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# Synthesis of Degradable Polyethylene and Poly(ethylene-*co*-vinyl acetate) by Radical Co- and Ter-polymerization of Ethylene, $\epsilon$ -Thionocaprolactone and Vinyl acetate

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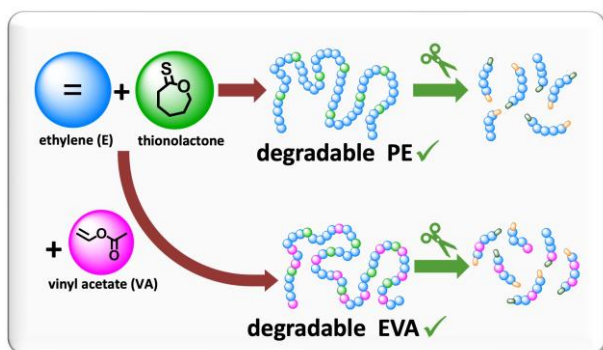
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KEYWORDS. Polyethylene • degradable • copolymerization • rROP • thionolactone • vinyl acetate



ABSTRACT. We report the synthesis of PE and poly(ethylene-*co*-vinyl acetate) (EVA) bearing a low content of in-chain thioester functions introduced via a co- or ter-polymerization approach involving ethylene (E), vinyl acetate (VAc) and  $\epsilon$ -thionocaprolactone (TCL). To achieve a homogenous incorporation of thioester functions along the chains resulting from the ring opening of TCL, a semi-batch process with an adjusted feed of TCL was employed. Characterizations of the polymers were conducted by combination of size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) analyses. The chemically-induced degradability of the obtained polymers was assessed by SEC.

## INTRODUCTION

The production of polyolefins, i.e. polyethylenes (PE) and isotactic polypropylene (iPP), occupies more than the half of the worldwide production of thermoplastics. With more than 130 million tons produced in 2021, PEs remain the most industrially produced polymers<sup>[1]</sup> either by radical or coordination-insertion polymerization. The popularity<sup>[2,3]</sup> of this material is mainly due to its intrinsic chemical inertness and thermal stability resulting from a combination of its ability

to crystallize and its lack of functionality. In the environmental context of end life of plastics and considering recyclability and (bio)degradability, it is thus of real interest to consider all possible means to confer these features to PE while retaining its desirable properties such as thermal stability. Therefore, the eco-design of polyethylene has recently emerged as an attractive topic.<sup>[4]</sup> The installation of a small amount of cleavable functions in the polyethylene backbone offers a possible solution to polyethylene recycling or degradability.<sup>[5-12]</sup> As PE is industrially produced by catalytic coordination-insertion polymerization or radical polymerization, any strategy devoted to degradable PE based on these techniques is of interest.

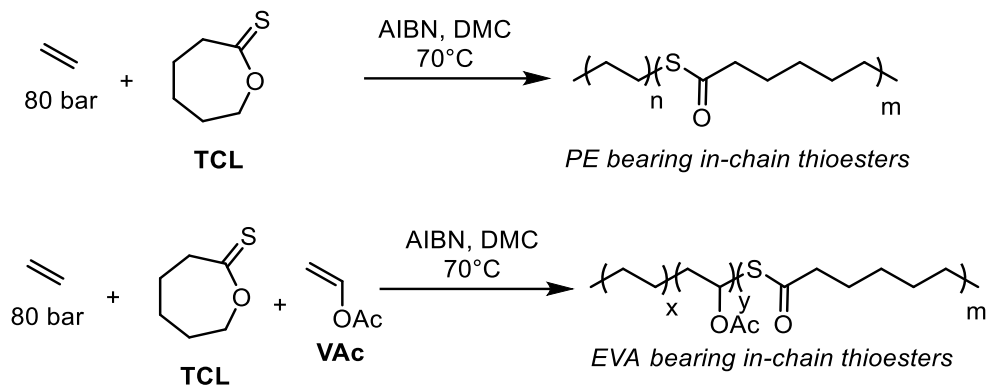
The introduction of cleavable bonds into polymer backbone has indeed been employed for polymers obtained by different polymerization techniques.<sup>[13]</sup> It has recently been rejuvenated for polymers whose backbones are composed of C-C bonds such as those obtained by radical polymerization.<sup>[14]</sup> The use of a cyclic comonomer that can ring open while copolymerizing has allowed degradable polymers to be produced via radical ring opening copolymerization (rROP).

The cyclic ketene acetals (CKAs) first reported by Bailey in the 1980's are an example of such ring-opening.<sup>[15]</sup> Among them, 2-methylene-1,3-dioxepane (MDO) has been homopolymerized to form a polyethylene-like polymer incorporating ester bonds in the backbone. Ethylene was further copolymerized with MDO by Bailey to produce copolymer with properties closer to those of PE. Biodegradability studies showed that rapid degradation occurred for chains containing ca 10% MDO.<sup>[16-17]</sup> Some attempts to control radical copolymerization of ethylene and MDO have been made using cobalt-mediated radical copolymerization<sup>[18]</sup> or reversible addition-fragmentation chain transfer (RAFT)<sup>[19]</sup> polymerization. Enzymatic degradation of the resulting copolymers confirmed the biodegradation results previously obtained by Bailey<sup>[16]</sup> and Lenz.<sup>[17]</sup>

The use of CKAs for the synthesis of degradable vinylic polymers has been widely reported.<sup>[14,20]</sup> These studies also revealed the limited stability of CKAs which may complicate their use in many polymerization systems.<sup>[21]</sup>

Thionolactones are a new class of monomers that ring-open to introduce thioester functions along the polymer backbone via thiocarbonyl radical addition- ring-opening (TARO) polymerization. This approach was reported independently by Roth and Gutekunst, via the use of biphenylic cyclic thionolactone (dibenzo[c,e]oxepane-5-thione, DOT) as a comonomer in the copolymerization with acrylates,<sup>[22,23]</sup> acrylamides,<sup>[24]</sup> styrene,<sup>[25-27]</sup> acrylonitrile<sup>[22]</sup> and maleimides.<sup>[28]</sup> DOT inhibits the copolymerization of less activated monomers such as vinyl acetate (VAc).<sup>[24]</sup> However, thionocaprolactone (TCL) has recently been shown to undergo TARO and to be compatible with VAc copolymerization.<sup>[29-30]</sup> TCL can be synthesized in high yield from the readily available  $\epsilon$ -caprolactone. Considering the known similarities in terms of reactivities of VAc and ethylene in radical polymerization,<sup>[31-33]</sup> we anticipate that the reactivity of propagating macroradicals produced during either the radical polymerization of ethylene or the copolymerization of ethylene with VAc would be compatible with TARO in the presence of TCL. To the best of our knowledge, the insertion of thioester linkages into the main chain of polyethylene or poly(ethylene-*co*-vinyl acetate) (EVA) has never previously been reported.

