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# Ethylene Free Radical Polymerization in Supercritical ethylene/CO<sub>2</sub> mixture

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**ABSTRACT:** Polymerization of ethylene *via* radical pathways involving high temperatures and pressures (>200 °C, >2000 bar) is the current process of choice to produce low-density polyethylene (LDPE). Here we report ethylene free radical polymerization in supercritical CO<sub>2</sub>/ethylene mixture as a reaction medium without any addition of organic solvent and under milder conditions (<100°C, <300 bar). The effect of CO<sub>2</sub> pressure on the yield and the molar masses of the polyethylenes (PE) produced is substantial and depends on the chosen initiator. The three selected initiators (AzobisIsoButyroNitrile, lauroyl peroxide, and benzoyl peroxide) all yield PE, with  $M_w$  up to ~20000 g/mol, confirming the non-transferring nature of CO<sub>2</sub>. We also investigated the divergences in initiation/transfer/termination for these 3 compounds embedded within the functionalities borne by the polyethylene chains, and in particular the influence of CO<sub>2</sub> over the polymerization. No CO<sub>2</sub>-derived moieties could be evidenced within the PE chains, neither for AIBN nor lauroyl peroxide. On the contrary, benzoic ester moieties could be identified within the produced PE when benzoyl peroxide was employed. This study paves the road towards functionalization of PE *via* radical processes.

## INTRODUCTION

Carbon Dioxide is a renewable, non-toxic, and inexpensive raw material that can be used for many synthetic applications & processes in chemistry.<sup>1</sup>

The use of CO<sub>2</sub> as a sustainable polymerization medium constitutes a valuable starting point to new industrial processes for material production. A straightforward implementation of scCO<sub>2</sub> as a solvent/diluent was realized when polysiloxanes and fluoropolymers were identified as materials displaying high solubilities in CO<sub>2</sub> at easily attainable temperatures ( $T < 100$  °C) and pressures ( $P < 350$  bar).<sup>2</sup> DeSimone and coworkers,<sup>3,4</sup> and later other groups,<sup>5,7</sup> concentrated on homo- and co-polymerization of fluorinated monomers in supercritical CO<sub>2</sub>. A comprehensive review classified the different forms of polymerizations that could be achieved in supercritical CO<sub>2</sub> such as free radical, cationic, emulsion and other polymerization processes.<sup>8</sup> CO<sub>2</sub> is now used as a multipurpose solvent, from impregnation of small molecules, to washing of residual monomers or contaminants to actual polymerization medium.<sup>9-11</sup>

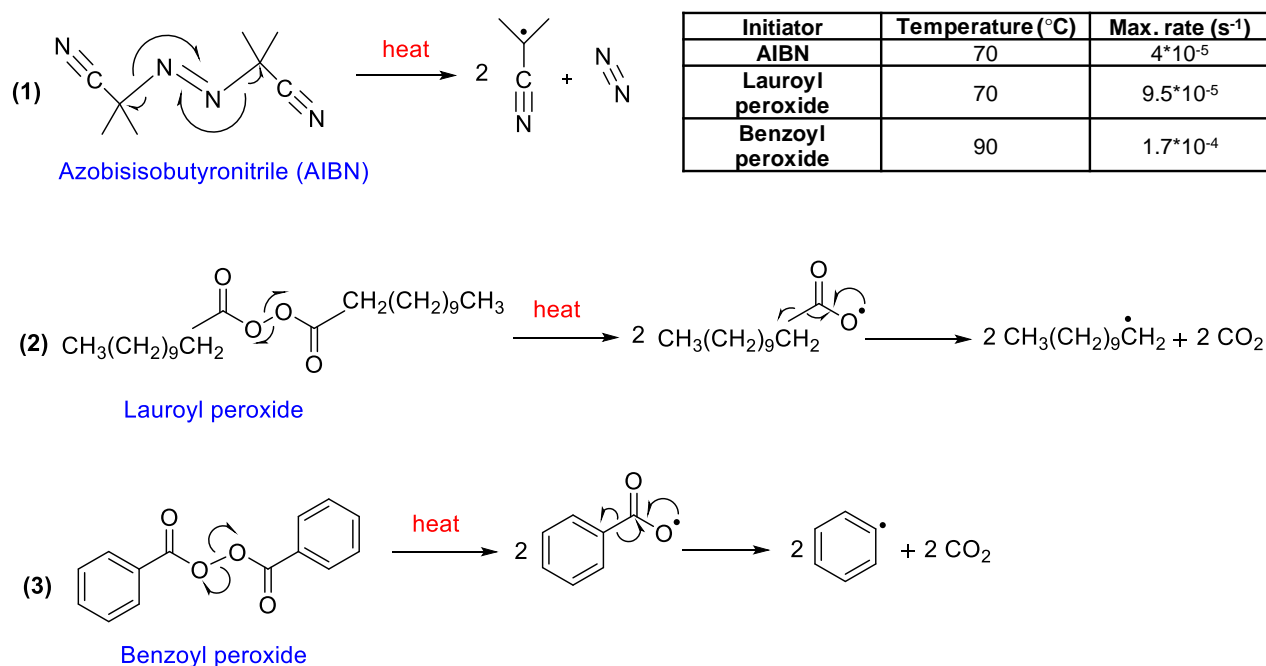
Free radical polymerization is one of the most utilized processes in polymer production. Not only does it account for a large fraction of polyolefin production in the form of low density polyethylene (LDPE) but it is also employed for most of the polar vinylic monomers including styrenics, acrylics, and vinyl esters. This radical process accounts for roughly 40-45 % of the plastics' global annual production.<sup>12</sup> LDPE is a widely demanded polyolefin, and is currently produced *via* radical polymerization processes under harsh conditions ( $T = 200-300$  °C,  $P = 1000-4000$  bar).<sup>13,14</sup> Recent work has been done in our research group on ethylene free

radical polymerization under milder conditions harnessing the activating effect of an organic solvent to promote the radical (co)polymerization of ethylene.<sup>15-19</sup> The mass of polyethylene produced as function of ethylene pressure was found to be highly dependent on the chosen organic solvent.<sup>15-17</sup> For instance, the activity in THF was determined as about fivefold that in toluene. However, all PE molar masses obtained were less than 3000 g/mol, which was attributed to transfer reactions to THF and evidenced by NMR spectroscopy.<sup>17</sup> By screening a series of solvents under the same conditions (50 mg of AIBN, 50 mL of toluene, 4 h at 70 °C under varying ethylene pressure) dimethylcarbonate (DMC) gave the highest molar masses for the produced polyethylene, with at 100 bar a  $M_n$  of 12000 g/mol and a yield of 1.6 g in 4 hours, using 50 mg of AIBN as initiator.<sup>17</sup> At 200 bar of ethylene, under the same conditions, 2.8 g of polyethylene with a  $M_n = 16600$  g/mol was produced.<sup>18</sup> One can note that under these conditions, the overall medium is supercritical and the solvent of reaction thus becomes a mixture of organic solvent and ethylene.<sup>16,19</sup>

