

Supporting information to :

## **Improving the Flame Retardancy of Polyethylenes through Palladium-Catalyzed Incorporation of Polar Comonomers**

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# 1. Experimental section

## 1.1 General consideration

All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Deuterated solvents used for NMR spectroscopy were dried and distilled prior to use.

$^1\text{H}$  NMR spectra were recorded with a Bruker Ascend 400 spectrometer at 120°C.

Differential scanning calorimetry (DSC) was measured with a DSC Q2000 (TA Ltd, USA) at a heating rate of 20°C/min under a nitrogen atmosphere.

The thermal properties of the samples were performed on a TGA SDT2960 thermal gravimetric analyzer (TA instruments) under both nitrogen and air at a heating rate of 20°C/min.

Water contact angles on polymer films were measured with Contact Angle Meter SL200B (Solon Tech. Co., Ltd.) by the dynamic sessile drop method. Samples for water contact angle measurements were prepared by the evaporation of 3 to 5 % (w/w) solutions in toluene onto glass slides under ambient conditions. The solvent was evaporated on top of a glass slide for 10 minutes, and a second layer of the polymer solution was then applied in order to make the film thicker. The water contact angles of the polymer thin films were measured using a contact angle goniometer at 25 °C with an accuracy of  $\pm 3^\circ$ . The reported values are the average of at least six measurements made at different positions of the film.

Mechanical properties of the polyethylene samples were measured Standard test method ASTM 638. Polymers were melt pressed at 30 to 35 °C above their melting point to obtain the test specimens. The test specimens had 28-mm gauge length, 3-mm width, and thickness of 0.4 mm. Stress/strain experiments were performed at 10m/min by means of S4a Universal Test Machine (UTM2502) at room temperature. At least two specimens of each copolymer were tested.

The Molecular weights and molecular-weight distributions of the polymers were determined by gel permeation chromatography (GPC) using an Agilent PL-220 chromatograph equipped with two Agilent PLgel Olexis columns operating at 150 °C using o-dichlorobenzene as the solvent. The system was calibrated with a polystyrene standard and chromatograms were corrected for linear polyethylene through universal calibration using the Mark–Houwink parameters of Rudin:  $K = 1.75 \times 10^{-2} \text{ cm}^3/\text{g}$  and  $R = 0.67$  for polystyrene, and  $K = 5.90 \times 10^{-2} \text{ cm}^3/\text{g}$  and  $R = 0.69$  for polyethylene. Dichloromethane, toluene and hexanes were purified in solvent purification systems.

The values of peak heat release rate (PHRR) and total heat release (THR) for the samples were obtained using a Govmak MCC-2 microscale combustion calorimeter (MCC). In the experiments, 5 mg of powdery samples was heated to 700 °C at a heating rate of  $1 \text{ K s}^{-1}$  under an inert gas stream ( $80 \text{ mL min}^{-1}$ ). The pyrolysis products were then mixed with oxygen ( $20 \text{ mL min}^{-1}$ ) prior to being placed in a 900 °C combustion

furnace. The heats of combustion of the pyrolysis products were measured by the oxygen consumption principle.

Real-time Fourier transform infrared spectra (RTIR) were recorded using a Nicolet 6700 FT-IR spectrophotometer equipped with a ventilated oven with a heating device, which was employed to study the thermo-oxidative degradation of the polymers. The cured samples were ground with KBr powder, and the mixtures were pressed into a tablet, placed into the oven, and heated at a rate of approximately 10 °C/min.

The limiting oxygen index (LOI) was measured according to ASTM D2863 by an HC-2 oxygen index meter (Jiangning Analysis Instrument Co., China). The specimens used for the test were of dimensions 100 × 6.5 × 3 mm<sup>3</sup>.

Scanning electron microscopy (SEM) images of fracture surface for composites were obtained using a Hitachi Model X650 SEM system.