In this work, we report the free-radical initiated copolymerization/terpolymerization of ethylene, VAc and TCL to produce degradable PE or EVA (**Scheme 1**).

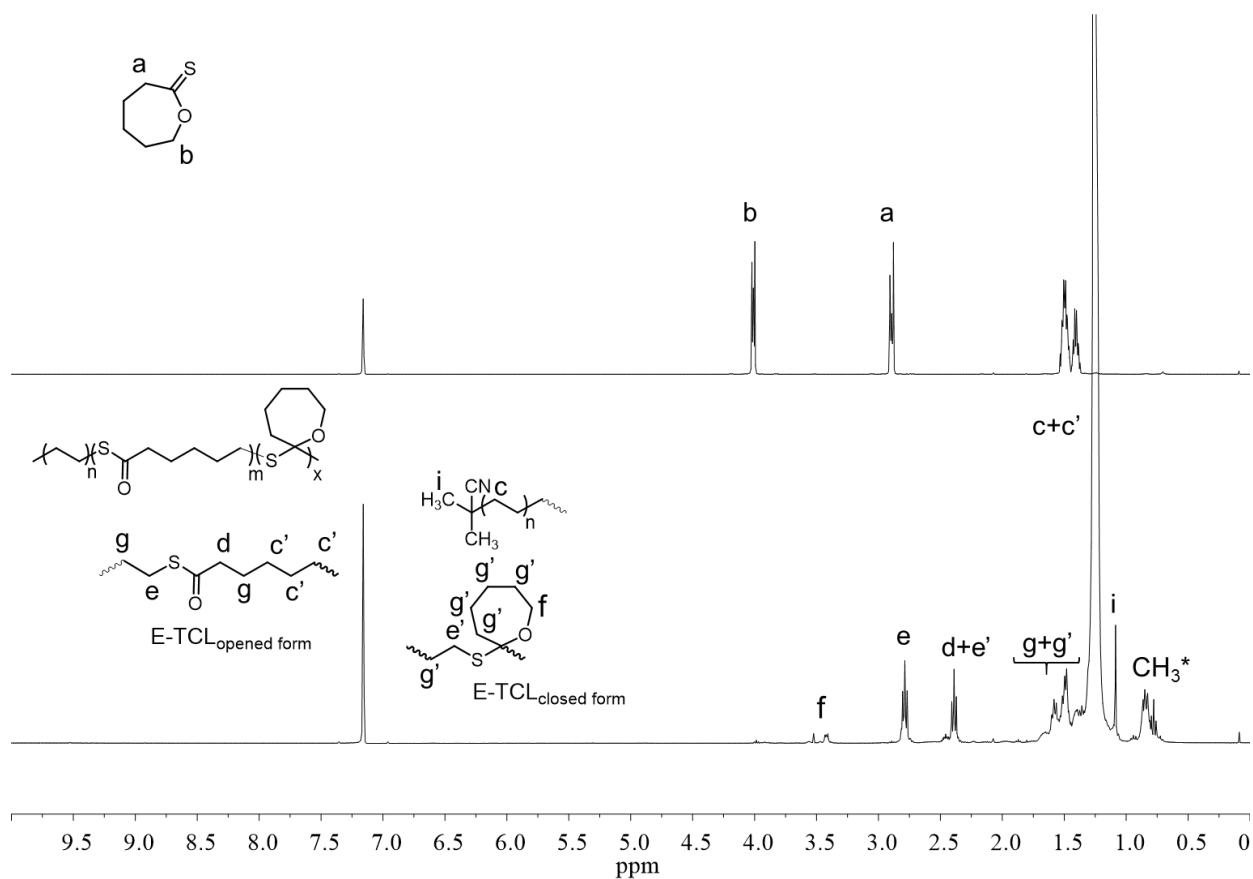


**Scheme 1.** Preparation of in-chain thioester PE and EVA. (AIBN: azobisisobutyronitrile, DMC: dimethylcarbonate)

## RESULTS AND DISCUSSION

### Copolymerization of Ethylene and TCL

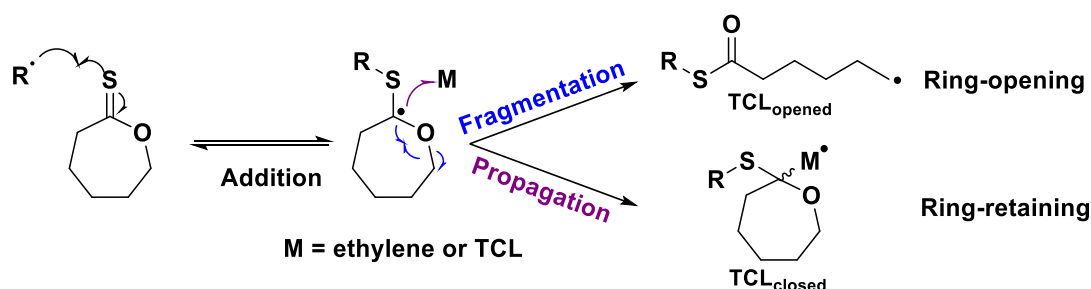
*Kinetic studies under batch conditions.* Copolymerizations were first carried out in dimethyl carbonate (DMC, 50 mL) as solvent in a 160 mL autoclave at 70 °C and 80 bar of ethylene in the presence of AIBN as initiator and TCL as presented in Table 1. The choice of these starting conditions was dictated by our previous works dealing with RDRP of ethylene<sup>[31]</sup> and the fact that DMC was shown to induce less transfer reaction than other candidates. The experiments were monitored by <sup>1</sup>H NMR spectroscopy analyses of the polymerization medium over 180 min, each experiment representing one polymerization time (Figure S1).



**Figure 1.**  $^1\text{H}$  NMR spectra of TCL ( $\text{C}_6\text{D}_6/\text{TCE}$ ,  $90^\circ\text{C}$ , top) and of the copolymer recovered from entry 4 of Table 1 (noted  $\text{poly}(\text{E}_{0.89}\text{-co-TCL}_{0.11})$  according its composition) ( $\text{C}_6\text{D}_6/\text{tetrachloroethylene}$  (TCE),  $90^\circ\text{C}$ , bottom, Table 1, entry 4); \* = methyl chain-end including branching.

TCL conversion was determined by  $^1\text{H}$  NMR by following the disappearance of the methylene protons of TCL at 3.9 ppm and 2.85 ppm (Figure 1, top) during polymerization (see calculation in SI). These protons were compared to the new signals appearing at 2.8, 2.4 and 3.5 ppm that were assigned to the opened-form ( $\text{SCH}_2$  and  $\text{CH}_2\text{-C=O}$ ) and closed-form ( $\text{OCH}_2$ ) of inserted TCL units<sup>[20]</sup> in the copolymer (Figure 1, bottom), respectively. The intense signal at 1.26 ppm is characteristic of the methylene protons of ethylene and TCL units in copolymer.

