

**Electronic Supplementary Information**

**Dithiocarbamate-Mediated Controlled Copolymerization of Ethylene with  
Cyclic Ketene Acetals towards Polyethylene-Based Degradable  
Copolymer**

**Supporting Information**

Tian-You Zeng, Lei Xia, Ze Zhang, Chun-Yan Hong,\* and Ye-Zi You\*

Key Laboratory of Soft Matter Chemistry, Chinese Academy of Science, Department of  
Polymer Science and Engineering, University of Science and Technology of China, Hefei,  
Anhui 230026, China.

E-mail: [zyyou@ustc.edu.cn](mailto:zyyou@ustc.edu.cn)

## Experimental Procedures

**Materials.** Di-tertbutyl peroxide (DTBP, 98%), dioxane (99%) and dimethyl carbonate (DMC, 99%) were purchased from Energy. Vinyl acetate (VAc, 99%) and tetrahydrofuran (THF, 99%) were purchased from Aladdin. Common PE and Lipase from *Candida antarctica* was purchased from Sigma-Aldrich. Cyanomethyl methyl(phenyl)carbamodithioate (CTA 4) was purchased from TCI. Methanol (99%), hexane (97%) and chloroform ( $\text{CHCl}_3$ , 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Pro. 2, 2'-Azobis(2-methylpropionitrile) (AIBN, 98%) was purified by recrystallization from ethanol. All other reagents were used as received. 2-methylene-1, 3-dioxepane (MDO) and 2-methylene-1, 3, 6-trioxocane (MTC) were prepared using the previously reported procedure<sup>1, 2</sup>. O-ethyl xantate (CTA 1), O-methyl xanthate (CTA 2) and *p*-methoxyphenyl xanthate (CTA 3) were prepared using the previously reported procedure<sup>3</sup>.

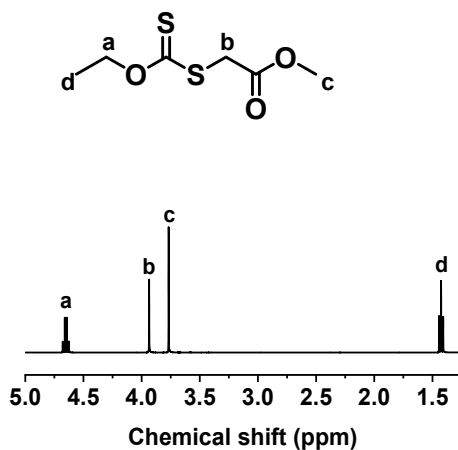


Figure S1.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) spectrum of CTA 1.

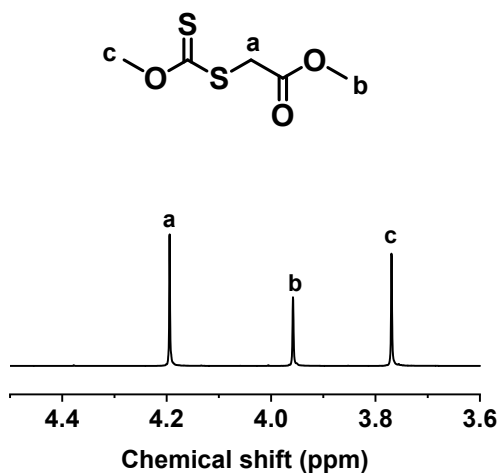
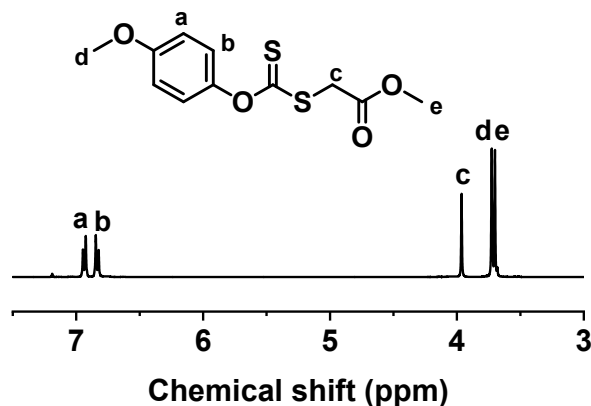


Figure S2.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) spectrum of CTA 2.



