

# Advances in the Synthesis of Copolymers from Carbon Dioxide, Dienes and Olefins

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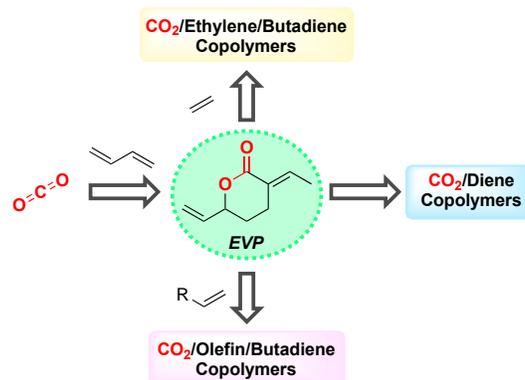
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**CONSPECTUS:** Carbon dioxide (CO<sub>2</sub>) has long been considered as a sustainable comonomer for polymer synthesis due to its abundance, easy availability and low toxicity. Polymer synthesis from CO<sub>2</sub> is highly attractive, and has received continuous interests from synthetic chemists. In this regard, alternating copolymerization of CO<sub>2</sub> and epoxides is one of the most well-established methods to synthesize aliphatic polycarbonates. Moreover, binucleophiles including diols, diamines, amino alcohols and diynes have been reported to copolymerize with CO<sub>2</sub> to give polycarbonates, polyureas, polyurethanes and polyesters, respectively. Nevertheless, little success has been made for incorporating CO<sub>2</sub> into the most widely used polyolefin materials.

Although extensive studies have been focused on the copolymerization of olefins and CO<sub>2</sub>, most of the attempted reactions resulted in olefin homopolymerization owing to the endothermic property and high energy barriers of CO<sub>2</sub> insertion during the chain propagation process. In this Account, we show how this challenge is addressed by taking advantage of a metastable lactone intermediate, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (EVP), which is produced from CO<sub>2</sub> and butadiene via palladium catalysis. Homopolymerization of EVP furnishes CO<sub>2</sub>/butadiene copolymers with up to 29 wt% of CO<sub>2</sub> content. This reaction strategy represents a breakthrough for the long-standing challenge of inherent kinetic and thermodynamically unfavorable CO<sub>2</sub>/olefin copolymerization. A new class of polymeric materials bearing repeating bicyclic lactone and unsaturated lactone units can be obtained. Importantly, one-pot copolymerization of CO<sub>2</sub>/butadiene or terpolymerization of CO<sub>2</sub>/butadiene/diene can be achieved to afford copolymers through a two-step reaction protocol. Interestingly, the bicyclic lactone units in the polymer chain can undergo ring-opening through hydrolysis and aminolysis, while reversible ring-closing of the hydrolyzed or aminolyzed units was also achieved simply by heating.

Over the past few years, more and more studies have utilized EVP as an intermediate to synthesize copolymers from olefins, butadiene and CO<sub>2</sub>. Recently, we successfully incorporated CO<sub>2</sub> into the most widely used polyethylene materials via the direct copolymerization of EVP and ethylene. Taking advantage of the bifunctional reactivity of EVP, we were able to access two types of main-chain-functionalized polyethylenes through palladium-catalyzed coordination/insertion copolymerization and radical copolymerization. Besides polyethylenes, CO<sub>2</sub> was also incorporated into poly(methyl methacrylate), poly(methyl acrylate), polystyrene, polymethylacrylate, polyvinylchloroacetate and polyvinylacetate materials via radical copolymerization of EVP and olefin monomers. The EVP/olefin copolymerization strategy provides a novel avenue for the synthesis of highly versatile copolymers from an olefin, CO<sub>2</sub> and butadiene.



## ■ KEY REFERENCES

- Nakano, R.; Ito, S.; Nozaki, K. Copolymerization of carbon dioxide and butadiene via a lactone intermediate. *Nat. Chem.* **2014**, *6*, 325–331.<sup>1</sup> A two-step reaction strategy was developed to circumvent the thermodynamic and kinetic barriers for copolymerization of carbon dioxide and butadiene.
- Moon, S.; Masada, K.; Nozaki, K. Reversible polymer-chain modification: ring-opening and closing of polylactone. *J. Am. Chem. Soc.* **2019**, *141*, 10938–10942.<sup>2</sup> Reversible polymer modifications involving structural

changes of the polymer chains were accomplished by hydrolysis or aminolysis of the CO<sub>2</sub>/butadiene copolymer.

- Tang, S.; Zhao, Y.; Nozaki, K. Accessing divergent main-chain-functionalized polyethylenes via copolymerization of ethylene with a CO<sub>2</sub>/butadiene-derived lactone. *J. Am. Chem. Soc.* **2021**, *143*, 17953–17957.<sup>3</sup> Two new copolymerization protocols were utilized for the synthesis of a diverse range of polyethylene materials made from ethylene, carbon dioxide and butadiene.

