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Supplemental Information

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

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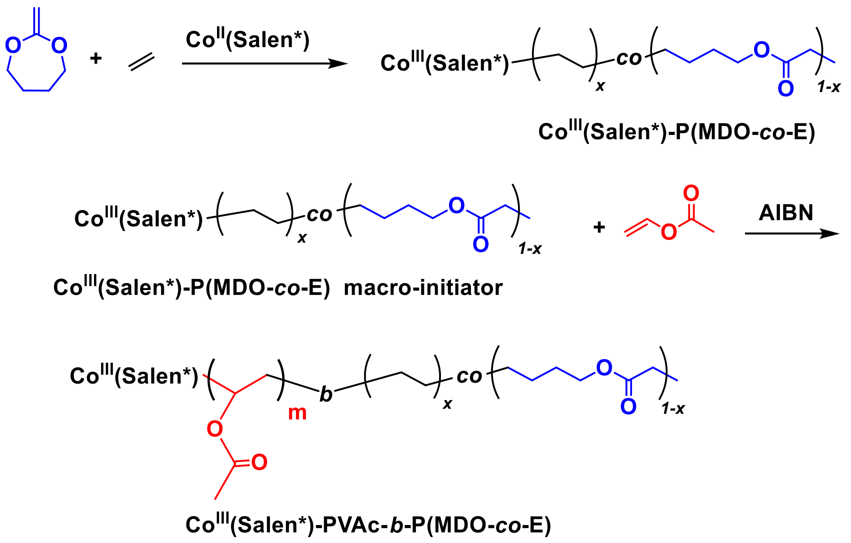
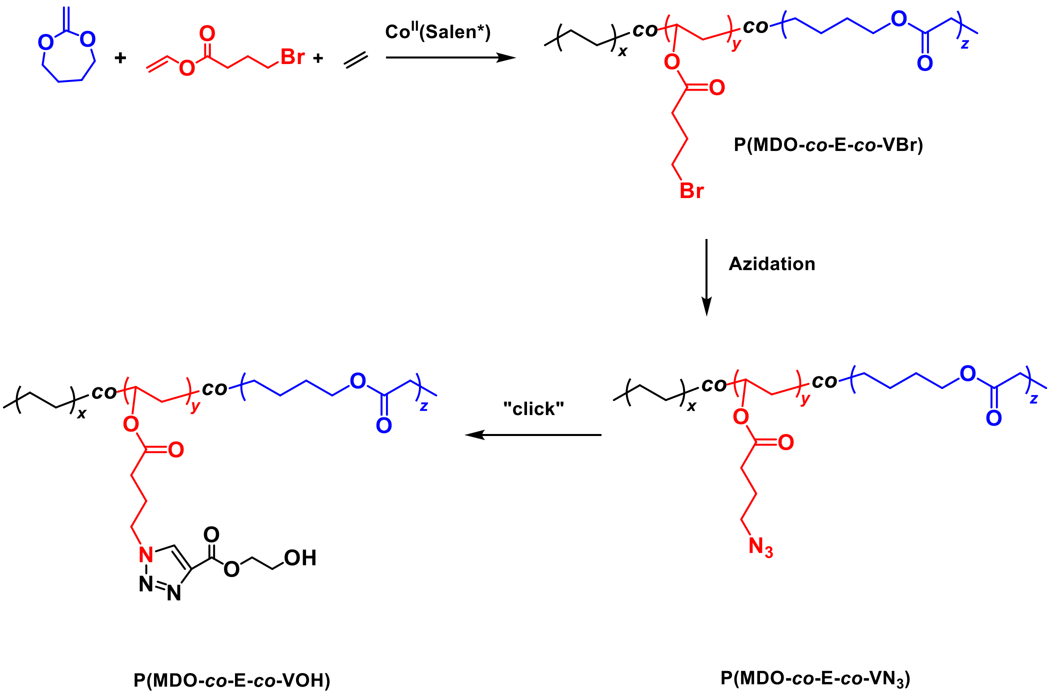
1. Figures and Schemes



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.