Probing the use of CO<sub>2</sub> as a medium of ethylene radical polymerization thus appeared attractive. In particular CO<sub>2</sub> was envisaged to replace the undesired organic solvent in the mild conditions polymerization process. We designed experiments with scCO<sub>2</sub> as the lone polymerization diluent other than the monomer itself, under mild conditions and using different initiators. Some reports do use CO<sub>2</sub> as a medium (in addition to other organic diluents) for catalytic polymerization, though in that case the advantage is less in terms of sustainability since catalytic processes in gas phase already exist.<sup>20-23</sup> To the best of our knowledge, the only mention in the literature of the use of CO<sub>2</sub> as ethylene

polymerization medium **via a free radical process** was reported by Kagiya and coworkers in 1960s,<sup>24</sup> where they used 1.22 mmol (0.2 g) of AIBN as an initiator, ethylene pressure of 392 bar (400 kg/cm<sup>2</sup>) at 55 °C for 4 h. In this example,<sup>24</sup> the yield obtained was 3 g, but they added 10 mL of 2-ethyl-hexyl adipate as an initiator diluent, therefore another organic solvent was required in their experiment. Here we report free radical polymerization of ethylene in CO<sub>2</sub> under mild conditions without the addition of any diluent other than scCO<sub>2</sub>, and screening AIBN, lauroyl peroxide and benzoyl peroxide as initiator to probe the effect of the polymerization medium on the activity and the initiation process. It is of note that in this particular case, the overall medium is likely to become supercritical (low critical points for both ethylene and CO<sub>2</sub>) and therefore the solvent of polymerization will be a mixture of ethylene and CO<sub>2</sub>. Polyethylene rapidly precipitates from the polymerization medium, as verified with the use of the sapphire-windowed reactor (see SI).

## RESULTS AND DISCUSSION



**Figure 1.** Thermal decomposition of the radical initiators and corresponding rates of decomposition.<sup>25,26</sup>

**Ethylene Free Radical Polymerization in CO<sub>2</sub>.** The process was done in CO<sub>2</sub> without any addition of organic solvent or diluent, thus the polymerization medium was exclusively constituted of ethylene, CO<sub>2</sub> and selected initiator. The variation of CO<sub>2</sub> pressure governs its state, above its critical point (the critical point of carbon dioxide occurs at  $P_c = 73$  bar and  $T_c = 31$  °C), CO<sub>2</sub> is in its supercritical state. Interestingly, since ethylene also has an easily reachable critical point ( $P_c = 50$  bar and  $T_c = 9$  °C), it is quite straightforward to achieve a supercritical mixture. Interestingly, the polymer is obtained straightforwardly by simply degassing the reactor after polymerization with no need for precipitation or filtration (see SI, Figures S19 and S20). All CO<sub>2</sub>-featuring experiments were compared to standard

**Radical initiators.** Three radical initiators were selected and evaluated in the polymerization of ethylene in CO<sub>2</sub> in its supercritical and gaseous states. The thermal decompositions of the three initiators (AIBN, lauroyl peroxide, and benzoyl peroxide) are shown in **Figure 1**. Reactions (2) and (3) show that the secondary decomposition of both peroxides produces CO<sub>2</sub>. We anticipated unusual kinetics of decomposition of these initiators yielding varying concentration of different radical species, depending on the CO<sub>2</sub> pressure/concentration.

In order to have comparable rates of decompositions of the three initiators (**Figure 1 ; Table**),<sup>25,26</sup> the reactions initiated by AIBN and lauroyl peroxide were conducted at 70 °C, while those initiated by benzoyl peroxide were done at 90 °C. In all cases, solubility of the initiating system was verified using a sapphire-windowed reactor, and solubilization was achieved when supercritical state was reached for the reaction mixture (see SI, Figure S18).

radical polymerization of ethylene in DMC, with comparable sets of conditions (see SI, p.2).

**1. AIBN-Initiated Reactions.** Using AIBN as an initiator, the quantity of polyethylene (PE) produced increases as the CO<sub>2</sub> pressure increases (**Figure 2**). The yield increases from 0.3 g in the absence of CO<sub>2</sub> to 1g under 80 bar of CO<sub>2</sub> added at 35 °C under the same concentration of ethylene (110 bar at 35 °C). Note that the total pressure at the reaction temperature (70 °C) varies from 180 to 280 bar under different CO<sub>2</sub> pressures, which means that the overall reaction mixture is under supercritical conditions.<sup>27</sup>

The molar masses of the PE produced increase as the CO<sub>2</sub> pressure increases. It ranges from 16000 g/mol in the absence of CO<sub>2</sub> to 24000 g/mol under 80 bar of CO<sub>2</sub> added at

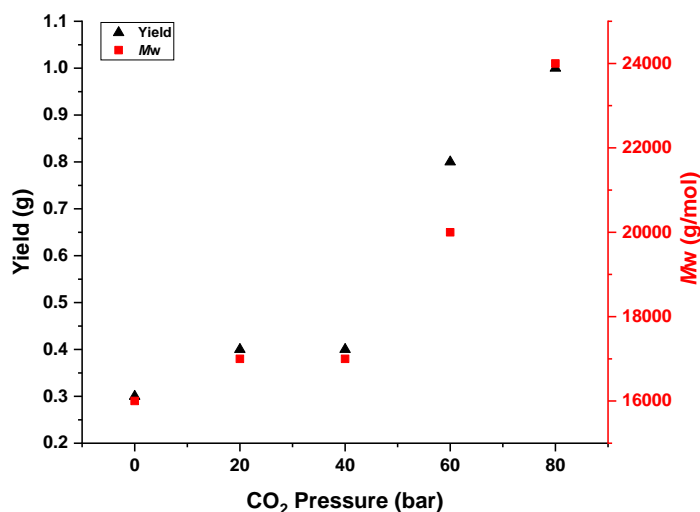
35 °C (**Figure 2**). The dispersity  $\bar{D}$  ( $M_w/M_n$ ) of the polymers produced varies from 2.2 to 2.6. The melting point obtained by "Differential Scanning Calorimetry" (DSC, see SI p.9) for all the PEs produced is close to 118 °C and crystallinities range from ~35 to 50%, which means the polyethylene produced is closer to MDPE than LDPE (m.p. of