Vertical burning test (UL-94) was conducted by a CZF-II horizontal and vertical burning tester (Jiangning Analysis Instrument Co., China) according to ASTM Standard D3801. The dimensions of the samples were 130 × 12.7 × 3 mm<sup>3</sup>.

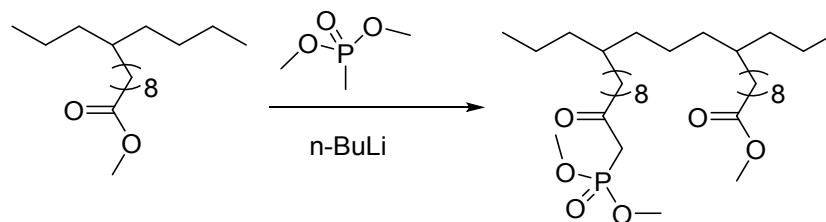
The combustion test was performed on the cone calorimeter (FTT, U.K.) test according to ISO 5660 standard procedures, with 100 × 100 × 3 mm<sup>3</sup> specimens. Each specimen was wrapped in an aluminum foil and exposed horizontally to 35 kW/m<sup>2</sup> external heat flux.

Comonomer P1, P2 and B1 were prepared according to previous literature procedures.<sup>1,2</sup>

## 1.2 Synthesis of comonomer P3, Poly(E-co-O1)\* and PE composites

**Preparation of (diethoxyphosphinyl) methyl ester (P3).** Diethyl hydroxymethylphosphonate (0.1 mol) and TEA (0.15 mol) were added to a 500-mL round-bottom flask containing 200 mL of anhydrous DCM, and the mixture was cooled using an ice-bath before the addition of acryloyl chloride (0.12 mol in 150 mL of anhydrous DCM). After 24 h of reaction at room temperature under stirring, the resulting mixture was evaporated and then redissolved in 300 mL THF to remove the triethylamine hydrochloride. The THF was then removed to obtain an oil, which was distilled under vacuum to yield the product as a colorless liquid (0.07 mol, 70%).

**Preparation of Poly(E-co-O1)\*.** To a solution of dimethyl methanephosphonate (3.74 g, 30 mmol in 100 mL dry toluene) at -78 °C under nitrogen was added dropwise n-BuLi (30 mmol) and stirred at -78 °C for 1 h. The copolymer (2 g, 3% incorporation ratio) was dissolved in toluene (50 mL) at 90 °C, after which lithium was carefully added dropwise. The reaction was stirred at 90 °C for 24 h, after which the solvent was evaporated and ethanol was added to obtain the copolymer. The copolymer was then washed several times to remove the dimethyl methanephosphonate, and after filtration, it was dried at 80 °C for 24 h under vacuum.



Scheme 1. Post-modification of poly(E-co-O1).

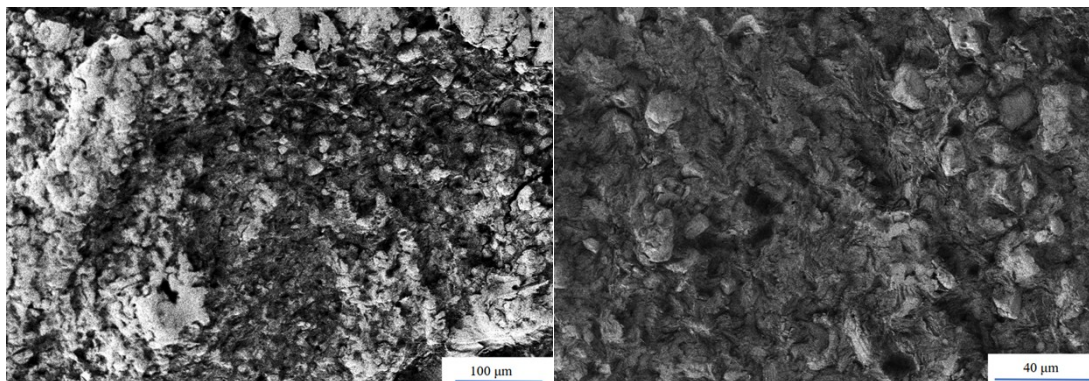
**Preparation of PE composites.** PE, commercial ammonium polyphosphate (APP) and pentaerythritol (PER) were dried under vacuum at 80 °C overnight in order to remove the solvent. All of the samples were prepared using a two roll mixing mill (Rheomixer XSS-300, Shanghai Ke Chuang, China) at 180 °C, and the roll speed was maintained at 60 rpm. TPU was first added into the mill at the beginning of the blending procedure. After the melting of PE, the desired amount of flame retardant was added, and the mixture was processed for about 10 min. The resulting samples were hotpressed at about 180 °C under 10 MPa for 10 min into sheets with a thickness of  $3.0 \pm 0.1$  mm for limiting oxygen index (LOI) measurements.