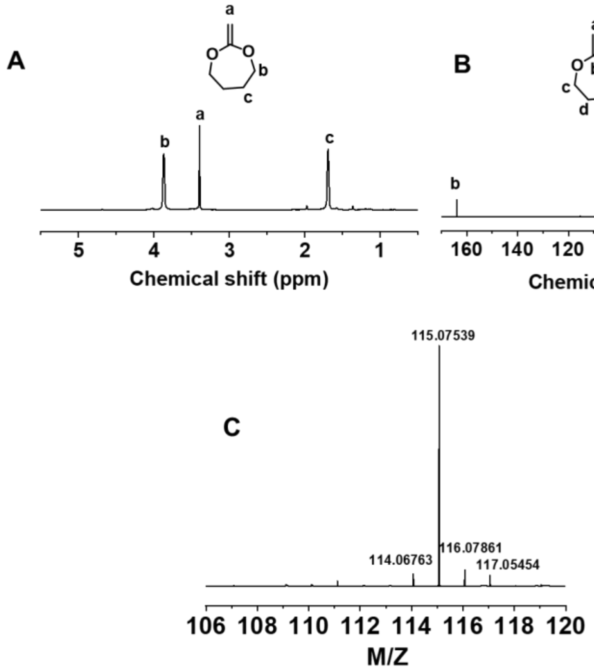


Figure S1. (A) ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of MDO, (B) ^{13}C NMR ($CDCl_3$, 300 MHz) spectrum of MDO, (C) ESI mass spectrum of MDO, related to Figure 1.

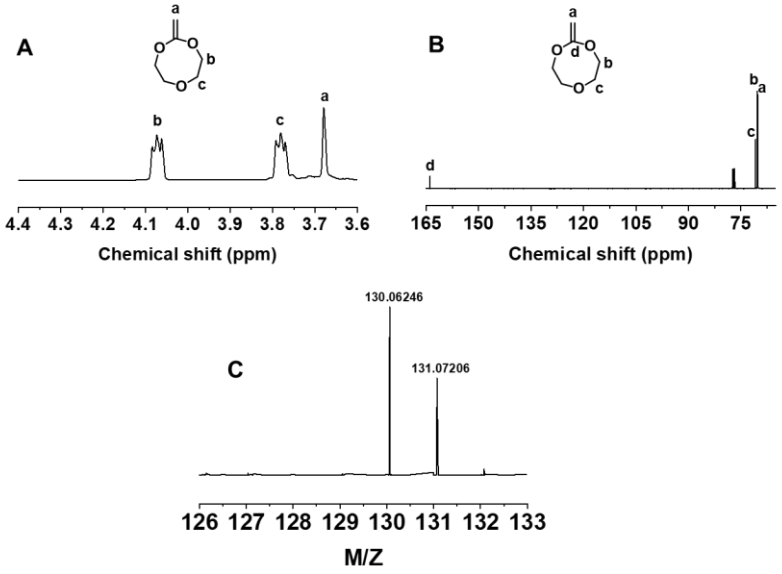


Figure S2. (A) ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of MTC, (B) ^{13}C NMR ($CDCl_3$, 300 MHz) spectrum of MTC, (C) ESI mass spectrum of MTC, related to Figure 1.

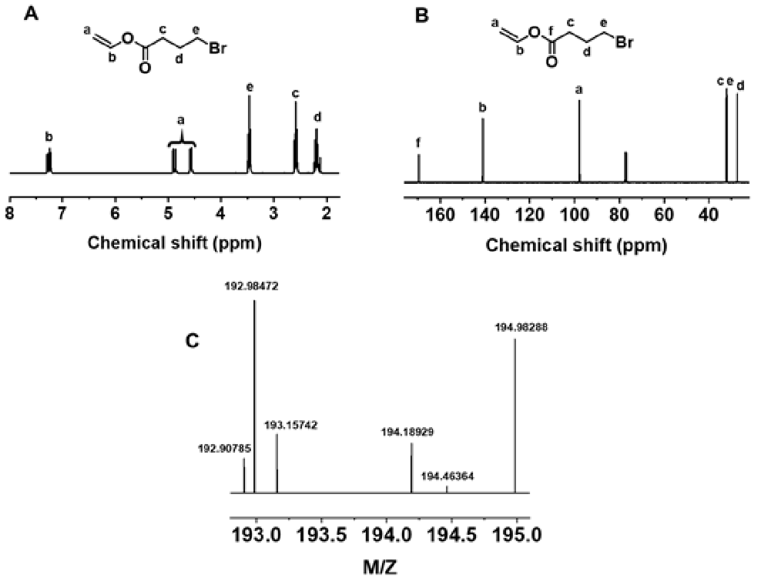


Figure S3. (A) ^{1}H NMR (CDCl$_3$, 300 MHz) spectrum of VBr, (B) ^{13}C NMR (CDCl$_3$, 300 MHz) spectrum of VBr, (C) ESI mass spectrum of VBr, related to Scheme 2.