## 1. INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is a stable and renewable C1 carbon source, which is also recognized as the major component of greenhouse gases in the atmosphere. Due to its abundance, easy availability and low toxicity, increasing attention has been paid to efficient transformation of CO<sub>2</sub> into useful chemical products.<sup>4-8</sup> Specifically, using CO<sub>2</sub> as a comonomer in the synthesis of useful polymers is a highly attractive research area.<sup>9-11</sup> However, activation of CO<sub>2</sub> is still challenging since that it is the most oxidized and stable form of carbon. Therefore, polymerization reactions with CO<sub>2</sub> usually rely on the use of a high-energy comonomer to circumvent thermodynamic and kinetic barriers. In this regard, the most explored transformation is the alternating copolymerization of CO<sub>2</sub> and epoxides to produce aliphatic polycarbonates.<sup>12-15</sup> Utilization of the high energy epoxides as comonomers is the key for the successful chain-growth polymerization with CO<sub>2</sub>. Numerous homogeneous and heterogeneous catalytic systems have been developed to achieve this polymerization reaction.<sup>16-17</sup>

Besides epoxides, diols were also utilized to copolymerize with CO<sub>2</sub> for the synthesis of polycarbonates. For example, the direct polycondensation of CO<sub>2</sub>, dihalides and diols was reported to furnish polycarbonates in the presence of K<sub>2</sub>CO<sub>3</sub>.<sup>18</sup> Later, polycarbonates were found to be produced from the direct polycondensation of CO<sub>2</sub> and diols in the presence of an alkylating reagent or a dehydrating reagent.<sup>19-22</sup> Similar reaction strategies were also applied to the copolymerization of CO<sub>2</sub> with amino alcohols,<sup>23</sup> diamines<sup>24</sup> and diynes,<sup>25-27</sup> affording corresponding polyurethanes, polyureas, and polyesters, respectively. Apart from direct copolymerization with CO<sub>2</sub>, great attention has also been paid to synthesize copolymers from CO<sub>2</sub>-derived comonomers via ring-opening copolymerization (ROCOP).<sup>9</sup>

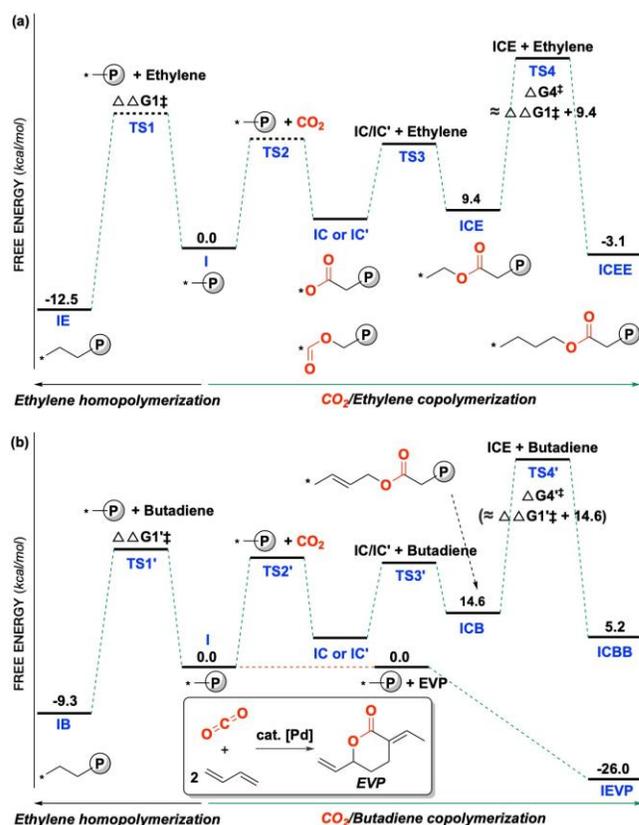
Polyolefins are highly important plastic materials, and produced in the largest volume among all polymer materials.<sup>28-29</sup> Although copolymerization of CO<sub>2</sub> and olefins has caught continuous research interest, little success has been made in producing copolymers.<sup>30-33</sup> In most cases, attempts on copolymerization of CO<sub>2</sub> and olefins resulted in olefin homopolymerization. There are examples for oligomerization of CO<sub>2</sub> with olefins such as dienes,<sup>34</sup> and vinyl ethers<sup>35-37</sup>, whereas they were only able to obtain oligomers with very low molecular weights. In this Account, we show how this challenging copolymer synthesis issue was addressed by taking advantage of a metastable lactone intermediate, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (EVP), which is produced from CO<sub>2</sub> and butadiene via palladium catalysis. Discussions on thermodynamics and kinetics will be presented to understand the obstacles for CO<sub>2</sub>/olefin copolymerization. Copolymers of olefins, butadiene and CO<sub>2</sub> synthesized by different polymerization mechanisms will be summarized. Moreover, efforts for the modification of the obtained copolymers will also be demonstrated.

