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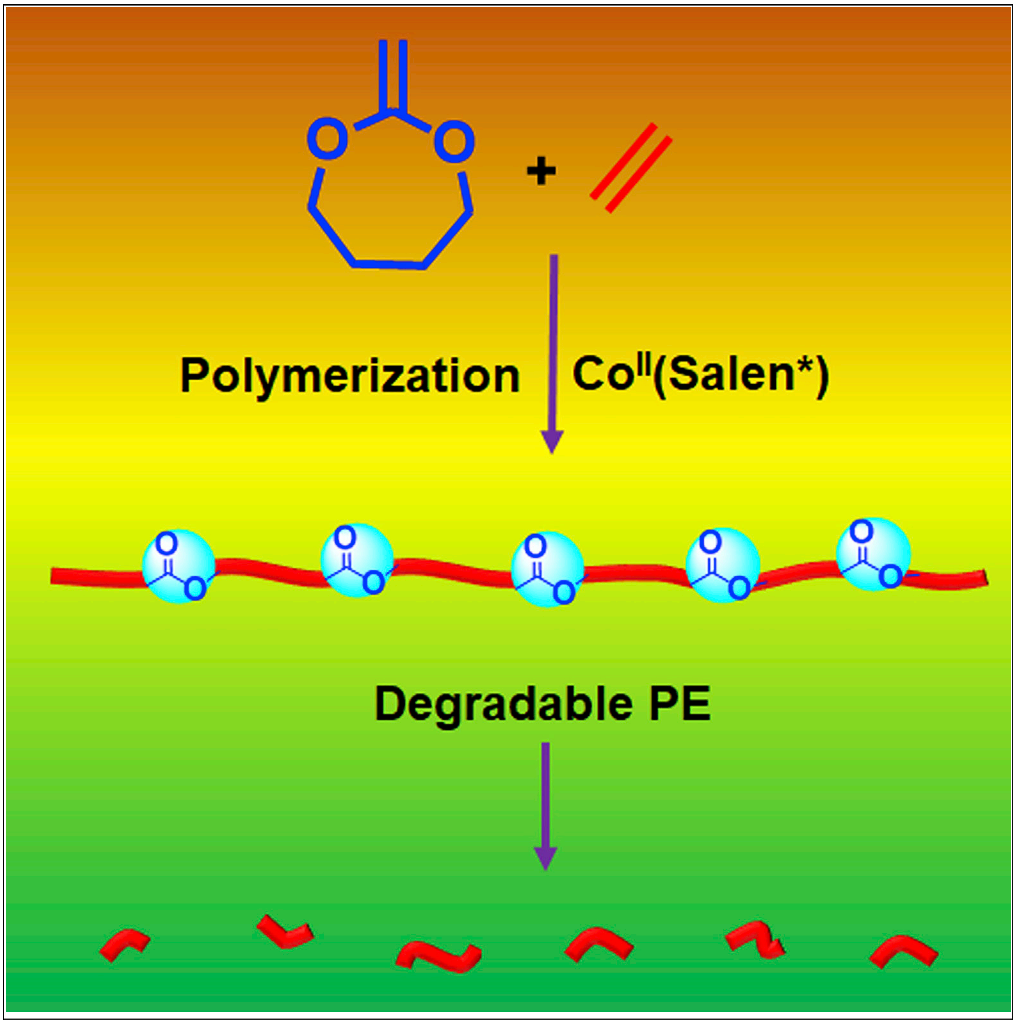

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HIGHLIGHTS

We report cobalt-mediated copolymerization for inserting ester unit into PE backbone

The molecular weight of degraded product varied from several hundreds to thousands

This method provides access to a diverse range of degradable functional PE materials

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Degradable PE-Based Copolymer with Controlled Ester Structure Incorporation by Cobalt-Mediated Radical Copolymerization under Mild Condition

Tianyou Zeng,[1] Wei You,[2] Guang Chen,[1] Xuan Nie,[1] Ze Zhang,[1,*] Lei Xia,[1] Chunyan Hong,[1,*] Changle Chen,[1,*] and Yezi You[1,3,*]

SUMMARY

Polyethylene (PE) is one of the most widely used materials in the world, but it is virtually undegradable and quickly accumulates in nature, which may contaminate the environment. We utilized the cobalt-mediated radical copolymerization (CMRP) of ethylene and cyclic ketene acetals (CKAs) to effectively incorporate ester groups into PE backbone as cleavable structures to make PE-based copolymer degradable under mild conditions. The content of ethylene and ester units in the produced copolymer could be finely regulated by CKA concentration or ethylene pressure. Also, the copolymerization of ethylene and CKA with other functional vinyl monomers can produce functional and degradable PE-based copolymer. All the formed PE-based copolymers could degrade in the presence of trimethylamine (Et_3N).

INTRODUCTION

Polyethylene (PE) is vital to our society, affecting practically every aspect of modern life because it has so many advantages such as high strength, resistance to corrosion, low weight, and longevity (Eagan et al., 2017; Gao et al., 2019; Kermagoret et al., 2014; Klein and Briscoe, 1977). The longevity of plastics is one of their major advantages, but today it is also considered to be one of their great disadvantages (Author Anonymous, 2018; Devanand and Selser, 1990; Jambeck et al., 2015). Large amounts of these materials were used only once and then discarded, they hardly decomposed and could stay in environment for many years, which has caused a considerable part of wastes accumulating in nature and affecting both terrestrial and marine ecosystems (Author Anonymous, 2018; Lebreton et al., 2017). Now plastic wastes in natural environment have gained global attention (Cózar et al., 2017; Geyer et al., 2017; Haider et al., 2019b). Therefore, the synthesis of degradable PE-based copolymer that is kind to environment is a major goal of chemists. Ideally, introducing cleavable structures into the main chain of PE could make PE degradable (Tardy et al., 2017a, 2017b). In 1980s, the copolymerizations of ethylene and carbon monoxide or vinyl ketone monomers have been employed to introduce carbonyl groups into the copolymer. The carbonyl group could undergo Norrish I and Norrish II photochemical reactions to cause chain scission (Ammala et al., 2011; Modi and Guillet, 1995; Scoponi et al., 1993). However, the incorporation of carbonyl group was very limited. Bailey et al. reported that the radical ring-opening polymerization of cyclic ketene acetals (CKAs) could yield polymers containing the same repeating unit as polylactones (Bailey and Gapud, 1984; Bailey et al., 1982); the ester units could degrade in the presence enzyme or base. The free radical copolymerization of ethylene and 2-methylene-1, 3-dioxepane (MDO) was also reported (Wu and Lenz, 1998); the copolymer with low molecular weight (M_n) was obtained, and the ester units distribution in the copolymer was essentially uniform and random. Recently, polyester formation from long-chain α, ω-diacids/diols, acyclic diene metathesis (ADMET) copolymerizations of dienes and nonfunctionalized α, ω-dienes with ester groups have also been reported. These routes provide access to PE-like degradable materials, but it is necessary for these methods to tailor the monomers (not directly from ethylene monomer) (Bauer et al., 2017; Haider et al., 2019a, 2019b; Steinbach and Wurm, 2015).

Cobalt-mediated radial polymerization (CMRP) based on the reversible deactivation of the growing radical chains by cobalt complexes is an efficient and versatile method to control the polymerization of vinyl monomers (Davis et al., 1995; Debuigne et al., 2005, 2009; Demarteau et al., 2019a; Guan, 2002; Hsu et al., 2014; Li et al., 2008; Miao et al., 2014; Peng et al., 2009; Wang et al., 2017). Reversible

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termination (RT) and degenerate transfer (DT) are two mechanisms that occur in CMRP. RT involves the trap and release of the radical chain via reversible metal-carbon bond homolysis and occurs when the total radical concentration is less than that of the trapping cobalt species, whereas DT occurs under higher radical concentration in which a radical species displaces the trapped radical bound to the metal (Debuigne et al., 2009; Li et al., 2008; Wayland et al., 2006). Cobalt complexes could be used to control the polymerization of both low-activated monomers such as vinyl acetate (VAc) and *N*-vinylpyrrolidone (NVP) (Debuigne et al., 2005, 2011; Demarteau et al., 2017; Hsu et al., 2014; Kermagoret et al., 2014; Wang et al., 2017) and more-activated monomers such as methyl acrylate (MA) with high living character (Liao et al., 2013; Lu et al., 2004). Up to now, only Co(acac)$_2$ has been reported to be able to control the copolymerization of ethylene and vinyl monomers (Bryaskova et al., 2007; Demarteau et al., 2018, 2019b; Kermagoret et al., 2014). Herein, we reported the preparation of degradable PE-based copolymers with well-tuned ester incorporation by Co^{II}(Salen*)-mediated radical copolymerization of ethylene and CKAs under mild conditions; the ring-opening reaction of CKAs could effectively incorporate ester structures into copolymer backbone to ensure degradation.

RESULTS AND DISCUSSION

Homo-Polymerization of MDO and Homo-Polymerization of Ethylene

The MDO monomer was commonly used to be copolymerized with vinyl monomers via radical mechanism for preparing degradable polymers (Hedir et al., 2014, 2015, 2017; Undin et al., 2014); the product of ring-opening polymerization of MDO has ester group in its backbone, which could easily degrade in acidic or basic conditions (Agarwal, 2010; Hill et al., 2017, 2018; Tardy et al., 2017b; Undin et al., 2012). The MDO propagating radicals lack stabilized group and generally result in unfavorable reactivity ratios toward more-activated monomers, usually leading to very limited incorporation in the final copolymer when copolymerizing with more-activated monomers (Seema and Liqun, 2009; Undin et al., 2013); however, the copolymerization of MDO and less-activated monomers (e.g., vinyl acetate, vinyl ethers) could yield statistical copolymers (Hedir et al., 2017; Tardy et al., 2017a). In our work, Co^{II}(Salen*)-mediated radical homopolymerization of MDO using AIBN as the initiator at 75°C was carried out. Generally, MDO is the isomer of the corresponding lactones, which can undergo radical addition at the double bond with subsequent possibilities of either ring opening or ring retaining or a combination of the two (Agarwal, 2007; Bailey et al., 1982; Carter et al., 2016), and the corresponding signals of acetal CH$_2$ of MDO (ring-retaining part) in polymer is at 3.5 ppm in the ^{1}H NMR spectrum. But, there was no signal at 3.5 ppm in ^{1}H NMR of the resulting polymer produced via CMRP of MDO (as shown in Figure 1E), which indicates that CMRP of MDO gave only ring-opening product without any ring-retaining product as shown in Figures 1A and 1E (Carter et al., 2016). The kinetics of the homopolymerization of MDO mediated by Co^{II}(Salen*) was also investigated, which exhibited living polymerization characters (Figures 1B–1D); the dispersity (Đ) of the resulting PMDO is low, and the molecular weight (M_n) of the resulting polymer increased almost linearly with MDO conversion (Figure 2C). The homopolymerization of ethylene mediated by Co^{II}(Salen*) was also carried out with AIBN as the initiator and dimethyl carbonate (DMC) as the solvent under the conditions of DMC (1.8 mL), Co^{II}(Salen*) (6 mg, 0.01 mmol), and AIBN (10.7 mg, 0.065 mmol) at 75°C (Grau et al., 2011), and PE was successfully obtained and the results are shown in Figure S4 and Table S1. M_n of the obtained PE increased almost linearly with the yield, indicating that the polymerization of ethylene is controlled (Wolpers et al., 2019).

Copolymerization of Ethylene and MDO Using CMRP Method

The concentration of radical initiator is critical to the CMRP of less-activated monomers since it dominates the radical concentration in the polymerization system. A higher radical concentration would give a faster and more economical polymerization process, but a lower radical concentration provides a better control to the polymeric product. According to the previously published research, the CMRP of vinyl acetate could be well controlled under the initiator/Co complex molar ratio range of 1–10 (Liao et al., 2013; Lu et al., 2004; Zhao et al., 2015a, 2015b). Herein, the CMRP of ethylene and MDO was performed at a molar ratio of Co^{II}(Salen*):AIBN = 1:6.5 according to previous reports on CMRP (Liao et al., 2013). MDO was successfully copolymerized with VAc mediated by Co(acac)$_2$, and a statistical copolymer was obtained (Ding et al., 2016). In the CMRP of ethylene in the presence of MDO, the growing radical can attack the double bond of MDO and immediately the MDO ring opens to form an ester unit in the main chain and another growing chain radical, which could further react with either ethylene or MDO (Scheme 1). Therefore, the CMRP of ethylene and MDO could provide a valuable route to introduce degradable ester units into the PE backbone under the mild conditions. After 22 h of copolymerization of MDO and ethylene mediated by Co^{II}(Salen*) in DMC at 75°C, the color turned from red of the initial mixture to dark green, which indicated that Co^{III} complex

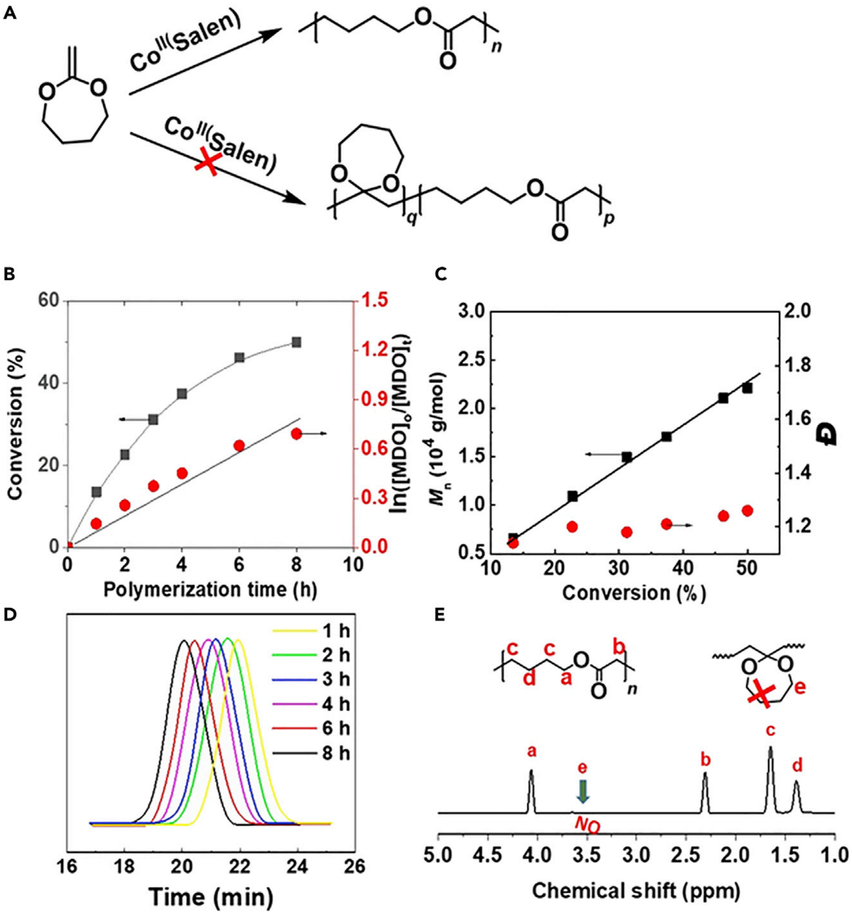


Figure 1. Homo-Polymerization of MDO Mediated by Co^{II}(Salen*)

Conditions: MDO (5.7 g, 50.0 mmol), Co^{II} (Salen*) (60.4 mg, 0.1 mmol), AIBN (82.0 mg, 0.5 mmol), 75°C.