LDPE are usually close to 105°C). This is also evidenced by calculating the number of branches per 1000 C atoms (see **Figure 3** and SI, NMR section, p.3) which are quite low (~5-6 for all polyethylenes, see **Table 1**).<sup>28</sup>

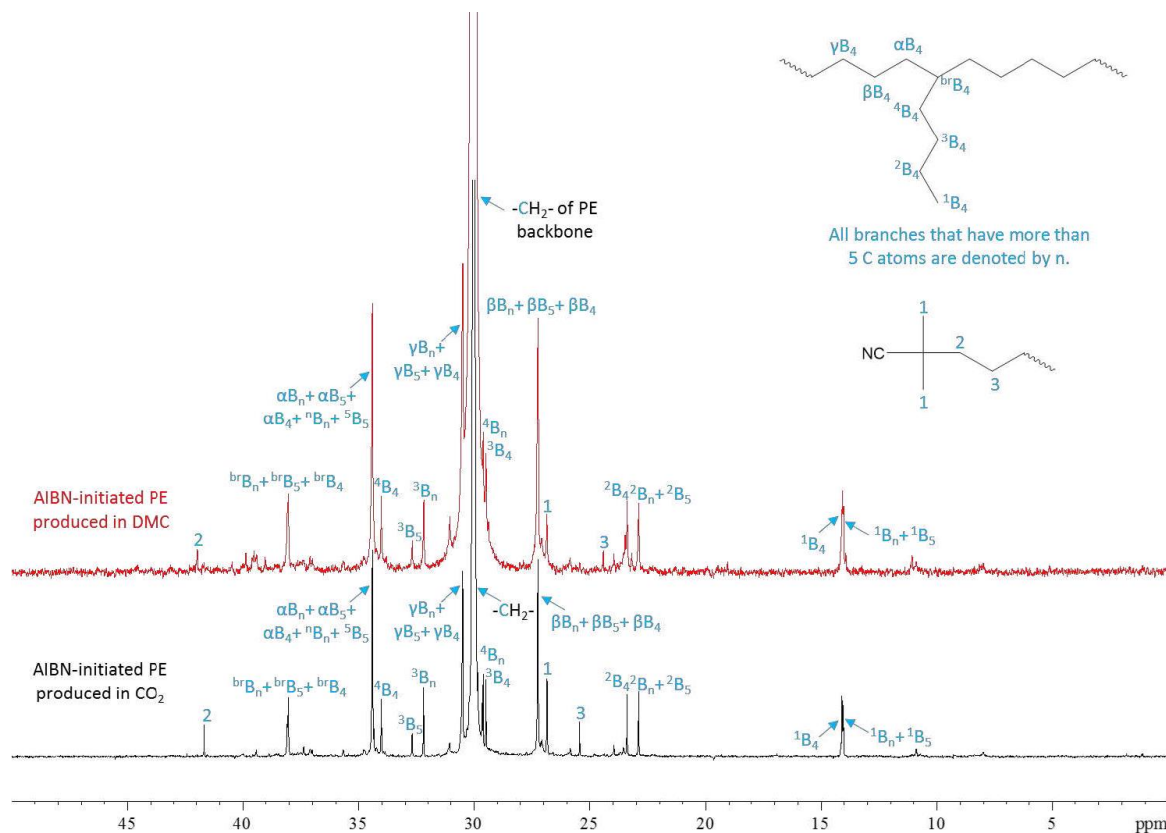
**Table 1.** Comparison between ethylene free radical polymerization reactions in CO<sub>2</sub> and those in DMC.

Initiator	Solvent	Yield (g)	$M_w^e$ (g/mol)	$M_w/M_n^e$	Melting point <sup>f</sup> (°C)	Number of branches (per 1000 C atoms) <sup>g</sup>
AIBN	CO <sub>2</sub> <sup>a</sup>	1	24 000	2.2	118	5.56
	DMC <sup>b</sup>	0.8	20 000	2.6	116	5.18
Lauroyl peroxide	CO <sub>2</sub> <sup>c</sup>	1	19 000	2.1	117	5.23
	DMC <sup>b</sup>	2.2	42 000	2.1	118	5.45
Benzoyl peroxide	CO <sub>2</sub> <sup>d</sup>	1.2	8 000	1.6	112	6.51
	DMC <sup>b</sup>	2.4	19 000	2.0	118	6.45

a) CO<sub>2</sub> pressure = 80 bar at 35 °C; b) 50 mL of DMC; c) CO<sub>2</sub> pressure = 20 bar at 35 °C; d) CO<sub>2</sub> pressure = 80 bar at 45 °C; e) determined by high-temperature SEC; f) Measured by DSC; g) see supporting information.



**Figure 2.** Variation of the PE yield of AIBN-initiated ethylene polymerizations and corresponding molar masses as function of CO<sub>2</sub> pressure. Conditions: 0.3 mmol of AIBN, 110 bar of ethylene at 35 °C, reaction temperature: 70 °C, total pressure at the reaction temperature: 180-280 bar, polymerization time: 3 h. Added CO<sub>2</sub> pressure is determined at 35 °C.