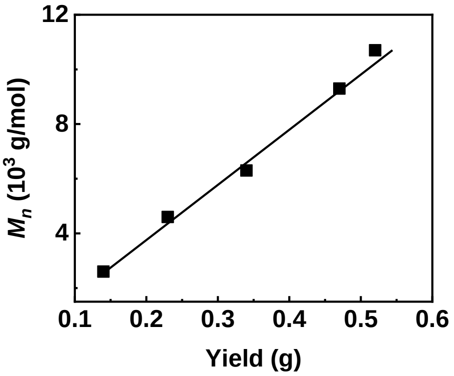


Figure S4. The variation of M_n and Đ for common PE with polymer yield, related to Table 1. Conditions: DMC (1.8 mL), ethylene (30 bar), Co^{II}(Salen*) (6.0 mg, 0.01 mmol), AIBN (10.07 mg, 0.065 mmol), 75 °C.

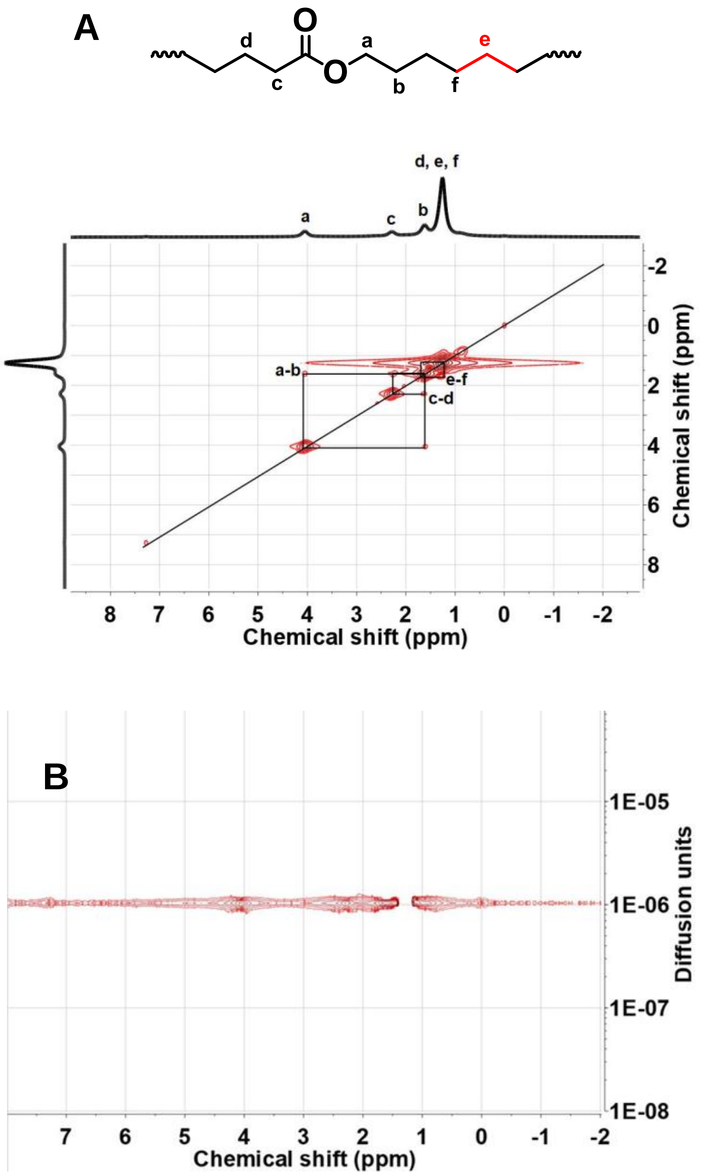


Figure S5. ^{1}H COSY NMR spectra (A) and ^{1}H DOSY NMR spectra (B) of P(MDO-*co*-E) with 76.9% ethylene content, related to Figure 2.