(A) The scheme of ring-opening radical homo-polymerization of MDO mediated by Co^{II}(Salen*).

(B) The evolution of monomer conversion and ln([MDO]$_0$/[MDO]$_t$) with polymerization time.

(C) The variation of M_n and Đ for PMDO with MDO conversion.

(D) GPC (THF, 35°C) traces of PMDO at different polymerization times.

(E) ^{1}H NMR spectrum of the produced PMDO.

formed from Co^{II} complex after trapping the propagating radicals (Debuigne et al., 2009; Kermagoret et al., 2014). The CMRP of ethylene and MDO was carried out at 30 bar of ethylene pressure and 1:3 volume ratio of MDO: DMC (Figures 2A–2C). The first order kinetic plot (Figure 2B) could be observed. The M_n of the obtained polymers increased almost linearly with the copolymer yield (Figure 2C), and Đ was low throughout the copolymerization (Figure 2C). Fourier transform infrared spectroscopy (FTIR) spectra of PE and PE-based copolymer with ester structures in the backbone are shown in Figure 2D; the absorptions at 2,850–2,950 cm^{-1} were assigned to the stretching mode of –CH$_2$–CH$_2$– in the PE backbone. The absorptions at 1,480 cm^{-1} came from the methylene scissors motion. Compared with the FTIR spectrum of PE, the FT-IR spectrum of PE-based copolymer with ester structures in the backbone showed a strong absorption at 1,738 cm^{-1}, which is attributed to the stretching vibration of C=O of the ester groups originating from the ring-opening structure of MDO, and the absorption at 1,166 cm^{-1} came from the C–O structure. We further used ^{1}H NMR to characterize the structure of the PE-based copolymer with 76.9% ethylene content, and the results are shown in Figure 2E. The signal at 4.06 ppm came from the methylene protons of –COOCH_2 structure, and the signal at 2.29 ppm was assigned to the methylene protons of –CH_2COO structure originating from MDO ring-opening structure. The signals for all other protons in the copolymer were present between 1.77 and 0.80 ppm. The strong signal at 1.25 ppm was typical –CH_2–CH_2 protons in the backbone. The amount of ethylene structures in the copolymer could be (I_t-6)/4 while setting the integral value of the peak around 4.06 ppm as 2 and the integral values from 1.77 to 0.80 ppm as I_t; the content of

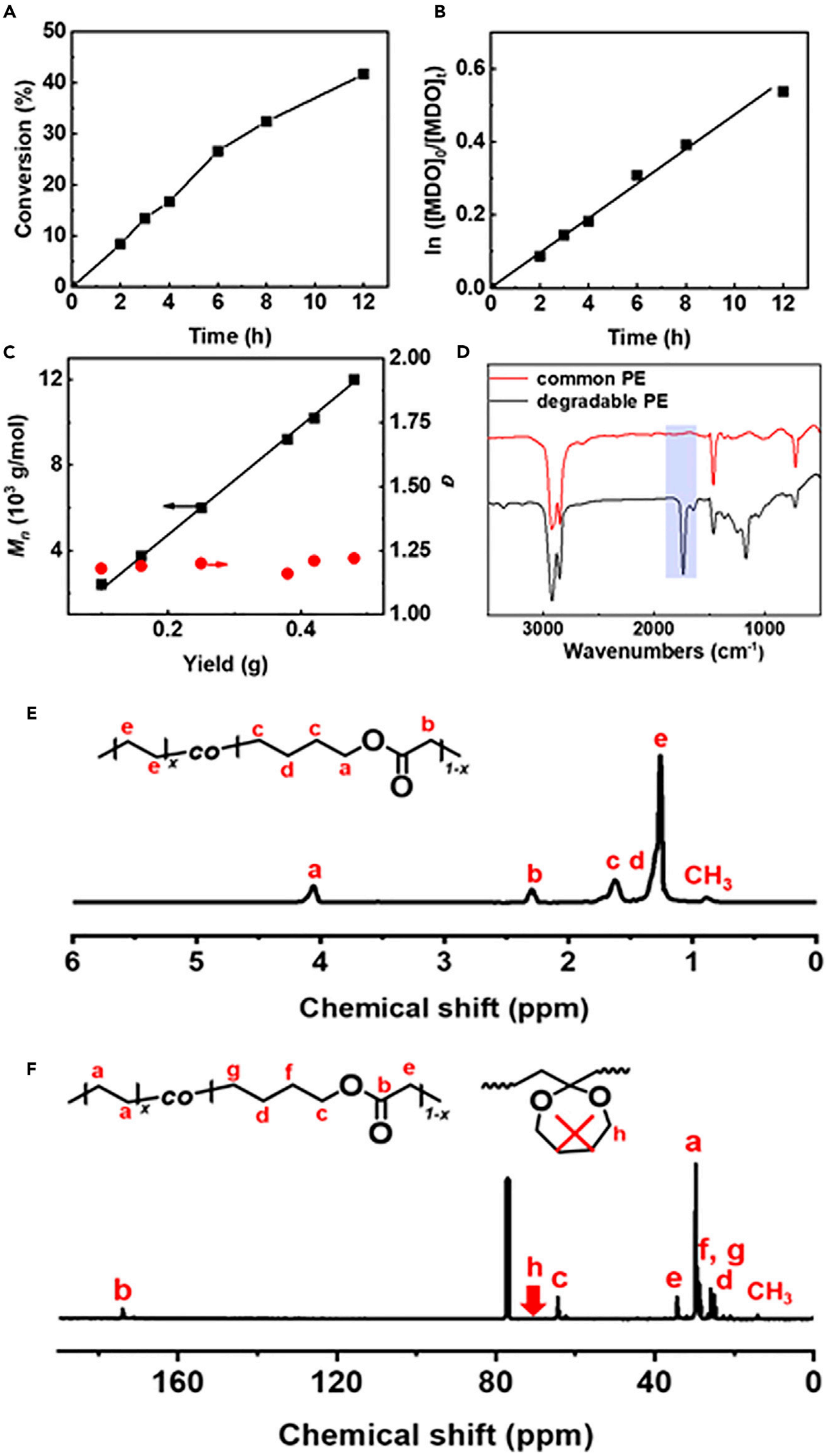


Figure 2. The Copolymerization of Ethylene and MDO Mediated by Co^{II}(Salen*)

Conditions: MDO (0.6 mL), DMC (1.8 mL), ethylene (30 bar), Co^{II}(Salen*) (6.0 mg, 0.01 mmol), AIBN (10.7 mg, 0.065 mmol), 75°C.

(A) The evolution of MDO conversion with polymerization time.

(B) The evolution of ln([MDO]$_0$/[MDO]$_t$) with polymerization time.

Figure 2. *Continued*

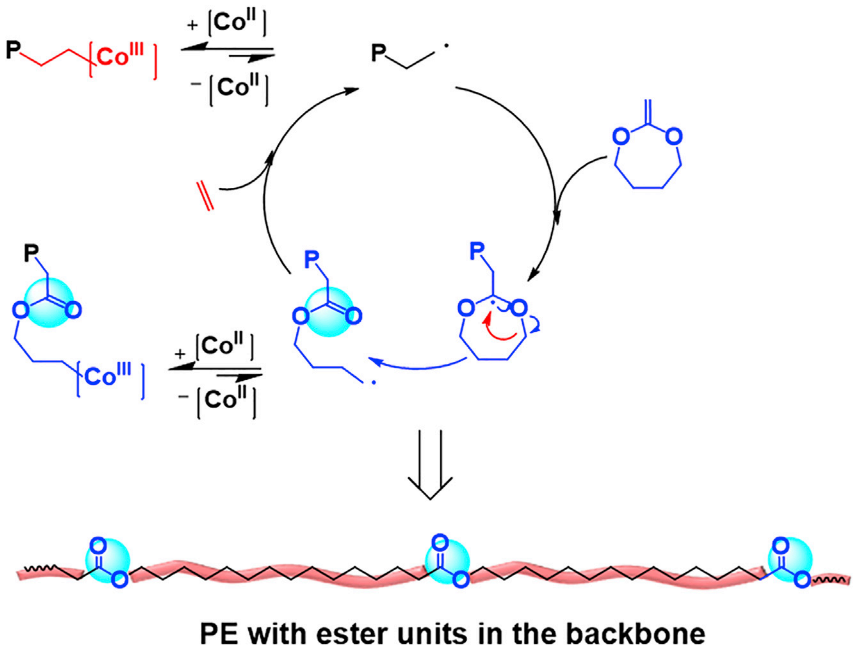
(C) The variation of M_n and Đ for produced PE-based copolymer with ester structures in the backbone with copolymer yield.

(D) FTIR spectra of common PE and produced PE-based copolymer with ester structures in the backbone.

(E) ^{1}H NMR spectrum of produced PE-based copolymer with 76.9% ethylene content.

(F) ^{13}C NMR spectrum of produced PE-based copolymer with 76.9% ethylene content.

ethylene could be further determined by the formula $[(I_t-6)/4]/[1+(I_t-6)/4]$. The signal around 0.88 ppm was assigned to –CH_3 groups of the branched ethylene units; the medium signals indicated that the produced copolymers have branched chains, and the degree of branching (DB, CH_3 branches/1000 C atoms) is listed in Table 1. The branched structure could also be confirmed in the ^{13}C NMR spectrum (Figure 2F); a medium signal at 14.1 ppm is attributed to the –CH_3 groups in the branched chain. The DB of the copolymer obtained by the CMRP method was close to the PE obtained by conventional free radical mechanism (determined to be 45) but was a litter higher than the EVA copolymers obtained using $Co(acac)_2$, which may result from that the polymerization temperature of CMRP is higher than that of the previously reported work (Kermagoret et al., 2014). Generally, higher polymerization temperature would produce PE with higher DB. The existence of ester units could also be confirmed by ^{13}C NMR spectrum (Figure 2F). The signal at 174.0 ppm was assigned to the carbon in –COO groups originating from the MDO ring-opening structure; the absence of a signal around 70.4 ppm, corresponding to a ketal carbon, indicated that MDO underwent ring-opening reaction and no ring remaining products formed. Furthermore, the ^{1}H COSY NMR spectrum could also prove the existence of ester structure in the PE backbone. The ^{1}H DOSY NMR spectrum of the produced polymer gave only single diffusion coefficiency (Figure S5), indicating that the produced polymer has one kind of polymer chain, is the copolymer, but not the mixture of PE and PMDO. On the other hand, we used ^{13}C NMR spectrum and HSQC NMR spectrum to identify the major sequence structural units in the produced PE-based copolymers (Figures 3 and S8). The strong signal at 29.7 ppm is attributed to methylene carbon in linear PE corresponding to EEE units in this case (Savant et al., 2007). Signals at 29.1 and 29.3 ppm are coupled with the ^{1}H NMR resonance at 1.64 ppm in the HSQC spectrum (Figure S8) and are assigned to the carbon in $–COOCH_2CH_2CH_2\boldsymbol{C}H_2–CH_2CH_2$ (ME) structure coming from MEE or EME; it is clear that the signal corresponding to EEE and ME structure are strong, whereas the signal corresponding to MMM and MEM units are weak (Figure 3). The presence of these signals could confirm the random incorporation of the MDO ring-opening structure in the copolymer backbone. The living character of the CMRP process was further confirmed by the chain extension experiment as shown in Scheme S1. Co^{III}(Salen*)-P(MDO-*co*-E)



Scheme 1. Formation of PE-Based Copolymer with Ester Structures in the Backbone via the CMRP of Ethylene and MDO

Entry	P (bar)	MDO:DMC (v:v)	X_{ethylene}[a] (%)	M_n[b] (10^3 G/mol)	Đ	Yield (g)	DB[c]
1	10	1:3	64.4	10.1	1.17	0.43	42
2	20	1:3	68.3	11.2	1.19	0.45	41
3	30	1:3	76.9	12.5	1.21	0.54	43
4	40	1:1	77.0	14.8	1.22	0.83	42
5	40	1:2	88.8	13.4	1.20	0.81	44
6	40	1:3	89.8	9.5	1.16	0.74	40
7	40	1:4	92.6	7.6	1.21	0.67	45

Table 1. Copolymerization of Ethylene and MDO under Different Volume Ratios of MDO:DMC and Ethylene Pressure

Conditions: MDO (0.6 mL), Co^{II}(Salen*) (6.0 mg, 0.01 mmol), AIBN (10.7 mg, 0.065 mmol), 75°C, 22 h.