**Figure 3.** Aliphatic regions of the  $^{13}\text{C}$ -NMR spectra of the AIBN-initiated PE respectively produced in DMC and in  $\text{CO}_2$  (80 bar at  $35^\circ\text{C}$ ).<sup>25</sup>

To compare with the recent results achieved in our laboratory,<sup>15-19</sup> an ethylene free radical polymerization reaction was realized under the same conditions of that of the  $\text{CO}_2$ -mediated reactions, but substituting dimethylcarbonate (DMC) as a solvent (see SI, p.2). The corresponding total pressure at  $70^\circ\text{C}$  was 237 bar. **Table 1** shows a comparison between the reaction done in 50 mL of DMC and that conducted under 80 bar of  $\text{CO}_2$  added at  $35^\circ\text{C}$  (the reaction with the highest activity in  $\text{CO}_2$  using AIBN). The yield, molar masses, and melting point of the PE produced from the polymerization reaction in DMC (0.8 g, 20000 g/mol,  $116^\circ\text{C}$ ) are slightly lower than those of the PE produced in  $\text{CO}_2$  (1 g, 24000 g/mol,  $118^\circ\text{C}$ ). Overlays of SECs are disclosed in the SI (p.10-13).  $\bar{M}_w$  of the PE produced in DMC (2.5) is slightly higher than that of PE produced in  $\text{CO}_2$  (2.2). Overall, ethylene polymerization in  $\text{scCO}_2$  gives slightly higher activity and produces higher molar-mass PE than that in DMC when initiated by AIBN. Additionally, the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of both polymers are extremely similar; **Figure 3** (see SI, Figure S1 for  $^1\text{H}$  NMR spectra) represents the aliphatic region of the  $^{13}\text{C}$ -NMR spectra for both polymers. On this superimposition, the  $\text{CH}_2$ -based main chain as well as the C4-chain branching (due to back-biting reactions: radical transfer from a cyclic 6-membered intermediate) and other chain branching can easily be identified, but no additional polar groups arising from  $\text{CO}_2$  interference.  $\text{CO}_2$  can therefore be considered a very-low to **non-transferring solvent** for the free radical polymerization of ethylene, which is a valuable feature

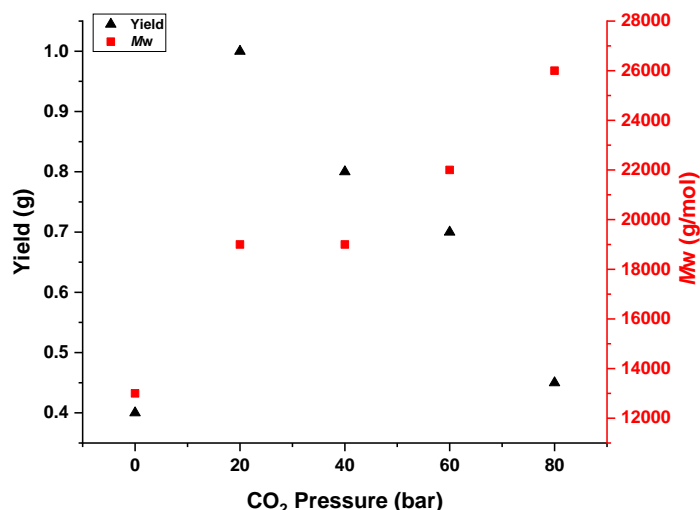
considering the extreme reactivity of the primary polyethylenyl radical.

**2. Lauroyl Peroxide-Initiated Reactions.** Using lauroyl peroxide as an initiator the yield of PE produced increases strictly by the primary addition of  $\text{CO}_2$  (20 bar at  $35^\circ\text{C}$ ) from 0.4 g in the absence of  $\text{CO}_2$  to 1g in presence of  $\text{CO}_2$ . However, by subsequently increasing the  $\text{CO}_2$  pressure, the mass of PE produced decreases gradually to reach 0.45 g under 80 bar of  $\text{CO}_2$  added at  $35^\circ\text{C}$  (**Figure 4**). This decrease might be due to a different secondary decomposition of lauroyl peroxide from the carboxylic radical to the primary  $-\text{CH}_2\cdot$  radical in the presence of a high  $\text{CO}_2$  concentration in the medium:<sup>29</sup> the kinetics of this decomposition could be affected thus changing the overall repartition of radical species and thus the efficiency of polymerization (**Figure 1** ; **Scheme 1-(2)**). In particular, the lauroyl peroxide carboxylic radical is either unsuccessful at initiating ethylene polymerization or is producing PE chains with very low molar masses, probably due to fast recombination of accumulated carboxyl radicals with initiated polyethylenyl chains. These oligomers along with leftover unreacted lauroyl peroxide are soluble in methanol (precipitation solvent to remove the traces of initiator by-products). Indeed, as shown in the  $^{13}\text{C}$ -NMR spectra in **Figure 5** (see also SI, Fig. S2), the signals corresponding to the  $\alpha$  and  $\beta$  carbon atoms to the oxygen of the carboxyl group at 63.2 ppm and 25.0 ppm, respectively, in addition to that corresponding to the  $\alpha$  carbon atom to the quaternary carbon of

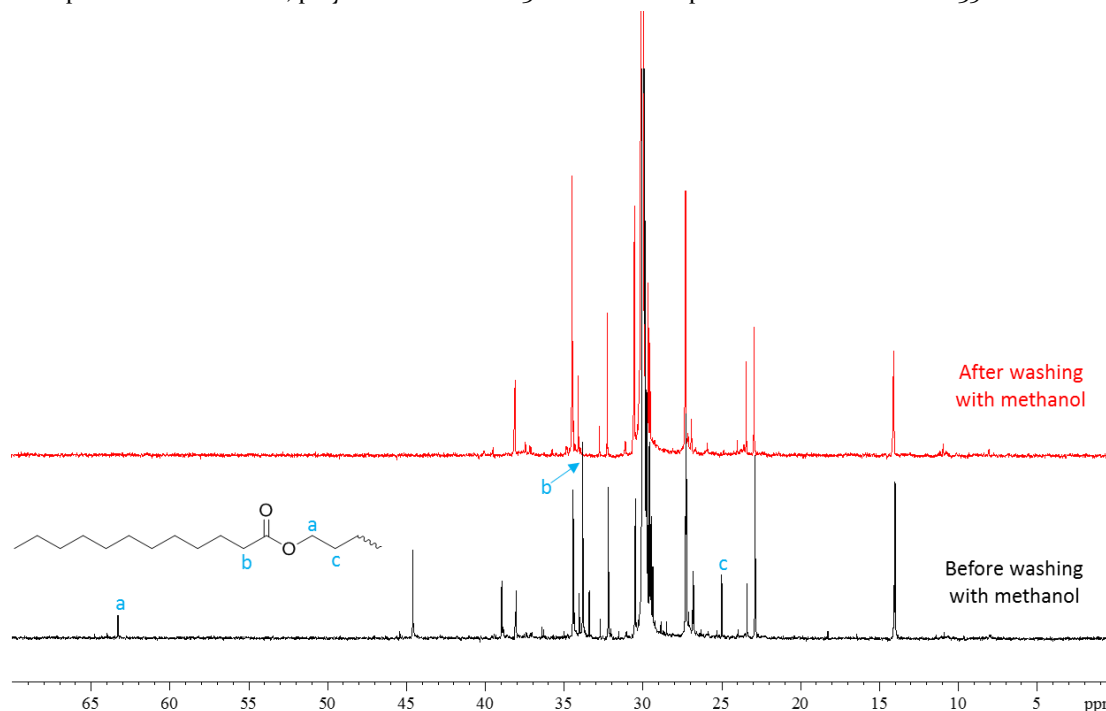
the carboxyl group at 33.8 ppm, disappear after washing with methanol. This is also evident in the IR spectra through the disappearance of the C-O single and double bonds after washing (see SI, Figure S10).