**Figure S3.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) spectrum of CTA 3.

**Characterization.** All NMR spectra were performed using Bruker AV300 NMR spectrometer, all samples were dissolved in chloroform-d with tetramethylsilane (TMS) as an internal reference. The molecular weight distribution, relative number-average molecular weights was 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. High temperature GPC was performed using PL-GPC-220 equipped with two Agilent PLgel Olexis columns at 150 °C using 1,2,4-trichlorobenzene as a solvent. The calibration curve was constructed on the basis of polyethylene standards. Infrared spectra were collected by a Nicolet 380 spectrometer using Attenuated Total Reflectance (ATR) in the range of wavenumbers of 4000-400  $\text{cm}^{-1}$ , for degradable PE-based copolymer, sample was prepared by the evaporation of 20 % (w/w) P(MDO-co-E) solution in  $\text{CHCl}_3$  onto transparent potassium bromide sheet and  $\text{CHCl}_3$  was evaporated under ambient conditions; common PE 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 20 °C to 110 °C.

**Copolymerization of ethylene and MDO using CTA 1-4.** In a typical experiment, to the mixture of MDO (0.6 mL, 5.26 mmol) and DMC (2.4 mL) was added AIBN (6.6 mg, 0.04 mmol) and CTA 4 (22.2 mg, 0.1 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 (3 MPa) and the mixture was heated to 70 °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 methanol followed by centrifugation, the

resulting polymer was dissolved into chloroform and precipitated into excess of methanol, and dried under vacuum. Also CTA 1-3 were used to mediate the copolymerization of MDO and ethylene. Under the following conditions: ethylene (55 bar), MDO (1.5 mL), DMC (10 mL), CTA 4 (33 mg), AIBN (10 mg), the yield of the copolymer increased obviously to ~1.8 g.

**Synthesis of P(MDO-co-E) macro-CTA and chain extension of VAc from P(MDO-co-E).** P(MDO-co-E) macro-CTA was obtained under 2.5 MPa of ethylene pressure and 1/3 volume ratio of MDO/DMC, the total volume of the solution was 2.4 mL and the weight of CTA 4 was 44.4 mg. After 22 h of polymerization at 70 °C, the polymerization was stopped to give a P(MDO-co-E) macro-CTA with  $M_n$  of 5500 g/mol and  $\bar{D}$  of 1.16, yield was 0.47 g. Polymerization of VAc (0.6 mL, 6.48 mmol) in the presence of P(MDO-co-E) macro-CTA (0.15 g, 0.027 mmol) and AIBN (3.3 mg, 0.02 mmol) in dioxane (1.2 mL) was carried out. After 16 h of polymerization at 70 °C, 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 18200 g/mol and  $\bar{D}$  of 1.36 was obtained, yield was 0.46 g.

**Synthesis of block-like copolymer composed of one PE-poor lock and one PE-rich block.** To the mixture of MDO (0.8 mL, 7.02 mmol) and DMC (3.2 mL) was added AIBN (6.6 mg, 0.04 mmol) and CTA 4 (22.2 mg, 0.1 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 (1 MPa) and the mixture was heated to 70 °C under stirring (400 rpm). Ethylene was continuously introduced to the reactor to maintain a constant ethylene pressure. After 4 h of polymerization, the reactor was cooled to room temperature and an aliquot was picked out to determine the conversion of MDO and  $M_n$  of the resulting copolymer, then ethylene pressure was increased to 4 MPa and allowed for another 4 h of copolymerization until the copolymer was formed.