[a] Ethylene content was calculated based on ^{1}H NMR spectra.

[b] M_n was determined by GPC (TCB, 150°C).

[c] Degree of branching, calculated based on ^{1}H NMR spectra.

with M_n of 11,000 g/mol and Đ of 1.15 was obtained after 22 h of polymerization under 10 bar of ethylene pressure, 6 mg of Co^{II}(Salen*), 1 mL of total mixture, and molar ratio of Co^{II}(Salen*):AIBN:MDO = 1:6.5:526 at 75°C. The obtained Co^{III}(Salen*)-P(MDO-*co*-E) was further used as macro-initiator for the bulk polymerization of VAc at 75°C. After 20 h of polymerization, the block copolymer Co^{III}(Salen*)-PVAc-*b*-P(MDO-*co*-E) was obtained with M_n of 35,300 g/mol and Đ of 1.26, as shown in Figures S6 and S7, which indicates that the CMRP of ethylene and MDO is living radical polymerization.

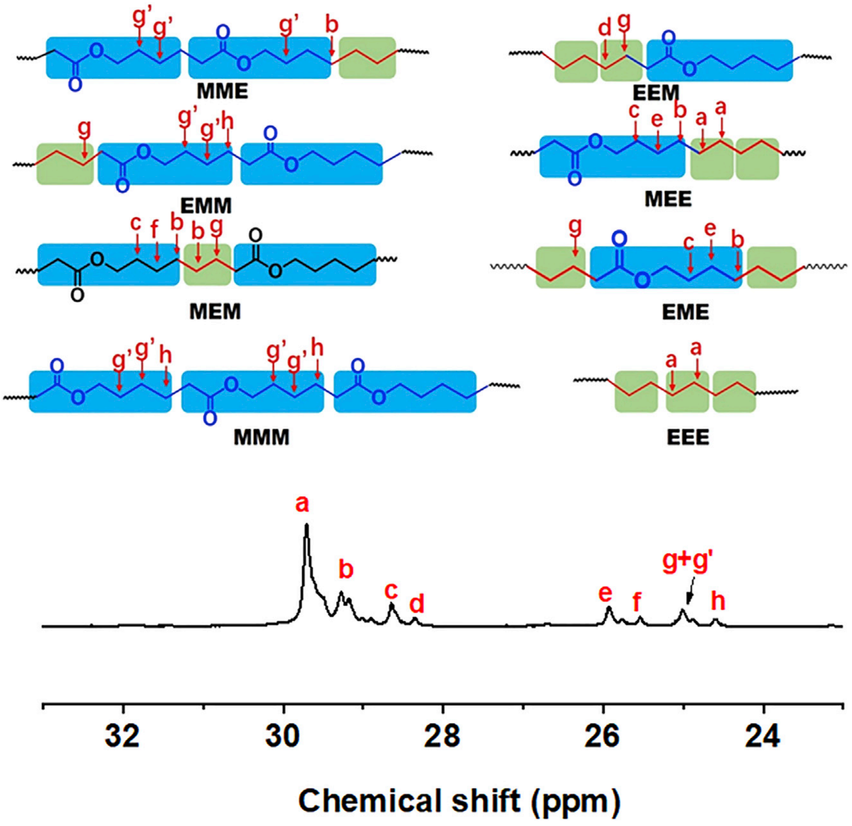


Figure 3. ^{13}C NMR Spectrum of the Major Sequence Structure Units in Produced PE-Based Copolymer with 76.9% Ethylene Content

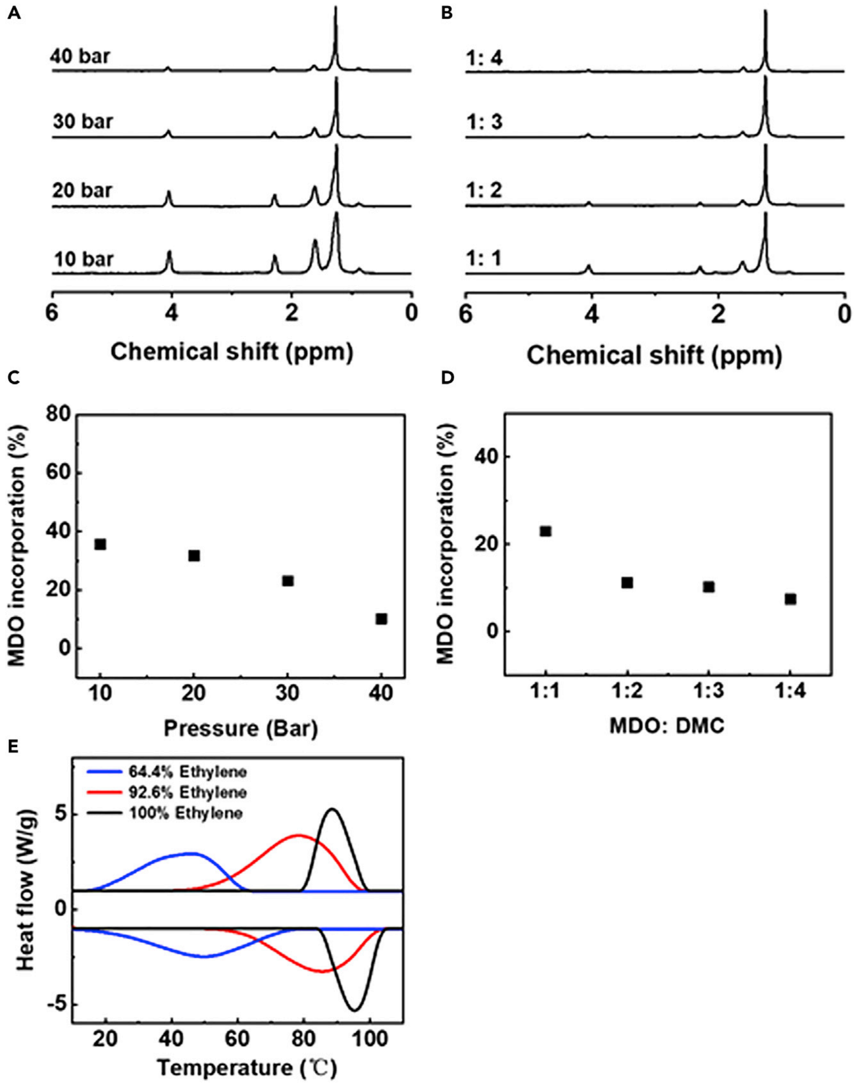


Figure 4. The Effect on Ethylene Content in the Produced Polymer

Conditions: MDO (0.6 mL), Co^{II}(Salen*) (6.0 mg, 0.01 mmol), AIBN (10.7 mg, 0.065 mmol), 75°C, 22 h.

(A) ^1H NMR spectra of produced PE-based copolymers prepared under different ethylene pressure (10–40 bar), MDO:DMC = 1:3.

(B) ^1H NMR spectra of produced PE-based copolymers prepared under different volume ratios of MDO:DMC (1:1 to 1:4), ethylene pressure was 40 bar.

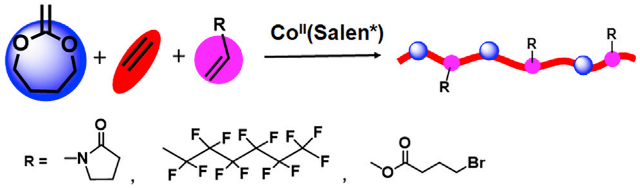
(C) MDO incorporation in the produced copolymer under different ethylene pressure.

(D) MDO incorporation in the produced copolymer under different volume ratios of MDO: DMC.

(E) DSC thermograms for PE-based copolymer with ester structures and common PE.

Regulation of Ethylene Content in the Copolymer

The pressure of ethylene and the concentration of MDO have an effect on the ethylene content in the produced copolymer. It is clear that by increasing ethylene pressure from 10 to 40 bar, the ethylene content in the produced copolymers increased from 64.4% to 89.8%, as shown in Table 1, and the intensity of the signal at 4.06 ppm decreased obviously when increasing ethylene pressure (Figures 4A and 4C). At higher ethylene pressure, more ethylene could dissolve in the mixture and more ethylene participated in the copolymerization; the ethylene content in the copolymers increased consequently. The ethylene content in the copolymer also depends on MDO concentration. At 40 bar of ethylene pressure with 0.6 mL of DMC, the ethylene content was around 77.0%, but it could reach up to 92.6% when quadrupling the solvent, the intensity of the signal at 4.06 ppm also decreased (Figures 4B and 4D). Ethylene



Scheme 2. The CMRP of Ethylene, MDO, and Functional Vinyl Monomers

concentration remained unchanged under the specific pressure and temperature; the concentration of MDO in DMC decreased when quadrupling the solvent. The lower concentration of MDO in DMC indicated the higher molar ratio of ethylene to MDO in the initial polymerization mixture, and ethylene content in copolymer is high consequently. The M_n of the copolymers and ethylene content in the produced copolymers are shown in Table 1; the M_n could reach up to 10,000 g/mol with low Đ. Because the CMRP of ethylene and MDO is living polymerization, the M_n of the produced PE-based copolymers could be further increased by decreasing the amount of Co^{II}(Salen*). When the amounts of Co^{II}(Salen*) and AIBN were halved and other conditions remained unchanged as Entry 5, Table 1, the M_n of the formed PE-based copolymer was nearly doubled to 27,700 g/mol, whereas the content of ethylene and yield of the copolymer did not vary too much, as shown in Figure S9 and Table S2. The polymerization kinetics changed very little in the presence of MDO; M_n and DB of the PE-based copolymer are similar to those of PE produced via the CMRP method (Figures 2C and S4 and Tables 1 and S1). The M_n could reach up to 10,000 g/mol and increased with polymer yield; the DB was around 40–50. However, the solubility of PE-based copolymer with ester structures in DMC is much better than that of PE. The incorporation of ester structures may destroy the crystallization of PE and caused the melting temperature (T_m) of the produced PE-based copolymer to decrease. T_m of common PE and the PE-based copolymers are shown in Figure 4E; T_m decreased with the increase of ester structures in the PE-based copolymer chain. The PE-based copolymer with 92.6% ethylene content has the T_m of 86.2°C, which is close to the T_m (92.4°C) of PE, but the melting range is broader than PE.

Copolymerization of Ethylene and Other CKA

We also prepared other CKA, such as 2-methylene-1, 3, 6-trioxocane (MTC), to copolymerize with ethylene. The homopolymerization of MTC using this CMRP method was conducted. The obtained PMTC was analyzed using ^1H NMR as shown in Figure S10. The signal at 4.27 ppm was assigned to the –COOCH_2, the signals between 3.71 and 3.46 ppm were assigned to the CH_2OCH_2, and the signal at 2.43 ppm was assigned to the –CH_2COO; the existence of these signals proved that MTC underwent ring-opening reaction during the polymerization. Similar to the mechanism of the CMRP of ethylene and MDO, in the copolymerization of MTC and ethylene, MTC could also ring open to introduce ester units as well as ether units into the polymer backbone without any ring remaining reactions when the double bond of MTC was attacked by a radical. The MTC ring-opening structure obviously exists in the ^1H NMR spectrum of the resulting P(MTC-*co*-E); the strong signal around 1.25 ppm came from $-CH_2-CH_2-$ structure of PE (Figure S11), and the ethylene content was determined to be 88.4% under the conditions of MTC (0.6 mL), DMC (1.8 mL), Co^{II}(Salen*) (6.0 mg, 0.01 mmol), 30 bar of ethylene pressure, and 75°C for 22 h. The CMRP of MTC and ethylene was also carried out at 75°C with AIBN as the initiator at 30 bar of ethylene pressure, MTC (0.6 mL) and DMC (1.8 mL); the results are shown in Figure S12. The M_n of the obtained copolymer increased almost linearly with the copolymer yield, and Đ was low throughout the copolymerization (Figure S12C); therefore, Co^{II}(Salen*) could also mediate the copolymerization of MTC and ethylene.

Functionalization of Degradable PE-Based Copolymer

The copolymerization of MDO and ethylene with other functional vinyl monomers could offer a promising method to design functional PEs with ester structures in the backbone (Scheme 2). Fluoropolymers have particular properties, such as chemical inertness, high thermal stability, and hydrophobicity. Introducing fluoro-containing units into the PE chain could significantly change its properties. The copolymerization of MDO, ethylene, and perfluorohexylethylene (PFHE) was carried out as shown in Scheme 2 and Figure S13. Gel permeation chromatography (GPC) (THF, 35°C) results showed unimodal peak for all samples, and the M_n of the formed fluoro-containing PE could reach up to 10,000 g/mol with low Đ. We also

Entry	PFHE (mL)	Pressure (bar)	Content[a] (%)			M_n[b] (10^3 G/mol)	Đ	Yield (g)
			E	PFHE	MDO			
1	0.3	20	47.6	15.3	37.1	10.6	1.17	1.05
2	0.6	20	62.1	17.8	20.1	14.1	1.21	1.31
3	0.6	40	69.8	13.6	16.6	17.8	1.18	1.78

Table 2. Copolymerization of Ethylene, MDO, and PFHE

Conditions: MDO (0.6mL), DMC (1.2 mL), Co^{II}(Salen*) (6.0 mg, 0.01 mmol), AIBN (10.7 mg, 0.065 mmol), 75°C, 22 h.