## 2. THERMODYNAMIC AND KINETIC ANALYSIS FOR COPOLYMERIZATION OF ETHYLENE/BUTADIENE WITH CARBON DIOXIDE

In 2006, Miller and coworkers conducted a comprehensive study on the thermodynamic and kinetics of the copolymerization of CO<sub>2</sub> and ethylene.<sup>30</sup> Density function theory (DFT) calculations revealed that CO<sub>2</sub>/ethylene alternating copolymerization is thermodynamically impossible at reasonable

temperatures. When the copolymerization ratio of ethylene/CO<sub>2</sub> is greater than 2.4, the thermodynamics for the copolymerization will be feasible. A later calculation study by Müller *et al.* also found that reasonable Gibbs free activation barriers were observed after insertion of three equivalents of ethylene prior to a CO<sub>2</sub> insertion.<sup>31</sup> Both studies claimed that the most challenging issue in achieving CO<sub>2</sub>/ethylene copolymerization was to find an effective kinetic favorable pathway for CO<sub>2</sub> insertion.

In order to explain the intrinsic difficulty for CO<sub>2</sub>/olefin copolymerization, we carried out thermodynamic calculations using the CBS-4M//B3LYP/6-31G\* method for CO<sub>2</sub>/olefin copolymerization (Figure 1a).<sup>1</sup> According to the calculation results, incorporation of ethylene and CO<sub>2</sub> resulted in Gibbs free-energy change of -12.5 and 21.9 kcal/mol, respectively (Figure 1a). Therefore, the thermodynamics for alternating copolymerization of CO<sub>2</sub> and ethylene is unfavorable, uphill by 9.4 kcal/mol. Similar to the conclusion by Miller *et al.*,<sup>30</sup> excess ethylene insertion (>63 mol%) is crucial for achieving successful ethylene/CO<sub>2</sub> copolymerization based on thermodynamic analysis. Furthermore, we also compared the energy barriers for ethylene homopolymerization and ethylene/CO<sub>2</sub> copolymerization. Compared to the transition state of ethylene insertion in homopolymerization (TS1), a higher free energy was determined for the transition state of the second ethylene insertion after CO<sub>2</sub> insertion (TS4). These results suggest that even non-alternating ethylene/CO<sub>2</sub> copolymerization is kinetically unfavorable.



**Figure 1.** (a) DFT calculations on CO<sub>2</sub>/ethylene copolymerization. (b) DFT calculations on CO<sub>2</sub>/butadiene copolymerization.

Additionally, copolymerization of butadiene and CO<sub>2</sub> was calculated by using the same method (CBS-4M//B3LYP/6-31G\*) as that of ethylene/CO<sub>2</sub> copolymerization (Figure 1b).<sup>1</sup> The Gibbs free-energy for the incorporation of butadiene through 1,4-addition was determined as -9.3 kcal/mol. In

comparison, the Gibbs free-energy for CO<sub>2</sub> propagation was 23.9 kcal/mol. Similar to the previously discussed ethylene/CO<sub>2</sub> copolymerization, excess butadiene insertion (72 mol%) is crucial for butadiene/CO<sub>2</sub> copolymerization via 1,4-addition. Higher free energy was also determined for CO<sub>2</sub>/butadiene via 1,4-addition (**TS4'**) than that of butadiene homopolymerization (**TS1'**). The thermodynamic and kinetic problems could be circumvented by the use of 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (EVP). EVP, produced from palladium-catalyzed coupling between CO<sub>2</sub> and butadiene, has attracted great attention as an intermediate for CO<sub>2</sub> utilization.<sup>38</sup> Continuous efforts have been taken to achieve a high yield and selectivity for the synthesis of EVP from CO<sub>2</sub> and butadiene.<sup>39-44</sup> The developed approaches for EVP synthesis rely on the use of noble palladium catalysts under inert reaction conditions. Development of robust catalysts such as nickel in the presence of possible impurities in row CO<sub>2</sub> is highly desirable. It is worthy of noting that EVP contains both an allylic ester unit and a tiglate ester unit. A formal copolymerization of CO<sub>2</sub> and butadiene may be achieved if we can take advantage of these two units to develop a method for EVP homopolymerization. According to our calculation results, almost no Gibbs free-energy change was determined for EVP formation via telomerization of butadiene with CO<sub>2</sub>, while EVP incorporation via cyclization to form bicyclic lactone intermediate was found to be exothermic of -26.0 kcal/mol (Figure 1b). These results indicate that a kinetically favored pathway for formal CO<sub>2</sub>/butadiene copolymerization can be accomplished via the homopolymerization of EVP.