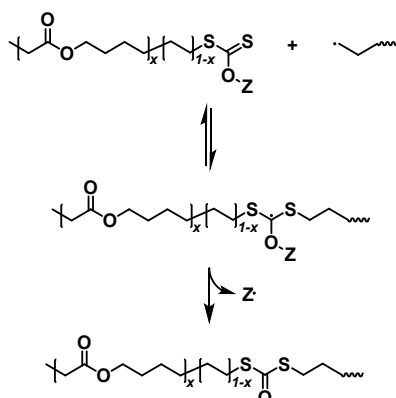
**Copolymerization of ethylene and MTC.** To the mixture of MTC (0.6 mL, 4.68 mmol) and DMC (1.8 mL) was added AIBN (6.6 mg, 0.04 mmol) and CTA 4 (22.2 mg, 0.1 mmol). The mixture was introduced into a 100 mL stainless steel reactor, followed by freeing from oxygen with argon. Ethylene was then introduced until the desired pressure (3 MPa) and the mixture was heated to 70 °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 methanol followed by centrifugation, the resulting polymer was dissolved into chloroform and precipitated into excess of methanol, and dried under vacuum. P(MTC-co-E) with  $M_n$  of 14200 g/mol and  $\bar{D}$  of 1.17 was obtained, yield was 0.78 g.

**Copolymerization of ethylene, VAc and MDO.** To the mixture of VAc (0.4 mL, 4.33 mmol), MDO (0.2 mL, 1.75 mmol) and DMC (1 mL) was added AIBN (6.6 mg, 0.04 mmol)

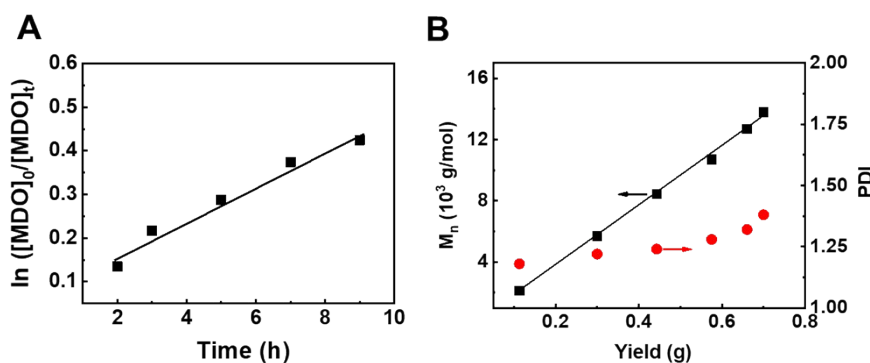
and CTA 4 (22.2 mg, 0.1 mmol). The mixture was introduced into a 100 mL stainless steel reactor, followed by freeing from oxygen with argon. Ethylene was then introduced until the desired pressure (3 MPa) and the mixture was heated to 70 °C under stirring (400 rpm). Ethylene was continuously introduced 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 hexane, and dried under vacuum.  $M_n = 15900$  g/mol,  $\bar{D} = 1.23$ , yield was 0.46 g.

**Hydrolysis.** The degradation of degradable PE-based copolymer was performed by enzymatic hydrolysis. The copolymer with 86.7% ethylene content was poured in 0.1 M PBS by the nano-precipitation technique. Copolymer (100.0 mg) was dissolved in 5 mL of THF and added dropwise to 20 mL of 0.1 M PBS under stirring. THF was then evaporated and lipase from *Candida antarctica* (100 U/mL) was added to the mixture (500.0 mg). After 20 days of incubation under stirring at 37 °C, the mixture was lyophilized, and 2 mL of chloroform was added, allowing removal of buffer salts by filtration. The degradation products were then analyzed by  $^1\text{H}$  NMR spectroscopy and GPC.