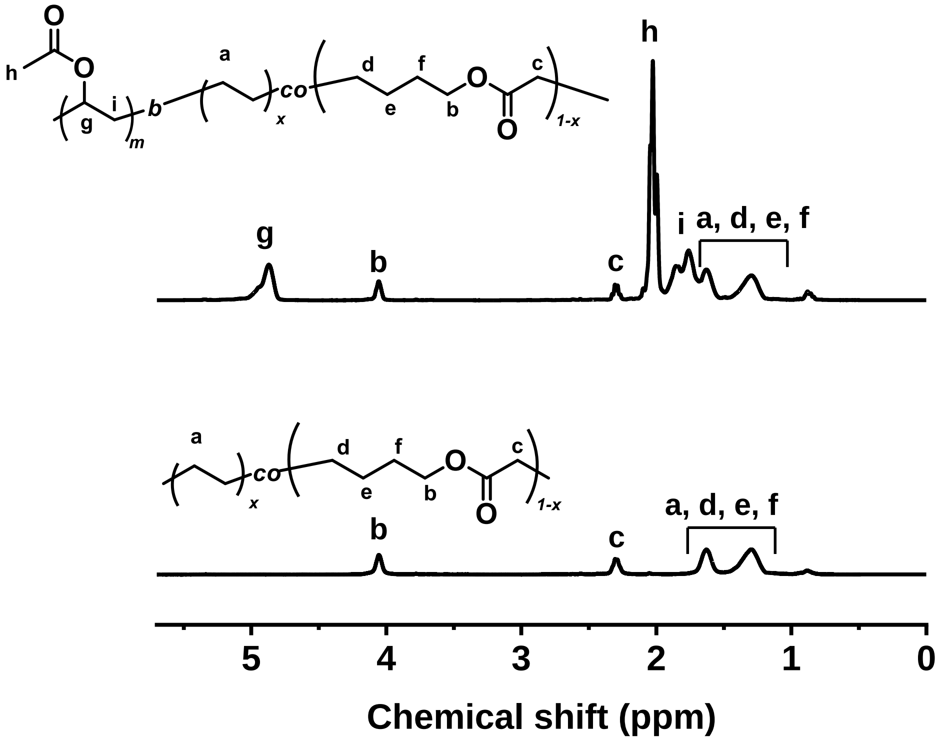


Figure S6. ^{1}H NMR ($CDCl_3$, 300 MHz) spectra of macro-initiator Co^{III}(Salen*)–P(MDO-*co*-E) and block copolymer PVAc-*b*-P(MDO-*co*-E), related to Figure 2.

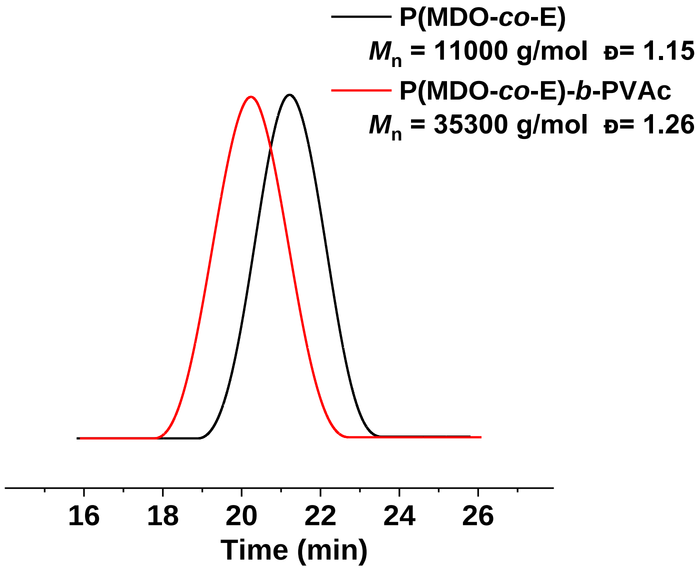


Figure S7. GPC (THF, 35 °C) curves of the resulting copolymer and block copolymer, related to Figure 2.

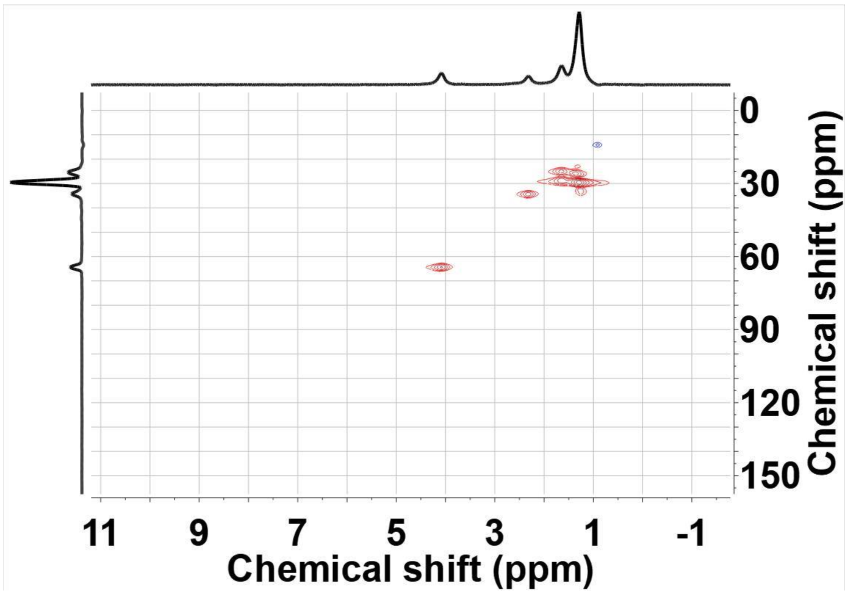


Figure S8. HSQC NMR spectrum of produced P(MDO-*co*-E) with with 76.9% ethylene content, related to Figure 3.