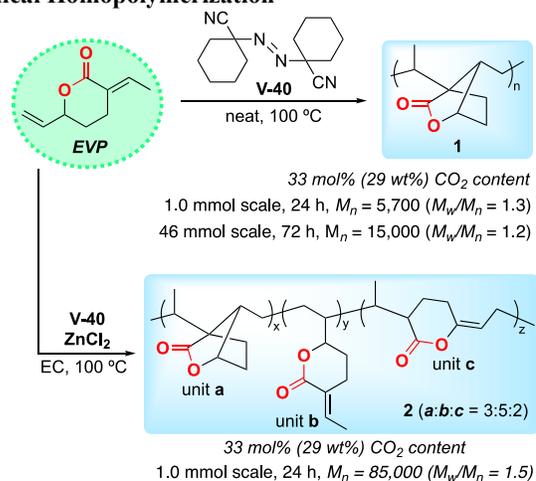
### 3. COPOLYMERS MADE FROM DIENES AND CARBON DIOXIDE

Based on the thermodynamic and kinetic analyses in the previous section, a formal copolymerization of CO<sub>2</sub> and butadiene is likely to be developed via the homopolymerization of EVP. Dinjus and co-workers have investigated the reaction conditions for EVP homopolymerization,<sup>45</sup> but unfortunately, no polymerization was observed under the conditions they examined. In 2014, we reported the radical polymerization in the presence of radical initiators (Scheme 1).<sup>1</sup> A polymeric material (Polymer **1**) was obtained in 22% yield simply by heating a mixture of EVP and 1,1'-azobis(cyclohexanecarbonitrile) (V-40) at 100 °C under neat conditions for 24 h. The molecular weight of polymer **1** is determined as  $M_n = 5,700$  ( $M_w/M_n = 1.3$ ) according to size exclusion chromatography (SEC) analysis. The glass-transition temperature of it was determined to be 178 °C. Therefore, polymer **1** may serve as a new engineering plastic made from derived from renewable feedstocks. When the polymerization was carried out with a longer reaction time of 72 h on a larger scale, the molecular weight of polymer **1** could be increased to  $M_n = 15,000$  ( $M_w/M_n = 1.2$ ).<sup>2</sup> Based on <sup>1</sup>H and <sup>13</sup>C NMR analyses, only a repeating bicyclic lactone unit was determined in the structure of polymer **1**, which suggested that EVP homopolymerization proceeded through alternating copolymerization of its allylic ester and tiglate ester moieties (Scheme 1).

Tiglate esters are believed to be relatively inert in radical polymerization due to the steric hindrance between the radical chain-end and the next monomer. During radical homopolymerization of EVP, the issue of steric hindrance for the tiglate ester unit incorporation was successfully dismissed by alternating incorporation of the allylic ester unit. Whereas less than 28 mol%

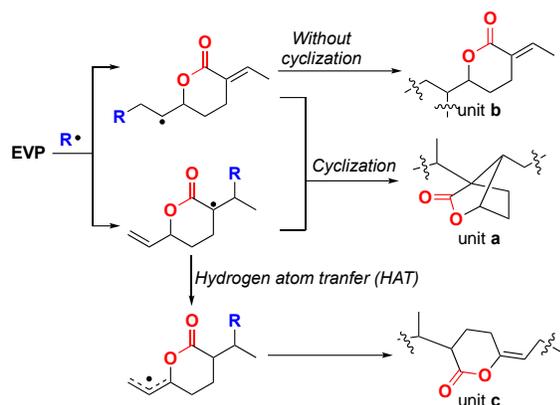
CO<sub>2</sub> can be incorporated in direct CO<sub>2</sub>/butadiene copolymerization via 1,4-addition according to our calculation results (Figure 1b), our reaction strategy furnished CO<sub>2</sub>/butadiene copolymers with 33 mol% of CO<sub>2</sub> incorporation. Two possible radical addition pathways for the formation of the bicyclic lactone unit (unit **a**) were proposed in Scheme 2. Both radical addition to the allylic ester moiety and the tiglate ester moiety may lead to the formation of unit **a** through intramolecular radical cyclization.

#### Scheme 1. Synthesis of CO<sub>2</sub>/Butadiene Copolymer via EVP Radical Homopolymerization



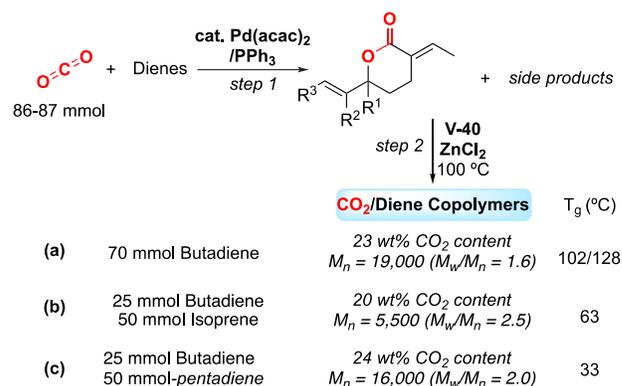
Lewis acids have been reported to interact with  $\alpha,\beta$ -unsaturated ester moiety during radical polymerization.<sup>46</sup> Utilizing a combination of V-40 and ZnCl<sub>2</sub> in ethyl carbonate (EC) solvent, the molecular weight of the EVP homopolymer was increased to  $M_n = 85,000$  ( $M_w/M_n = 1.5$ ). Compared to polymer **1**, higher glass transition temperatures were observed for polymer **2**. Besides the repeating bicyclic lactone units, two different unsaturated lactone units **b** and **c** were identified in the obtained new polymer **2**. Based on <sup>1</sup>H NMR analysis, the ratio of the three different units in polymer **2** was determined as **a:b:c** = 3:5:2 (Scheme 1). Unit **b** is believed to be generated from radical chain propagation of the allylic ester moiety of EVP without cyclization, while unit **c** is likely formed from hydrogen atom transfer of  $\alpha$ -carbonyl radical intermediate during radical chain propagation (Scheme 2). ZnCl<sub>2</sub> has been reported to accelerate the polymerization of allylic acetate since it may suppress degradative chain transfer of allylic acetate. In addition, ZnCl<sub>2</sub> was also believed to enhance the electrophilicity of  $\alpha$ -carbonyl radicals through coordination, which accelerated the intramolecular hydrogen abstraction to form allyl radicals. Therefore, units **b** and **c** were observed aside from unit **a** during the homopolymerization of EVP in the presence ZnCl<sub>2</sub>.<sup>46</sup> Three years later, Lin and coworkers developed an alternative method for radical homopolymerization of EVP by using air as the radical initiator at 180 °C.<sup>47</sup> Although no additive or solvent was added, they detected the formation of different structure units in addition to **a-c** in the polymer chain.