### 1.3 Polymerization procedure

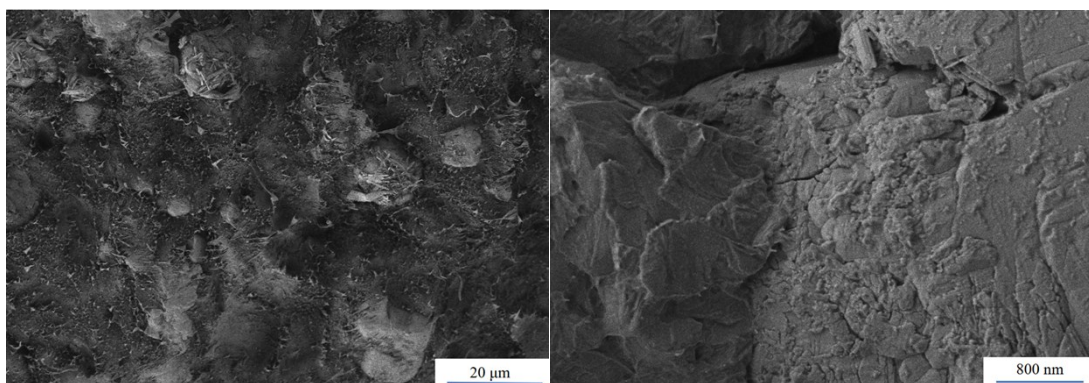
**Procedure for copolymerization.** In a typical experiment, a 350-mL glass thick-walled pressure vessel was charged with toluene, the desired amount of the comonomer, and a magnetic stir bar in a glovebox. The pressure vessel was connected to a high-pressure line, and the solution was degassed. The vessel was warmed to 80 °C using an oil bath and allowed to equilibrate for 5 min. The metal complex in 2 mL  $\text{CH}_2\text{Cl}_2$  was injected into the polymerization system via syringe with rapid stirring, and the reactor was pressurized with ethylene. The desired pressure was maintained and the system was stirred continuously for 3 h. The polymer was precipitated using excess EtOH. After filtration, the copolymer was obtained and dried at 80 °C for 24 h under vacuum. The polar monomer incorporation (%) was calculated from  $^1\text{H}$  NMR analysis.

**Procedure for terpolymerization.** In a typical experiment, a 350-mL glass thick-walled pressure vessel was charged with toluene, the desired amount of the two comonomers, and a magnetic stir bar in a glovebox. The pressure vessel was connected to a high-pressure line, and the solution was degassed. The vessel was warmed to 80 °C using an oil bath and allowed to equilibrate for 5 min. The metal complex in 2 mL  $\text{CH}_2\text{Cl}_2$  was injected into the polymerization system via syringe with rapid stirring, and the reactor was pressurized with ethylene. The desired pressure was maintained and the system was stirred continuously for 3 h. The polymer was precipitated using excess EtOH. After filtration, the copolymer was obtained and dried at 80 °C for 24 h under vacuum. The polar monomer incorporation (%) was calculated from  $^1\text{H}$  NMR analysis.