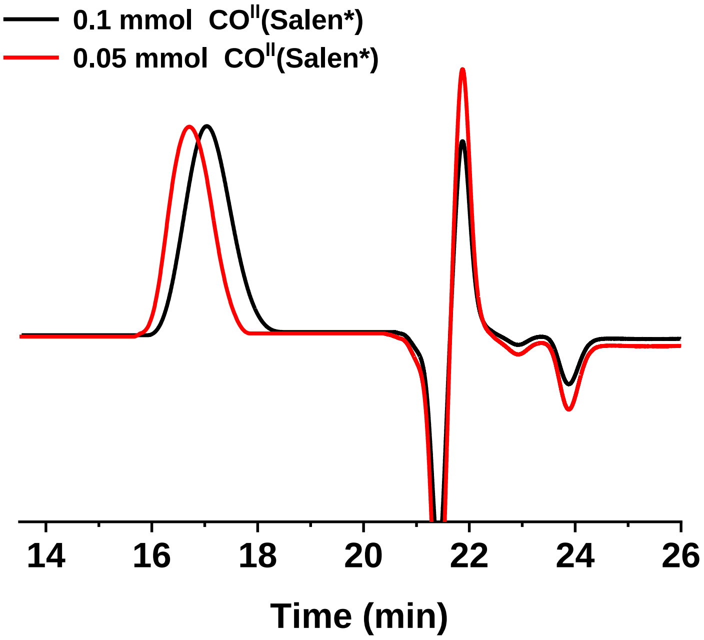


Figure S9. GPC (TCB, 150 °C) curves of produced PE with ester units in the backbone using various amount of Co^{II}(Salen*), related to Table 1.

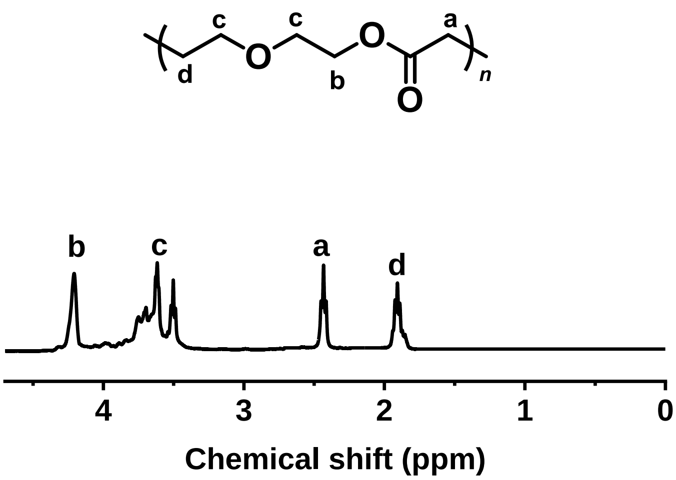


Figure S10. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of homo-PMTC, related to Scheme 1.

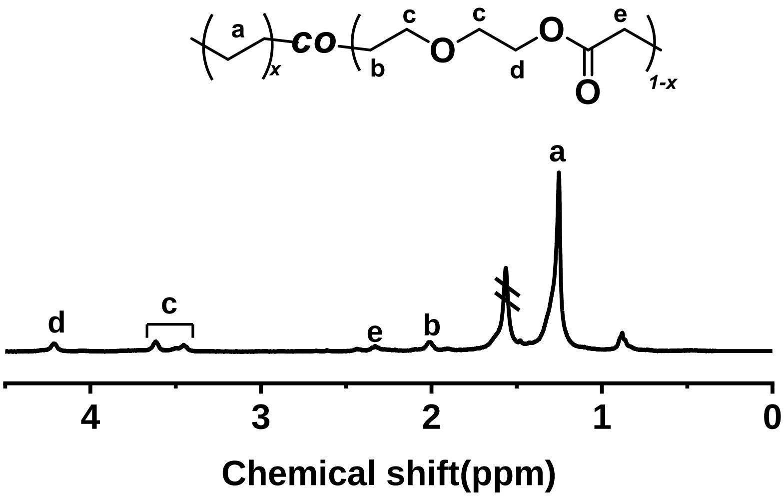


Figure S11. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of P(MTC-*co*-E) with 88.4% ethylene content, related to Scheme 1.