#### Scheme 2. Proposed Mechanism for the Formation Units of **a**, **b** and **c** in Polymer **2**.



The copolymerization of butadiene and CO<sub>2</sub> can be achieved through a one-pot/two-step approach (Scheme 3).<sup>1</sup> In the first step, palladium-catalyzed telomerization of butadiene and CO<sub>2</sub> was carried out in ethylene carbonate. After removing all the volatiles, followed by addition of ZnCl<sub>2</sub> and V-40, the reaction mixture was heated at 100 °C for 24 h. A good isolated polymer yield of 47% based on the initial butadiene was obtained in this formal CO<sub>2</sub>/butadiene copolymerization. Elementary analysis of the obtained homopolymer demonstrated 23 wt% of CO<sub>2</sub> incorporation (Scheme 3a). Interestingly, attempts for terpolymerization of carbon dioxide, butadiene and another 1,3-diene were also successful through this one-pot/two-step protocol. Elemental analysis revealed that 20 wt% CO<sub>2</sub> was incorporated in the case of CO<sub>2</sub>/butadiene/isoprene terpolymerization while 24 wt% of CO<sub>2</sub> was incorporated that of CO<sub>2</sub>/butadiene/1,3-pentadiene terpolymerization (Scheme 3b and 3c). Differential scanning calorimetry (DSC) analysis of these terpolymers revealed much lower glass transition temperatures than CO<sub>2</sub>/butadiene copolymers, which is likely caused by the introduction of methyl substituents into the lactone units.

**Scheme 3. One-pot/Two-step Co/Terpolymerization of CO<sub>2</sub> and Dienes.**

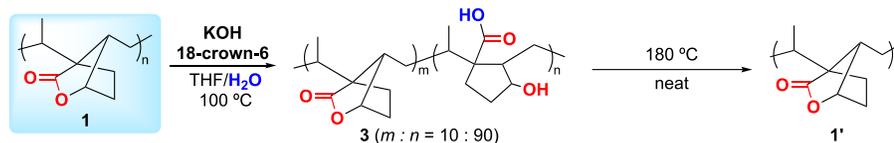


In order to demonstrate the diversity of our copolymerization protocol, efforts were taken to modify the obtained CO<sub>2</sub>/butadiene copolymers.<sup>2</sup> Since that polymer **1** consists of only strained bicyclic lactone units, hydrolysis and aminolysis of the ester group were both explored. Using 10 eq. of KOH and 1.0 eq. of 18-crown-6 in a mixed THF/H<sub>2</sub>O solution, 90% of the bicyclic lactone units in polymer **1** underwent hydrolysis at 100 °C after 72 h (Scheme 4a). A new polymer (Polymer **3**) bearing repeating *trans*-cyclopentan-1,2-diyl units was obtained after hydrolysis, while the carboxyl and hydroxy groups are located *cis* to each other on the cyclopentane ring. Notably, the reversible dehydrative lactonization of polymer **3** proceeded simply by heating polymer **3** at 180 °C under neat conditions (Scheme 4a). It is worthy of noting that the molecular weight and polydispersity did not change during the reversible ring-opening hydrolysis/ring-closing dehydration process. Because of the dehydrative lactonization, gravimetric loss was observed twice at around 180 °C and 350 °C during thermogravimetric (TG) analysis of polymer **3**. Nevertheless, similar gravimetric loss and glass transition behaviors to polymer **1** were determined by TG and DSC analyses.

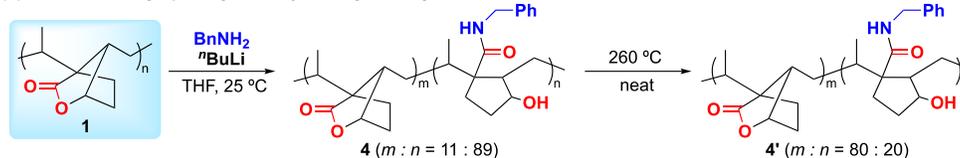
Aminolysis of polymer **1** was also successful at room temperature with a mixture of benzylamine and <sup>n</sup>BuLi, affording polymer **4** with 89% conversion of the bicyclic lactone units (Scheme 4b). Compared with ring-closing of the hydrolyzed polymer **3**, a higher temperature (260 °C) was required to achieve partial ring-closing deamination of bicyclic lactone units for the aminolyzed polymer **4** (Scheme 4b). The obtained polymer **4'** contains both lactone and amide/alcohol units in 8:2 ratio. TG measurements of polymer **4** also exhibit twice gravimetric losses at around 260 °C and 350 °C. The weight loss at around 260 °C was caused by ring-closing deamination. Similar to that of reversible hydrolysis, there is no obvious change in molecular weight and polydispersity during the partially ring-opening aminolysis/ring-closing deamination process.

