Accessing Divergent Main-Chain-Functionalized Polyethylenes via Copolymerization of Ethylene with a CO_2/Butadiene-derived Lactone

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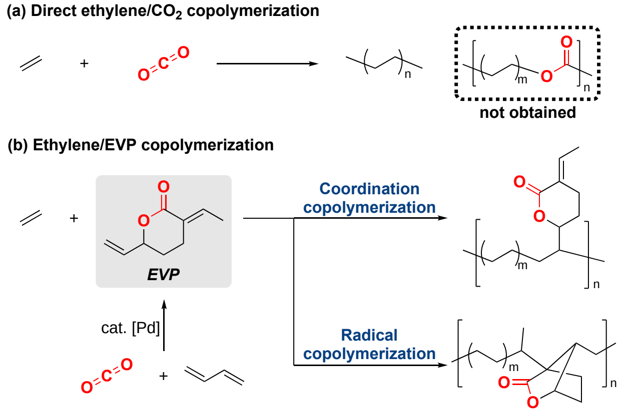
ABSTRACT: Carbon dioxide (CO_2) has been used as a sustainable comonomer in the synthesis of different functional polymers including polycarbonates, polyurea and polyurethane. Until today, despite of the great interest, little success has been made for incorporating CO_2 into the most widely used polyethylene materials. Herein, we report the incorporation of CO_2 to polyethylenes through the copolymerization of ethylene with a CO_2/butadiene-derived lactone, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (EVP). Two-types of main-chain-functionalized polyethylenes can be synthesized through different copolymerization strategies. Palladium-catalyzed coordination/insertion copolymerization furnished polyethylenes bearing unsaturated lactones, while radical copolymerization afforded polyethylenes bearing bicyclic lactones. Modification of the polyethylene chains was successfully accomplished through Michael addition or aminolysis. This highly versatile copolymerization protocol provides access to a diverse range of polyethylene materials made from ethylene, CO_2 and 1,3-butadiene.

Due to its abundance, easy availability and low toxicity, carbon dioxide (CO_2) has been considered as a green and useful one-carbon (C1) building block for chemical synthesis.[1-4] Copolymerization with CO_2 is one of the most widely studied transformations, and has attracted continuous interest from synthetic chemists. The synthesis of polycarbonates, polyurea, and polyurethane has been well established via alternating copolymerization of CO_2 with epoxides, diols, diamine, or amino alcohols.[5-8] Polyethylenes are known to be highly important plastic materials which are produced in the largest volume among all plastic materials.[9-10] Aiming at accessing sustainable polyethylene copolymers, copolymerization of ethylene with CO_2 has long been considered to be an important but synthetically challenging transformation.[11] Although significant efforts have been devoted to develop methods for incorporating CO_2 into polyethylene chains, most of the attempts resulted in ethylene homopolymerization due to the endothermic property of CO_2 insertion (Scheme 1a).[12-15]

In 2014, our group reported the radical copolymerization of CO_2 with 1,3-butadiene via a lactone intermediate, 3-ethyli-dene-6-vinyltetrahydro-2H-pyran-2-one (EVP).[16] This polymerization strategy successfully furnished CO_2/butadiene copolymers with 29 wt% of CO_2 incorporation. Later on, a similar homopolymerization of EVP was reported by using air as the radical initiator instead of 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40).[17] In another study, Ni and coworkers converted EVP to a trivinyl monomer (MEDMA) by a two-step procedure including methanolysis and following acylation with methacryloyl chloride.[18] MEDMA was found to be reactive both in radical homopolymerization and palladium catalyzed copolymerization with ethylene.[18-19] Although there are three olefin moieties in MEDMA, the key reactivity in polymerization originates from the introduced methacrylate moiety. The allylic ester moiety originating from EVP also participated in polymerization but led to the formation of complicated polymer structures.[18-19] Recently, Meier, Detrembleur and coworkers reported the synthesis of functionalized polyethylene copolymers via copolymerization of ethylene with a CO_2-based α-alkylidene carbonate comonomer.[20] We wondered if EVP could be directly employed as a polar monomer for incorporating CO_2 into polyethylene chains through copolymerization. Different from common polar comonomers, EVP contains both an allylic ester unit and a tiglate ester unit. Therefore, it can be considered either as an allyl comonomer with a bulky substituent or a tiglate ester comonomer. Taking advantage of the bifunctional reactivity of EVP, it would be possible to tune the microstructure of the obtained polyethylene copolymers.

