforward alkene reactions after polymerization. Tonks *et al.* demonstrated the successfully modification of **poly-8** via radical thiol-ene click reaction with butyl-3-mercaptopropionate, 2-diethylaminoethane thiol and trimethylolpropane tris(3-mercaptopropionate) (Scheme 9b and 9c).[76] The glass transition temperature was further decreased to -57 °C in the case of butyl-3-mercaptopropionate. When trimethylolpropane tris(3-mercaptopropionate) was used with various molar ratios, cross-linked polymers (**poly-8''**) with 15-76% gel fraction were produced, which were more solid than **poly-8** and were slightly sticky (Scheme 9c). Similarly, Lin *et al.* conducted the post-modification of **poly-8** via thiol-ene addition to produce **poly-8'''**. Interestingly, **poly-8'''** was found to be a light-sensitive and hydrophobicity-tunable coating material (Scheme 9e).[80] These studies by Tonks and Lin have demonstrated the feasibility of producing precisely structured polyesters derived from both CO_2 and butadiene with high CO_2 weight content (28.5 wt% for **poly-8** and 28.2 wt% for **poly-9**).

Scheme 9. Chemical Recycling and Post-modification of Poly-8



The activation of EVP for ROP via 1,4-conjugate addition or hydrogenation sacrifices the functionality of the internal carbon-carbon double irreversibly. In a recent report, Ni *et al.* developed a novel reversible activation and functionalization strategy for EVP (Scheme 10).[81] EVP derivatives with various thiol functional groups (RS-EVP) were prepared through Michael addition of EVP with thiols (Scheme 10a). Retro-Michael additions of RS-EVP were carried out with calcium hydride to recover both EVP and thiols (Scheme 10b, yield up to 99% and 87%, respectively), which were reused in another synthesis of EVP with original or an altered functional group. The controlled anionic ROP of RS-EVP in the presence of TBD generated polyesters (**poly-10**) with tunable M_n ranging between 6.9 kg·mol^{-1} and 14.8 kg·mol^{-1} and narrow distributions ($M_w/M_n < 1.2$) (Scheme 10c). The ROP exhibits first-order kinetics with respect to monomer concentration. A positive linear relationship between M_n and conversion was observed in the kinetic study, suggesting living polymerization behavior. The ceiling temperature of **poly-10** was determined to be -2.4 °C at 1M concentration, calculated from the enthalpy change (ΔH_p^0) of -3.3 kcal·mol^{-1} and entropy change (ΔS_p^0) of -0.012 kcal·mol^{-1}·K^{-1}. Accordingly, chemical recycling of **poly-10** was achieved at 60 °C through TBD-catalyzed depolymerization, resulting in a 90% yield in 48 h (Scheme 10d). Under the same conditions, **poly-10** with comparable M_n and M_w/M_n was obtained from recycled RS-EVP. As sulfur-containing polyesters, the refractive indices of **poly-10** were determined to be up to 1.85 when bearing a benzyl group, indicating their potential in optical materials applications.

Scheme 10. Accessing Recyclable CO_2/Butadiene/Thiol Terpolymers via Ring-opening Polymerization of Thiol-modified EVP