## Results

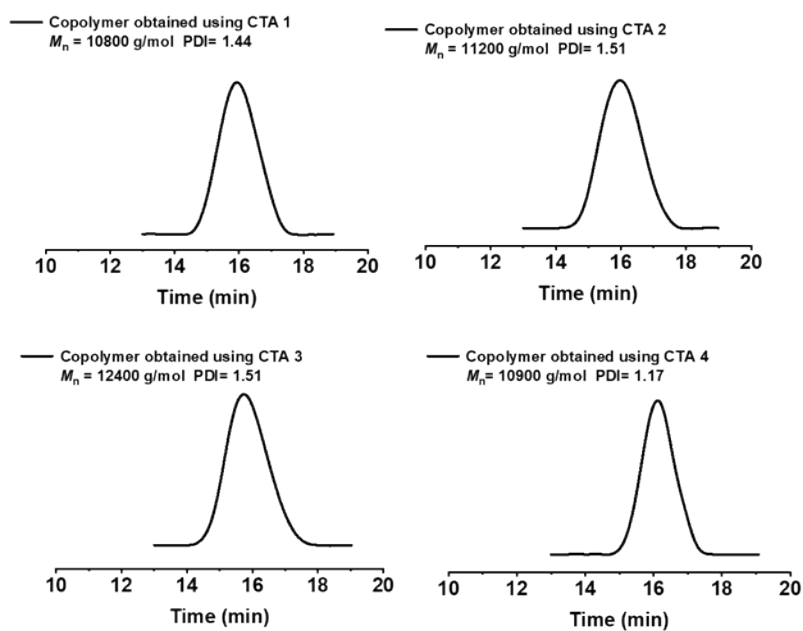


**Scheme S1.** Side fragmentation of the Z-group of CTA 1 and CTA 2 in the polymerization.

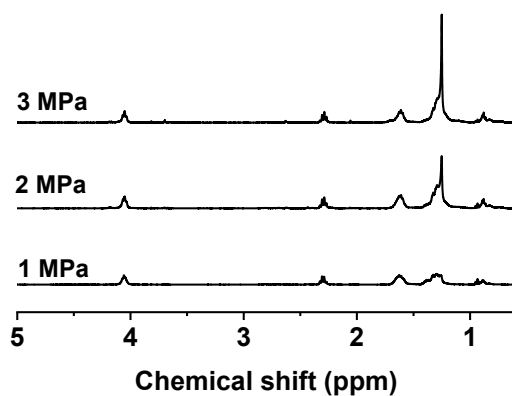


**Figure S4.** Synthesis of P(MDO-co-E) with CTA 3. Conditions: ethylene (3 MPa), MDO (0.6 mL, 5.26

mmol), DMC (1.8 mL), CTA 3 (27.2 mg, 0.1 mmol), AIBN (6.6 mg, 0.04 mmol), 70 °C. (A) The evolution of  $\ln([MDO]_0/[MDO]_t)$  with polymerization time. (C) The variation of  $M_n$  and  $\bar{D}$  for the copolymer with copolymer yield.



**Figure S5.** High temperature GPC curves of P(MDO-co-E) obtained using CTA 1-4.

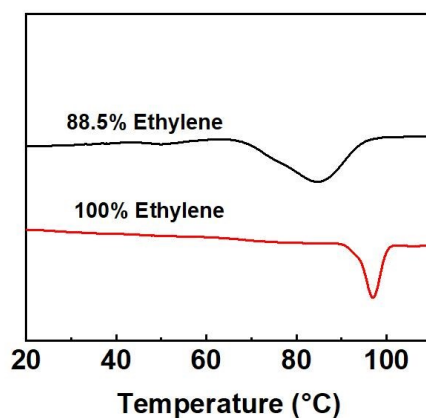


**Figure S6.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) spectra of P(MDO-co-E) prepared at 120 °C. Conditions: MDO (0.6 mL, 5.26 mmol), DMC (2.4 mL), CTA 4 (22.2 mg, 0.1 mmol), DTPB (5.8 mg, 0.04 mmol), 120 °C, 22 h.