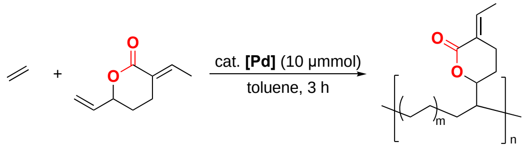
Scheme 1. Strategies for incorporating CO_2 into polyethylene chains



Herein, we report a novel strategy for incorporation of CO_2 into polyethylene main-chains via the copolymerization of ethylene with EVP (Scheme 1b). EVP can be easily synthesized from CO_2 and 1,3-butadiene by utilizing a catalytic combination of $Pd(dba)_2$ and tris(o-methoxyphenyl)phosphine.[21] Copolymerization was achieved through a Pd-catalyzed coordination/insertion copolymerization as well as an azobisisobutyronitrile (AIBN)-promoted radical copolymerization. Two different types of copolymers were synthesized with high regioselectivities. Whereas coordination/insertion copolymerization afforded polyethylenes bearing unsaturated lactones, radical copolymerization gave polyethylenes bearing bicyclic lactones. Post-polymerization grafting of the obtained polymers is also presented to further demonstrate the diversity of polymers accessible by our method.

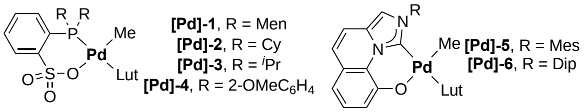
First, the coordination/insertion copolymerization of ethylene and EVP was investigated with different palladium complexes. The reactions were first conducted at 80 °C and 3.0 MPa of ethylene using 10 μmol of palladium catalyst in toluene (10 mL). The obtained copolymers were purified by precipitation with methanol. Palladium complexes of both phosphine-sulfonates (**[Pd]-1–4**)[22-23] and carbene-phenolates (**[Pd]-5–6**)[21] furnished EVP-incorporated polyethylenes (Table 1, entries 1-6). Much higher incorporation ratios of EVP but lower catalytic reactivity was observed when carbene-phenolic palladium complexes were used as catalysts (Table 1, entries 5 and 6). Complex **[Pd]-6** gave a relatively high EVP incorporation ratio (2.0 mol%) and moderate copolymer molecular weight (M_n = 6,000) (Table 1, entry 6, polymer **1**). The ^1H NMR spectrum of polymer **1** showed characteristic resonances of the α,β-unsaturated lactone at 7.08 (m, **C**), 4.21 (m, **E**), and 1.82 (d, **D**) (Figure 1a), which suggested that only the allylic ester moiety of EVP participated in the copolymerization reaction and the tiglate ester moiety was left untouched. Moreover, absorption peaks at 1717 and 1640 cm^{-1}, corresponding to the C=O and C=C stretching of the tiglate ester group, were observed in the IR spectrum of polymer **1** (Figure 2a). In the $^{13}C\{^1H\}$ NMR spectrum (See Supporting Information, Figure S16), the resonance of the carbonyl carbon was observed at 166.5 ppm while the sp^2-carbons of the carbon–carbon double bond were found at 139.4 and 127.2 ppm. The sp^3-carbon adjacent to oxygen was also observed at 81.7 ppm.

Table 1. Palladium-Catalyzed Coordination/Insertion Copolymerization of Ethylene with EVP[a]



entry	[Pd]	EVP (mL)	temp. (ºC)	yield (g)[b]	actvity (g•mmol^{-1}•h^{-1})	M_n (Kg/mol)[c]	M_w/M_n[c]	i. r. (%)[d]
1	**[Pd]-1**	1.0	80	0.509	17	25.3	2.9	0.04
2	**[Pd]-2**	1.0	80	1.479	48	8.7	2.5	0.12
3	**[Pd]-3**	1.0	80	0.549	18	6.5	2.7	0.14
4	**[Pd]-4**	1.0	80	0.382	13	6.4	3.1	0.32
5	**[Pd]-5**	1.0	80	0.017	0.6	0.7	4.7	3.7
6	**[Pd]-6**	1.0	80	0.073	2.4	6.0	2.9	2.0
7	**[Pd]-6**	1.0	60	0.061	2.0	6.1	2.2	2.2
8	**[Pd]-6**	1.0	100	0.061	2.0	6.5	2.2	2.2
9	**[Pd]-6**	0.5	80	0.150	5.0	15	1.9	1.1
10	**[Pd]-6**	0.2	80	0.284	9.5	32	1.7	0.47

[a] A mixture of **[Pd]** (10 μmol) and EVP in toluene (10 mL) was stirred under 3.0 MPa ethylene for 3 h. [b] Yields of isolated polymers after precipitation with methanol. [c] Molecular weights determined by size-exclusion chromatography (SEC) corrected by universal calibration using narrow polystyrene standards. [d] EVP incorporation ratio (i. r.) in mol% was determined by ^1H NMR analysis.