[a] Monomer content, calculated based on ^{1}H NMR spectra.

[b] Determined by GPC (THF, 35°C).

changed the concentration of PFHE and ethylene pressure to regulate the content of each component in the copolymer, and the results are listed in Table 2. In contrast to the hydrophobicity of poly(perfluorohexylethylene), poly(*N*-vinyl -pyrrolidone) exhibits hydrophilicity. The copolymerization of ethylene, MDO, and *N*-vinyl pyrrolidone (NVP) was also conducted. After 22 h of polymerization, the mixture became dark green and was of high viscosity; the pyrrolidone-containing PE copolymers were analyzed using ^{1}H NMR and GPC (THF, 35°C). Ethylene pressure was also changed to regulate the composition of the produced copolymers, and the results are shown in Table 3 and Figure S14. The content of each component in the copolymer could be regulated by ethylene pressure or monomer concentration; higher pressure would produce copolymer with high ethylene content. The surface properties of the produced copolymers could be significantly varied after introducing different hydrophilic groups or hydrophobic groups into PE-based copolymers. For common PE, the contact angle with water was 115.5°, whereas the PE-based copolymer with 7.4% MDO content in the backbone has a contact angle of 107.9°. The contact angle could be raised to 126.7° for the PE copolymer with 17.8% PFHE and 20.1% MDO contents, whereas it could decrease to 96.9° for the copolymer with 15.6% NVP and 8.0% MDO contents (Figure S15). Also, the copolymerization of ethylene, MDO, and vinyl bromobutanoate (VBr) could yield the copolymer (P(MDO-*co*-E-*co*-VBr)) with pendent bromine functional groups that are able to be modified via post-polymerization modification as shown in Scheme S2 and Figures S16 and S17 under the conditions of MDO (0.6 mL), VBr (0.3 mL), DMC (1.2 mL), Co^{II}(Salen*) (6 mg, 0.01 mmol), AIBN (10.7 mg, 0.065 mmol), 30 bar of ethylene pressure, and 75°C for 22 h; the contents were determined to be 15.1% for MDO, 43.3% for VBr, and 41.6% for ethylene, respectively. The side bromine unit of the resulting P(MDO-*co*-E-*co*-VBr) can be further replaced by azide group after reacting with NaN_3 in DMF for 48 h to yield P(MDO-*co*-E-*co*-VN_3). In the ^{1}H NMR spectrum (Figure S16), a clear shift of CH_2–Br ($\delta = 3.50$ ppm) to the CH_2–N_3 ($\delta = 3.40$ ppm) was observed, indicating that all bromine units have been completely replaced by azide group. GPC (THF, 35°C) results showed almost the same curves for copolymer before and after azidation (Figure S17). Via "click" chemistry of 1, 3-dipolar cycloaddition reaction of azides with alkynes, glycol units can be easily linked onto the PE copolymer chain. Propynyl glycol acrylate and the copolymer P(MDO-*co*-E-*co*-VN_3) were dissolved in DMF and allowed for reacting at 80°C; the appearance of new resonances at 8.25 (the triazole proton) and 3.66 ppm coming from propynyl glycol acrylate units and the absence of the resonance at $\delta = 3.40$ ppm (CH_2–N_3), which shifted to 4.50 ppm after connection with the triazole ring, indicated successful linking of the propynyl glycol acrylate group onto the PE copolymer. GPC (THF, 35°C) results showed that the resulting copolymer after "click" has an increase in M_n (Figure S17). The advantage of this method is the versatility in the approaches that can be used to prepare the functional copolymers.

Entry	Pressure (bar)	Content[a] (%)			M_n[b] (10^3 G/mol)	Đ	Yield (g)
		E	NVP	MDO			
1	40	76.4	15.6	8.0	8.6	1.21	0.78
2	20	53.9	30.1	16.0	6.6	1.18	0.52

Table 3. Copolymerization of Ethylene, MDO, and NVP

Conditions: MDO (0.6mL), NVP (0.6 mL), DMC (1.2 mL), Co^{II}(Salen*) (6.0 mg, 0.01 mmol), AIBN (10.7 mg, 0.065 mmol), 75°C, 22 h.

[a] Monomer content, calculated based on ^{1}H NMR spectra.

[b] Determined by GPC (THF, 35°C).

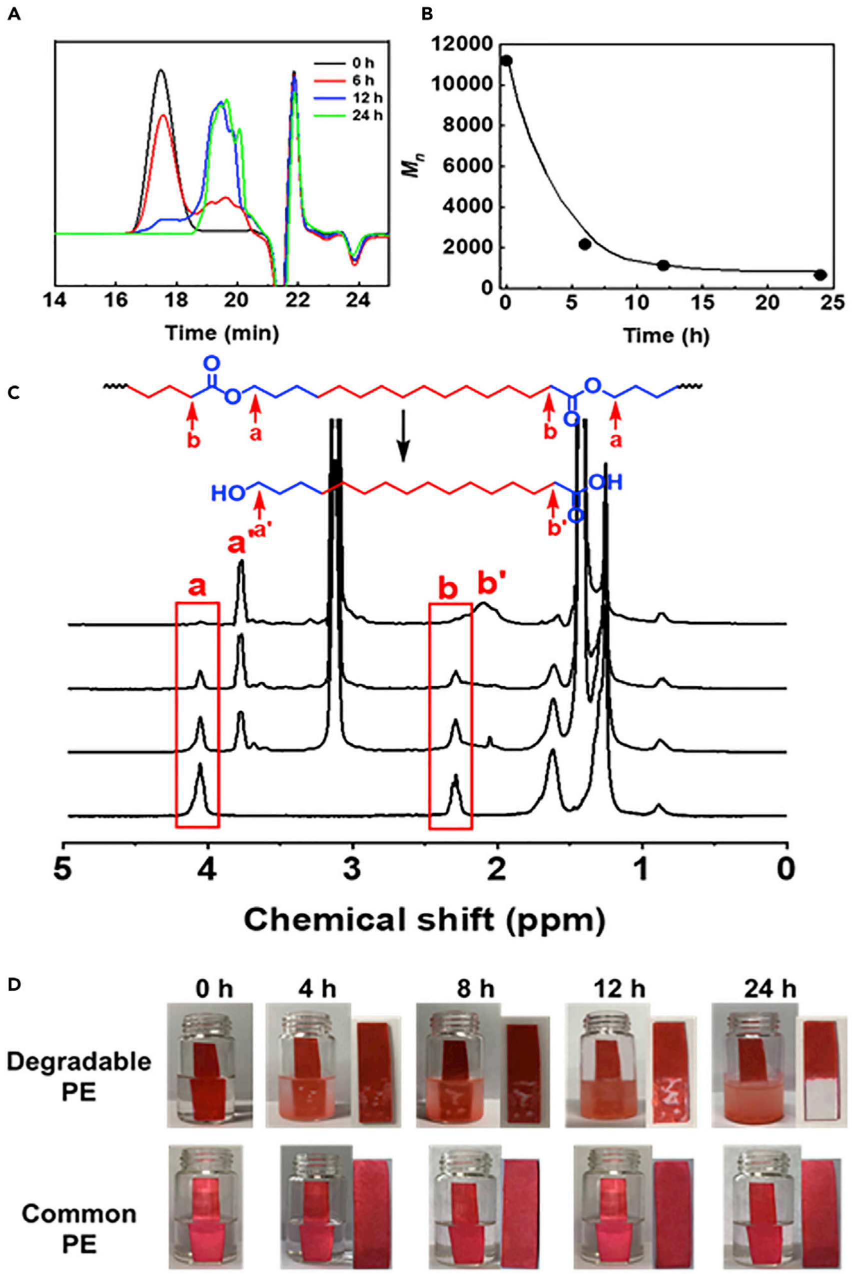


Figure 5. The Degradation of PE-Based Copolymer with Ester Structures in the Backbone

(A) GPC (TCB, 150°C) curves of PE-based copolymer with ester structures in the backbone treated with Et_3N at different times.

(B) Percent decrease of M_n of PE-based copolymer with ester structures in the backbone treated with Et_3N at different times.

(C) ^1H NMR spectra of the copolymer treated with Et_3N at different times.

(D) The picture of film of PE-based copolymer with ester structures in the backbone and common PE film treated with Et_3N at different times.

Degradation of the PE-Based Copolymer with 68.3% Ethylene Content

The degradation behavior was investigated by the hydrolysis of PE-based copolymer in mixed triethylamine (Et_3N) and chloroform (Mattsson et al., 2007). When 40 mg of PE-based copolymer with 68.3% ethylene content (Entry 2, Table 1) was dissolved in the solution of 1 mL Et_3N in 4 mL of chloroform by heating to 70°C in the presence of small amount of water, the intensity of the resonance at 4.06 ppm (–CH_2OOC–, a) decreased obviously and a new resonance at 3.75 ppm (–CH_2OH, a') was present, and the intensity of the resonance at 2.3 ppm (–CH_2COOCH$_2$–, b) decreased obviously and a new resonance at 2.1 ppm (–CH_2COOH, b') was present, which was attributed to the degradation of ester group into hydroxyl group, since the resonance of CH_2 group connected to hydroxyl group usually occurred at 3.75 ppm. When prolonging the reaction time, the resonance at 4.06 ppm became weaker and the resonance at 3.75 ppm became stronger obviously as shown in Figure 5C. After 24 h, the resonance at 4.06 ppm was almost absent (Figure 5C), which could prove that the ester group was fully degraded. GPC (TCB, 150°C) results showed that PE with M_n of 11,200 g/mol has degraded into the products with M_n of 670 g/mol in 24 h (Figures 5A, 5B, and S18). We also prepared films of common PE and degradable PE films with purple color; subsequently, two films emerged in the mixed solvent of CH_3OH and Et_3N in presence of small amount of water. It is very clear that the PE film completely degraded and the solvent became purple from colorless, whereas the common PE film and the solvent remained unchanged as shown in Figure 5D.

Conclusion

We utilized the CMRP method to copolymerize ethylene and CKAs to effectively incorporate ester groups into PE backbone for making PE-based copolymer that degrades under mild conditions. Ethylene content in the copolymer was regulated by ethylene pressure or MDO concentration, and it could be easily tuned in a wide range. Also, the functionalization of the PE-based copolymer was investigated; the copolymerization of ethylene and MDO with other functional vinyl monomers could produce functional and degradable PE-based copolymer. All the formed PE-based copolymer could degrade. This CMRP method would provide access to a diverse range of degradable and functional polyolefin materials.

Limitations of the Study

Although the degradable PE-based copolymer with ester structures in the backbone was successfully obtained with the ethylene content varying in a wide range, it is still a challenge to further improve the M_n of the copolymer for affording PE-based copolymers with good mechanical properties. Also, the degradation under natural environment need to be investigated in the future.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.100904.

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AUTHOR CONTRIBUTIONS

T.Z. and W.Y. conducted the experiments. C.H., C.C., and Y.Y. designed the experiments, prepared the manuscript, and wrote the paper. G.C, X.N., Z.Z., and L.X. have done some characterization on the polymers.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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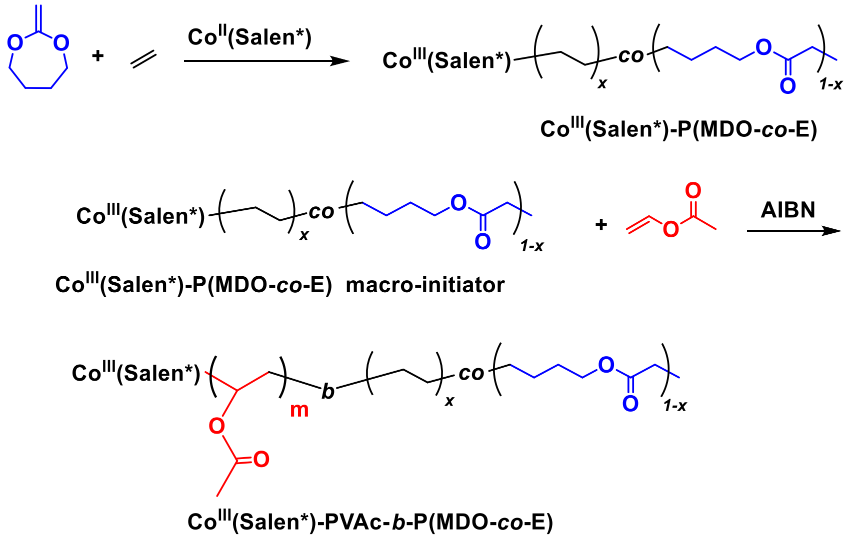
Supplemental Information

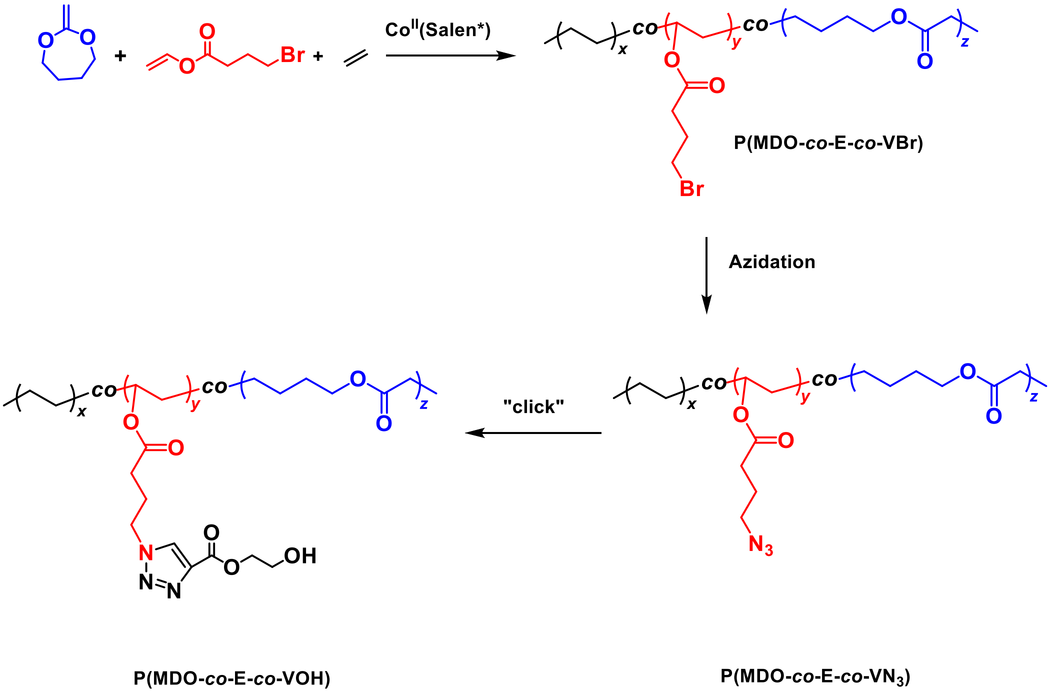
Degradable PE-Based Copolymer with Controlled Ester Structure Incorporation by Cobalt-Mediated Radical Copolymerization under Mild Condition

Tianyou Zeng, Wei You, Guang Chen, Xuan Nie, Ze Zhang, Lei Xia, Chunyan Hong, Changle Chen, and Yezi You

1. Figures and Schemes



Scheme S1. Chain extension reaction, related to Figure 2.