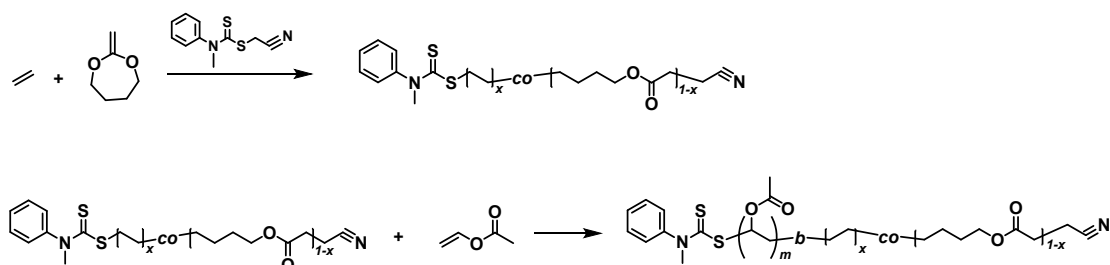
**Table S1.** Copolymerization of MDO and ethylene at 120 °C.

Entry	P (MPa)	Conversion <sup>[a]</sup> (%)	$M_n$ , NMR <sup>[b]</sup> (g/mol)	$M_n$ <sup>[c]</sup> (g/mol)	$DP_E$ <sup>[d]</sup>	$DP_{MDO}$ <sup>[d]</sup>	$\bar{D}$	X <sup>[e]</sup> (%)	Yield (g)	DB <sup>[f]</sup>
1	1	66.3	7600	5400	52	52	1.18	50.0	0.68	105
2	2	57.8	8800	6900	123	46	1.15	27.2	0.73	112
3	3	51.2	9300	7800	171	38	1.17	18.0	0.75	110

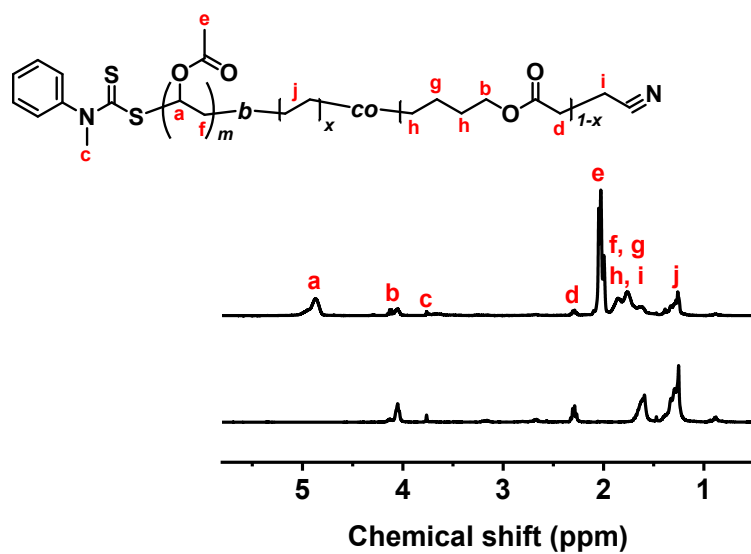
Conditions: MDO (0.6 mL, 5.26 mmol), DMC (2.4 mL), CTA 4 (22.2 mg, 0.1 mmol), DTPB (5.8 mg, 0.04 mmol), 120 °C, 22 h. [a] MDO conversion, determined by <sup>1</sup>H NMR spectroscopy. [b] Molecular weight, determined by <sup>1</sup>H NMR spectroscopy. [c] Molecular weight, determined by GPC. [d] Degree of polymerization, determined by <sup>1</sup>H NMR spectroscopy. [e] X = MDO content (mol %), determined by <sup>1</sup>H NMR spectroscopy. [f] Degree of branching, determined by <sup>1</sup>H NMR spectroscopy.



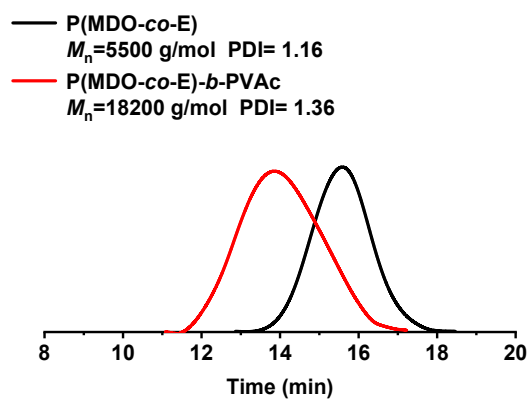
**Figure S7.** DSC thermograms for PE-based copolymer and common PE.