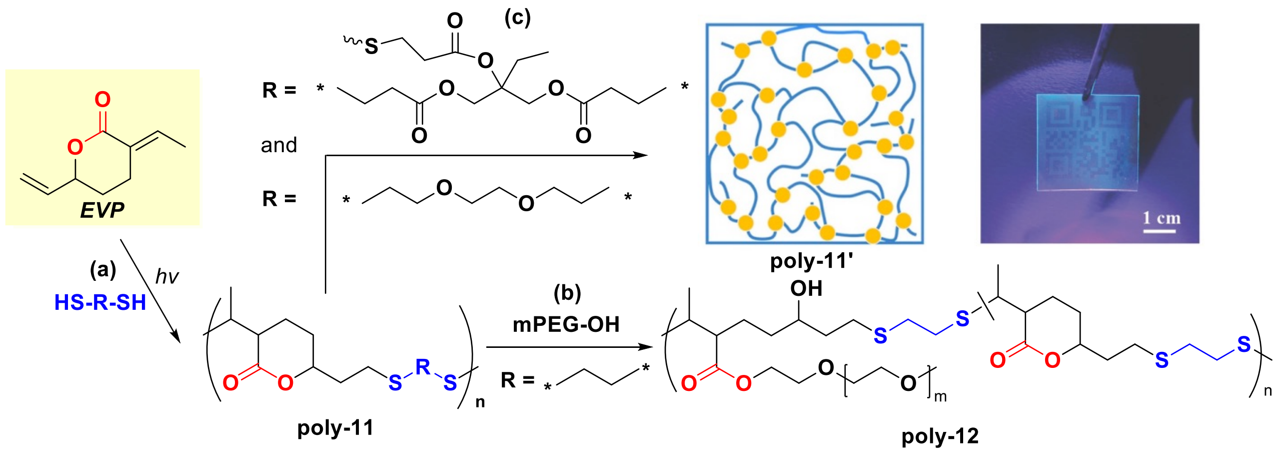


5. COPOLYMERIZATION OF A CO_2/BUTADIENE-DERIVED LACTONE OR ITS DERIVATIVES WITH COMONOMERS

5.1. Thiol-ene Click Copolymerization with Multi-thiols

Since EVP has historically shown relatively low reactivity in both radical polymerization and ring-opening polymerization, attention was also paid toward introducing reactive comonomers for EVP copolymerization. In 1998, Dinjus and coworkers reported a step-growth polymerization of EVP with dithiols via thiol-ene addition.[66] They were able to produce linear polymers (M_n up to 7.6 kg·mol^{-1}) from EVP with an intact lactone ring structure in the main chain for the first time. When multi-thiols were added as comonomers, network polymers were formed as polymer films or molded parts. Based on Dinjus's pioneering report, Ni *et al.* investigated the kinetics of the thiol-ene click polymerization of EVP with ethanedithiol (Scheme 11a).[82] The polymerization was carried out under UV light with 4 wt% of the photo-initiator DMPA. According to ^{1}H NMR spectroscopic analysis, the tiglate moiety exhibits higher reactivity, with ca. 1.5 times higher conversion than the allylic ester moiety in 10 min, owing to its electron-deficient character. The resulted alternating copolymer **poly-11** contains lactone rings that are ready for modification. Ring-opening by methoxy polyethylene glycol (mPEG) was achieved by a TBD-catalyzed alcoholysis, resulting in a maximum degree of grafting of 21.1% in 16 h, where the grafted mPEG side chain was identified by MALDI-TOF MS analysis (Scheme 11b, **poly-12**). With hydrophilic PEG segments, the copolymer behaved as an amphiphilic polymer that self-assemble to micelles in aqueous solution, where the spherical morphology was illustrated by transmission electron microscopy (TEM). In further work, tri-thiol trimethylolpropane tris(3-mercaptopropionate) (TMPT) was used as the cross-linker with EVP in a photoinitiated thiol-ene click copolymerization with tri(ethylene glycol)dithiol (TEGDT), providing a copolymer network in 30 min (Scheme 11c, **poly-11'**).[83] Increasing the initial ratio of TMPT/TEGDT led to increases of cross-link density, glass transition temperature (T_g) and decomposition temperature (T_d). The network without TEGDT exhibited a maximum tensile strength of 6.18 ± 0.16 MPa, while strain at break reached 5.74 ± 0.23 mm^{-1} when feeding 90% TEGDT. The thioether networks have good affinities for metal ions such as Cu^{2+}, Ni^{2+}, Fe^{3+} and Co^{2+}. When complexed with Fe^{3+}, the network exhibited a higher tensile strength of 3.3 MPa compared to the initial one of 2.1 MPa. Since the polymerization was initiated by UV light, various patterns, which consisted of stripes with different cross-linking density, were designed through light masking. In fact, a patterned QR code could be clearly observed under UV light (365 nm) thanks to the fluorescence behavior of the highly cross-linked copolymer.

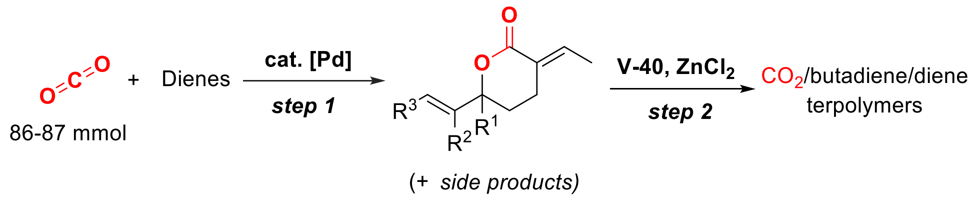
Scheme 11. Accessing CO_2/Butadiene/Multi-thiol Terpolymers via Thiol-Ene Click Polymerization



5.2. Coordination/Insertion and Radical Copolymerization with Olefins

Because EVP contains two carbon-carbon double bonds, it can also potentially function as a polar comonomer in olefin copolymerization reactions. Combining an olefin with EVP offers a potential route for the formal terpolymerization of CO_2, butadiene, and an olefin. EVP can be viewed as either an allyl carboxylate comonomer with a bulky substituent or a tiglate ester comonomer. Due to the limited reactivity of its two olefin groups, little prior attention has been given to direct copolymerization of EVP. In section 3.1, we have discussed the synthesis and radical polymerization of EVP in two separate steps. However, it is also possible to produce EVP radical polymers and copolymers using a one-pot/two-step approach.[65] In the initial step, a Pd-catalyzed telomerization of butadiene and CO_2 was conducted in ethylene carbonate. After the removal of all volatiles, $ZnCl_2$ and V-40 were added to the reaction mixture, which was then heated at 100 °C for 24 hours. This process yielded a high-quality polymer with an isolated yield of 47% based on the initial amount of butadiene used in the formal CO_2/butadiene copolymerization. Elementary analysis of the obtained homopolymer demonstrated that it contained 23 wt% of CO_2 incorporation. Utilization of alternative dienes, rather than 1,3-butadiene, in telomerization with CO_2 remains quite challenging due to increased steric hindrance and the generation of intricate mixtures containing constitutional isomers. However, investigation by Behr *et al.* into the three-component coupling of carbon dioxide, butadiene, and isoprene/1,3-pentadiene using Pd catalysis yielded reasonable results.[84] Consequently, attempts to carry out terpolymerization involving carbon dioxide, butadiene, and another 1,3-diene have also yielded success using this one-pot/two-step procedure (Scheme 12).[65] Elemental analysis revealed that in the case of CO_2/butadiene/isoprene terpolymerization, 20 wt% of CO_2 was incorporated (**poly-13**), while in the CO_2/butadiene/1,3-pentadiene terpolymerization, 24 wt% of CO_2 was incorporated (**poly-14**). DSC analysis of these terpolymers indicated significantly lower glass transition temperatures compared to CO_2/butadiene copolymers. This reduction in glass transition temperature is likely due to the introduction of methyl substituents into the lactone units.