Scheme S2. Post-modification of the resulting PE with ester units in the backbone, related to Scheme 2.

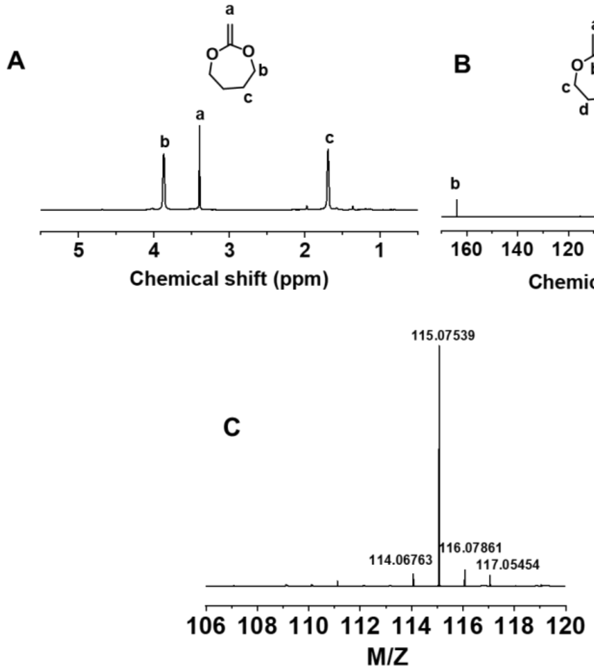


Figure S1. (A) ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of MDO, (B) ^{13}C NMR ($CDCl_3$, 300 MHz) spectrum of MDO, (C) ESI mass spectrum of MDO, related to Figure 1.

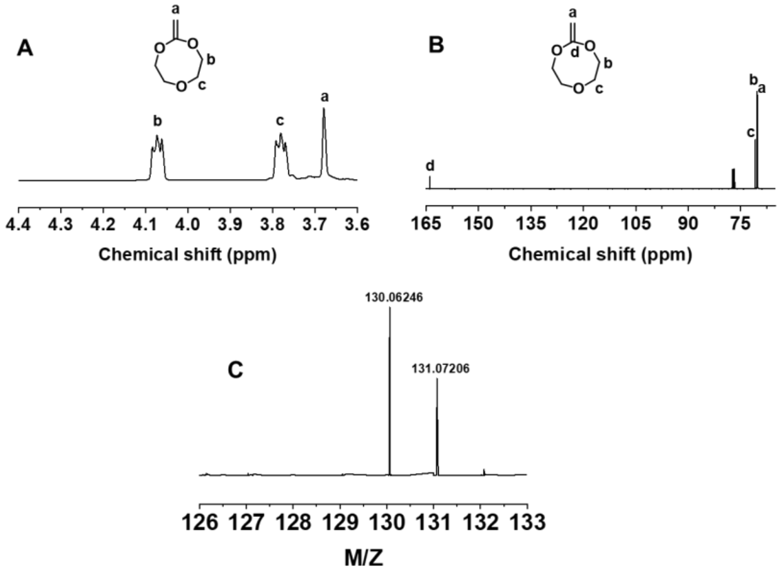


Figure S2. (A) ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of MTC, (B) ^{13}C NMR ($CDCl_3$, 300 MHz) spectrum of MTC, (C) ESI mass spectrum of MTC, related to Figure 1.

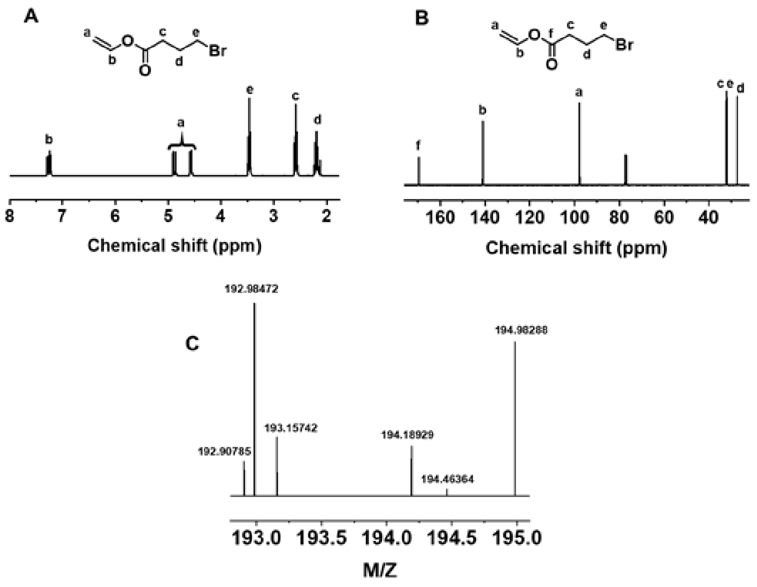


Figure S3. (A) ^{1}H NMR (CDCl$_3$, 300 MHz) spectrum of VBr, (B) ^{13}C NMR (CDCl$_3$, 300 MHz) spectrum of VBr, (C) ESI mass spectrum of VBr, related to Scheme 2.

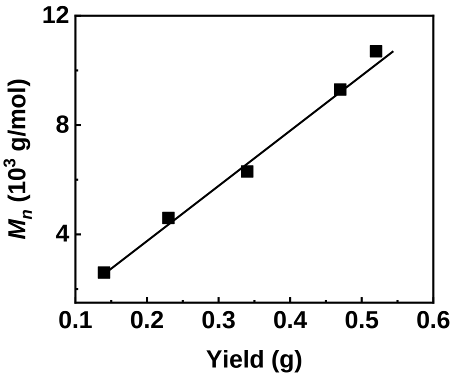


Figure S4. The variation of M_n and Đ for common PE with polymer yield, related to Table 1. Conditions: DMC (1.8 mL), ethylene (30 bar), Co^{II}(Salen*) (6.0 mg, 0.01 mmol), AIBN (10.07 mg, 0.065 mmol), 75 °C.

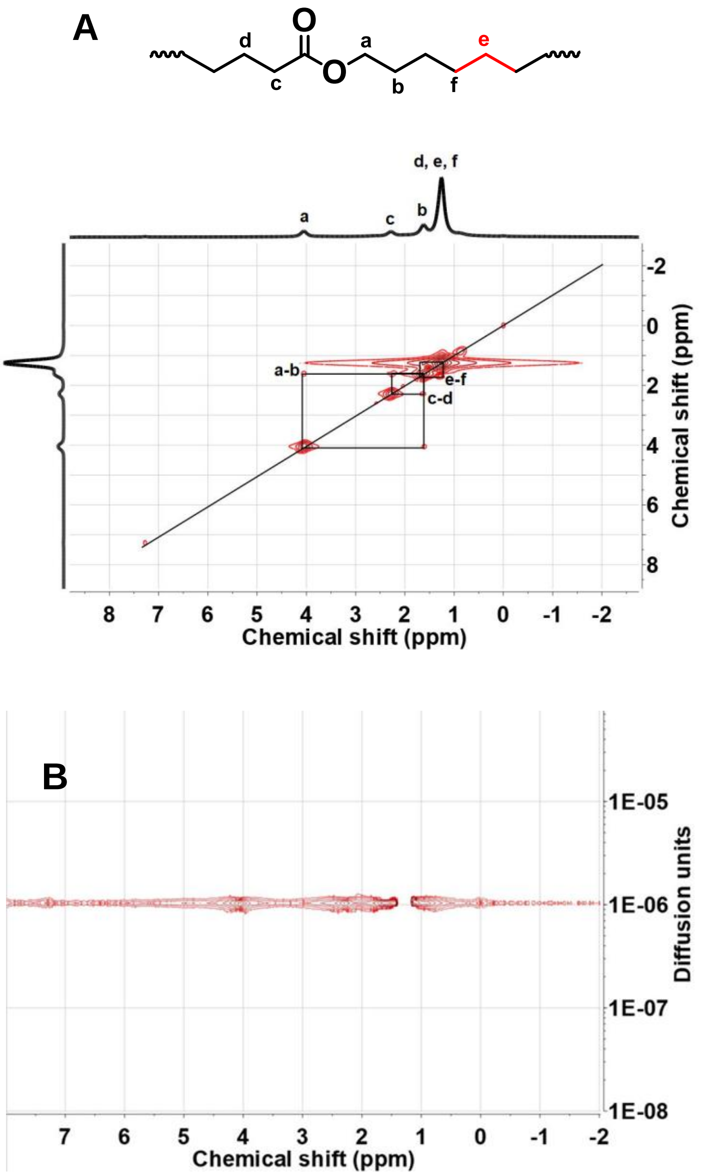


Figure S5. ^{1}H COSY NMR spectra (A) and ^{1}H DOSY NMR spectra (B) of P(MDO-*co*-E) with 76.9% ethylene content, related to Figure 2.

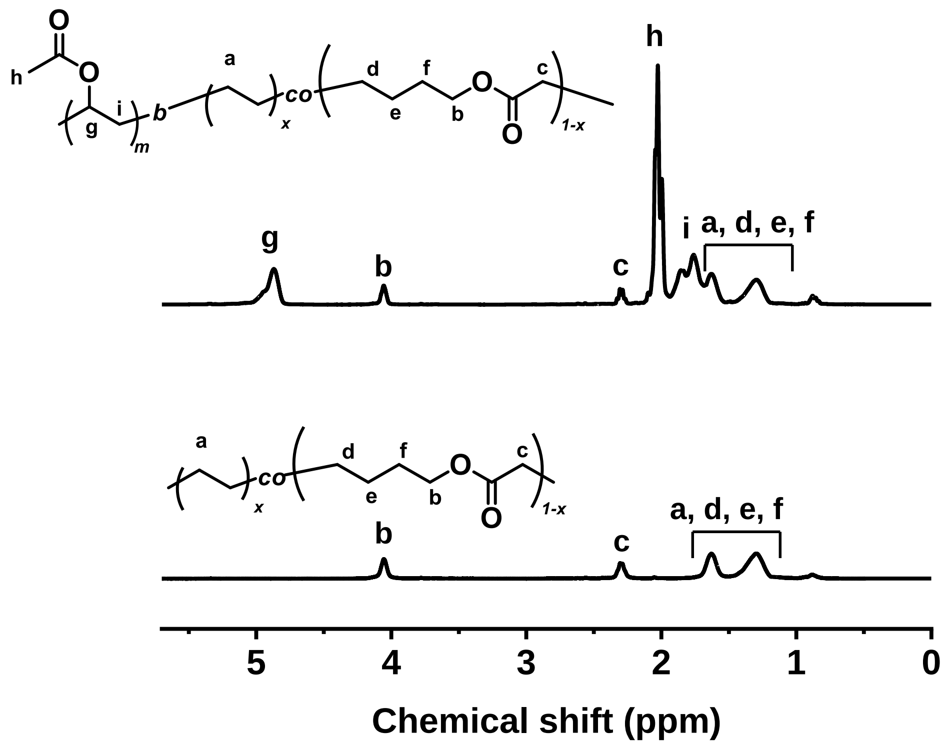


Figure S6. ^{1}H NMR ($CDCl_3$, 300 MHz) spectra of macro-initiator Co^{III}(Salen*)–P(MDO-*co*-E) and block copolymer PVAc-*b*-P(MDO-*co*-E), related to Figure 2.

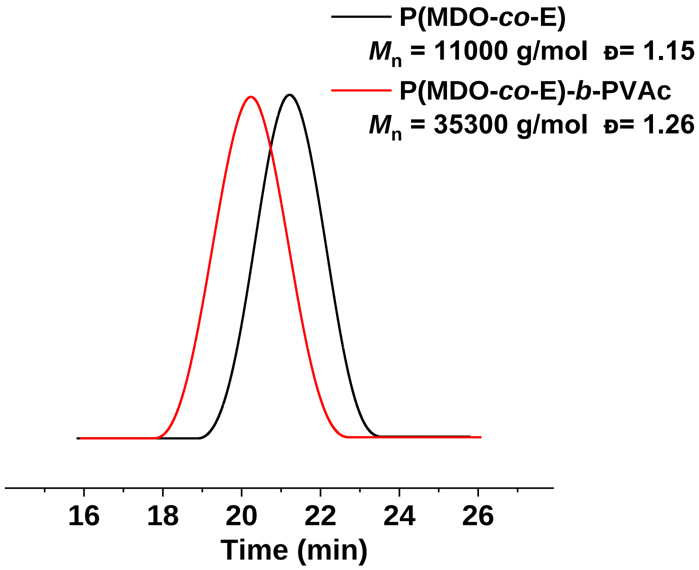


Figure S7. GPC (THF, 35 °C) curves of the resulting copolymer and block copolymer, related to Figure 2.