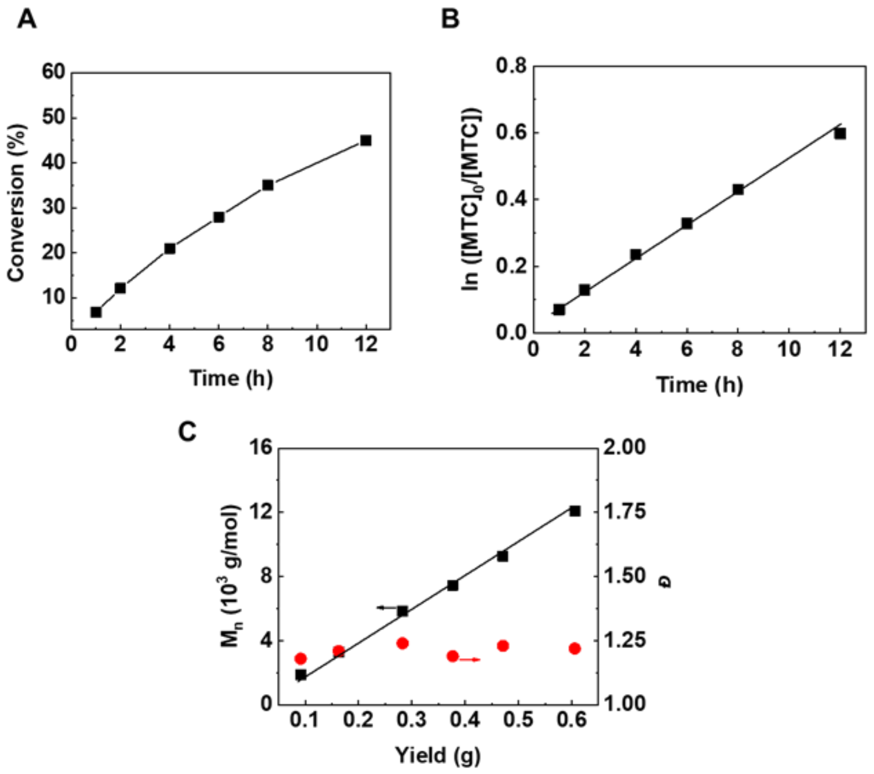


Figure S12. Copolymerization of MTC and ethylene, related to Scheme 1. Conditions: MTC (0.6 mL), DMC (1.8 mL), ethylene (30 bar), $\mathrm{Co^{II}}$(Salen*) (6.0 mg, 0.010 mmol), AIBN (10.7 mg, 0.065 mmol), 75 °C. (A) The evolution of MTC conversion with polymerization time. (B) The evolution of $\ln([\mathrm{MTC}]_0/[\mathrm{MTC}]_t)$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

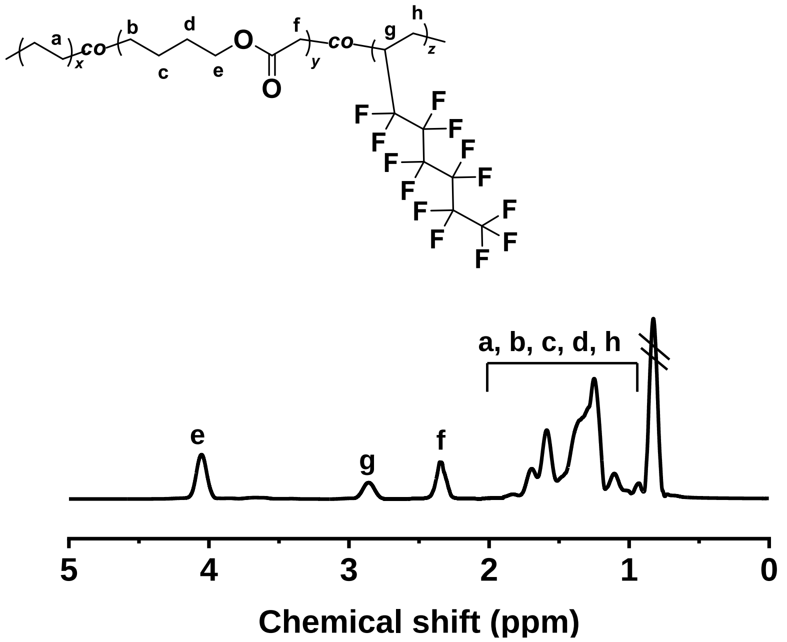


Figure S13. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of P(MDO-*co*-E-*co*-PFHE), related to Table 2. Conditions: PFHE (0.3 mL), MDO (0.6 mL), ethylene (20 bar), DMC (1.2 mL), Co^{II}(Salen*) (6.0 mg), AIBN (10.7 mg), under 75 °C.