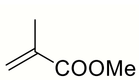
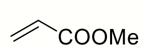
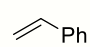
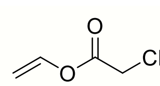
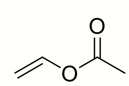
Scheme 12. One-pot/Two-step Terpolymerization of CO_2, Butadiene and Another Dienes



	Dienes	CO_2/Diene copolymers	T_g (ºC)
poly-13	25 mmol Butadiene 50 mmol Isoprene	*20 wt% CO_2 content* M_n = 5,500 (M_w/M_n = 2.5)	63
poly-14	25 mmol Butadiene 50 mmol 1,3-Pentadiene	*24 wt% CO_2 content* M_n = 16,000 (M_w/M_n = 2.0)	33

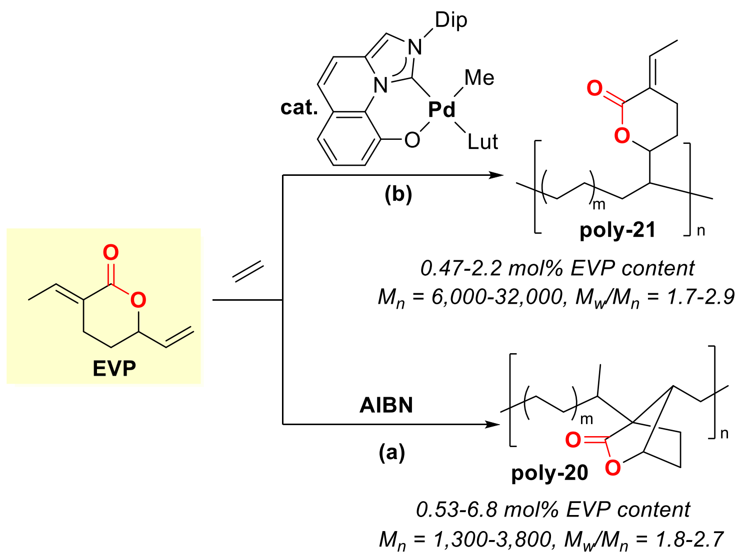
In 2021, Lin and coworkers reported a combination of air and 1 mol% EVP to initiate the radical polymerization of neat methyl methacrylate (MMA) under air at 60-90 °C.[85] Incorporation of EVP into the resultant polymers were observed by NMR spectroscopy. The NMR signals are consistent with those of repeat units α, β, γ and δ in **poly-3**. In contrast, no polymerization of MMA was observed without EVP under similar conditions, again suggesting that the special reactivity between EVP and O_2 may allow for discoveries of unusual radical polymerization chemistry of olefins in the presence of O_2.[68] Later on, Nozaki and coworkers reported the radical copolymerization of EVP with a range of commercially available functional monomers.[86] By employing similar reaction conditions as those used in the radical homopolymerization of EVP to afford **poly-1**, copolymerizations of EVP with methyl methacrylate (MMA), methyl acrylate (MA), styrene (Sty), vinyl chloroacetate (VAcCl), and vinyl acetate (VAc) were successfully achieved, resulting in EVP incorporation ranging from 3.5% to 90% (Scheme 13, **poly-15** to **poly-19**). Since the reactivity of the olefin comonomers varied from each other, the selection of radical initiators and the mole fraction of comonomers played crucial roles in achieving reasonable EVP incorporation. Different from the work of Lin, only bicyclic lactone units, corresponding to repeat unit α, were observed in the obtained copolymers. Due to the rigid nature of these bicyclic lactone units, their incorporation into poly(methyl acrylate), polystyrene, polymethyl acrylate, polyvinyl chloroacetate, and polyvinyl acetate resulted in elevated glass transition temperatures when compared to the convertional homopolymers.