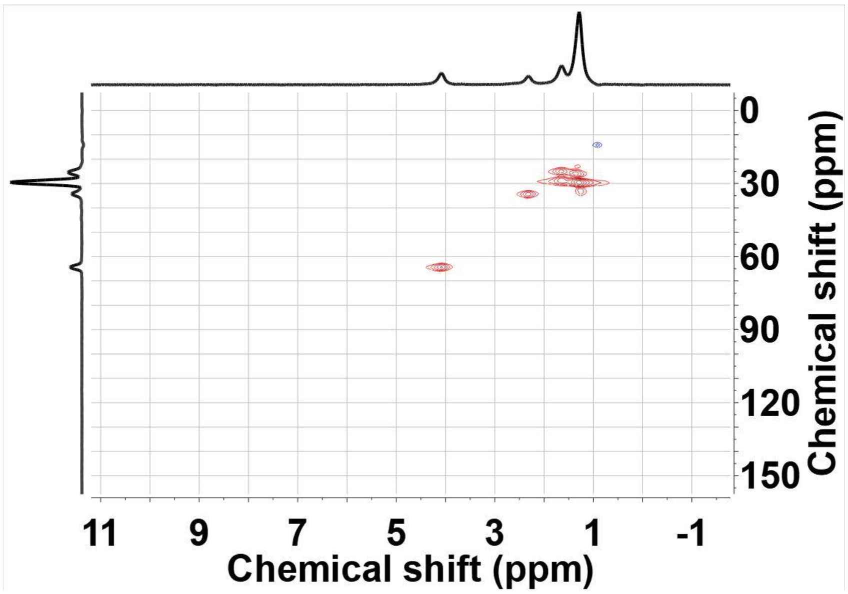


Figure S8. HSQC NMR spectrum of produced P(MDO-*co*-E) with with 76.9% ethylene content, related to Figure 3.

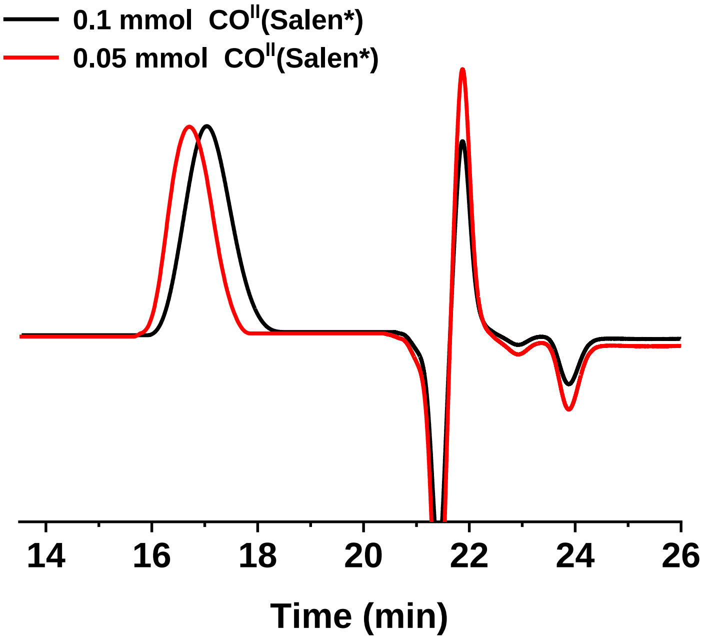


Figure S9. GPC (TCB, 150 °C) curves of produced PE with ester units in the backbone using various amount of Co^{II}(Salen*), related to Table 1.

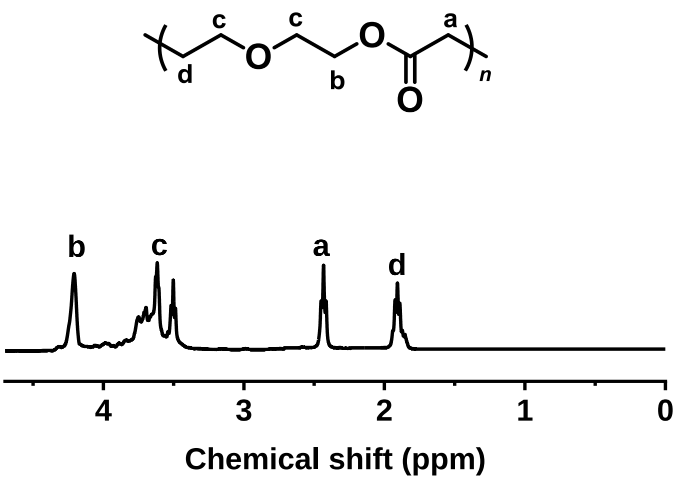


Figure S10. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of homo-PMTC, related to Scheme 1.

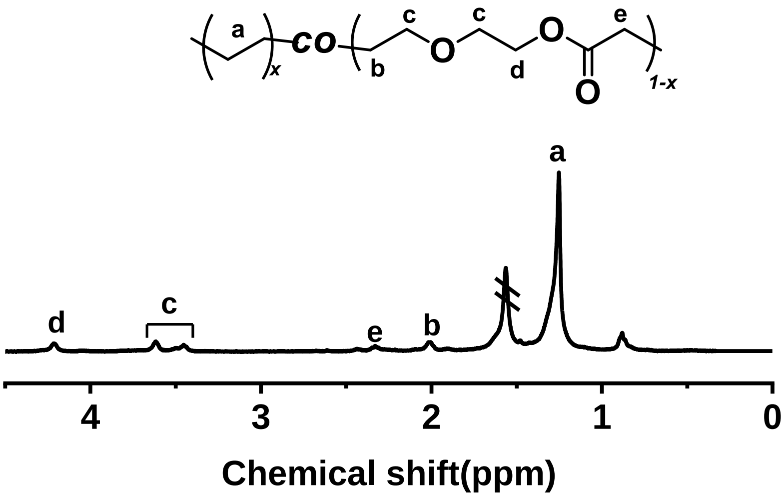


Figure S11. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of P(MTC-*co*-E) with 88.4% ethylene content, related to Scheme 1.

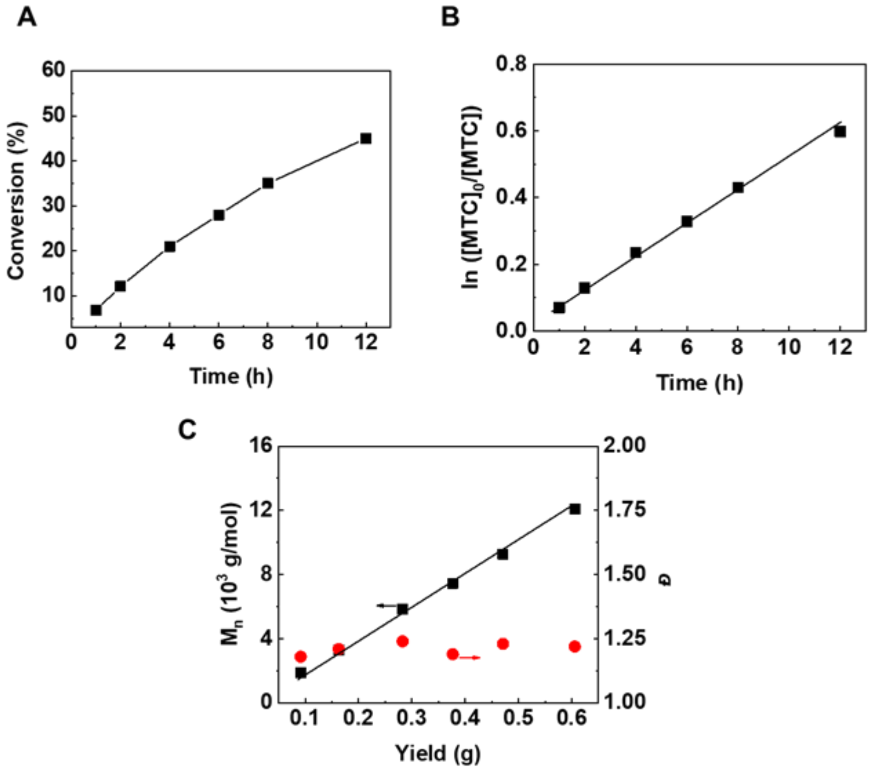


Figure S12. Copolymerization of MTC and ethylene, related to Scheme 1. Conditions: MTC (0.6 mL), DMC (1.8 mL), ethylene (30 bar), Co^{II}(Salen*) (6.0 mg, 0.010 mmol), AIBN (10.7 mg, 0.065 mmol), 75 °C. (A) The evolution of MTC conversion with polymerization time. (B) The evolution of $\ln([MTC]_0/[MTC]_t)$ with polymerization time. (C) The variation of M_n and Đ with copolymer yield.

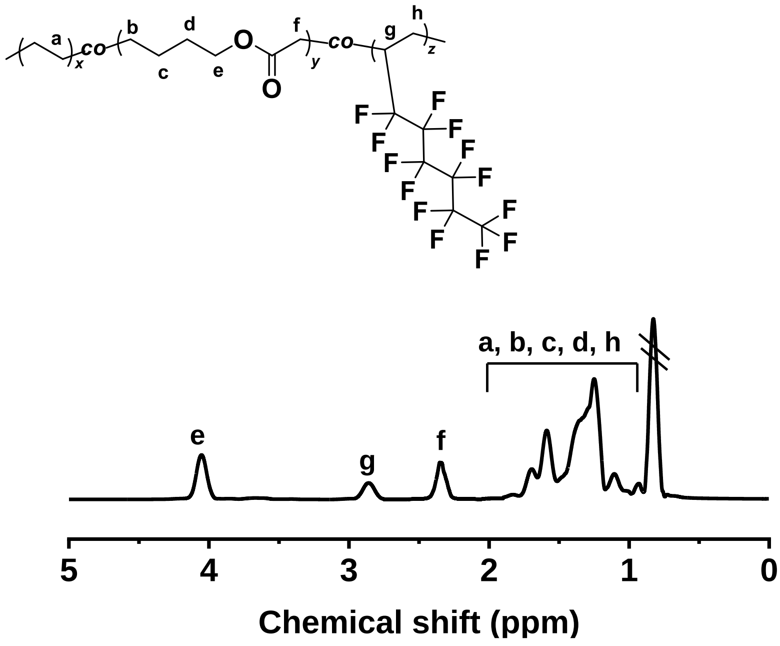


Figure S13. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of P(MDO-*co*-E-*co*-PFHE), related to Table 2. Conditions: PFHE (0.3 mL), MDO (0.6 mL), ethylene (20 bar), DMC (1.2 mL), Co^{II}(Salen*) (6.0 mg), AIBN (10.7 mg), under 75 °C.

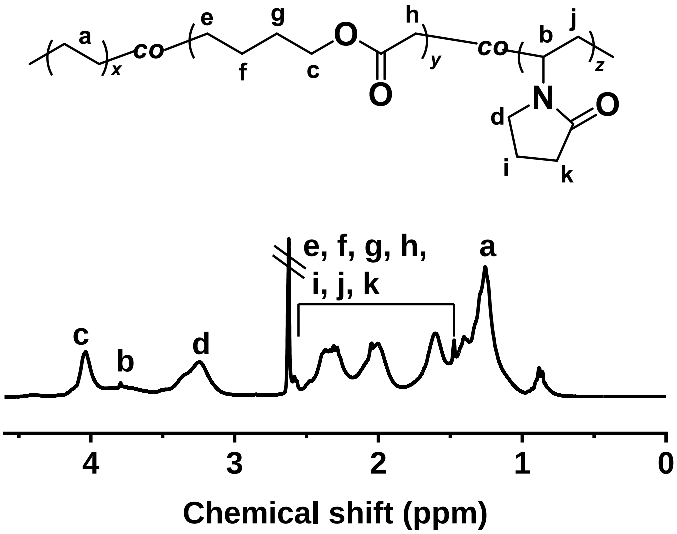


Figure S14. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of P(MDO-*co*-E-*co*-NVP), related to Table 3. Conditions: NVP (0.6 mL), MDO (0.6 mL), ethylene (20 bar), DMC (1.2 mL), Co^{II}(Salen*) (6.0 mg), AIBN (10.7 mg), under 75 °C.

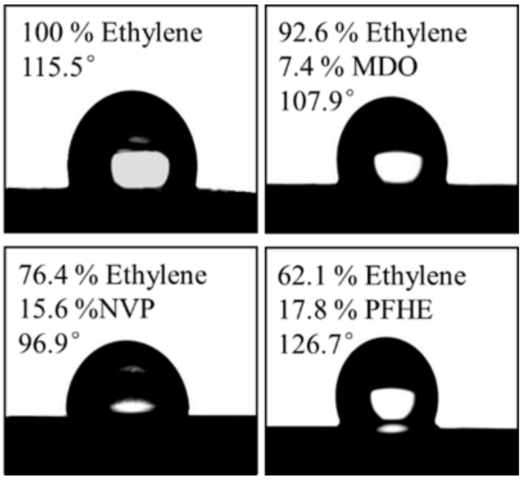


Figure S15. Water contact for copolymers, related to Scheme 2.