The molar masses of the PE produced increases as the CO<sub>2</sub> pressure increases, from 13000 g/mol in the absence of CO<sub>2</sub> to 26000 g/mol under 80 bar of CO<sub>2</sub> added at 35 °C (**Figure 4**). Polymers' *D*'s produced varies from 1.6 to 2.5 showing narrower distribution than that of PE produced by AIBN-initiated reactions. The melting point obtained by DSC for all the PEs produced using lauroyl peroxide is ~117°C (see

SI for SEC & DSC, and **Table 1**). The comparison between the results obtained from the CO<sub>2</sub>-mediated reaction (under 20 bar at 35 °C; the most active reaction) and those obtained from the reaction done in DMC under the same conditions evidences the advantages of the lauroyl peroxide solubilization in DMC here. Yields and molar masses of the corresponding PE produced are higher (see **Table 1**). Solubility of lauroyl peroxide in CO<sub>2</sub>/ethylene supercritical medium is likely very low, even though slightly enhanced as compared to neat supercritical ethylene, as visually verified using a sapphire-windowed reactor. This could result in the inefficient radical initiation of polymerization.



**Figure 4.** Variation of the PE yield of lauroyl peroxide-initiated ethylene polymerizations and corresponding molar masses as function of CO<sub>2</sub> pressure. 0.3 mmol of lauroyl peroxide, 10 bar of ethylene at 35 °C, reaction temperature: 70 °C, total pressure at the reaction temperature: 180-280 bar, polymerization time: 3 h. Added CO<sub>2</sub> pressure is determined at 35 °C.



**Figure 5.** Aliphatic regions of the <sup>13</sup>C-NMR spectra of the lauroyl peroxide-initiated PE produced in CO<sub>2</sub> before and after washing with methanol.



**3. Benzoyl Peroxide-Initiated Reactions.** Using benzoyl peroxide as an initiator, the yield of PE produced increases noticeably with the presence of CO<sub>2</sub>. Even at low CO<sub>2</sub> concentration (20 bar at 45 °C), 1.2 g can be produced as opposed to 0.4 g in the absence of CO<sub>2</sub> (**Figure 6**). Increasing the CO<sub>2</sub> pressure further does not provide additional PE productivity as the yield remains constant (**Figure 6**). This plateau obtained could again be consistent with a different repartition of radical species due to varying kinetics of decomposition in the presence of CO<sub>2</sub>.<sup>30-33</sup> Moreover, the secondary decomposition of benzoyl peroxide is unfavorable due to the unpaired electron lying in an orbital perpendicular to the ring  $\pi$ -system (**Figure 1** ; **Scheme 1**-(3)). Consequently, the yield remaining constant while increasing the CO<sub>2</sub> pressure could suggest concomitant initiation processes by both benzoyl-peroxide derived carboxylic radicals and phenyl radicals in ethylene polymerization in scCO<sub>2</sub>, both processes compensating each other. To verify this assessment, <sup>1</sup>H and <sup>13</sup>C-NMR and infrared spectra of the PE produced by the benzoyl peroxide-initiated reactions were realized (**Figure 7**), as well as SEC and DSC characterization (see SI).

The  $M_w$  of the produced PE is 16000 g/mol in the absence of CO<sub>2</sub>, then it decreases suddenly to 6000 g/mol by adding CO<sub>2</sub> (20 bar at 45 °C), then it re-increases gradually as the CO<sub>2</sub> pressure increases till it reaches 8000 g/mol at 80 bar of CO<sub>2</sub> added at 45 °C (**Figure 6**). This is consistent with a higher concentration of radicals in the medium, either initiating or terminating polyethylene chains. The flux and repartition of radicals (carboxyl and phenyl) and the efficiency of initiation/transfer/termination thus strongly depends on the presence of CO<sub>2</sub> in the polymerization medium. Ester end groups could then be formed *via* transfer to initiator and radical recombination, for instance.<sup>32,33</sup>

Indeed, when characterizing spectroscopically the polyethylene obtained in the presence of CO<sub>2</sub>, two triplets appear at 2.5 ppm and 4.2 ppm in the <sup>1</sup>H-NMR spectrum, corresponding to the protons on the  $\alpha$ -Carbon to the phenyl ring and that adjacent to the oxygen atom of the carboxyl group, respectively (**Figure 7-A**, and Fig S5 in SI). In the <sup>13</sup>C-NMR spectrum, the signals corresponding to the  $\alpha$  and  $\beta$  carbon atoms to the oxygen of the carboxyl group at 64.7 ppm and 31.5 ppm, respectively, appear even after washing with methanol, in addition to the signal corresponding to the quaternary carbon of the carboxyl group at 176.5 ppm (**Figure 7-B**, and Fig S6 in SI). The initiation and/or termination *via* the carboxylic radical of benzoyl peroxide is also verified by the IR spectra, showing the C-O single bond absorption band at 1272 cm<sup>-1</sup> and the C-O double bond band at 1724 cm<sup>-1</sup> (**Figure 7-C**).