Scheme 13. Accessing CO_2/Butadiene/Olefin Terpolymers via Radical Copolymerization of EVP and An Olefin

Olefin comonomer					
Reactivity ratios (r_M/r_{EVP})	920	24	25	0.59	-
Terpolymer	**poly-15**	**poly-16**	**poly-17**	**poly-18**	**poly-19**
EVP incorporation ratio (mol%)	*3.9-28*	*13.7-55*	*3.5-46*	*34-90*	*13-48*
M_n (kg·mol^{-1})	20.0-49.0	20.5-115.5	18.8-20.1	15.9-35.4	45.0-71.8
M_w/M_n	1.3-1.6	1.4-1.9	1.2-1.5	1.2	1.1-1.2

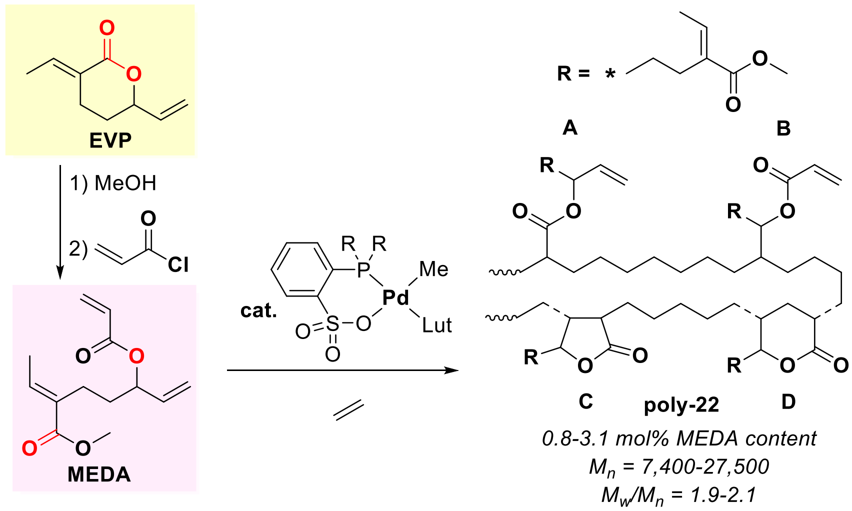
Apart from polar vinyl monomers, radical copolymerization of EVP with ethylene was also achieved by Nozaki and coworkers (Scheme 14a).[87] Using AIBN as a radical initiator, both the tiglate ester and allylic ester groups in EVP participated in the copolymerization, affording polyethylene copolymers (**poly-20**) bearing exclusively bicyclic lactone units (α) in the main chain (0.53-6.8 mol% content). Interestingly, it is possible to alter the microstructure of the incorporated EVP-derived functional groups by changing the copolymerization strategy. When a carbene-phenolate Pd complex was used as the catalyst, EVP could copolymerize with ethylene through a coordination/insertion mechanism, resulting in a 0.47-2.2 mol% incorporation (Scheme 14b). According to ^{1}H NMR spectroscopic analysis, only the allylic ester group participated in the copolymerization with ethylene, leading to polyethylenes with unsaturated lactone side groups (**poly-21**). Coordination/insertion copolymerization produced highly linear polyethylene copolymers with high molecular weights, whereas radical copolymerization resulted in more branched polyethylene copolymers with lower molecular weights.

Scheme 14. Accessing CO_2/Butadiene/Ethylene Terpolymers via Copolymerization of EVP and Ethylene



Ni, Jian and coworkers reported the coordination/insertion copolymerization of ethylene with an EVP derivative (Scheme 15).[88] Methyl-2-ethylidene-5-hydroxyhept-6-enoate acrylate (MEDA) was synthesized following a similar procedure with that of MEDMA. Utilizing Pd phosphine-sulfonates complexes as catalysts, the copolymerization of MEDA with ethylene resulted in polyethylenes functionalized with (cyclic)ester groups (0.8-3.1 mol% content) (**poly-22**). Although the tiglate moiety was inert in the copolymerization, the insertion of the other two moieties generated various microstructures in the copolymers. Noncyclic structures were generated via acrylate insertion and allylic insertion, respectively. The combined acrylate-allylic insertion resulted in five-membered or six-membered lactone structures incorporated in the main chain, depending on the insertion regioselectivity.

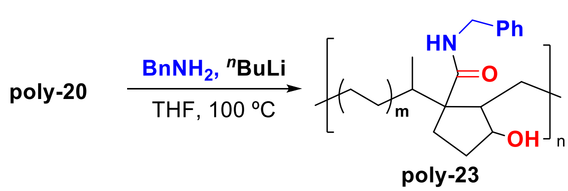
Scheme 15. Accessing CO_2/Butadiene/Ethylene Terpolymers via Copolymerization of An EVP derivative and Ethylene



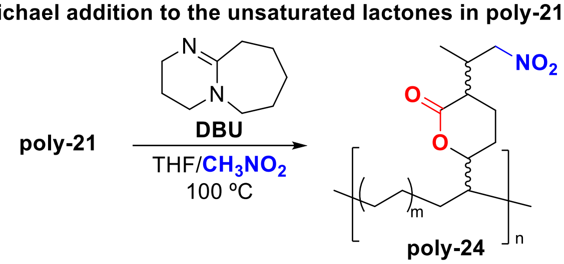
Similar to the post-polymerization modification of **poly-1**, Nozaki *et al.* also delved into the ring-opening aminolysis of bicyclic lactone units in **poly-20**.[87] Using a combination of benzyl amine and ^{n}BuLi, the ring-opening aminolysis of the bicyclic units in **poly-20** proceeded with high conversion after heating at 100 °C for 24 hours (Scheme 16a). A new copolymer containing both amide and hydroxyl groups could be obtained (**poly-23**). Given that tiglate esters can serve as Michael acceptors, experiments were conducted to showcase their ability to facilitate late-stage grafting onto **poly-21**. For instance, nitromethane was observed to react via Michael addition with the unsaturated lactones when 1,5-diazabicyclo[5,4,0]undec-5-ene (DBU) was present, following heating at 100°C for 24 hours (Scheme 16b, **poly-24**). Consequently, the unsaturated lactone units can be regarded as an entry point for accessing variously functionalized polyethylenes. DSC analyses were performed on the obtained copolymers to investigate their thermal properties. **Poly-21** and **poly-23** exhibited a lower melting temperature compared to highly linear polyethylene within a similar molecular weight range. In contrast to the linear polyethylene materials obtained through coordination/insertion copolymerization, **poly-20** and **poly-24** exhibited much broader endothermic peaks at 100-102 °C.