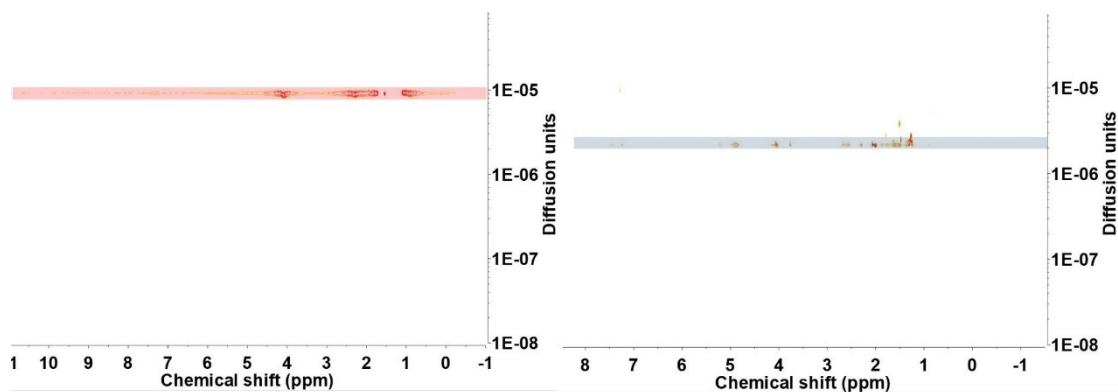
**Scheme S2.** Synthesis of P(MDO-co-E) macro-CTA and chain extension of VAc from P(MDO-co-E).



**Figure S8.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) spectra of P(MDO-co-E) macro-CTA and P(MDO-co-E)-b-PVAc.

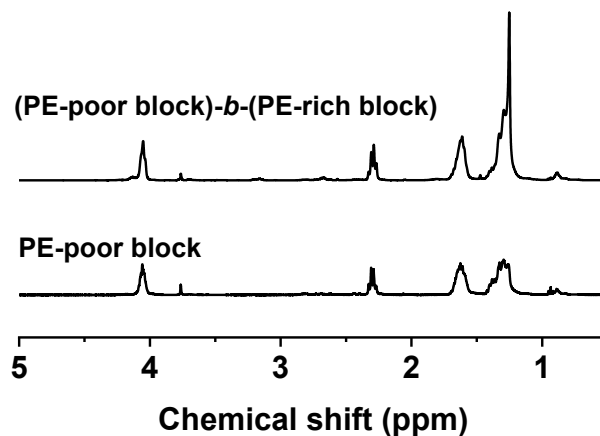


**Figure S9.** GPC curves of P(MDO-co-E) macro-CTA and P(MDO-co-E)-b-PVAc.



**Figure S10.** The DOSY spectra of P(MDO-co-E) macro-CTA and P(MDO-co-E)-b-PVAc.



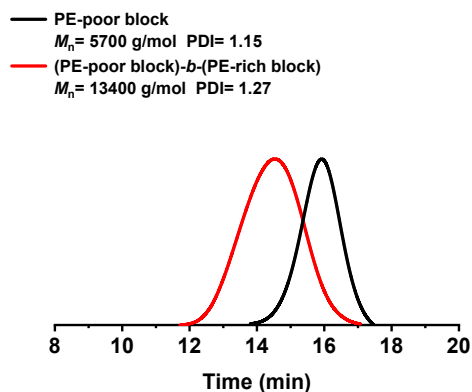


**Figure S11.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) spectra of PE-poor block and (PE-poor block)-*b*-(PE-rich block).