Next, the effect of temperature on the copolymerization was then explored. Slightly decreased catalytic activity were observed when the copolymerization was performed at 60 °C or 100 °C (Table 1, entries 7 and 8). The result in entry 8 is comparable to the copolymerization of allyl acetate and ethylene under similar conditions (the same conditions except the ethylene pressure was 4.0 MPa: activity: 4.5 g · $mmol^{-1}$ · h^{-1}; Mn 7,400; Mw/Mn 2.5; i.r. 1.4 mol%).[23] In order to increase the catalytic activity and molecular weight of the copolymers, efforts were taken to carry out the copolymerization by decreasing the amount of EVP. As expected, higher catalytic activities and copolymer molecular weights were observed when the copolymerization was performed with less EVP (Table 1, entries 9 and 10).

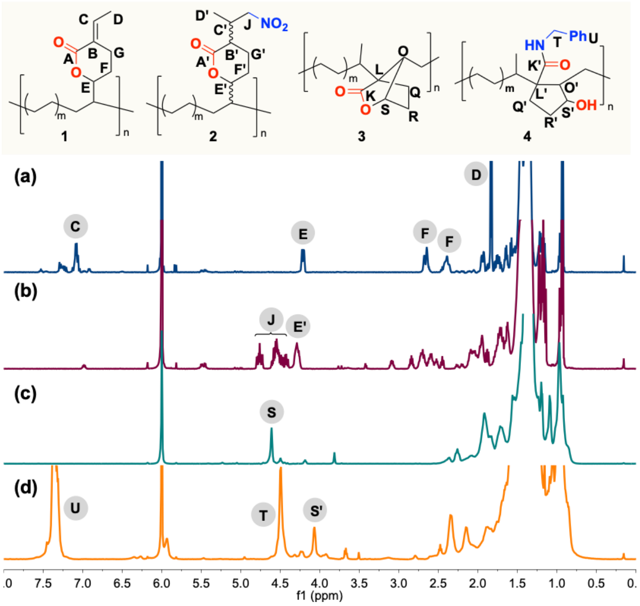
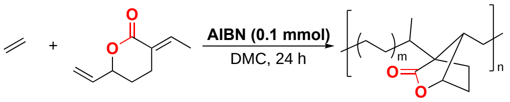


Figure 1. ^1H NMR spectra of the copolymers. (a) Copolymer in entry 6 of Table 1: polymer **1**. (b) Copolymer of Scheme 2a: polymer **2**. (c) Copolymer in entry 7 of Table 2: polymer **3**. (d) Copolymer of Scheme 2b: polymer **4**.

As revealed in our former study, EVP can undergo radical homopolymerization to form homopolymers.[16] We assumed that the copolymerization of ethylene and EVP might also be accomplished through a radical process. After certain condition optimization, we found that radical copolymerization of ethylene and EVP can be achieved by mixing EVP (0.02–0.10 mL) with AIBN (0.10 mmol) in DMC[24-25] at 80 ºC and 5.0 MPa of ethylene (Table 2). The amount of EVP, reaction concentration and temperature all had significant effects on the EVP incorporation ratio and molecular weights of the copolymers. Increasing the amount of EVP led to increased EVP incorporation ratios but decreased the copolymer molecular weights (Table 2, entries 1-3).

Compared with the copolymer in entry 2, using less DMC during copolymerization afforded a copolymer with higher EVP incorporation ratio and lower molecular weight (Table 2, entry 4), whereas more DMC led to a lower EVP incorporation ratio and a higher molecular weight of the copolymer (Table 2, entry 5). This can be explained that the tertiary α-carbonyl radical generated by radical addition to the tiglate moiety of EVP is very stable and thus the subsequent polymer growth is retarded. Last, the effect of the reaction temperature was also investigated. Since that reaction temperature can affect the decomposition of radical initiator and thus influence the chain propagation process, both decreasing and increasing the reaction temperature resulted in higher EVP incorporation but lower copolymer molecular weights (Table 2, entries 6 and 7). Addition of a Lewis acid additive, $ZnCl_2$, was beneficial for improving the molecular weight and EVP incorporation ratio of the copolymer (Table 2, entry 8).[16] Compared with the copolymer obtained in entry 1 of Table 2, performing the radical copolymerization under 3.0 MPa of ethylene afforded a copolymer with a higher EVP incorporation ratio (1.1 mol%) but with a lower molecular weight (Table 2, entry 9).