Scheme 16. Post-modification of Poly-20 and Poly-21

(a) Ring-opening aminolysis of the bicyclic lactones in poly-20



(b) Michael addition to the unsaturated lactones in poly-21

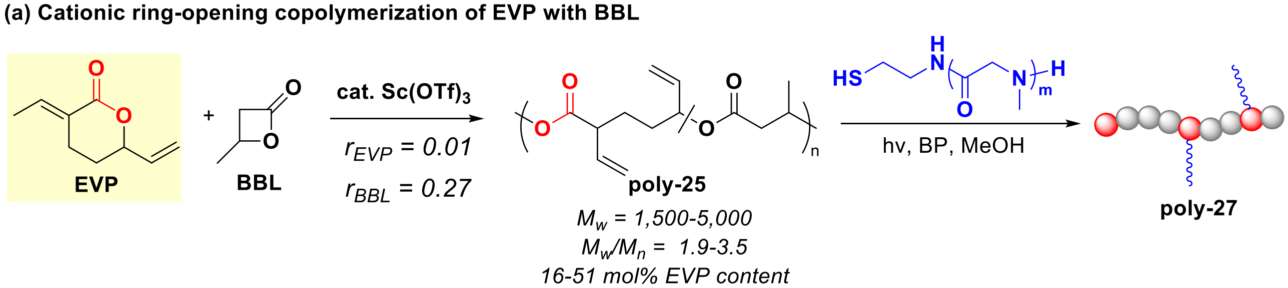


5.3. Ring-Opening Copolymerization with Lactones

Reactive lactones can also be introduced as comonomers to enhance the reactivity of EVP via ring-opening mechanisms. The first successful ring-opening polymerization (ROP) of EVP was reported by Ni *et al*. in its copolymerization with another lactone.[89] β-Butyrolactone (BBL),[90] a four-membered lactone with large ring strain, was selected as the comonomer to copolymerize with EVP in the presence of a strong Lewis acid, scandium triflate ($Sc(OTf)_3$). The cationic ring-opening copolymerization resulted in copolymer with M_w up to 5.0 kg·mol^{-1} (Scheme 16a, **poly-25**). The uncontrollable molecular weight was due to unavoidable proton transfer reactions, which is also common side reaction in the cationic ROP of BBL. The reactivity ratios (r) of EVP and β-BL were determined as 0.01 and 0.27, respectively, which is consistent with the absence of sequential EVP units and the limited EVP content (lower than 51%) in **poly-25**. DFT calculations (Scheme 17a) revealed the challenge of cationic ROP homopolymerization of EVP, where the homopropagation of EVP onto an EVP chain end exhibited the highest energy barrier ($\Delta G^{\neq}$ = 38.0 kcal·mol^{-1}) and ΔG_p (27.7 kcal·mol^{-1}). The energy barriers were decreased to 25.4 kcal·mol^{-1} for EVP onto a BBL chain end and 31.9 kcal·mol^{-1} for BBL onto a EVP chain end, confirming that the introduced BBL aided through reducing the transition state energy for ROP of EVP. Since that the energy barriers of BBL-onto-EVP-end and EVP-onto-BBL-end are both lower than those of the corresponding homopropagations, a random copolymer with alternating tendency was generated (**poly-25**). The remaining allylic ester moiety could be functionalized with a mercapto-terminated polysarcosine (PSar-SH) by thiol-ene click reaction to produce an amphiphilic graft copolymer poly(EVP-*r*-β-BL)-*g*-PSar (**poly-27**), which self-assembles to form micelles in water.

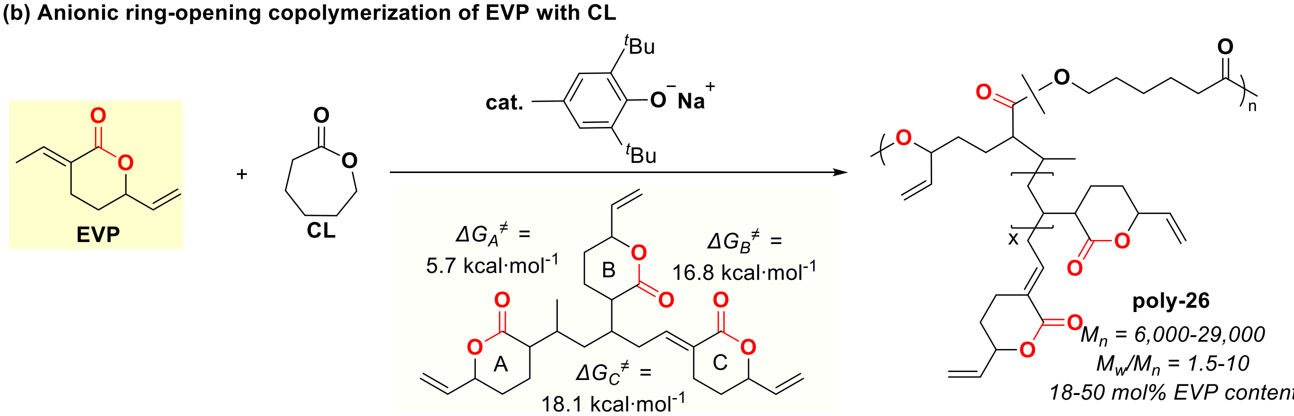
Scheme 17. Accessing CO_2/Butadiene/Lactone Terpolymers via Ring-Opening Copolymerization of EVP with Lactones