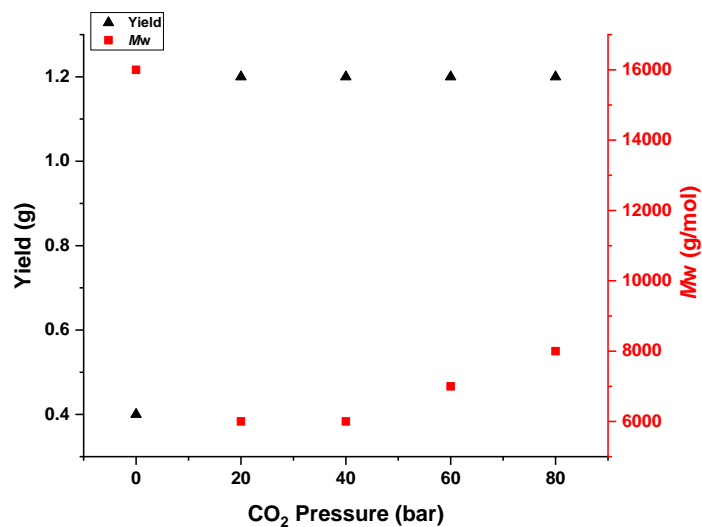
In absence of CO<sub>2</sub> pressure, neither phenyl nor carboxyl chain ends appear in the NMR spectra (see SI), but the signals corresponding to the benzoyl peroxide appear in the <sup>1</sup>H-NMR spectrum (the protons at the *ortho*, *para* and *meta* positions of the phenyl ring, respectively at 7.9 ppm, 7.3 ppm, and 7.1 ppm). In absence of diluent (CO<sub>2</sub> or an organic solvent) benzoyl peroxide is almost inefficient at initiating ethylene radical polymerization, probably due to

its very low solubility in supercritical ethylene, as the low yield in PE suggests. On the contrary, when CO<sub>2</sub> is present in the reaction mixture, benzoic ester moieties along phenyl chain-ends can be evidenced by NMR spectroscopy, signifying that carboxylic radicals are either efficiently initiating or terminating the polymerization of ethylene, *via* transfer to initiator and radical recombination most likely.<sup>30-33</sup> The higher the CO<sub>2</sub> proportion in the supercritical mixture, the higher the concentration of benzoic ester chain-ends. It is worth mentioning that the molar masses are increasing by increasing CO<sub>2</sub> pressure.  $\bar{D}$  varies from 1.6 to 2.2 showing slightly narrower distribution than that of PEs produced by AIBN- and lauroyl peroxide-initiated reactions. The melting point obtained by DSC for all the PEs produced is ~112 °C lower than that of the PEs produced by AIBN- and lauroyl peroxide-initiated reactions (**Table 1**), probably due to the lower molar masses.

In order to produce higher molar masses of benzoyl peroxide-initiated PE, a reaction was performed at 70 °C pressurized by 80 bar of CO<sub>2</sub> and 110 bar of ethylene at 35 °C. This reaction yielded 0.7 g of PE in 3 h, with an  $M_w$  = 19000 g/mol and  $\bar{D}$  of 1.9. By decreasing the temperature the rate of decomposition of the initiator decreases, thus the concentration of radicals in the medium decreases and termination reactions consequently decrease resulting in an increase in molar masses.

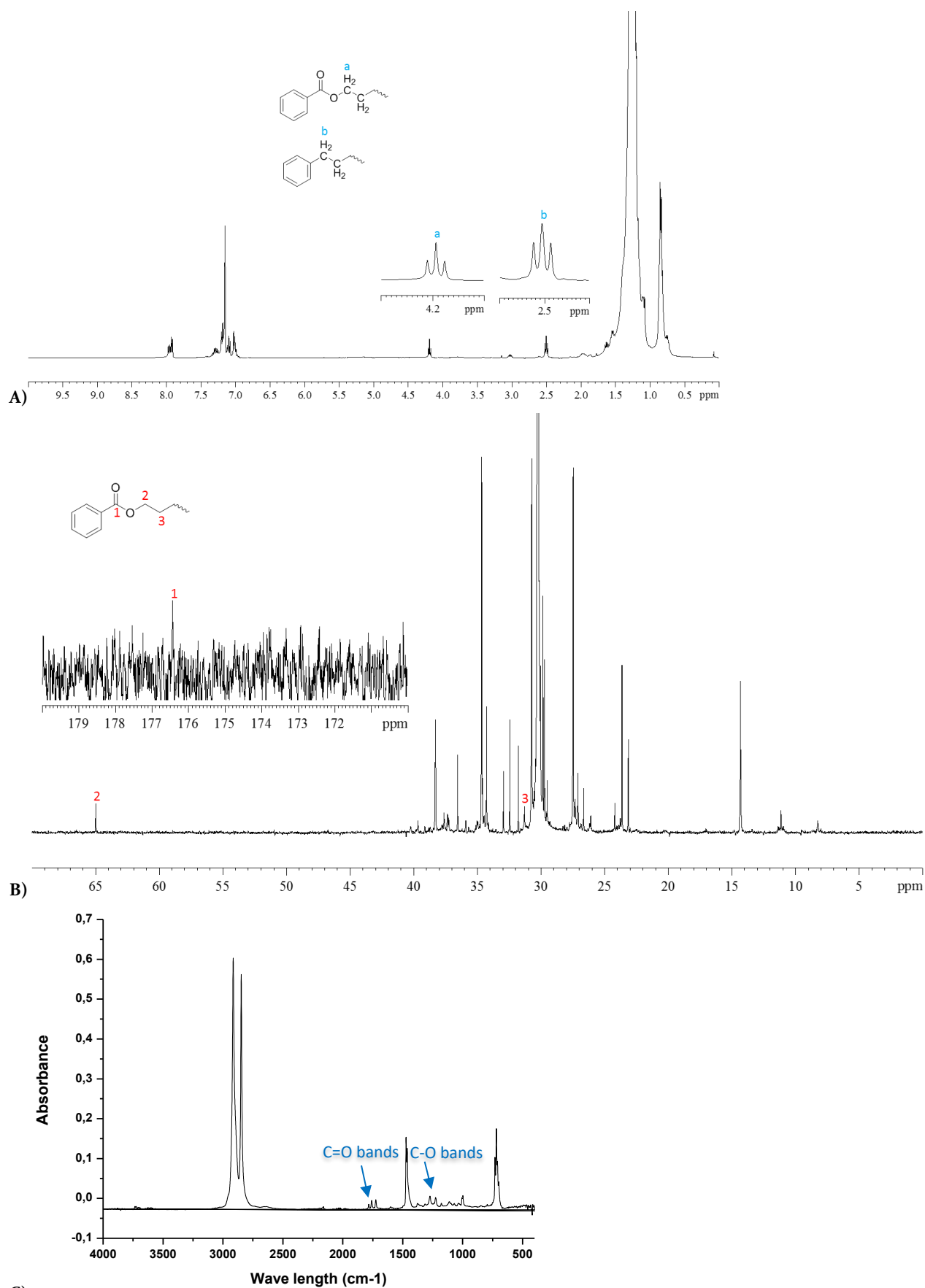
Finally, when comparing CO<sub>2</sub> and DMC as diluent, polyethylenes resulting from the ethylene polymerization with CO<sub>2</sub> (80 bar added at 45 °C) and from the reaction run in DMC contrast starkly (**Table 1**). The yield, molar masses, and melting point of the PE produced from the DMC-diluted polymerization (2.4 g, 19000 g/mol, 116 °C) are higher than those of the PE produced in CO<sub>2</sub> (1.2 g, 8000 g/mol, 112 °C); whereas  $\bar{D}$  is slightly lower in CO<sub>2</sub> (1.6 vs. 2.0). This difference in activity is due to the higher solubility of benzoyl peroxide in DMC than in CO<sub>2</sub>. Even though the activity in DMC is higher, there is minimal initiation/termination by recombination by the benzoyl-peroxide derived carboxylic radical as evidenced by the NMR spectra (see SI, Figures S7 and S8), and in addition some transfer to DMC can be evidenced.<sup>19</sup> Therefore, only an ethylene radical polymerization in sc(CO<sub>2</sub>/ethylene) using benzoyl peroxide as an initiator yields ester-functionalized PE chains, potentially post-modifiable.<sup>34-36</sup>