During rROP, after addition of a propagating radical to TCL, two mechanistic pathways are possible: fragmentation leading to the ring-opening or propagation leading to ring-retention (Scheme 2).



**Scheme 2.** Different mechanistic pathways during the TCL copolymerization leading to either ring-opening or ring-retention.<sup>[29]</sup>

In the literature, ring-retention was observed during the TCL copolymerization with vinyl esters.<sup>[29-30, 34a]</sup> In these works, the ratio  $TCL_{\text{closed}}/TCL_{\text{opened}}$  depends on both the overall monomer concentration and temperature. In bulk copolymerization with vinyl pivalate (VPi), the fraction of  $TCL_{\text{closed}}$  units decreases from 34% at 70°C to 15% at 100°C.<sup>[34a]</sup> Also, bulk copolymerization of  $TCL_{\text{closed}}$  units decreases from 34% at 70°C to 15% at 100°C.<sup>[34a]</sup> Also, bulk copolymerization of TCL with VAc leads to 35-45% of  $TCL_{\text{closed}}$  at 70°C<sup>[29]</sup> whereas in dilute solution exclusively ring-opening polymerization is observed.<sup>[30]</sup> The presence of some  $TCL_{\text{closed}}$  in copolymerization with ethylene, even though the polymerizations take place in dilute solution, may be explained by the lower steric bulk of ethylene compared to VAc, which facilitates its reaction with the ring-closed macroradical. We note that while ring-retention can be considered to be a side reaction, the resulting thioketal groups are also sensitive to oxidative hydrolysis and could contribute to the backbone degradation.<sup>[34]</sup>



In the remainder of the paper, TCL content refers to the total content of inserted TCL units including ring-closed and opened forms. The fraction of ring-closed units from the total TCL incorporated in the copolymer was also calculated using  $^1\text{H}$  NMR. They typically comprise 14-18% of the overall inserted TCL units (see SI and Figure S2-S3). The molar mass and dispersity of resulting copolymers were determined by SEC analyses. Due to their different solubilities, copolymers with TCL content of less than 11 mol% were analyzed by high temperature SEC (HT-SEC, trichlorobenzene eluent at 150 °C) whereas for the copolymers with higher TCL content, SEC-THF (THF eluent, 25°C) was preferred. Neither SEC analysis gives an absolute molar mass, making molar mass evaluation and comparison difficult. The molar mass of the copolymers is less than 5000 g mol<sup>-1</sup> with dispersities between 2.2 and 3.0 (Figures S4 and S5). After 30 minutes, 0.047 g of TCL has reacted (47% conversion) but only 0.023 g of ethylene had been incorporated into the copolymer (Table 1, entry 1). The mass of copolymer produced continued to increase after all the TCL had been consumed (105 min). This indicates a marked compositional drift and the formation of homopolyethylene once TCL has been consumed. Thus, although poly(E-co-TCL) appeared to form, the strong compositional drift observed would lead to chains with different degradability, including non-degradable PE chains. To avoid the formation of such non-degradable chains once TCL has been consumed, the polymerization would need to be stopped at a very early stage of the reaction, leading to a very limited yield of product.

**Table 1.** Kinetic studies under batch conditions of the copolymerization of ethylene and TCL<sup>[a]</sup>

The reaction scheme shows ethylene (CH<sub>2</sub>=CH<sub>2</sub>) reacting with a thiolane ring (a seven-membered ring containing one oxygen and one sulfur atom). The reaction conditions are AIBN, DMC, and 70°C. The products are copolymers consisting of ethylene units (represented by a zigzag line with two bonds extending from the vertices) and TCL units. The 'opened form' is a chain segment where the sulfur atom is part of a thioether linkage (-S-) and the oxygen atom is part of a carbonyl group (-C(=O)-). The 'closed form' is a chain segment where the sulfur atom is part of a thioether linkage (-S-) and the oxygen atom is part of a cyclic ether ring fused to the polymer backbone.

Entry	Time [min]	TCL conv. [b] [%]	Yield [c] [g]	TCL content <sup>[d]</sup> [mol %]	TCL <sup>closed</sup> <sup>[e]</sup> [%]	$M_n$ ( $\bar{D}$ ) [g mol <sup>-1</sup> ]
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1	30	47	0.07	30	14	2100(2.3) <sup>[f]</sup>
2	60	79	0.16	18	14	3000(2.2) <sup>[f]</sup>
3	90	94	0.21	15	18	3500(2.7) <sup>[f]</sup>
4	105	99	0.27	11	18	2600(3.0) <sup>[g]</sup>
5	120	100	0.39	7	18	3100(2.3) <sup>[g]</sup>
6	180	100	0.60	4	18	4300(2.6) <sup>[g]</sup>

[a] Reaction conditions: AIBN (50 mg, 0.3 mmol), at 70 °C and 80 bar ethylene in DMC (50 mL) with [TCL]:[ethylene]:[AIBN] = 3:1900:1; [b] TCL conversion was determined by <sup>1</sup>H-NMR of crude product, following equation S1; [c] yield of reaction was determined by the mass of copolymers observed after drying; [d] Determined by mass balance, following equation S2; [e] Determined by <sup>1</sup>H NMR, following equation S3; [f] Determined by SEC-THF, using polystyrene standards; [g] Determined by HT-SEC (150°C, trichlorobenzene), using a universal calibration corrected by Mark–Houwink–Sakurada coefficients with polystyrene standards.

*Semi-batch copolymerization of ethylene and TCL.* To compensate for the compositional drift, the copolymerization was conducted under semi-batch conditions with a constant feed of TCL. The polymerization conditions were similar to those previously described (80 bar of ethylene, AIBN, 70 °C in DMC) but TCL was fed continuously as a solution in DMC. The feed rate was varied from 0.04 to 0.2 mL min<sup>-1</sup> (Table 2). In all cases, the conversion of TCL was very high (> 90%), while decreasing the feed rate led to higher overall yields of copolymer of lower TCL content. For example, when the feed rate was decreased from 0.2 to 0.11 mL min<sup>-1</sup> (Table 2, entries 1-4), the yield of copolymer increased from 0.29 to 0.64 g while the TCL content dropped from 10 to 3.5 mol%. When the TCL was fed at very low rates (0.04 to 0.07 mL min<sup>-1</sup>, Table 2, entries 5-7), significant amounts of copolymers (1-2.5 g) were obtained, containing 1.0 to 2.2 mol% TCL. SEC analyses showed monomodal molar mass distributions (Figure S6) with number-average molar masses ( $M_n$ ) of up to 6600 g mol<sup>-1</sup> (for a feed rate of 0.04 mL min<sup>-1</sup>, Table 2, entry 7) and dispersities ( $D$ ) around 2.