(a) Cationic ring-opening copolymerization of EVP with BBL



ROP pathway	BBL-onto-BBL-end	EVP-onto-BBL-end	EVP-onto-EVP-end	BBL-onto-EVP-end
Energy barriers $\Delta G^{\neq}$ (kcal·mol^{-1})	30.4	25.4	38.0	31.9
ΔG_P (kcal·mol^{-1})	11.4	-1.8	27.7	19.3

(b) Anionic ring-opening copolymerization of EVP with CL

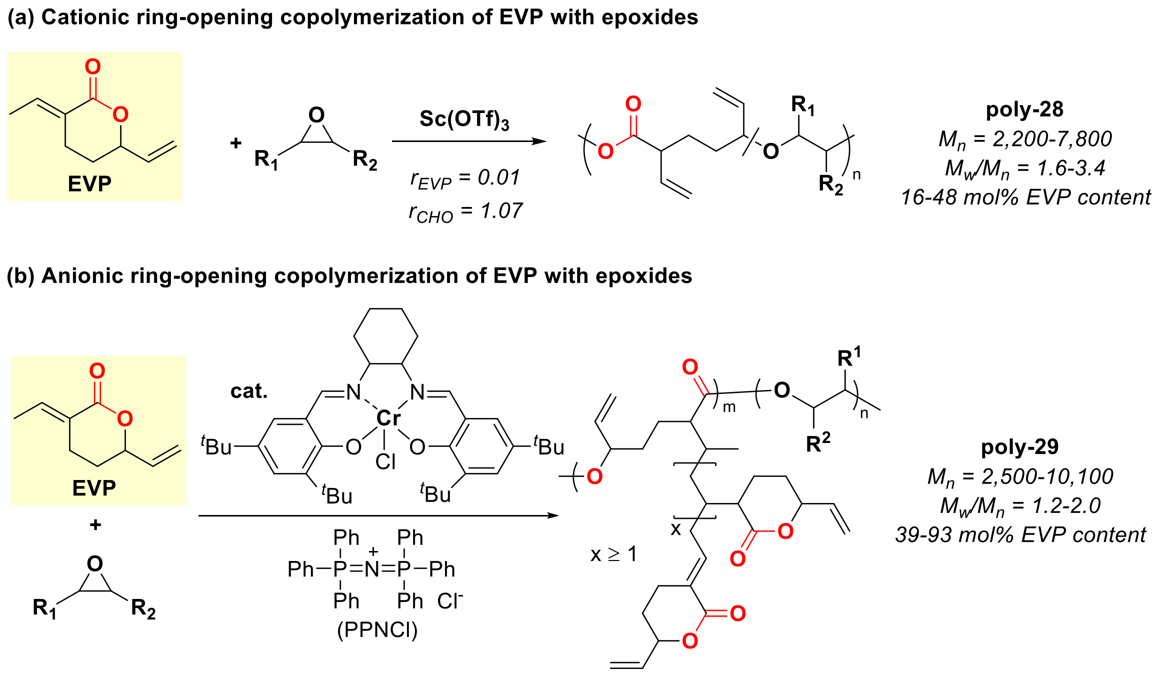


Later on, the same group utilized a novel anionic ring-opening strategy to copolymerize EVP with ε-caprolactone (CL), resulting in polyesters with controllable topologies (Scheme 17b, **poly-26**).[91] As is shown in the DFT calculations of an EVP trimer, the ring-cleavage energy barrier of the conjugated lactone ring **C** was as high as 18.1 kcal·mol^{-1} ($\Delta G_C^{\neq}$), while it was decreased to 5.7 kcal·mol^{-1} ($\Delta G_A^{\neq}$) in the nonconjugated lactone ring **A** (Scheme 17b). Therefore, in the presence of catalytic sodium 2,6-ditert-butyl-4-methylphenolate (NaOAr), EVP could undergo addition-oligomerization to yield nonconjugated lactones along with concurrent copolymerization with CL via anionic ROP. In the presence of NaOAr, **poly-26** with EVP content up to 50 mol% was prepared in 5 h. The M_n reaches 29 kg·mol^{-1} under a 1/4 initial CL/EVP ratio. According to kinetic studies, the copolymerization was divided to three stages. In the first stage, activated EVP oligomers and long PCL chains, which was generated from the rapid but uncontrolled ROP of CL, were obtained simultaneously, and conversions of EVP and CL were 58% and 99% in 1 min, respectively. The copolymer was obtained in the second stage, where transesterification reactions happened frequently between the most active nonconjugated lactone ring in the EVP oligomer and the ester groups in PCL. The copolymer was entirely scrambled over the course of 4 h, and correspondingly the T_m peak disappeared from the DSC curve. A cyclic topology was determined as the major polymer topology by MALDI-TOF MS analysis, which is consistent with the intramolecular transesterification occuring during copolymerization. Finally in the third stage, the unconjugated lactone rings in the middle of EVP oligomer with medium reactivity (similar to **B** from the trimer) participated in intermolecular transesterification reactions, providing branching points for the copolymer. As a result, the topology switched to a branched or further cross-linked one. The copolymer network behaved as a degradable and non-cytotoxic elastomer with available tensile strength (up to 1.7 MPa), almost complete recovery (> 97 % under tensile strain of 200 %) and high elongation at break (up to 733 %).