Table 2. Radical Copolymerization of Ethylene with EVP[a]



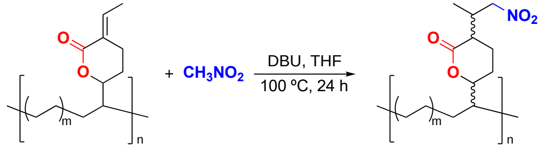
entry	EVP (mL)	DMC (mL)	temp. (°C)	yield (g)[b]	M_n (Kg/mol)[c]	M_w/M_n[c]	i. r. (%)[d]
1	0.02	5.0	80	0.603	3.8	2.7	0.53
2	0.05	5.0	80	0.360	2.7	2.5	1.8
3	0.10	5.0	80	0.134	1.3	2.5	6.8
4	0.05	2.5	80	0.127	1.6	2.6	4.8
5	0.05	10.0	80	0.658	3.7	2.6	1.1
6	0.05	5.0	60	0.113	1.8	2.3	5.6
7	0.05	5.0	100	0.246	2.0	2.4	2.7
8[e]	0.05	5.0	100	0.115	2.6	2.0	3.6
9[f]	0.02	5.0	80	0.074	2.2	1.8	1.1

[a] A mixture of AIBN (0.1 mmol) and EVP in DMC was stirred under 5.0 MPa ethylene in a 50 mL autoclave for 24 h. [b] Yields of isolated polymers after precipitation with methanol. [c] Molecular weights determined by SEC corrected by universal calibration using narrow polystyrene standards. [d] EVP incorporation ratio (i. r.) in mol% was determined by ^1H NMR analysis. [e] 0.38 mmol of $ZnCl_2$ was added. [f] 3.0 MPa of ethylene was used.

In contrast to that of coordination/insertion copolymerization, both of the carbon-carbon double bonds in the allylic ester and the tiglate ester moieties of EVP participated in the radical copolymerization, resulting in exclusive formation of bicyclic lactone units (Figure 1c, *vide infra* for characterizations). Compared with polymer **1**, the carbonyl carbon of the copolymer corresponding to entry 7, Table 2 (Polymer **3**) exhibits a clear downfield chemical shift to 178.3 ppm in the $^{13}C\{^1H\}$ NMR spectrum (See Supporting Information, Figure S40). At the same time, the oxygen-adjacent sp^3-carbon was also observed at 80.5 ppm. In the ^1H NMR spectrum, a characteristic signal, corresponding to the $C(sp^3)$-H adjacent to oxygen, was observed at 4.61 ppm (m, **S**) (Figure 1c). Moreover, a sharp peak at 1774 cm^{-1}, corresponding to the carbonyl stretching of the 5-membered lactone, was observed in its IR spectrum (Figure 2c). These data are in agreement with the chemical shifts of the bicyclic lactone units which were previously observed in the EVP homopolymers.[16]

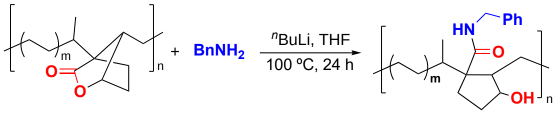
Scheme 2. Modification of the Obtained Copolymers

(a) Michael addition to polymer 1



1 2

(b) Aminolysis of polymer 3



3 4

It is well known that tiglate esters can serve as Michael acceptors.[26] Therefore, we thought that the incorporated unsaturated lactones may allow late-stage grafting of the obtained copolymers. A simple Michael addition of nitromethane was performed to confirm our assumption. By employing DBU as the base and THF as the solvent, Michael addition of nitromethane to the unsaturated lactone unit of polymer **1** proceeded smoothly, affording polymer **2** in quantitative yield (Scheme 2a). The IR absorption peak corresponding to the C=C stretching disappeared and the C=O absorption peak moved to a higher wave number of 1732 cm^{-1} (Figure 2b). In addition, the absorption peaks corresponding to N-O stretching of nitro groups were detected at 1553 and 1377 cm^{-1}. The ^1H NMR spectrum in Figure 1b shows the characteristic resonances corresponding to the nitromethylene groups among 4.85-4.35 ppm (m, **E**). Multiple peaks corresponding to the nitromethylene carbon were found at around 80.0 ppm in the $^{13}C\{^1H\}$ NMR spectrum (See Supporting Information, Figure S48). The observation of different resonances corresponding to the nitromethylene groups was possibly due to the low diastereoselectivity of the nitromethane addition process. This assumption is also supported by the observation of different resonances of the carbonyl carbons at 173.0, 172.6, 171.0 and 170.8 ppm. The successful addition of nitromethane shows that the incorporated unsaturated lactone units provide an entrypoint for diversely functionalized polyethylene materials through late-stage Michael addition and thiol-ene addition[27].