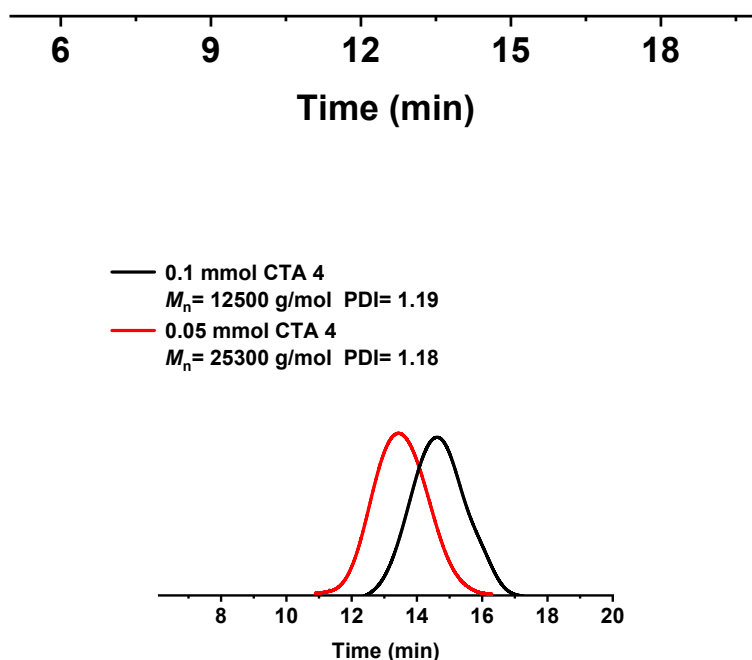
**Table S2.** Synthesis of PE-poor block and (PE-poor block)-*b*-(PE-rich block).

	MDO conversion (%) <sup>[a]</sup>	Composition		$M_n$ <sup>[d]</sup> (g/mol)	$\bar{D}$ <sup>[b]</sup>
		$X_1$ <sup>[b]</sup> (%)	$X_2$ <sup>[b]</sup> (%)		
Block-1	20.2	47.3	52.7	5700	1.15
Block-2	37.0	91.2 <sup>[c]</sup>	8.8 <sup>[c]</sup>	7700	-
Copolymer	-	67.2	32.8	13400	1.27

Conditions: MDO (0.8 mL, 7.02 mmol), DMC (3.2 mL), CTA 4 (22.2 mg, 0.1 mmol), AIBN (6.6 mg, 0.04 mmol), 70 °C. First block was obtained after 4 h of copolymerization under 1 MPa of ethylene pressure, second block was formed after another 4 h of polymerization under 4 MPa of ethylene pressure. [a] Determined by  $^1\text{H}$  NMR spectroscopy. [b]  $X_1$  = Ethylene content (mol %), determined by  $^1\text{H}$  NMR spectroscopy,  $X_2$  = MDO content (mol %), calculated from  $X_1$ . [c] Calculated based on the incorporation in block-1 and the copolymer. [d] Molecular weight, determined by GPC.