**Table 2.** Semi-batch copolymerization of ethylene and TCL<sup>[a]</sup>

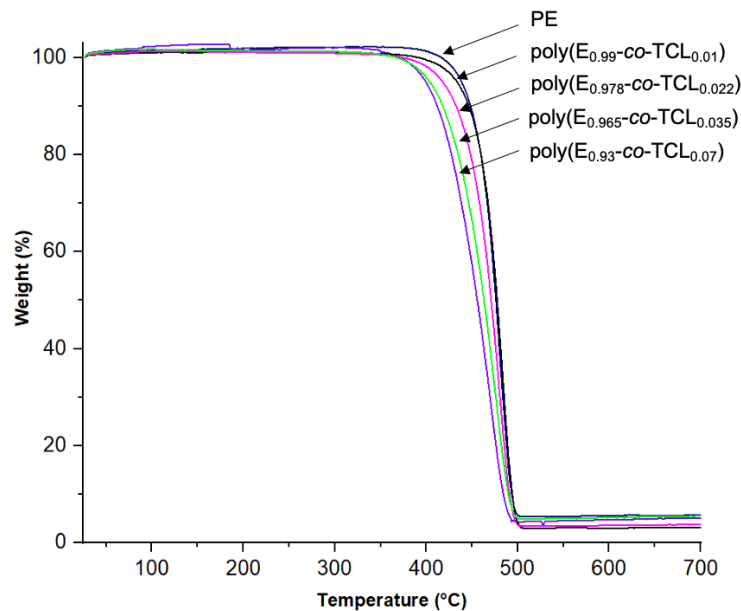
Entry	Overall of TCL [mg]	mass	Feed rate [mL min <sup>-1</sup> ]	Time [min]	TCL conversion [b] [%]	Yield [c] [g]	TCL content[d] [mol %]	TCL <sub>closed</sub> [e] [%]	M <sub>n</sub> [f] [g mol <sup>-1</sup> ]	Đ [f]
1	100		0.2	100	98	0.29	10	19	3600	1.9
2	100		0.16	135	98	0.37	7	18	3800	1.8
3	100		0.13	154	98	0.43	6	20	3600	2.2
4	100		0.11	180	92	0.64	3.5	19	3100	2.3
5	100		0.07	270	96	0.97	2.2	18	6000	1.6
6	100		0.05	400	97	1.5	1.5	13	5900	2.1
7	100		0.04	480	90	2.0	1.0	35	6600	2.5
8	0		-	270	-	1.05	-	-	9100	1.8
9	200		0.07	270	99	0.79	7	18	4300	1.9

[a] Reaction conditions: AIBN (50 mg, 0.3 mmol), at 70 °C and 80 bar Ethylene in DMC (50 mL) with [TCL]:[ethylene]:[AIBN] = 3:1900:1; [b] Determined by <sup>1</sup>H NMR of crude product, following equation S1; [c] Determined by the mass of copolymers observed after drying under vacuum (50° C, 0,1 mbar, 5 h); [d] Determined by mass balance, following equation S2; [e] Determined by <sup>1</sup>H-NMR of copolymer, following equation S3; [f] Determined by HT-SEC (150°C, trichlorobenzene), using a universal calibration corrected by Mark–Houwink–Sakurada coefficients with polystyrene standards

The homopolymerization of ethylene was also conducted at the same temperature and pressure but without a TCL feed and gave 1.05 g of PE with M<sub>n</sub> around 9100 g mol<sup>-1</sup> with Đ of 1.8 (Table 2, entry 8). A slight retardation was observed for semi-batch copolymerizations conducted over 4.5 hours (Table 2, entry 5 and 9), since 0.97 g and 0.79 g of poly(E-co-TCL) were obtained in those cases. Besides, the molar masses of these copolymers were lower than that of the PE. These results suggest that additional side reactions such as transfer and/or termination induced by the presence of TCL monomer or inserted TCL unit in the chains take place. Indeed, Plummer et al. reported that during copolymerization of TCL with VAc, intermolecular or intramolecular transfer reactions could occur by abstraction of hydrogen atoms from the methylene adjacent to the sulfur of the thioester function functions.<sup>[30]</sup> Extensive NMR characterization by <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT-135 and <sup>1</sup>H/<sup>13</sup>C HSQC NMR (see SI Figures S7-11) performed on poly(E<sub>0.93</sub>-co-TCL<sub>0.07</sub>)

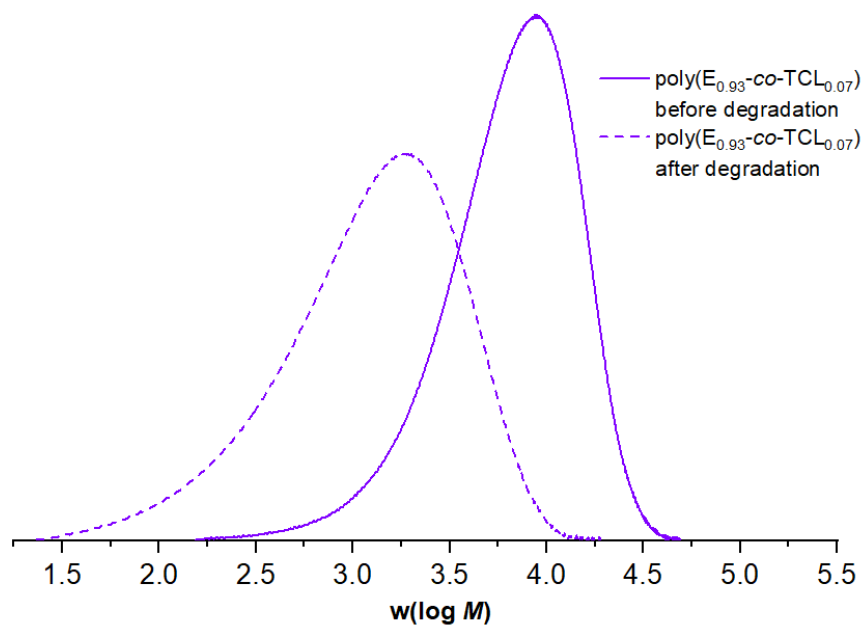
(Table 2, entry 2) revealed that in our case branching takes place on the methylene adjacent to the carbonyl of the thioester. Increasing the TCL feed from 100 to 200 mg produced a 0.79 g of copolymer (c.f. 0.97 at 100 mg of TCL) with similar molar mass, but containing 7% of TCL units (c.f. 2.2 at 100 mg TCL). Finally, a range of poly(E-co-TCL) copolymers were synthesized with a number-average molar masses of 3100-6600 g mol<sup>-1</sup> and TCL contents of 1 to 7 mol% (Figure S6). For the rest of the study, a copolymer containing x mol% of TCL inserted unit will be labelled poly(E<sub>1-x/100</sub>-co-TCL<sub>x/100</sub>).