## 2. SEM micrographs of fracture surface for composites



**Figure S1.** SEM micrographs of fracture surface for PE/APP (70/30 wt%).



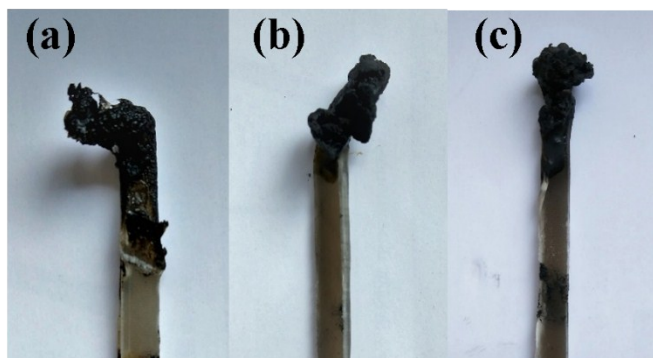
**Figure S2.** SEM micrographs of fracture surface for PE/Poly(E-co-O1)/APP (60/10/30 wt%).

## 3. LOI and cone calorimeter data for PE composites

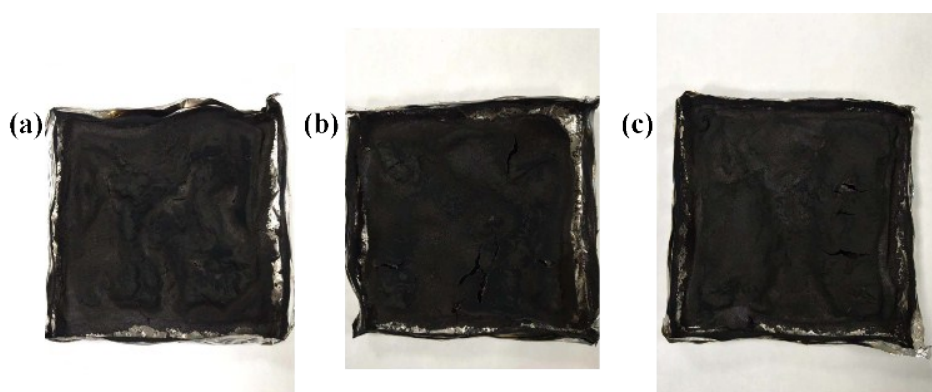
Table S1. LOI and Cone Calorimeter Data for PE composites

Sample	LOI (vol %)	TTI (s)	pHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )
PE/APP/PER	25.5	35	755.9	139.9

PE/APP/PER/1 wt% <b>Poly(E-co-O1)</b>	26.5	33	678.9	137.7
PE/APP/PER/3 wt% <b>Poly(E-co-O1)</b>	27	32	570.6	133.4