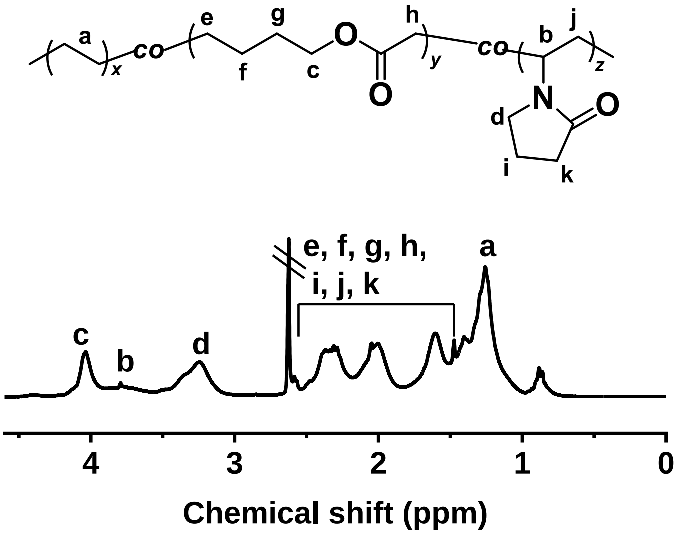


Figure S14. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of P(MDO-*co*-E-*co*-NVP), related to Table 3. Conditions: NVP (0.6 mL), MDO (0.6 mL), ethylene (20 bar), DMC (1.2 mL), Co^{II}(Salen*) (6.0 mg), AIBN (10.7 mg), under 75 °C.

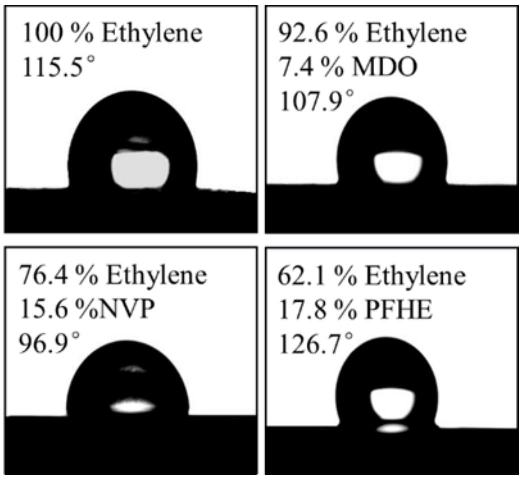


Figure S15. Water contact for copolymers, related to Scheme 2.