*Thermal properties and thermal stability of poly(E-co-TCL).* A comparison of the properties of the copolymers obtained with, example given, a commercial LDPE would not be appropriate. The latter is obtained by gas phase radical polymerization performed at much higher pressure and temperature and its structure cannot be compared with the solution process employed here. Nevertheless, DSC and TGA analyses were performed on a PE (Table 2, entry 8) and on different poly(E-co-TCL) (Table 2, entries 4-5, 7, 9) obtained under our polymerization conditions. As expected, when the TCL content increased in the copolymers, the melting temperature (T<sub>m</sub>) and the crystallization temperature (T<sub>c</sub>) decreased from 110 to 90°C which are similar to those of PE (Figure S12). More importantly, thermal decomposition profiles obtained by TGA were very similar (420-460°C) between the different poly(E-co-TCL) copolymers and PE (**Figure 2**). Although a slight shift towards lower temperatures was observed when TCL content increased, these results indicate that the incorporation of up to 7 mol% (28 wt%) TCL has a minor effect on the physical properties of the copolymer.



**Figure 2.** TGA curves of poly(E-co-TCL) containing 1-7 mol% TCL content, PE obtained under similar conditions.

*Chemical degradation studies.* Poly(E<sub>0.93</sub>-co-TCL<sub>0.07</sub>) from entry 9 in Table 2 ( $M_n$  of 4300 g mol<sup>-1</sup>) was chosen as a model substrate. As previously reported,<sup>[23-26]</sup> copolymers containing thioester functions can be degraded by aminolysis. The degradation of poly(E<sub>0.93</sub>-co-TCL<sub>0.07</sub>) was investigated using an excess of allyl amine (400 equiv.) in toluene at 90°C for 24 hours. The degradation was followed by comparing the molar mass distributions of the copolymer before and after treatment (**Figure 3**).



**Figure 3.** Molar mass distributions of poly( $E_{0.93}$ -co-TCL $_{0.07}$ ) and its degradation products after treatment with allylamine.

Following aminolysis, the  $M_n$  of the copolymer decreased from 4300 to 630 g mol $^{-1}$ . This decrease in  $M_n$  is consistent with the TCL content.<sup>[29]</sup> However, due to the difficulty of obtaining accurate molar masses for PE samples, it would be unwise to draw any firm conclusions from these results. It is also worth mentioning that the small amount of thioketal closed form (see Figure S14) does not degrade under the conditions employed.<sup>[34a]</sup>

A PE obtained under the same conditions (Table 2, entry 8) was unaffected by aminolysis (Figure S13). After purification, the fragments were analyzed by  $^1\text{H}$  NMR and compared to the starting allyl amine and poly( $E_{0.93}$ -co-TCL $_{0.07}$ ) (Figure S14). The characteristic resonances of inserted TCL disappeared and new resonances were observed at 5.7 (CH), 5.0 (CH $_2$ ) and 3.6 (CH $_2$ ) ppm in the degraded polymer, confirming the presence of allyl moiety. In addition, a triplet

appearing at 1.8 ppm corresponding to  $\text{CH}_2\text{-CONH}$ , and a broad singlet at 4.7 ( $\text{CH}_2\text{-CONH}$ ) ppm reveal the presence of allyl amide as a chain-end. On the other chain-end, an expected triplet at 1.0 ppm, due to the formation of a thiol<sup>[35]</sup> is not observed. However, the unassigned triplet at 2.6 ppm may be due to methylenes adjacent to a disulfide group<sup>[35]</sup> that could form upon thiol coupling.<sup>[26]</sup>

The degradation studies were then extended to a series of copolymers containing different TCL contents (Table 3). In all cases, aminolysis led to a reduction of the molar mass of the copolymers (Figures S15-S16).

**Table 3.** Degradation of copolymers through aminolysis<sup>[a]</sup>

poly(E-co-TCL)  
0-7 mol% thioester in-chain

Entry	Copolymer	Before degradation	After degradation
		$M_n$ (g mol <sup>-1</sup> ) / ( $\mathcal{D}$ ) <sup>[b]</sup>	$M_n$ (g mol <sup>-1</sup> ) / ( $\mathcal{D}$ ) <sup>[b]</sup>
1	PE	9100 / 1.8	9100 / 1.9
2	P(E <sub>0.99</sub> -CO-TCL <sub>0.01</sub> )	6600 / 2.5	3100 / 2.7
3	P(E <sub>0.985</sub> -CO-TCL <sub>0.015</sub> )	5900 / 2.1	2200 / 2.7
4	P(E <sub>0.978</sub> -CO-TCL <sub>0.022</sub> )	6000 / 1.6	1500 / 2.5
5	P(E <sub>0.965</sub> -CO-TCL <sub>0.035</sub> )	3100 / 2.3	1100 / 2.3
6	P(E <sub>0.94</sub> -CO-TCL <sub>0.06</sub> )	3600 / 2.2	750 / 2.4
7	P(E <sub>0.93</sub> -CO-TCL <sub>0.07</sub> )	4300 / 1.8	630 / 3.0

<sup>[a]</sup> Degradation conditions: copolymer (50 mg), allylamine (2 mL, 400 equiv.), toluene (3 mL) at 90 °C for 24 hours;<sup>[b]</sup> Determined by HT-SEC (150°C, trichlorobenzene), using a universal calibration corrected by Mark–Houwink–Sakurada coefficients with polystyrene standards.

### Towards degradable EVAs: terpolymerization of ethylene, VAc, and TCL

Building on the results obtained in the case of the copolymerization of ethylene and TCL, the terpolymerization of ethylene, VAc and TCL was investigated under semi-batch conditions (Table

4). The feed rate of TCL solution in DMC was varied from 0.06 to 0.25 mL min<sup>-1</sup> (Table 4, entries 1-4). As observed in copolymerization of ethylene and TCL, the conversion of TCL was very high (> 91%, (see SI for calculation), Figure S17) and decreasing the feed rate led to higher yields of polymers with lower TCL contents. SEC analyses of poly(E-co-VAc-co-TCL) systematically provided monomodal molar mass distributions (Figure S18) with  $M_n$  ranging from 12 to 29 kg mol<sup>-1</sup>. A copolymer of ethylene and VAc obtained under the same conditions in absence of TCL feed (Table 4, entry 5) had an  $M_n$  of 34 kg mol<sup>-1</sup> ( $D = 1.6$ ). The decrease of the molar mass observed on increasing incorporation of TCL again suggests TCL-induced transfer and/or termination reactions.