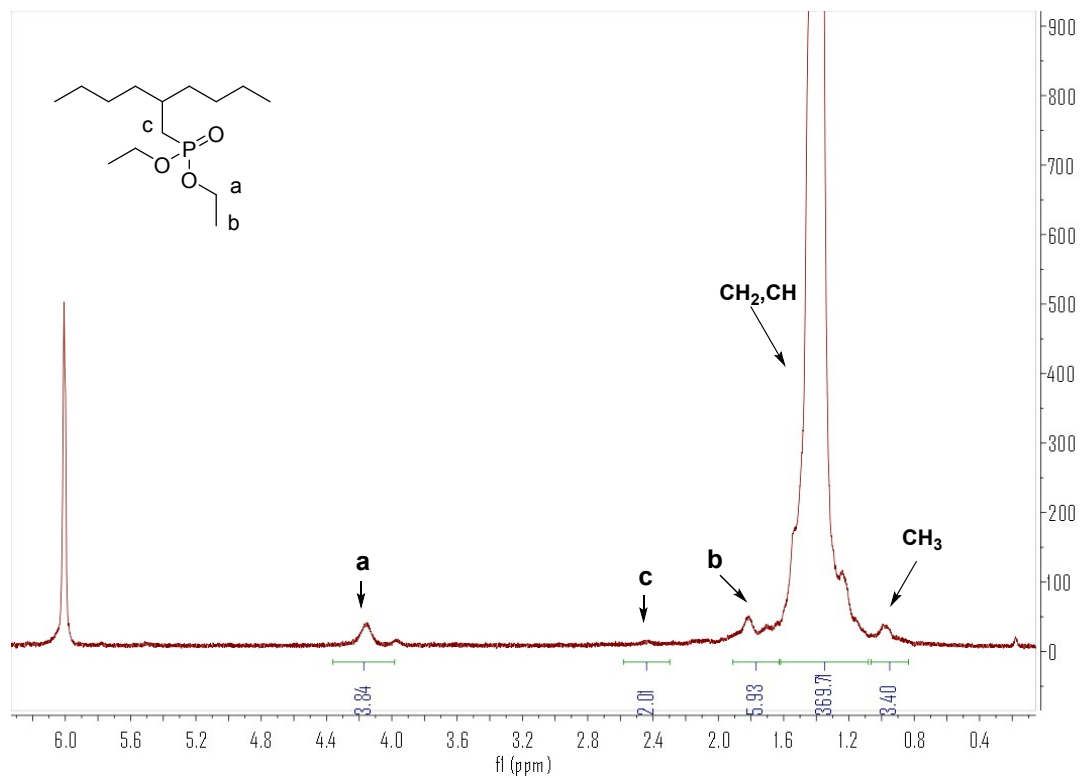
**Figure S3.** Photos of residues at the end of LOI tests: (a) PE/APP/PER (75:18:7 wt%); (b) with 1 wt% **Poly(E-co-O1)**; (c) with 3 wt% **Poly(E-co-O1)**.



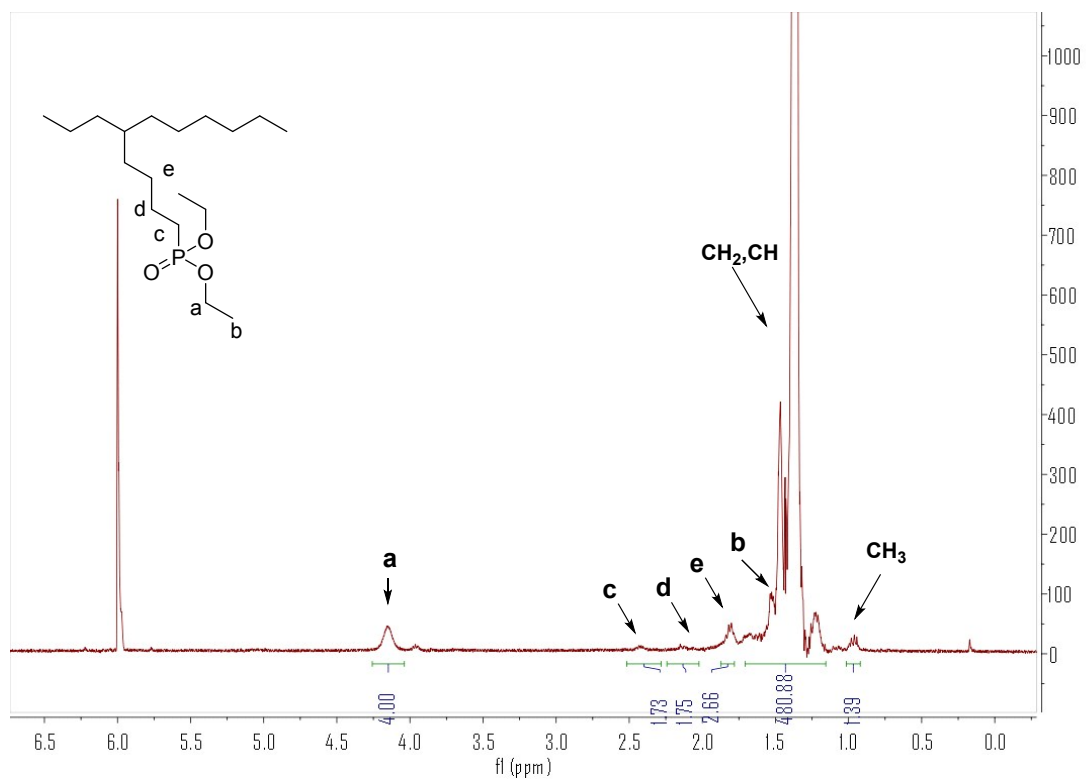
**Figure S4.** Photos of residues at the end of cone calorimetry tests: (a) PE/APP/PER (75:18:7 wt%); (b) with 1 wt% **Poly(E-co-O1)**; (c) with 3 wt% **Poly(E-co-O1)**.