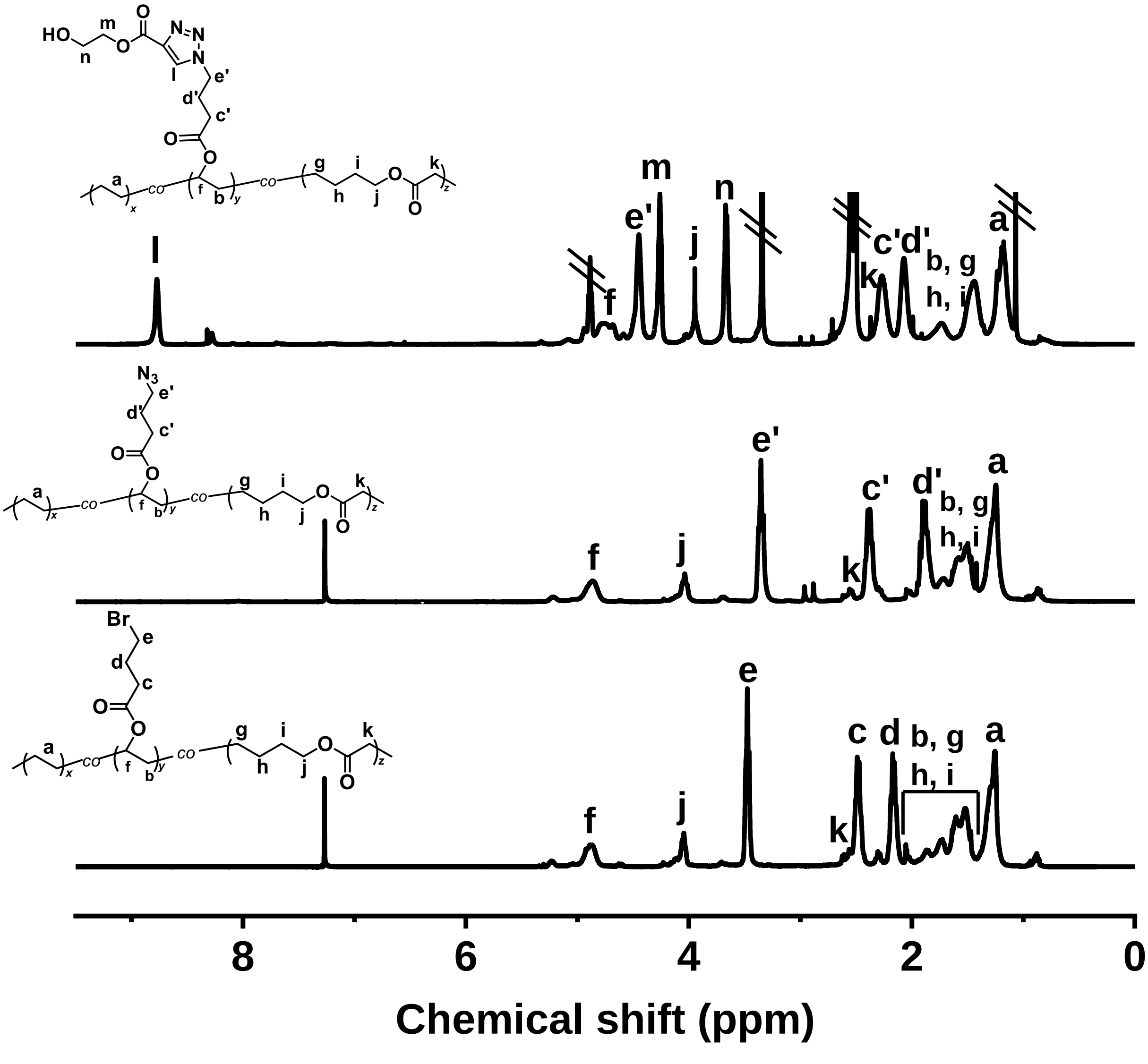


Figure S16. ^1H NMR ($CDCl_3$, 300 MHz) spectra of P(MDO-*co*-E-*co*-VBr), P(MDO-*co*-E-*co*-VN_3) and ^1H NMR (DMSO-d_6, 300 MHz) spectrum of the copolymer after “click”, related to Scheme 2.

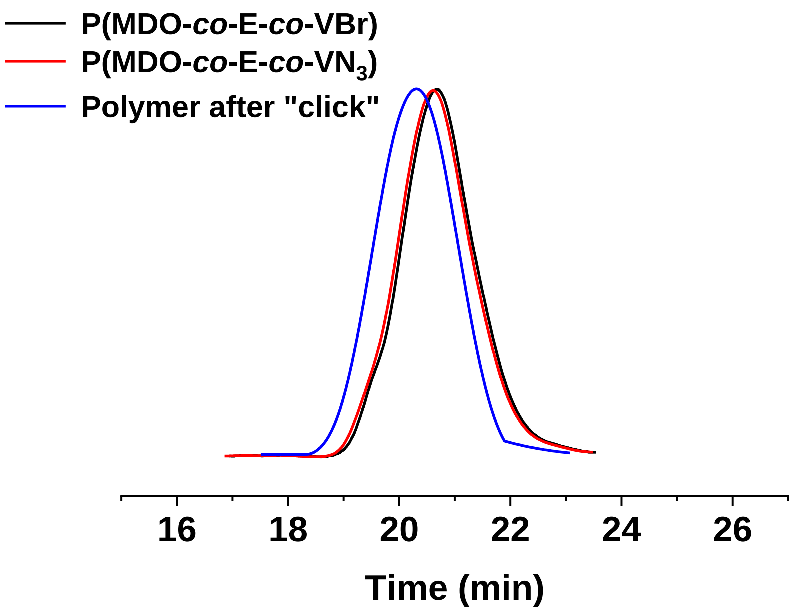


Figure S17. GPC (THF, 35 °C) curves of (MDO-*co*-E-*co*-VBr), P(MDO-*co*-E-*co*-VN$_3$) and the copolymer after “click”, related to Scheme 2.

Figure S18. Images of PE with ester units in the backbone before (left) and after (right) degradation, related to Figure 5.

2. Tables

Table S1. Homo-polymerization of ethylene mediated by Co^{II}(Salen*), related to Table 1.

Entry	Yield (g)	M_n[a] (10^3 g/mol)	Đ	DB[b]
1	0.14	2.6	1.89	43
2	0.23	4.6	2.02	42
3	0.35	6.3	2.15	44
4	0.47	9.3	2.26	43
5	0.52	10.7	2.36	46

Conditions: Co^{II}(Salen*) (6.0 mg, 0.01 mmol), AIBN (10.7 mg, 0.065 mmol), ethylene (30 bar), DMC (1.8 mL), 75 °C. [a] Molecular weights were determined by GPC (TCB, 150 °C). [b] Degree of branching, calculated based on ^{1}H NMR spectra.

Table S2. Copolymerization of ethylene and MDO, related to Table 1.

Entry	Co^{II}(Salen*) (mmol)	AIBN (mmol)	$X_{ethylene}$[a] (%)	M_n (10^3 g/mol)	Đ	Yield (g)	DB
1	0.1	0.065	88.8	13.4	1.20	0.81	41
2	0.05	0.032	85.9	27.7	1.17	0.79	43

Conditions: MDO (0.6 mL), DMC (1.2 mL), 75 °C, 40 bar, 22 h. [a] Ethylene content was calculated based on ^{1}H NMR spectra, [b] Molecular weights were determined by GPC (TCB, 150 °C). [c] Degree of branching, calculated based on ^{1}H NMR spectra.

3. Transparent Methods

3.1 Materials. *N*-Vinyl pyrrolidone (NVP, 99%), cobalt(II) [*N,N'*-bis(3, 5-ditert-butylsalicylidene)-1, 2-cyclohexanediamine] [(Co^{II}(Salen*), >99%)], 2-bromo-1, 1-dimethoxyethane (98%), 1, 4-dibromo-2-butene (99%), diethyl malonate (98%) and dimethyl carbonate (DMC, 99%) were purchased from Energy. Vinyl acetate (VAc, 99%), triethylamine (Et_3N, 99%), 4-bromobutyric acid (98%), palladium acetate ($Pd(OAc)_2$, 98%), sodium azide (NaN_3, 97%) and perfluorohexylethylene (PFHE, 98%) were purchased from Aladdin. Diethylene glycol (99%), sodium, methanol (CH_3OH, 99%), 1, 4-butanediol (99%), tetrahydrofuran (THF, 99%), ether (99%), vinyl acetate (99%), hexane (97%) and chloroform (99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Pro. 2, 2'-Azobis(2-methylpropionitrile) (AIBN, 98%) was purified by recrystallization from ethanol, and THF was distilled over sodium. All other reagents were used as received. Propynyl glycol acrylate was prepared using a previously reported procedure, to a solution of 2-propynoic acid (3.50 g, 50.0 mmol) and ethylene glycol (46.8 mL, 755 mmol) was added p-toluenesulfonic acid monohydrate (1.63 g, 8.64 mmol). The mixture was stirred at 60 °C for 24 h, then poured into 100 mL of saturated aqueous sodium bicarbonate. The organic layer was extracted four times with 30 mL of ethyl acetate. The combined organic layers were dried over anhydrous magnesium sulfate. After the evaporation of the solvents, the residue was purified by vacuum distillation to give 3.87 g (33.9 mmol, yield: 67.9%) of propynyl glycol acrylate. PE by conventional free radical mechanism was obtained by the polymerization of ethylene (30 bar) in DMC (1.8 mL) with AIBN (10.7 mg, 0.065 mmol) as the initiator at 75 °C, M_n was determined to be 11700 g/mol, yield was 0.57 g, DB (degree of branching) was determined to be 45.

3.2 Characterization. NMR spectra were recorded on Bruker AV300 NMR spectrometer, all copolymers were dissolved in chloroform-d ($CDCl_3$) or dimethyl sulfoxide-d$_6$ (DMSO-d$_6$) with tetramethylsilane (TMS) as an internal reference at ambient temperature. DB was calculated based on the ^{1}H NMR ($C_2D_2Cl_4$, 300 MHz, 120 °C) of related common PE and PE based-copolymers obtained using CMRP method. The molecular weight distribution and relative number-average molecular weight of common PE, PE-based copolymers obtained using CMRP method and degradation products were determined at 150 °C by a high-temperature chromatograph, PL-GPC 220 instrument equipped with a triple detection array, including a differential refractive index (RI) detector, a two-angle light scattering (LS) detector, and a four bridge capillary viscometer. The detection angles of the LS detector were 15 and 90, and the laser wavelength was 658 nm. 1, 2, 4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of 1.0 mL min^{-1}. The viscometer and the light scattering (LS) as on-line detectors allow the direct measure of the true molecular weight of the sample. The molecular weight distributions and relative number-average molecular weights of PMDO, P(MDO-*co*-E) macro-initiator and all other copolymers were determined at 35 °C by gel permeation chromatography (GPC, Waters 1515) equipped with a refractive index detector (Waters 2414) and a series of Styragel HR1, HR3 and HR5 (THF) column with the eluent at 1.0 mL/min, the molecular weights were calibrated against polystyrene standards. Water contact angles on polymer films were measured with Contact Angle Meter SL200B (Solon Tech. Co., Ltd.) by the dynamic sessile drop method, samples were prepared by the evaporation of 20 % (w/w) solutions in dry THF onto silicon slides and THF was evaporated. Infrared spectra were collected by a Niclolet 380 spectrometer using Attenuated Total Reflectance (ATR) in the range of wavenumbers of 4000-400 cm^{-1}. For PE with ester structure in the backbone, sample was prepared by the evaporation of 20 % (w/w) polymer solution in $CHCl_3$ onto transparent potassium bromide sheet and $CHCl_3$ was evaporated. For common PE, the sample was measured directly. Differential scanning calorimetry (DSC) analysis was performed using a TA Q2000 differential scanning calorimeter instrument with a heating rate of 10 °C/min under a flowing nitrogen atmosphere from 10 °C to 110 °C.

3.3 Synthesis of 2-methylene-1, 3-dioxepane (MDO). 1,4-Butanediol (18.0 g, 200.0 mmol), 2-bromo-1,1-dimethoxyethane (33.8 g, 200.0 mmol) and *p*-toluenesulfonic acid (379.8 mg, 2.0 mmol) were added into a 100 mL round-bottom flask with a distillation apparatus and receiving flask. The mixture was stirred at 120 °C for 16 h, and 90% of the theoretical mass of ethanol byproduct was collected. The crude mixture was distilled to yield 25.8 g product of 2-bromo-1, 3-dioxepane. 2-Bromo-1, 3-dioxepane (21.7 g, 111.2 mmol) and aliquat 336 (902.3 mg, 2.2 mmol) in 100 mL of anhydrous THF were added to a 250 mL round-bottom flask. The solution was vigorously stirred in ice bath while potassium tert-butoxide (24.9 g, 221.4 mmol) was added within 45 min. The mixture was allowed to react for 75 min, subsequently, warmed to room temperature and stirred for an additional 12 h. After ether (100 mL) was added, the mixture was stirred vigorously and filtered. The filtered solids were collected and washed with ether (3 × 70 mL). The slurry was vacuum filtered, concentrated, and then filtered again, ether was then removed using rotary evaporation. The crude product was distilled at reduced pressure to yield 6.6 g (51.9%) of 2-methylene-1, 3-dioxepane (MDO). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (m, 4H,$-OCH_2-CH_2-CH_2-CH_2O-$), 3.45 (s, 2H, $-C=CH_2$), 3.92 (m, 4H, $-OCH_2-CH_2-CH_2-CH_2O-$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.0 ($-OCH_2-CH_2$-CH_2-CH_2O-), 67.4 (-CH_2=$(CO)_2-$), 70.4 ($-OCH_2$), 164.0 ($-C=CH_2$).