The terpolymers were analyzed by <sup>1</sup>H NMR (Figures S17, S18-20). As for the P(E-co-TCL) copolymers, the new triplets appearing at 2.8 and 2.5 ppm were assigned to the signal of the opened-form of TCL inserted unit while a broad peak at 3.5 ppm was assigned to the closed-form. Resonances due to VAc units ((-CH<sub>2</sub>-CH)-O(C=O)CH<sub>3</sub>) at 4.8 ppm and ((-CH<sub>2</sub>-CH)-O(C=O)CH<sub>3</sub>) at 2.1 ppm) and E units ((-CH<sub>2</sub>-CH<sub>2</sub>)- at 1.26 ppm confirmed the formation of the targeted terpolymers. No signal was found between 6 and 7 ppm that could be assigned to the CH of a VAc inserted unit adjacent to a S atom.<sup>[29]</sup> Thus, it appears that propagating macroradicals carrying a terminal VAc unit react selectively with ethylene. The TCL content in the chains was quantified by <sup>1</sup>H NMR analyses (see SI for calculation). As observed for poly(E-co-TCL) copolymers, the decrease in the TCL feed rate led to a decrease of the TCL content in the polymer backbone (from 6 to 0.9 mol%) while the VAc content was similar in all cases (12-18 mol%).

**Table 4.** Semi-batch terpolymerization of ethylene, VAc and TCL<sup>[a]</sup>

Entry	Rate of feeding [mL min <sup>-1</sup> ]	Time [min]	TCL conv. <sup>[b]</sup> [%]	Yield <sup>[c]</sup> [g]	TCL content <sup>[d]</sup> [mol %]	TCL <sub>closed</sub> <sup>[e]</sup> [%]	$M_n$ <sup>[f]</sup> [g mol <sup>-1</sup> ]	$D$ <sup>[f]</sup>	VAc content <sup>[g]</sup> [mol %]
1	0.25	80	91	0.38	6.0	28	12000	2.2	12.9



2	0.2	105	100	0.51	3.3	29	15500	2.1	12.0
3	0.1	210	100	2.5	1.3	28	23000	2.4	16.6
4	0.06	310	100	4.3	0.9	28	29000	2.5	18.0
5 <sup>h</sup>	-	210	-	2.7	-	-	34000	1.6	15

[a] VAc (10 mL), TCL (100 mg), AIBN (50 mg, 0.3 mmol), at 70 °C and 80 bar in DMC (50 mL) with [TCL]:[ethylene]:[AIBN] = 3:1900:1; [b] Determined by <sup>1</sup>H NMR of crude product, following equation S4; [c] Determined by the mass of terpolymer observed after drying under vacuum (50°C, 0,1 mbar, 5 h); [d] Determined by <sup>1</sup>H NMR, following equation S5; [e] Determined by <sup>1</sup>H NMR of terpolymer, following equation S7; [f] Determined by SEC-THF, using polystyrene as standards; [g] Determined by <sup>1</sup>H NMR of terpolymer, following equation S6; [h] no TCL was used.

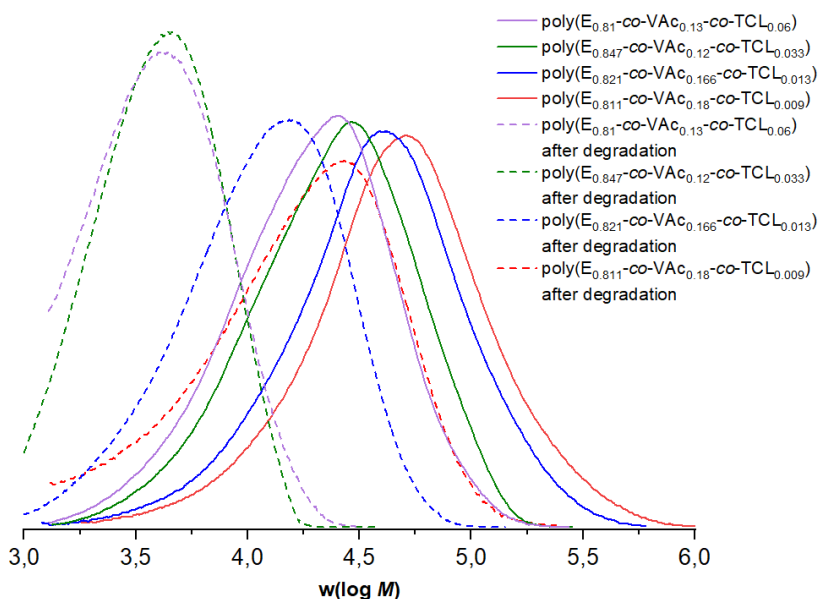
*Thermal properties of poly(E-co-VAc-co-TCL).* The obtained samples were analyzed by DSC (Table 5). As expected, the melting temperature is decreasing with the incorporation of TCL. Nevertheless, as both ethylene and VAc contents are changing for samples having different contents of TCL this is difficult to draw a tendency, particularly on the decrease of T<sub>g</sub> observed.

**Table 5.** DSC analyses of poly(E-co-VAc-co-TCL)

Entry	Terpolymer	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)
1	Poly(E <sub>0.85</sub> -co-VAc <sub>0.15</sub> )	-35.6	48.2
2	Poly(E <sub>0.811</sub> -co-VAc <sub>0.18</sub> -co-TCL <sub>0.009</sub> )	-36.2	38.1
3	Poly(E <sub>0.821</sub> -co-VAc <sub>0.166</sub> -co-TCL <sub>0.013</sub> )	-36.7	39.1
4	Poly(E <sub>0.847</sub> -co-VAc <sub>0.12</sub> -co-TCL <sub>0.033</sub> )	-42.0	35.3
5	Poly(E <sub>0.81</sub> -co-VAc <sub>0.13</sub> -co-TCL <sub>0.06</sub> )	-44.1	29.6

*Chemical degradation studies of poly(E-co-VAc-co-TCL).* The terpolymers were treated with a solution of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) in THF (2.5 wt%), following a protocol reported by Guillaneuf *et al.* for copolymers based of VAc and TCL.<sup>[30,36]</sup> These degradation conditions revealed to be more efficient and leading to an easier recovery of the degraded chains than when allylamine was used (see SI) as previously employed for the copolymers. A poly(E-co-

VAc) obtained under similar conditions (Table 6, entry 1) was subjected to the same treatment, with no effect on its molar mass distribution (Figure 4).



**Figure 4.** Molar mass distribution of poly(E-co-VAc-co-TCL) (entries 1-4, Table 4, solid lines) and their corresponding degradations after treatment with TBD (dashed lines).

The terpolymers, however, significantly decreased in molar mass in all cases ( $M_n$  between 2900 and 10000  $\text{g mol}^{-1}$ , Table 6, entries 2-5, Figure S18) confirming the incorporation of degradable TCL units.