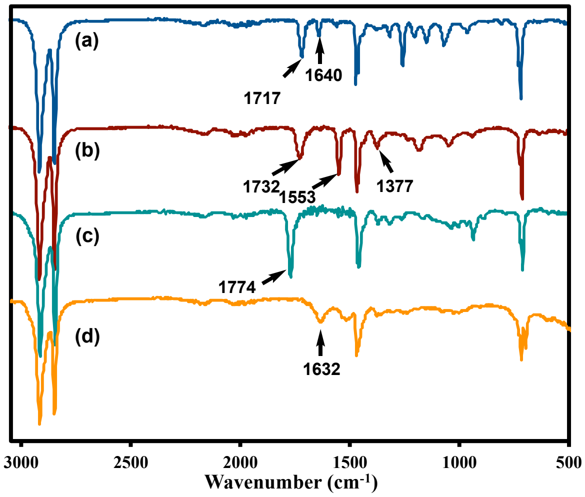


Figure 2. IR spectra of the copolymers. (a) Polymer **1**. (b) Polymer **2**. (c) Polymer **3**. (d) Polymer **4**.

For polymer **3**, aminolysis of the bicyclic lactone unit was successfully achieved with an *in-situ* mixture of benzylamine and *n*-butyl lithium (Scheme 2b).[28] A new copolymer (Polymer **4**) bearing both amide and hydroxyl groups was obtained after workup. In the IR spectrum of polymer **4**, the absorption peak at around 1774 cm^{-1} corresponding to the bicyclic lactone carbonyl disappeared, while an absorption peak at 1632 cm^{-1} corresponding to amide carbonyl stretching was observed (Figure 2d). In the ^{1}H NMR spectrum of polymer **4**, aromatic peaks at around 7.36 ppm (m, **U**) and benzyl proton peaks at 4.50 ppm (m, **T**) were observed (Figure 1d). The C(sp^3)-H adjacent to oxygen exhibited an upfield chemical shift to 4.07 ppm (**S'**) when compared with copolymer **3**. In the ^{13}C{^{1}H} NMR spectrum of polymer **4**, the methylene carbon of the benzyl amine moiety was detected at 44.2 ppm (See Supporting Information, Figure S52).

Last, thermal properties of the obtained copolymers were then evaluated via differential scanning calorimetry (DSC) analysis (See Supporting Information, Figures S68-71). During the coordination/insertion polymerization, the pendant tiglate ester moiety in EVP acted as a side chain, which may take their places in crystalline regions.[29] A clear endothermic peak was detected at T_m = 106 °C for the high-density polyethylene copolymer **1**, which is much lower than that of the highly linear polyethylene in the similar molecular weight range.[30] Polymer **2**, which was obtained from Michael addition to polymer **1**, exhibit a slightly increased melting temperature (T_m = 108 °C). Different from that of coordination/insertion copolymerization, more branched polyethylene segments were obtained through radical copolymerization. Moreover, considering that EVP comonomers are unable to participate in crystalline lattice,[28] both amorphous phases are progressively enriched in polyethylene segments, originating from the crystalline phase[31-32]. As a consequence, multiple endothermic peaks were detected for polymer **3** at around T_m = 102 °C. Polymer **4**, which was obtained through aminolysis of polymer **3**, showed a broad endothermic peak at T_m = 100 °C.

In summary, we reported a novel strategy for incorporation of CO_2 into polyethylene materials via the copolymerization of ethylene with EVP. Taking advantage of the bifunctional reactivity of EVP, divergent main-chain-functionalized polyethylenes were synthesized through palladium-catalyzed coordination/insertion copolymerization and radical copolymerization. The two new copolymerization protocols allow access to a diverse range of highly versatile polyethylene materials made from ethylene, CO_2 and 1,3-butadiene.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental details, materials, methods, NMR spectra, SEC and DSC data. (PDF)

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Notes

The authors declare no competing financial interest.

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