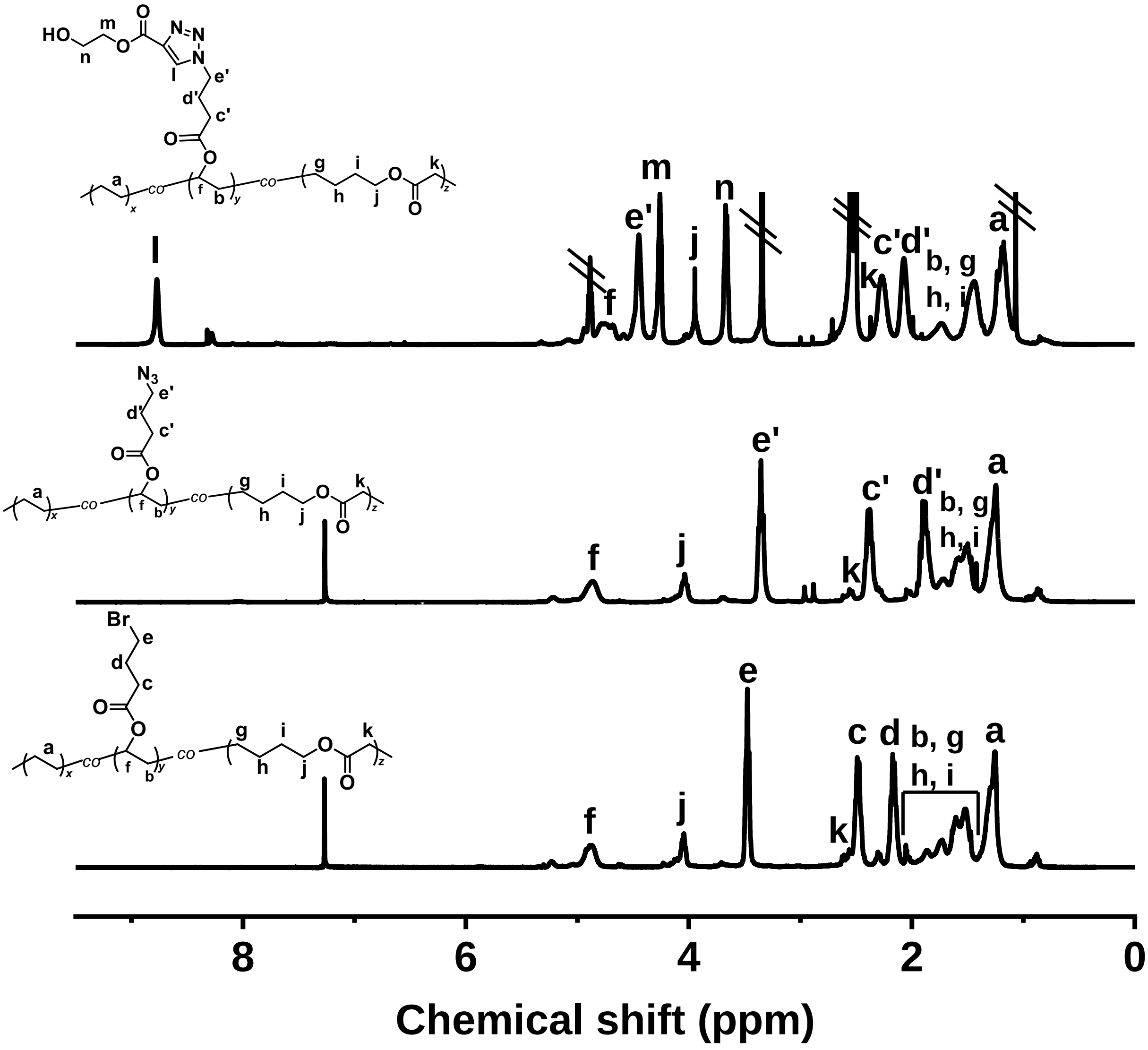


Figure S16. ^{1}H NMR ($CDCl_3$, 300 MHz) spectra of P(MDO-*co*-E-*co*-VBr), P(MDO-*co*-E-*co*-VN_3) and ^{1}H NMR (DMSO-d_6, 300 MHz) spectrum of the copolymer after “click”, related to Scheme 2.

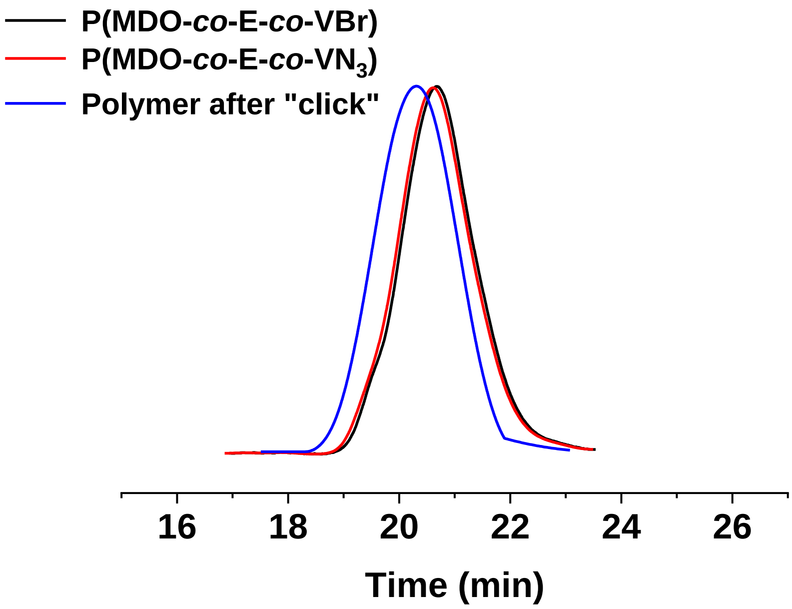


Figure S17. GPC (THF, 35 °C) curves of (MDO-*co*-E-*co*-VBr), P(MDO-*co*-E-*co*-VN$_3$) and the copolymer after “click”, related to Scheme 2.

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$_3$N, 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 ^1H 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 ^{1}H 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$^{\mathrm{III}}$(Salen*)-P(MDO-*co*-E) macro-initiator and chain extension of VAc from Co$^{\mathrm{III}}$(Salen*)-P(MDO-*co*-E). The synthesis of Co$^{\mathrm{III}}$(Salen*)-P(MDO-*co*-E) macro-initiator was performed under the condition of Co$^{\mathrm{II}}$(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$^{\mathrm{II}}$(Salen*) was 6.0 mg. After 22 h of polymerization, the polymerization was stopped to give a Co$^{\mathrm{III}}$(Salen*)-P(MDO-*co*-E) macro-initiator with M_n of 11000 and Đ of 1.15. Then, Co$^{\mathrm{III}}$(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$^{\mathrm{III}}$ (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$^{\mathrm{II}}$(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$^{\mathrm{II}}$(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$^{\mathrm{II}}$(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$^{\mathrm{II}}$(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.