**Scheme 4. Reversible Modification of Polymer 1 via Ring-Opening and Ring Closing of the Bicyclic Lactone Units**

(a) Reversible ring-opening hydrolysis/ring-closing dehydration



(b) Reversible ring-opening aminolysis/ring-closing deamination



Ring-opening polymerization (ROP) of lactones is a well-known approach for the synthesis of polyesters.<sup>48</sup> In addition to an olefin monomer, EVP can also be considered as a lactone monomer. Therefore, butadiene/CO<sub>2</sub> copolymers may also be synthesized via ROP of EVP. Intensive efforts have been devoted to developing suitable conditions for ROP of EVP.<sup>20, 49</sup> Only recently, Eagan and coworkers reported a homopolymerization of EVP via an organocatalyzed combined vinylogous 1,4-conjugate addition/ROP process.<sup>50</sup> Unfortunately, the polymerization proceeded through a noncontrolled chain propagation mechanism, affording amorphous polymer materials with low molecular weights ( $M_n < 3,800$ ) and low glass transition temperatures (25–52 °C). Almost at the same time, Tonks *et al.* reported an organocatalyzed ROP of the semi-hydrogenated or fully hydrogenated form of EVP.<sup>51</sup> Utilizing 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as the catalyst, ROP of semi-hydrogenated EVP furnished a degradable polyester with a high  $M_n$  of 13,600. The polymer has a low ceiling temperature of 138 °C and a low glass transition temperature of -38.8 °C, which may be utilized as a soft block in thermoplastic elastomers. Later on, Lin *et al.* also achieved the ROP of hydrogenated form of EVP by utilizing phosphazene bases as catalysts.<sup>52</sup> When <sup>t</sup>Bu-P4 was employed as the only catalyst, they were able to synthesize degradable polyesters with ultrahigh molecular weight (up to 613,800). The obtained polyesters demonstrated high thermal stability ( $T_d$ , 5% > 325 °C) while the glass transition temperatures were detected at around -30 °C. Importantly, they were able to process the obtained polyesters into transparent and flexible membranes with pressure-sensitive adhesive (PSA) properties comparable with their commercial counterparts.

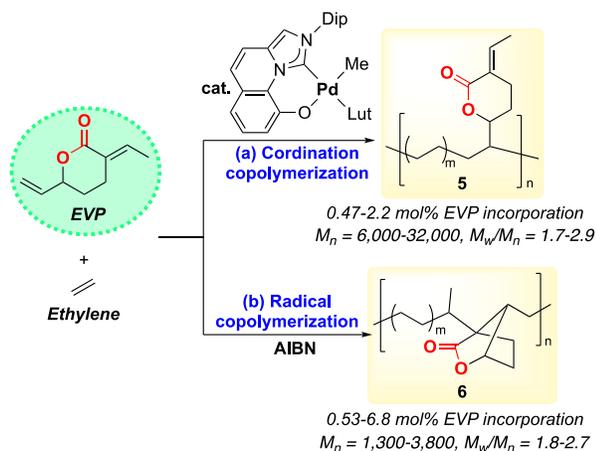
#### 4. COPOLYMERS MADE FROM AN OLEFIN, BUTADIENE AND CARBON DIOXIDE

Since that EVP contains carbon-carbon double bonds, it may also serve as a comonomer in copolymerization reactions. Copolymerization of an olefin and EVP may provide an avenue for the formal terpolymerization of an olefin, butadiene and CO<sub>2</sub>. In 2017, Ni *et al.* reported the transformation of EVP via methanolysis and following acylation with methacryloyl, affording a trivinyl monomer, methyl-2-ethylidene-5-hydroxyhept-6-enoate methacrylate (MEDMA).<sup>53</sup> Using a combination of azobisisobutyronitrile (AIBN) and 2-cyanoprop-2-yl-dithiobenzoate (CPDB), they were able to achieve chemoselective radical homopolymerization of MEDMA. Whereas only the introduced methacrylate moiety participated in radical

homopolymerization of MEDMA to afford linear polymers, the tiglate ester moiety still reacted at the late period of polymerization to give hyperbranched polymers. In a later report by the same group, they also developed a palladium-catalyzed copolymerization of MEDMA with ethylene.<sup>54</sup> Among the three olefin moieties of MEDMA, the reactivity of MEDMA in polymerization reactions mainly attributes to the introduced methacrylate moiety. The participation of the tiglate ester and allylic ester moieties led to complicated microstructures in the synthesized copolymers.