5.4. Ring Opening Copolymerization with Epoxides

Very recently, Ni *et al.* developed a new terpolymer of CO_2, butadiene with epoxides via the cationic ROCOP of EVP with epoxides (Scheme 18a).[92] Catalyzed by $Sc(OTf)_3$, copolymers of EVP with propylene oxide were obtained with M_n of 2.6 kg·mol^{-1}. Cyclohexene oxide (CHO) was found to be a better comonomer, resulting in higher M_n of the copolymer (**poly-28**) ranging from 2.2 kg·mol^{-1} to 7.8 kg·mol^{-1}. The uncontrollable M_n and broad dispersity ($M_w/M_n \geq 1.9$) were attributed to significant chain transfer reactions in the cationic polymerization at high temperature (40 ^oC). According to ^1H NMR spectroscopic analysis, there were twice as many CHO-EVP dyads as CHO-CHO dyads. This result is consistent with the fact that CHO exhibited twice the conversion of EVP, and the calculated reactivity ratios (r) of 0.01 for EVP and 1.07 for CHO. Backbiting and β-proton elimination were proposed to be the major side reactions that led the uncontrollable copolymerization. The copolymer was further cross-linked via the photoinitiated radical reaction between the preserved C=C double bonds. The obtained network exhibits strong fluorescence, which was not observed for the linear copolymer, with maximum emission wavelengths of 444 nm under 365 nm UV light. Both linear and cross-linked copolymers were proved to be degradable in basic ethanol solution.

Scheme 18. Accessing CO_2/Butadiene/Epoxide Terpolymers via Ring Opening Copolymerization of EVP with Epoxides



Almost at the same time, Tang *et al.* reported the synthesis of terpolymers comprising CO_2, butadiene, and epoxides through an anionic ring-opening copolymerization of EVP (Scheme 18b, **poly-29**).[93] Different from the work of Ni *et al.*, propylene oxide (PO) showed a higher reactivity than CHO. By employing a combination of a chromium salen complex and hexaphenyldiphosphazenium chloride (PPNCl), they successfully generated functional polyester-ethers with varied EVP content, ranging from 39% to 93 mol% (equivalent to 22% to 32 mol% CO_2 incorporation), with molecular weights reaching up to 10.1 kg·mol^{-1} in the copolymerization of EVP with PO. The resulting CO_2/butadiene/PO terpolymers exhibited high thermal stability (5% weight loss temperature, $T_{d,\,5\%}$ > 296 °C) and adjustable glass transition temperatures (-15.8 °C to 13.5 °C). Interestingly, it was discovered that epoxides played a crucial role in both the dimerization of EVP and the subsequent copolymerization. Notably, no conversion of EVP occurred in the absence of PO. Additionally, homopolymerization of PO produced polypropylene oxide (PPO) with a number-average molecular weight (M_n) of 5.9 kg·mol^{-1} and a narrow polydisperity (M_w/M_n = 1.2), underscoring the essential role of PO in the process. Both the EVP dimer and thiophenol-functionalized EVP were found to be active comonomers in ROCOP reactions. Conversely, attempts to copolymerize semi-hydrogenated EVP with CHO under similar conditions failed to yield a polymer, possibly due to backbiting reactions leading to the formation of cyclic esters. These results suggested that the *in-situ* generation of EVP dimer through Cr-catalyzed 1,4-vinylogous Michael addition mitigated the electronic effects of conjugated esters and enhanced steric hindrance to prevent backbiting during chain propagation. The resulting polyester-ethers could be easily degraded into oligomers in a basic methanol solution.

6. CONCLUSION AND OUTLOOK

In this review, we have provided a comprehensive overview of recent developments in the creation of eco-friendly copolymers using carbon dioxide (CO_2) and butadiene with diverse structures via various polymerization methods. Although non-alternating CO_2/olefin copolymerization (olefin:$CO_2 \geqslant 3$) is calculated to be thermodynamically favorable, the activation energy associated with CO_2 incorporation is still higher than that of olefin homopolymerization. A CO_2/butadiene-derived δ-valerolactone (EVP) has been discovered as an effective intermediate to circumvent the thermodynamic and kinetic barriers for synthesizing CO_2/butadiene copolymers. Since that there are two active carbon-carbon double bonds and a lactone unit, EVP and its derivatives serve as versatile intermediates for creating sustainable CO_2-derived copolymers.