**Table 6.** TBD-assisted chemical degradation of poly(E-co-VAc-co-TCL)<sup>[a]</sup>

Entry	Terpolymer	Before degradation	After degradation
		$M_n$ ( $\mathcal{D}$ ) <sup>[b]</sup> [ $\text{g mol}^{-1}$ ]	$M_n$ ( $\mathcal{D}$ ) <sup>[b]</sup> [ $\text{g mol}^{-1}$ ]
1	Poly(E <sub>0.85</sub> -co-VAc <sub>0.15</sub> )	34000(1.6)	33000(1.9)
2	Poly(E <sub>0.811</sub> -co-VAc <sub>0.18</sub> -co-TCL <sub>0.009</sub> )	29000(2.4)	10000(2.4)
3	Poly(E <sub>0.821</sub> -co-VAc <sub>0.166</sub> -co-TCL <sub>0.013</sub> )	23000(2.4)	7300(2.2)
4	Poly(E <sub>0.847</sub> -co-VAc <sub>0.12</sub> -co-TCL <sub>0.033</sub> )	15500(2.1)	3400(1.6)

5	Poly(E <sub>0.81</sub> -co-VAc <sub>0.13</sub> -co-TCL <sub>0.06</sub> )	11900(2.2)	2900(1.4)
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<sup>[a]</sup> Degradation conditions: terpolymer (50 mg), TBD (1 mL, 2.5wt% in THF), THF (1 mL) at 50 °C for 1 hour; <sup>[b]</sup> Determined by SEC-THF (25°C), using polystyrene standards.

## CONCLUSION

Radical copolymerization of ethylene and TCL allows thioester functions to be incorporated into polyethylene backbones. A semi-batch approach consisting of feeding TCL during the polymerization gave the most homogeneous incorporation of TCL and the highest overall yield of copolymer. Depending on the TCL feed rate, poly(E-co-TCL) containing from 1 to 7 mol% of TCL was obtained. Poly(E-co-TCL) retains the main physical properties of LDPE (*e.g.*  $T_m$  and  $T_c$ , thermal stability up to 450°C) and can be degraded by chemical treatment with allyl amine. The terpolymerization of ethylene, VAc and TCL also provides a wide range of poly(E-co-VAc-co-TCL) terpolymers under semi-batch conditions. TBD-assisted chemical degradation led to selective cleavage of thioester linkages as attested by comparison of experimental  $M_n$  values of degradation products and the TCL content of starting terpolymers. The incorporation of thioesters by radical copolymerization of thionolactones allows the production of chemically degradable analogues of PE or EVA.

**Supporting Information.** Experimental section, Calculation of TCL conversion, overall TCL content in the copolymers and proportion of TCL-closed form among inserted TCL units, Degradation experiments of poly(E-co-TCL), Calculation of TCL conversion, overall TCL and VAc contents in poly(E-co-VAc-co-TCL) terpolymer and proportion of TCL-closed form among inserted TCL units, Degradation experiments of poly(E-co-VAc-co-TCL) terpolymers, additional

data.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## REFERENCES

[1] Scholten, P. B. V.; Cartigny G.; Grignard B.; Debuigne A.; Cramail H.; Meier M. A. R.; Detrembleur C. Functional Polyethylenes by Organometallic-Mediated Radical Polymerization of Biobased Carbonates. *ACS Macro Lett.* **2021**, *10*, 313-320.

- [2] Geyer R.; Jambeck J. R.; Law K. L. Production, Use, and Fate of All Plastics Ever Made. *Sci. Adv.* **2017**, *3*, e1700782.
- [3] Stürzel M.; Mihan S.; Mülhaupt R. From Multisite Polymerization Catalysis to Sustainable Materials and All-Polyolefin Composites. *Chem. Rev.* **2016**, *116*, 1398-1433.
- [4] Garcia J. M.; Robertson M. L. The Future of Plastics Recycling. *Science* **2017**, *358*, 870-872.
- [5] Brubaker M. M.; Coffman D. D.; Hoehn H. H. Synthesis and Characterization of Ethylene/Carbon Monoxide Copolymers, A New Class of Polyketones. *J. Am. Chem. Soc.* **1952**, *74*, 1509-1515.
- [6] Stempfle F.; Ortmann P.; Mecking S. Long-Chain Aliphatic Polymers To Bridge the Gap between Semicrystalline Polyolefins and Traditional Polycondensates. *Chem Rev.* **2016**, *116* (7), 4597-4641.
- [7] Baur M.; Lin F.; Morgen T. O.; Odenwald L.; Mecking S. Polyethylene Materials with In-Chain Ketones From Non-Alternating Catalytic Copolymerization. *Science* **2021**, *374*, 604-607.
- [8] Tang S.; Seidel F. W.; Nozaki K. High Density Polyethylenes Bearing Isolated In-Chain Carbonyls. *Angew. Chem. Int. Ed.* **2021**, *60*, 26506-26510.
- [9] Morgen T. O.; Baur M.; Göttker-Schnetmann I.; Mecking S. Photodegradable Branched Polyethylenes from Carbon Monoxide Copolymerization Under Benign Conditions. *Nat. Commun.* **2020**, *11*, 3693-3699.
- [10] Fuchs A.; Mecking S. Controlled Cobalt-Mediated Free-Radical Co- and Terpolymerization of Carbon Monoxide. *J. Am. Chem. Soc.* **2022**, *144* (34), 15879–15884.

[11] Baur M.; Mast N. K.; Brahm J. P.; Habé R.; Morgen T. O.; Mecking S. High-Density Polyethylene with In-Chain Photolyzable and Hydrolyzable Groups Enabling Recycling and Degradation. *Angew. Chem.Int. Ed.* **2023**, *62*, e202310990.

[12] Johnson A. M.; Johnson J. A. Thermally Robust yet Deconstructable and Chemically Recyclable High-Density Polyethylene (HDPE)-Like Materials Based on Si–O Bonds. *Angew. Chem. Int. Ed.* **2023**, *62*, e202315085.

[13] Lefay C.; Guillaneuf Y. Recyclable/Degradable Materials via the Insertion of Labile/Cleavable Bonds Using a Comonomer Approach. *Prog. Polym. Sci.* **2023**, *147*, 101764.

[14] Tardy A.; Nicolas J.; Gigmes D.; Lefay C.; Guillaneuf Y. Radical Ring-Opening Polymerization: Scope, Limitations, and Application to (Bio)Degradable Materials. *Chem. Rev.* **2017**, *117* (3), 1319–1406.

[15] Bailey W. J.; Ni Z.; Wu S.-R. Synthesis of Poly- $\epsilon$ -caprolactone Via a Free Radical Mechanism. Free Radical Ring-Opening Polymerization of 2-Methylene-1,3-dioxepane. *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 3021-3030.

[16] Bailey W. J.; Gapud B. Synthesis of Biodegradable Polyethylene. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1984**, *27*(1), 58-59.

[17] Wu B.; Lenz R. W. Synthesis, Characterization, and Hydrolytic Degradation of Copolymers of 2-Methylene-1,3-dioxepane with Ethylene and with Styrene. *J. Polym. Environ.* **1998**, *6*, 23-29.

[18] Zeng T.; You W.; Chen G.; Nie X.; Zhang Z.; Xia L.; Hong C.; Chen C.; You Y. -Z. Degradable PE-Based Copolymer with Controlled Ester Structure Incorporation by Cobalt-Mediated Radical Copolymerization under Mild Condition. *iScience* **2020**, *23*, 100904.