**Figure S12.** GPC curves of PE-poor block and (PE-poor block)-*b*-(PE-rich block).

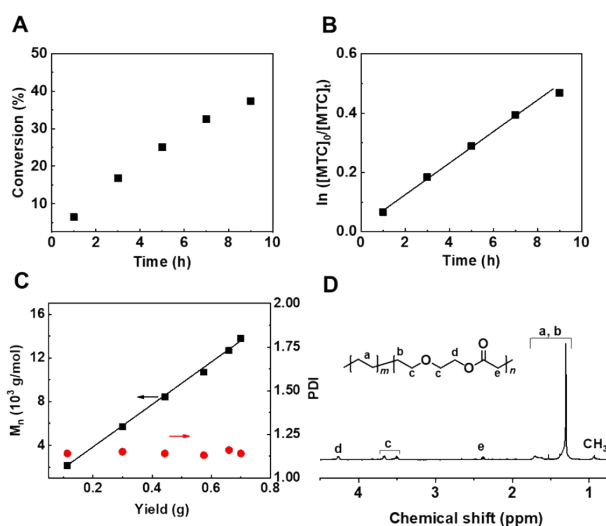


**Figure S13.** GPC curves of P(MDO-co-E) using different amount of CTA 4.

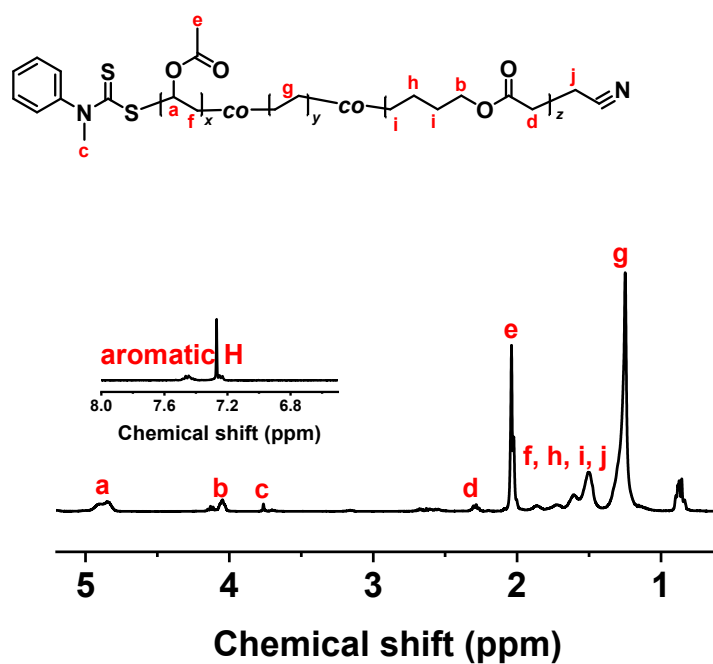
**Table S3.** Synthesis of P(MDO-co-E) using different amount of CTA 4

Entry	CTA 4 (mmol)	$M_n$ , NMR <sup>[a]</sup> (g/mol)	$M_n$ <sup>[b]</sup> (g/mol)	DP <sub>E</sub> <sup>[c]</sup>	DP <sub>MDO</sub> <sup>[c]</sup>	Đ	X <sup>[d]</sup> (%)	Yield (g)	DB <sup>[e]</sup>
1	0.1	8900	12500	205	27	1.19	11.5	0.67	47
2	0.05	18600	25300	419	60	1.18	12.6	0.65	44

Conditions: Ethylene (3 MPa), MDO (0.6 mL, 5.26 mmol), DMC (2.4 mL), 70 °C, 22 h. [a] Molecular weight, determined by <sup>1</sup>H NMR spectroscopy. [b] Molecular weight, determined by GPC. [c] Degree of polymerization, determined by <sup>1</sup>H NMR spectroscopy. [d] X = MDO content (mol %), determined by <sup>1</sup>H NMR spectroscopy. [e] Degree of branching, determined by <sup>1</sup>H NMR spectroscopy.



**Figure S14.** Synthesis of P(MTC-co-E) using CTA 4. Conditions: ethylene (3 MPa), MTC (0.6 mL, 4.68 mmol), DMC (1.8 mL), CTA 4 (22.2 mg, 0.1 mmol), AIBN (6.6 mg, 0.04 mmol), 70 °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 for P(MTC-co-E) with copolymer yield. (D) <sup>1</sup>H NMR spectrum of P(MTC-co-E).



**Figure S15.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) spectrum of P(MDO-co-E-co-VAc).

## References

1. M. C. Carter, J. Jennings, V. Appadoo and D. M. Lynn, *Macromolecules*, 2016, **49**, 5514-5526.
2. J. Undin, P. Pliikk, A. Finne - Wistrand and A. C. Albertsson, *Journal of Polymer Science Part A: Polymer Chemistry*, 2010, **48**, 4965-4973.
3. M. H. Stenzel, L. Cummins, G. E. Roberts, T. P. Davis, P. Vana and C. Barner - Kowollik, *Macromolecular Chemistry and Physics*, 2003, **204**, 1160-1168.