Homopolymerization of EVP provides a feasible way to access CO_2/butadiene copolymers with 29 wt% CO_2 content. Radical copolymerization of its allylic ester and tiglate ester functional groups produces CO_2/butadiene copolymers with repeating bicyclic lactone units or a mixture of bicyclic lactone units and unsaturated lactone units. The highly strained bicyclic lactone unite enables reversible post-polymerization modification via ring-opening hydrolysis/aminolysis, while the unsaturated bonds provide an entry point for structure modification via thiol-ene addition. The radical polymerization reactivity could be increased by the installation of methacrylate moiety into the structure of EVP. Though with a low efficiency, a conjugated addition/ring-opening homopolymerization of EVP was developed to afford main-chain degradable polymers. Although direct ROP of EVP to form recyclable polyesters was calculated to be feasible by Hoye et al.,[75] there is still a lack of suitable catalytic systems that favor ROP over self-conjugated addition. Furthermore, current polymerization systems usually suffered from low polymerization efficiency, while lacking of regio- and stereoselectivity control.

To increase the ring-opening polymerization reactivity, hydrogenation of EVP to DEtP and EtVP was done to remove the conjugated carbon-carbon double bond. The ring-opening polymerization of DEtP and EtVP proceeds smoothly to produce recyclable polyesters with low ceiling temperatures. Alternative to the hydrogenation of EVP, reversible Michael addition of EVP with thiols was also used for removing the conjugated carbon-carbon double bond to enhance the reactivity of EVP in ring-opening polymerization. Besides the transformation of EVP to its reactive derivatives, comonomers were also used to enhance the reactivity of EVP in polymerization reactions. These copolymerizations extend the potential to access new CO_2/butadiene-derived polymers. The incorporation of EVP into existing polymer products as well as the discovery of new compositions will continue to be a frontier for the field. Unfortunately, the ROP/ROCOP of EVP derivatives is still not very well behaved. There is still a lot of work to understand the ROP behavior of these interesting lactones: it is not as simple as with lactide or caprolactone. There is so much opportunity in the copolymer space (understanding degradation, better polymer properties, etc) that can be explored once ROP is better understood. Efforts are needed to develop stereoselective or retentive ROP for various EVP-derivative enantiomers, as this can significantly impact overall polymer properties. Especially in ROP, we are away behind to polylactide and there are still more room for catalyst development.

The highly efficient and selective synthesis of δ-valerolactone intermediate from CO_2 and butadiene is the most critical factor for the application of these sustainable copolymers. Although significant progress has been made for the efficient synthesis of EVP, all the reported methods depend on the use of noble palladium catalysts under inert reaction conditions. The creation of resilient and efficient catalysts, especially base-metal catalysts or heterogeneous catalysts, in the presence of potential impurities in raw CO_2, is strongly desirable. Moreover, little is really known about the CO_2/butadiene telomerization reaction. Mechanistic insights on the CO_2/butadiene telomerization reaction are necessary, which may provide guidance for the selective creation of analogues of EVP from other dienes and/or olefins. The creation of new CO_2/diene or olefin-derived lactones may produce opportunities to access divergent CO_2-derived polymers in the future. Furthermore, understanding the structure-property relationships has only just begun. Mechanical properties have been reported in only a few studies and systematic methods for tuning the thermal or rheological properties are lacking. With the dynamic and reversible functionalization that has been demonstrated, we can expect advanced material applications from this sustainable platform to continue advancing in the coming years. Ultimately, the environmental impacts of products and processes along their entire life cycles should be also analyzed carefully for the future utilization of EVP-based materials.

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James Eagan was born in Austin, Texas, United States of America, and graduated from Emory University with a B.S. degree in 2009. He received his Ph.D. in 2014 from Columbia University under the guidance of Prof. Scott Snyder. After completing his Ph.D., he joined the group of Prof. Geoffrey Coates at Cornell University as a postdoctoral fellow from 2014 to 2017. He worked at Aramco Performance Materials and Ascribe Bioscience before moving to the University of Akron. He has been an assistant professor in Polymer Science and Polymer Engineering since 2019. His research interests are focused on polymer synthesis and sustainable materials.

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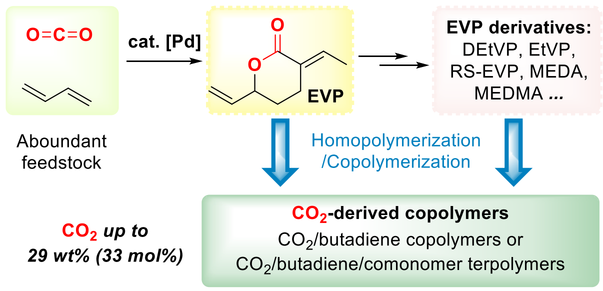

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EVP
EVP derivatives:
DEtVP, EtVP,
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Abundant
feedstock
Homopolymerization
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CO_2 up to
29 wt% (33 mol%)
CO_2-derived copolymers
CO_2/butadiene copolymers or
CO_2/butadiene/comonomer terpolymers