[19] Zeng T.-Y.; Xia L.; Zhang Z.; Hong C.-Y.; You Y.-Z. Dithiocarbamate-mediated Controlled Copolymerization of Ethylene with Cyclic Ketene Acetals Towards Polyethylene-Based Degradable Copolymers *Polym. Chem.* **2021**, *12*, 165-171.

[20] a) Agarwal S. Chemistry, Chances and Limitations of the Radical Ring-Opening Polymerization of Cyclic Keteneacetals for the Synthesis of Degradable Polyesters. *Polym. Chem.* **2010**, *1*, 953–964; b) Pesenti T.; Nicolas J. 100th Anniversary of Macromolecular Science Viewpoint: Degradable Polymers from Radical Ring-Opening Polymerization: Latest Advances, New Directions, and Ongoing Challenges. *ACS Macro Lett.* **2020**, *9*, 1812–1835.

[21] Carter M. C. D.; Hejl A.; Woodfin S.; Einsla B.; Janco M.; DeFelippis J.; Cooper R. J.; Even R. C. Backbone-Degradable Vinyl Acetate Latex: Coatings for Single-Use Paper Products. *ACS Macro Lett.* **2021**, *10* (5), 591–597.

[22] Bingham N. M.; Roth P. J. Degradable Vinyl Copolymers Through Thiocarbonyl Addition–Ring-Opening (TARO) Polymerization. *Chem. Commun.* **2019**, *55*, 55-58.

[23] Smith R. A.; Fu G.; McAteer O.; Xu M.; Gutekunst W. R. Radical Approach to Thioester-Containing Polymers. *J. Am. Chem. Soc.* **2019**, *141*, 1446-1451.

[24] Bingham N. M.; Qamar un Nisa Q.; Chua S. H. L.; Fontugne L.; Spick M. P.; Roth P. J. Thioester-Functional Polyacrylamides: Rapid Selective Backbone Degradation Triggers Solubility

Switch Based on Aqueous Lower Critical Solution Temperature/Upper Critical Solution Temperature. *ACS Appl. Polym. Mater.* **2020**, *2*, 3440–3449.

[25] Galanopoulo P.; Gil N.; Gignes D.; Lefay C.; Guillaneuf Y.; Lages M.; Nicolas J.; Lansalot M.; D'Agosto F. One-Step Synthesis of Degradable Vinyllic Polymer-Based Latexes via Aqueous Radical Emulsion Polymerization. *Angew. Chem. Int. Ed.* **2022**, *61*, e202117498.

[26] Kiel G. R.; Lundberg D. J.; Prince E.; Husted K. E. L.; Johnson A. M.; Lensch V.; Li S.; Shieh P.; Johnson J. A. Cleavable Comonomers for Chemically Recyclable Polystyrene: A General Approach to Vinyl Polymer Circularity. *J. Am. Chem. Soc.* **2022**, *144*, 12979–12988.

[27] Rix M.; Collins K.; Higgs S.; Dodd E.; Coles S.; Bingham N. M.; Roth P. J. Insertion of Degradable Thioester Linkages into Styrene and Methacrylate Polymers. *Macromolecules* **2023**, *56*, 9787–9795.

[28] Spick M. P.; Bingham N. M.; Li Y.; de Jesus J.; Costa C.; Bailey M. J.; Roth P. J. Degradable Linear and Bottlebrush Thioester-Functional Copolymers through Atom-Transfer Radical Ring-Opening Copolymerization of a Thionolactone. *Macromolecules* **2020**, *53*, 539–547.

[29] Ivanchenko O.; Authesserre U.; Coste G.; Mazières S.; Destarac M.; Harrisson S.  $\epsilon$ -Thionocaprolactone: an Accessible Monomer for Preparation of Degradable Poly(vinyl esters) by Radical Ring-Opening Polymerization. *Polym. Chem.*, **2021**, *12*, 1931–1938.

[30] Plummer C. M.; Gil N.; Dufils P.-E.; Wilson D. J.; Lefay C.; Gignes D.; Guillaneuf Y. Mechanistic Investigation of  $\epsilon$ -Thiono-Caprolactone Radical Polymerization: An Interesting Tool to Insert Weak Bonds into Poly(vinyl esters). *ACS Appl. Polym. Mater.* **2021**, *3*, 3264–3271.



[31] a) Dommangeat C.; D'Agosto F.; Monteil V. Polymerization of Ethylene through Reversible Addition–Fragmentation Chain Transfer (RAFT). *Angew. Chem. Int. Ed.* **2014**, *53*, 6683-6686.; b) Nakamura Y.; Ebeling B.; Wolpers A.; Monteil V.; D'Agosto F.; Yamago S. Controlled Radical Polymerization of Ethylene Using Organotellurium Compounds. *Angew. Chem. Int. Ed.* **2018**, *57*, 305-309.; c) Wolpers A.; Bergerbit C.; Ebeling B.; D'Agosto F.; Monteil V. Aromatic Xanthates and Dithiocarbamates for the Polymerization of Ethylene through Reversible Addition–Fragmentation Chain Transfer (RAFT). *Angew. Chem. Int. Ed.* **2019**, *58*, 14295-14302.

[32] Ehrlich P.; Mortimer G. A. Fundamentals of the Free Radical Polymerization of Ethylene. *Adv. Polym. Sci.* **1970**, 386-448.

[33] Kissin Y.V., Olefin Polymers. Polyethylene. In Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed.; Howe-Grant, M., Ed.; John Wiley & Sons, Inc.: New York, **1996**, Vol. *17*, 702–784.

[34] a) Ivanchenko O.; Mazières S.; Harrisson S.; Destarac M. On-Demand Degradation of Thioester/Thioacetal Functions in Vinyl Pivalate-Derived Copolymers with Thionolactones. *Macromolecules* **2023**, *56*, 4163–4171.; b) Uchiyama M.; Murakami Y.; Satoh K.; Kamigaito M. Synthesis and Degradation of Vinyl Polymers with Evenly Distributed Thioacetal Bonds in Main Chains: Cationic DT Copolymerization of Vinyl Ethers and Cyclic Thioacetals. *Angew. Chem. Int. Ed.* **2023**, *62*, e202215021.

[35] Mazzolini F.; Mokthari I.; Briquel R.; Boyron O.; Delolme F.; Monteil V.; Bertin D.; Gignes D.; D'Agosto F.; Boisson C. Thiol-End-Functionalized Polyethylenes. *Macromolecules* **2010**, *43*, 7495-7503.

[36] Gil N.; Caron B.; Siri D.; Roche J.; Hadiouch S.; Khedaioui D.; Ranque S.; Cassagne C.; Montarnal D.; Gimes D.; Lefay C.; Guillaneuf Y. Degradable Polystyrene via the Cleavable Comonomer Approach. *Macromolecules* **2022**, *55* (15), 6680–6694.