Interestingly, in all polymerizations conducted in sc(CO<sub>2</sub>+ethylene), the obtained PEs display relatively narrow molar-mass distributions and are devoid of very low molar masses *a.k.a.* waxes. All SECs are realized on the raw material directly collected from the reactor, and do not feature any tailing at high elution volumes, characteristic of waxes (see SI, p.10-13). These compounds, inherent to the harsh conditions industrially employed to produce LDPE (>200 °C, >2000 bar) are problematic since they require an additional separation step in the industrial process to allow for polymer processing and to abide to the regulations regarding VOCs.<sup>37</sup> Their absence is another advantage of our milder polymerization process.



**Figure 6.** Variation of the PE yield of benzoyl peroxide-initiated ethylene polymerization and corresponding molar masses as a function of CO<sub>2</sub> pressure. 0.3 mmol of benzoyl peroxide, 90 bar of ethylene at 45°C, reaction temperature: 90°C, total pressure at the reaction temperature: 180-280 bar, polymerization time: 3 h. Added CO<sub>2</sub> pressure is determined at 45°C.





**Figure 7.** A)  $^1\text{H}$ -NMR spectrum for a benzoyl peroxide-initiated PE produced in  $\text{CO}_2$  after washing with methanol. B)  $^{13}\text{C}$ -NMR spectrum for a benzoyl peroxide-initiated PE produced in  $\text{CO}_2$  after washing with methanol. C) Infrared spectrum for a benzoyl peroxide-initiated PE produced in  $\text{CO}_2$  after washing with methanol.

## CONCLUSION

Ethylene free radical polymerization in supercritical CO<sub>2</sub>/ethylene mixture without addition of any external organic solvent and under mild conditions (< 100 °C and < 300 bar) has been achieved to produce LDPE with no wax. Several initiators can be used as long as they possess a substantial solubility in scCO<sub>2</sub> or sc(CO<sub>2</sub>/ethylene). Interestingly, using benzoyl peroxide as initiator, one can obtain ester-functionalized LDPE in a very straightforward manner. The initiation or termination, including by transfer reactions, of PE chains *via* the carboxylic radical produced by the primary decomposition of benzoyl peroxide is possible in the presence of CO<sub>2</sub>, whereas the phenyl radical produced by the secondary decomposition preferentially initiates in the absence of CO<sub>2</sub>. We are now focusing on the study and control of the mechanisms of initiation, transfer and termination using this particular class of carboxy-radical precursors, in order to expand the scope of ester-functionalization of LDPE, as well as working on the morphology of the scCO<sub>2</sub>-born PE.

## EXPERIMENTAL SECTION

All experiments were conducted in a high-pressure (up to 350 bar) 160 mL reactor from "PARR INSTRUMENT COMPANY", connected to a main ballast (1.5 L) which itself is connected to two intermediate ballasts of 2 L each, one for ethylene and the other for CO<sub>2</sub>. The main ballast is used for condensation of gases to get high pressures up to 340 bar; the temperature varies in the ballast *via* oil circulation using an oil bath, the fluid temperature has a functioning range from -60 °C to 80 °C. Heating the reactor was done using another oil bath with a fluid temperature functioning range from 30 °C to 200 °C.

In each reaction, 0.3 mmol of the initiator were added into the reactor, then the reactor was closed and evacuated from air and moisture. After that, the reactor temperature was set at 35 °C for AIBN- and lauroyl peroxide-initiated reactions, and at 45 °C for benzoyl peroxide-initiated reactions. Then, the reactor was pressurized by ethylene (110 bar for AIBN- and lauroyl peroxide-initiated reactions; 90 bar for benzoyl peroxide-initiated reactions) followed by CO<sub>2</sub>. Finally, the reactor temperature was set at 70 °C for AIBN- and lauroyl peroxide-initiated reactions, and at 90 °C for benzoyl peroxide-initiated reactions. Each reaction lasted for 3 hours after CO<sub>2</sub> addition. The stirring speed was set at 600 rpm.

## ASSOCIATED CONTENT

### Supporting Information

All NMR spectra, FTIR spectra, DSC thermograms, SEC chromatograms, as well as photos and SEM pictures are included in the SI.