3.4 Synthesis of 2-methylene-1, 3, 6-trioxocane (MTC). Diethylene glycol (21.2 g, 200.0 mmol), 2-bromo-1, 1-dimethoxyethane (33.8 g, 200.0 mmol) and *p*-toluenesulfonic acid (379.8 mg, 2.0 mmol) were added to a 100 mL round-bottom flask with distillation apparatus and receiving flask. The mixture was stirred at 120 °C for 16 h. The crude mixture was distilled to yield 20.3 g of 2-bromo-1, 3, 6-trioxocane. 2-Bromo-1, 3, 6-trioxocane (18.7 g, 88.6 mmol) and aliquat 336 (717.2 mg, 1.8 mmol) in 100 mL of anhydrous THF were added to a 250 mL round-bottom flask. This solution was vigorously stirred in ice bath while potassium tert-butoxide (29.6 g, 177.2 mmol) was added within 45 min. The mixture was allowed to react for 75 min, then warmed to room temperature and stirred for an additional 12 h. Ether (100 mL) was added, and the mixture was stirred vigorously and filtered. The solids were collected and washed with ether (3 × 70 mL). The slurry was filtered, concentrated, and then filtered again, ether was removed using rotary evaporation. This crude product was distilled to yield 4.3 g (47.9%) of 2-methylene-1, 3, 6-trioxocane (MTC). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.47 (s, 2H, $C=CH_2$), 3.76–3.91 (m, 4H, 2 -OCH_2-), 1.72–1.78 ppm (m, 4H, -$OCH_2CH_2CH_2CH_2O$-). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 ($C=CH_2$), 70.8 (-$OCH_2CH_2CH_2CH_2O$-), 70.3 (=$CHOCH_2$), 70.2 (-$C=CH_2$).

3.5 Synthesis of vinyl bromobutanoate (VBr). A mixture of 4-bromobutanoic acid (15.5 g, 92.8 mmol), KOH (0.52 g, 9.3 mmol) and $Pd(OAc)_2$ (1.0 g, 4.6 mmol) in vinyl acetate (79.9 g, 928.0 mmol) was stirred at 60 °C for 16 h. The mixture was then filtered over neutral alumina and thoroughly washed with hexane in order to remove the excess of $Pd(OAc)_2$. The excess of vinyl acetate and hexane were evaporated using rotary evaporation. The crude product was purified and isolated by a column chromatography (100% CH_2Cl_2) before dried over anhydrous $MgSO_4$. Yield was 12.2 g (67.3%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (t, 1H, $COOCHCH_2$), 4.89 (d, 2H, COOCHCHH), 4.58 (d, 2H, COOCHCHH), 3.47 (t, 2H, CH_2CH_2Br), 2.60 (t, 2H, CH_2CH_2COOCH), 2.22 (m, 2H, $CH_2CH_2CH_2Br$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.8

(CH_2CHCOO), 141.3 (CH_2CHCOO), 98.2 (CH_2CHCOO), 32.9 ($CH_2CH_2CH_2Br$), 34.1 ($CH_2CH_2CH_2Br$), 27.5 ($CH_2CH_2CH_2Br$).

3.6 Homo-polymerization of ethylene (common PE) using CMRP method. In a typical experiment, Co^{II}(Salen*) (6.0 mg, 0.01 mmol) and AIBN (10.7 mg, 0.065 mmol) were weighed into DMC (1.8 mL) and the mixture was introduced into a 100 mL stainless steel reactor followed by freeing from oxygen with argon. Ethylene was then introduced until the desired pressure (30 bar) and the mixture was heated to 75 °C under stirring (400 rpm). Ethylene was continuously introduced to the reactor to maintain a constant ethylene pressure. After 22 h of polymerization, the reactor was cooled to room temperature. The crude polymerization mixture was precipitated into hexane followed by centrifugation, and then dried under vacuum.

3.7 Homo-polymerization of MDO at Co^{II}(Salen*) : AIBN : MDO = 1 : 5 : 500. The polymerization was performed in bulk. MDO (5.7 g, 50.0 mmol), Co^{II} (Salen*) (60.4 mg, 0.1 mmol) and AIBN (82.0 mg, 0.5 mmol) were added into a 20 mL round-bottomed flask equipped with a three-way valve and a magnetic stirrer. The system was cooled in liquid nitrogen and air was removed by three freeze-vacuum-thaw cycles. The flask was immersed in an oil bath at 75 °C under stirring (400 rpm). After the given time of polymerization, an aliquot was taken out to determine the conversion of MDO using ^1H NMR spectroscopy. PMDO was obtained by precipitating the mixture into cold hexane followed by centrifugation. The resulting polymer was dissolved into chloroform, precipitated into excess of cold hexane, and then dried under vacuum.

3.8 Copolymerization of MDO and ethylene at Co^{II}(Salen*) : AIBN : MDO = 1 : 6.5 : 526. In a typical experiment, to the mixture of 0.60 mL of MDO and 1.8 mL of DMC were added AIBN (10.7 mg, 0.065 mmol) and Co^{II}(Salen*) (6.0 mg, 0.010 mmol). The mixture was introduced into a 100 mL stainless steel reactor, followed by freeing from oxygen with argon. Ethylene was then introduced until the pressure of 30 bar and the mixture was heated to 75 °C under stirring (400 rpm). Ethylene was continuously introduced to the reactor to maintain a constant ethylene pressure. After 22 h of polymerization, the reactor was cooled to room temperature and an aliquot was taken out to determine the conversion of MDO. The crude polymerization mixture was precipitated into hexane followed by centrifugation, the resulting polymer was dissolved in chloroform and precipitated into excess of cold hexane, and dried under vacuum. Also, the copolymerizations under different ethylene pressure or different DMC volume were carried out.

3.9 Copolymerization of MDO and ethylene at Co^{II}(Salen*) : AIBN : MDO = 1 : 6.5 : 1052. To the mixture of 0.60 mL of MDO and 1.20 mL of DMC were added AIBN (5.3 mg, 0.032 mmol) and Co^{II}(Salen*) (3.0 mg, 0.005 mmol). The mixture was introduced into a 100 mL stainless steel reactor followed by freeing from oxygen with argon. Ethylene was then introduced until the desired pressure (40 bar) and the mixture was heated to 75 °C under stirring (400 rpm). Ethylene was continuously introduced to the reactor to maintain a constant ethylene pressure. After 22 h of polymerization, the reactor was cooled to room temperature. The crude polymerization mixture was precipitated into hexane followed by centrifugation, the resulting polymer was dissolved in chloroform, precipitated into excess of cold hexane, and then dried under vacuum.

3.10 Synthesis of the Co^{III}(Salen*)-P(MDO-*co*-E) macro-initiator and chain extension of VAc from Co^{III}(Salen*)-P(MDO-*co*-E). The synthesis of Co^{III}(Salen*)-P(MDO-*co*-E) macro-initiator was performed under the condition of Co^{II}(Salen*) : AIBN : MDO = 1: 6.5 : 526 in DMC at 75 °C under 10 bar of ethylene pressure. The total volume of the solution was 1.0 mL and the weight of Co^{II}(Salen*) was 6.0 mg. After 22 h of polymerization, the polymerization was stopped to give a Co^{III}(Salen*)-P(MDO-*co*-E) macro-initiator with M_n of 11000 and Đ of 1.15. Then, Co^{III}(Salen*)-P(MDO-*co*-E) was used as macro-initiator for the polymerization of VAc to form block copolymer. Bulk polymerization of VAc (1.72 g, 20 mmol) in the presence of Co^{III} (Salen*)-P(MDO-co-E) (650 mg, 0.050 mmol) was carried out in the presence of AIBN (5.3 mg, 0.032 mmol) at 75 °C. After 20 h of polymerization, the reactor was cooled to room temperature and crude polymerization mixture was precipitated into hexane followed by centrifugation, the resulting polymer was dissolved into chloroform and precipitated into excess of cold hexane, and dried under vacuum. PVAc-*b*-P(MDO-*co*-E) with M_n of 35300 g/mol and Đ of 1.26 was obtained, yield was 1.68 g.

3.11 Homo-polymerization of MTC. The polymerization was performed in bulk. MTC (650.0 mg, 5.0 mmol), Co^{II}(Salen*) (6.0 mg, 0.010 mmol) and AIBN (10.7 mg, 0.065 mmol) were added into a 10 mL round-bottomed flask equipped with a three-way valve and a magnetic stirrer. The system was cooled in liquid nitrogen and air was removed by three freeze-vacuum-nitrogen-thaw cycles. The flask was immersed in an oil bath at 75 °C. After 22 h of polymerization, the reaction was exposed to air, and PMTC was obtained by precipitating the mixture into cold hexane and followed by centrifugation. The resulting polymer was dissolved into chloroform and precipitated into tenfold excess of cold hexane and dried under vacuum. M_n = 16300 g/mol, Đ = 1.25, yield was 0.14 g.

3.12 Copolymerization of MTC and ethylene. To the mixture of 0.6 mL of MTC and 1.8 mL of DMC were added Co^{II}(Salen*) (6.0 mg, 0.010 mmol) and AIBN (10.7 mg, 0.065 mmol). The mixture was introduced into a 100 mL stainless steel reactor, followed by freeing from oxygen with argon. Ethylene was then introduced until the desired pressure (30 bar) and the mixture was heated to 75 °C under stirring (400 rpm). Ethylene was continuously introduced to the reactor to maintain a constant ethylene pressure. After 22 h of polymerization, the reactor was cooled to room temperature and crude polymerization mixture was precipitated into hexane followed by centrifugation. The resulting polymer was dissolved into chloroform and precipitated into excess of cold hexane, and dried under vacuum. MTC incorporation was 11.6%, M_n = 10600 g/mol, Đ = 1.22. Yield was 0.64 g. The investigations on the kinetics of Co^{II}(Salen*)-mediated radical copolymerization of ethylene and MTC were carried out at 30 bar of ethylene pressure and 1 : 3 volume ratio of MDO : DMC and the results were shown in Figure S12.

3.13 Copolymerization of MDO, ethylene and polar vinyl monomers. In a typical experiment, to the mixture of 0.6 mL of MDO, 0.3 mL of perfluorohexylethylene (PFHE) and 1.2 mL of DMC were added Co^{II}(Salen*) (6.0 mg, 0.010 mmol) and AIBN (10.7 mg, 0.065 mmol). The mixture was introduced into a 100 mL stainless steel reactor, followed by freeing from oxygen with argon. Ethylene was then introduced until the desired pressure (20 bar) and the mixture was heated to 75 °C under stirring (400 rpm). Ethylene was continuously introduced to the reactor to maintain a constant ethylene pressure. After 22 h of polymerization, the reactor was cooled to room temperature and the crude polymerization mixture was precipitated into hexane followed by centrifugation, the resulting polymer was dissolved into chloroform and precipitated into excess of cold hexane, and dried under vacuum.

3.14 Post-modification of the resulting PE with ester units in the PE backbone. To the mixture 0.6 mL of MDO, 0.3 mL of VBr and 1.2 mL of DMC were added Co^{II}(Salen*) (6.0 mg, 0.01 mmol) and AIBN (10.7 mg, 0.065 mmol). The mixture was introduced into a 100 mL stainless steel reactor followed by freeing from oxygen with argon. Ethylene was then introduced until the desired pressure (30 bar) and the mixture was heated to 75 °C under stirring (400 rpm). Ethylene was continuously introduced to the reactor to maintain a constant ethylene pressure. After 22 h of polymerization, the reactor was cooled to room temperature and the crude polymerization mixture was precipitated into hexane followed by centrifugation, the resulting polymer was dissolved into chloroform, precipitated into excess of cold hexane, and then dried under vacuum to yield P(MDO-*co*-E-*co*-VBr), M_n = 12300 g/mol, Đ = 1.20, yield was 0.62 g. The post-modification included two steps. Firstly, P(MDO-*co*-E-*co*-VBr) (0.31 g) was dissolved in DMF (10 mL) and NaN_3 (0.070 g, 1.07 mmol) was added to the mixture before being stirred at room temperature for 2 days. DMF was then removed, the polymer was dissolved in a small amount of toluene before being precipitated into cold hexane. The polymer was dried under vacuum to yield P(MDO-*co*-E-*co*-VN_3), M_n = 12400 g/mol, Đ = 1.21, yield was 0.28 g. Secondly, P(MDO-*co*-E-*co*-VN_3) (0.2 g) was dissolved in DMF (5 mL) and propynyl glycol acrylate (0.060 g, 0.61 mmol) was added to the mixture. The mixture was stirred for 15 min and then heated to 80 °C for 48 h. The solvent was removed, the polymer was dissolved in a small amount of $CHCl_3$, precipitated into excess of cold hexane, and then dried under vacuum. M_n = 15300 g/mol, Đ = 1.34, yield was 0.34 g.

3.15 Degradation. The degradation of P(MDO-*co*-E) was performed in chloroform solution with triethylamine in the presence small amount of water. P(MDO-*co*-E) (40 mg) containing 68.3% ethylene were weighed into a round-bottomed flask and stirred at 70 °C. After a certain time, an aliquot was taken out for analyzing via ^{1}H NMR spectroscopy and GPC (TCB, 150 °C).

3.16 Film degradation. P(MDO-*co*-E) (400 mg) containing 68.3% ethylene was dissolved in 2 mL of $CHCl_3$ and 10 mg of Eosin Y (purple color), P(MDO-*co*-E) film was formed by coating the solution in glass slides and washed with CH_3OH to remove the residual Eosin Y on the surface. The film was then emerged in methanol with triethylamine in the presence of a small proportion of water.