EVP can be considered either as an allyl carboxylate comonomer with a bulky substituent or as a tiglate ester comonomer. Owing to the low reactivity of its two olefin moieties, little attention has been paid to the direct copolymerization with EVP. In 2021, we reported the incorporation of CO<sub>2</sub> into the most widely used polyethylene materials via the direct copolymerization of ethylene and EVP.<sup>3</sup> The microstructure of the incorporated functional group was controlled by the utilized polymerization strategies. When a carbene-phenolate palladium complex was applied as the catalyst, EVP was able to copolymerize with ethylene via a coordination/insertion mechanism with 0.47–2.2 mol% incorporation (Scheme 5a). According to <sup>1</sup>H NMR analysis, only the allylic ester moiety participated in the copolymerization with ethylene, furnishing polyethylenes bearing unsaturated lactone units (Polymer 5). Different from that of coordination/insertion copolymerization, both the tiglate ester moiety and the allylic ester moiety participated in the AIBN-promoted radical copolymerization of ethylene and EVP, furnishing polyethylenes bearing bicyclic lactones (0.53–6.8 mol% content) in the main chain (Scheme 5b, polymer 6). Whereas coordination/insertion copolymerization afforded highly linear polyethylene copolymers with high molecular weights, radical copolymerization gave more branched polyethylene copolymers with low molecular weights.

#### Scheme 5. Synthesis of CO<sub>2</sub>/Ethylene/Butadiene Copolymers via EVP/Ethylene Copolymerization

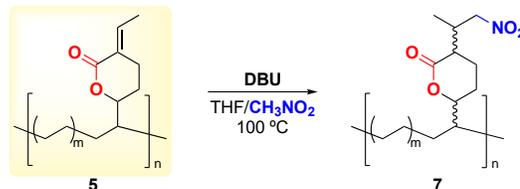


The incorporated functional units from EVP can be used for further modification of the obtained copolymers. Since that tiglate esters may serve as Michael acceptors, experiments were carried out to show their ability in achieving late-stage grafting of copolymers. For example, nitromethane was found to be reactive in the Michael addition to the unsaturated lactone units in the presence of DBU after heating at 100 °C for 24 h (Scheme 6a, polymer 7). Therefore, the unsaturated lactone units can be seen as an entypoint for accessing diversely functionalized polyethylenes. We have also explored the ring-opening hydrolysis and aminolysis of bicyclic lactone units in polymer 6. Whereas the ring-opening hydrolysis of polyethylene copolymer 6 was unsuccessful due to its poor solubility in the presence of water, the ring-opening aminolysis of the bicyclic units in polyethylene copolymer 6 proceeded with high conversion (Scheme

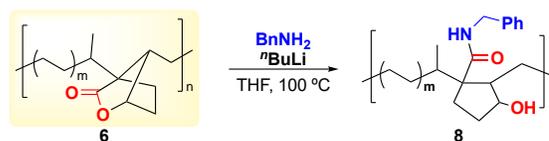
6b). After workup, a new copolymer bearing both amide and hydroxyl groups in the main chain of polyethylene could be obtained (Polymer 8). Overall, the two copolymerization strategies offer opportunities for the synthesis of divergent main-chain functionalized polyethylene materials made from ethylene, butadiene and CO<sub>2</sub>.

### Scheme 6. Modification of the CO<sub>2</sub>/Ethylene/Butadiene Copolymers

#### (a) Michael addition to polymer 5

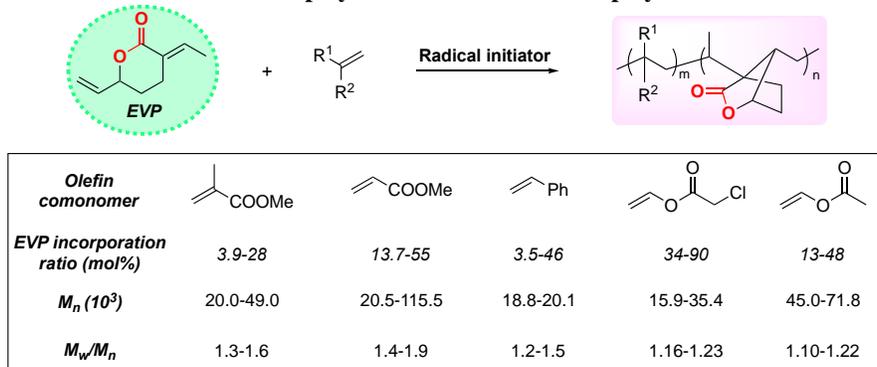


#### (b) Ring-opening aminolysis of polymer 6



DSC analyses of the obtained copolymers was conducted to explore their thermal properties. The melting temperature of polymer 5 was lower than that of the highly linear polyethylene in the similar molecular weight range. Polymer 7 demonstrated a similar melting property to polymer 5. Different from the linear polyethylene materials obtained through coordination/insertion copolymerization, much broader endo endothermic peaks were detected for polymers 6 and 8 at 100-102 °C.<sup>3</sup>