The Supporting Information is available free of charge on the ACS Publications website.

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## Conflicts of Interest

There are no conflicts of interest to declare.

## REFERENCES

- (1) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107* (6), 2365–2387.
- (2) McHugh, M.; Krukonis, V. *Supercritical Fluid Extraction: Principles and Practice*; Elsevier, **2013**.
- (3) Romack, T. J.; DeSimone, J. M.; Treat, T. A. *Macromolecules* **1995**, *28* (24), 8429–8431.
- (4) Michel, U.; Resnick, P.; Kipp, B.; DeSimone, J. M. *Macromolecules* **2003**, *36* (19), 7107–7113.
- (5) Renault, B.; Cloutet, E.; Lacroix-Desmazes, P.; Cramail, H. *Macromol. Chem. Phys.* **2008**, *209* (5), 535–543.
- (6) André, P.; Lacroix-Desmazes, P.; Taylor, D. K.; Boutevin, B. *J. Supercrit. Fluids* **2006**, *37* (2), 263–270.
- (7) Hosemann, B.; Siegmann, R.; Beuermann, S. Chapter 7: Supercritical Carbon Dioxide as Reaction Medium for Fluoropolymer Synthesis and Kinetic Investigations into Radical Polymerizations of VDF and HFP. In *Fluorinated Polymers*; **2016**; pp 211–232.
- (8) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, *99* (2), 543–564.
- (9) Hyatt, J. A. *J. Org. Chem.* **1984**, *49* (26), 5097–5101.
- (10) Morgenstern, D. A.; LeLacheur, R. M.; Morita, D. K.; Borkowsky, S. L.; Feng, S.; Brown, G. H.; Luan, L.; Gross, M. F.; Burk, M. J.; Tumas, W. Supercritical Carbon Dioxide as a Substitute Solvent for Chemical Synthesis and Catalysis. In *Green Chemistry*; ACS Symposium Series; American Chemical Society, **1996**; Vol. 626, pp 132–151.
- (11) Ramsey, E.; Sun, Q.; Zhang, Z.; Zhang, C.; Gou, W. *J. Environ. Sci.* **2009**, *21* (6), 720–726.
- (12) Nesvadba, P. Radical Polymerization in Industry. *Encycl. Radic. Chem. Biol. Mater.* **2012**.
- (13) Doak, K. W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley Interscience: New York, **1985**; Vol. 6, pp 386–428.
- (14) Aggarwal, S. L.; Sweeting, O. J. *Chem. Rev.* **1957**, *57*, 665–742.
- (15) Grau, E.; Broyer, J.-P.; Boisson, C.; Spitz, R.; Monteil, V. *Macromolecules* **2009**, *42*, 7279–7281.
- (16) Grau, E.; Broyer, J.-P.; Boisson, C.; Spitz, R.; Monteil, V. *Phys. Chem. Chem. Phys.* **2010**, *12* (37), 11665–11669.
- (17) Grau, E.; Broyer, J.-P.; Boisson, C.; Spitz, R.; Monteil, V. *Polym. Chem.* **2011**, *2* (10), 2328–2333.
- (18) Dommanget, C.; D'Agosto, F.; Monteil, V. *Angew. Chem. Int. Ed.* **2014**, *53* (26), 6683–6686.
- (19) Wolpers, A.; Bergerbit, C.; Ebeling, B.; D'Agosto, F.; Monteil, V. *Angew. Chem. Int. Ed.* **2019**, *Early View*; DOI: 10.1002/anie.201905629
- (20) Guironnet, D.; Friedberger, T.; Mecking, S. *Dalton Trans.* **2009**, 8929–8934.
- (21) Guironnet, D.; Göttker-Schnetmann, I.; Mecking, S. *Macromolecules* **2009**, *42* (21), 8157–8164.
- (22) Bastero, A.; Francio, G.; Leitner, W.; Mecking, S. *Chem. Eur. J.* **2006**, *12*, 6110–6116.
- (23) Daigle, J.-C.; Lucien, F. P.; Zetterlund, P. B.; Claverie, J. P. *Chem. Asian J.* **2017**, *12*, 2057–2061.
- (24) Kagiya, T.; Machi, S.; Hagiwara, M.; Kise, S. Polymerization of ethylene by means of radical initiation using carbon dioxide as reaction medium. US3471463 A, October 7, **1969**.
- (25) Bowes, P. C.; Harris, J. Thermal Decomposition of Lauroyl Peroxide, *Fire Research Notes* 684, **1967**, Table 1, page 3.
- (26) Denisov, E. T.; Denisova, T. G.; Pokidova, T. S. Handbook of Free Radical Initiators, John Wiley & Sons, **2003**, DOI: DOI: 10.1002/0471721476
- (27) Henderson, N.; Sacco, W. F.; Barufatti, N. E.; Ali, M. M. *Ind. Eng. Chem. Res.* **2010**, *49* (4), 1872–1882.
- (28) Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32* (5), 1620–1625
- (29) Guillet, J. E.; Gilmer, J. C. *Canadian J. Chem.* **1969**, *47*, 4405–4411.
- (30) Barnett, B.; Vaughan, W. E. *J. Phys. Chem.* **1947**, *51* (4), 942–955.
- (31) Nicholson, A. E.; Norrish, R. G. W. *Discuss. Faraday Soc.* **1956**, *22*, 97–103.
- (32) Mayo, F. R.; Gregg, R. A.; Matheson, M. S. *J. Am. Chem. Soc.* **1951**, *73* (4), 1691–1700.
- (33) Tarbelle, D. S.; Longosz, E. J. *J. Org. Chem.* **1959**, *24* (6), 774–778.
- (34) Cheng, C.; Brookhart, M. *Angew. Chem. Int. Ed.* **2012**, *51* (37), 9422–9424.
- (35) Fischer, C.; Sparr, C. *Angew. Chem. Int. Ed.* **2018**, *57* (9), 2436–2440.
- (36) Stadler, S. M.; Göttker-Schnetmann, I.; Mecking, S. *ACS Catal.* **2019**, *9* (4), 2760–2767.
- (37) As an example of chemical process for the production of LDPE: <https://www.lyondellbasell.com/globalassets/products-technology/technology/lupotech-brochure.pdf>.