### Scheme 7. Synthesis of CO<sub>2</sub>/Olefin/Butadiene Copolymers via EVP/Olefin Copolymerization



Besides ethylene, a series of commercially available functional monomers were tested in the copolymerization with EVP. Employing similar reaction conditions for radical homopolymerization of EVP, copolymerizations of EVP with methyl methacrylate (MMA), methyl acrylate (MA), styrene (Sty), vinyl chloroacetate (VAcCl) and vinyl acetate (VAc) were achieved with 3.5-90 mol% EVP incorporation (Scheme 7).<sup>55</sup> The choice of radical initiators and mole fraction of the comonomers were both important for EVP incorporation. In these radical copolymerization studies, EVP incorporation resulted in exclusive formation of bicyclic lactone units in the copolymers. Owing to the rigid nature of the bicyclic lactone units, incorporation of rigid bicyclic lactone units into poly(methyl acrylate), polystyrene, polymethylacrylate, polyvinylchloroacetate and

polyvinylacetate led to increased glass transition temperatures comparing to that of the traditional homopolymers.

### CONCLUSION AND PERSPECTIVE

In this Account, we have provided an overview of our studies on the synthesis of copolymers from CO<sub>2</sub>, dienes and olefins referring the related publications. Because of its endothermic nature and the high energy barriers of CO<sub>2</sub> insertion during the chain propagation process, most of the trials on olefins/CO<sub>2</sub> copolymerization result in olefin homopolymerization. According to the calculation results by us and the others, the key for successful CO<sub>2</sub>/olefin copolymerization is to find an effective kinetically favored pathway for CO<sub>2</sub> insertion. Herein, the formal

CO<sub>2</sub>/butadiene copolymerization has been developed via the homopolymerization of a metastable lactone intermediate, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (EVP), which is produced from CO<sub>2</sub> and butadiene via palladium catalysis. CO<sub>2</sub>/butadiene copolymers with up to 29 wt% of CO<sub>2</sub> were obtained via radical homopolymerization of EVP, as a new class of polymeric materials bearing repeating bicyclic lactone and/or unsaturated lactone units. Moreover, the unique bicyclic lactone units were able to undergo reversible ring-opening hydrolysis or aminolysis. Along with our study, great success from the other groups has been made for the synthesis of copolymer from olefins and CO<sub>2</sub> utilizing EVP as an intermediate.

EVP has also been shown to be a reactive bifunctional polar comonomer in olefin copolymerization. EVP/olefin copolymerization provides a feasible pathway to synthesize highly versatile copolymers made from an olefin, CO<sub>2</sub> and butadiene. We were able to access divergent main-chain-functionalized polyethylene materials via palladium-catalyzed coordination/insertion copolymerization or radical copolymerization of EVP and ethylene. Besides ethylene, common olefin monomers including MMA, MA, Sty, VAcCl and VAc were all able to copolymerize with EVP via radical processes.

Although there is still a lack of methods for direct olefin/CO<sub>2</sub> copolymerization, continuous efforts have been devoted to the synthesis of copolymers from olefins and CO<sub>2</sub>.<sup>11</sup> In this regard, copolymerization of CO<sub>2</sub>-based comonomers with olefins has received increasing attention.<sup>56-57</sup> Due to the importance of polyolefins, we believe that olefin/CO<sub>2</sub> copolymerization will remain to be a hot research topic. The key motivation for achieving this transformation is to produce sustainable polyesters that exhibit similar mechanical properties of polyolefins, but are degradable because of the ester functionality located in the polymer backbone. Although the thermodynamics for the non-alternating copolymerization are feasible for sufficiently high olefin/CO<sub>2</sub> ratios, existing competing routes especially olefin homopolymerization prevent successful CO<sub>2</sub> insertion into the main chain of polyolefins. Successful olefin/CO<sub>2</sub> copolymerization may rely on the utilization of new reaction mechanisms for CO<sub>2</sub> activation. The design of new catalysts and novel polymerization strategies may provide solutions for direct CO<sub>2</sub>/olefin copolymerization in the future.

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### Notes

The authors declare no competing financial interest.

### Biographies

**Shan Tang** was born in Xiaogan, Hubei, China. He received his B.S. degree in 2012 and Ph.D. degree in 2017 at Wuhan University under the supervision of Prof. Aiwen Lei. After completing his Ph.D., he joined the group of Prof. David Milstein at the Weizmann Institute of Science in Israel as a postdoctoral fellow from 2017 to

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**Kyoko Nozaki** was born in Osaka, Japan, and graduated from Kyoto University with a B.Sc. degree in 1986. She received her Ph.D. in 1991 from the same university under the guidance of Prof. Kiitiro Utimoto. During her Ph.D. studies, she joined Prof. Clayton H. Heathcock's group at the University of California, Berkeley, as an exchange student for 1 year in 1988. Since 1991, she has been a faculty member at Kyoto University, moved to the University of Tokyo in 2002, and has been a Professor at the University of Tokyo since 2003. Her research interests are focused on the development of homogeneous and heterogeneous catalysts for polymer synthesis and organic synthesis.

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