## 4. Spectra data

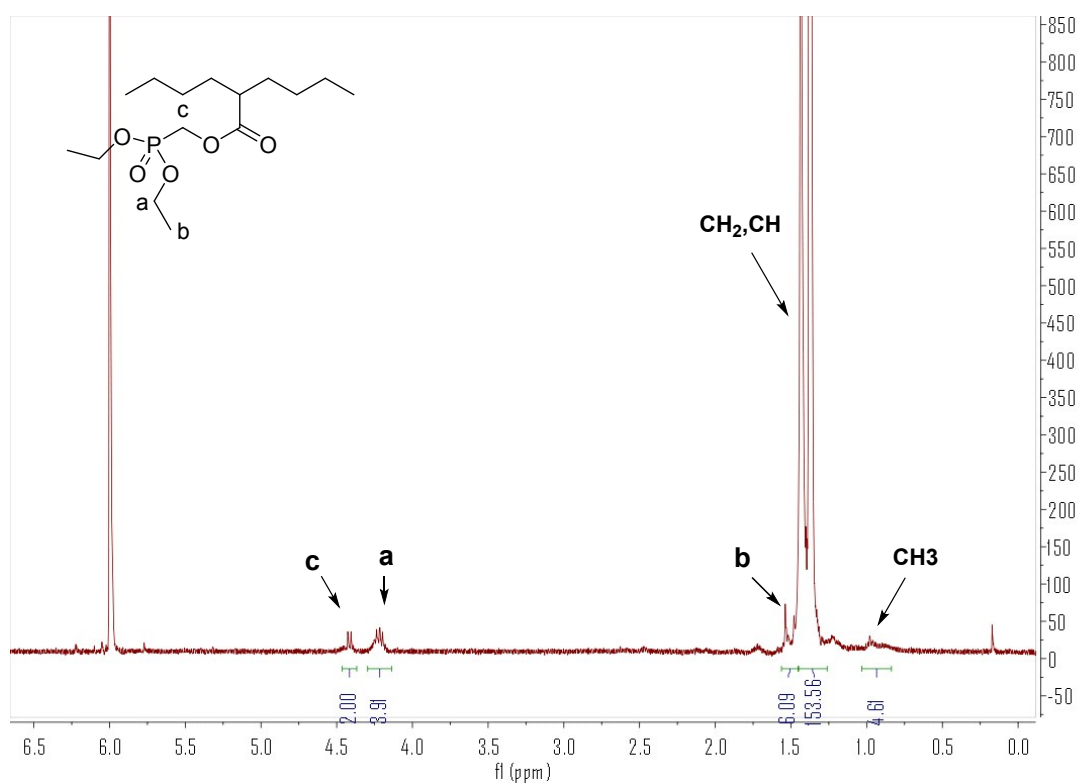
### 4.1 NMR and FT-IR spectra



**Figure S5.** <sup>1</sup>H NMR spectrum of the polymer from Table 1, Entry 2. (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 120 °C)

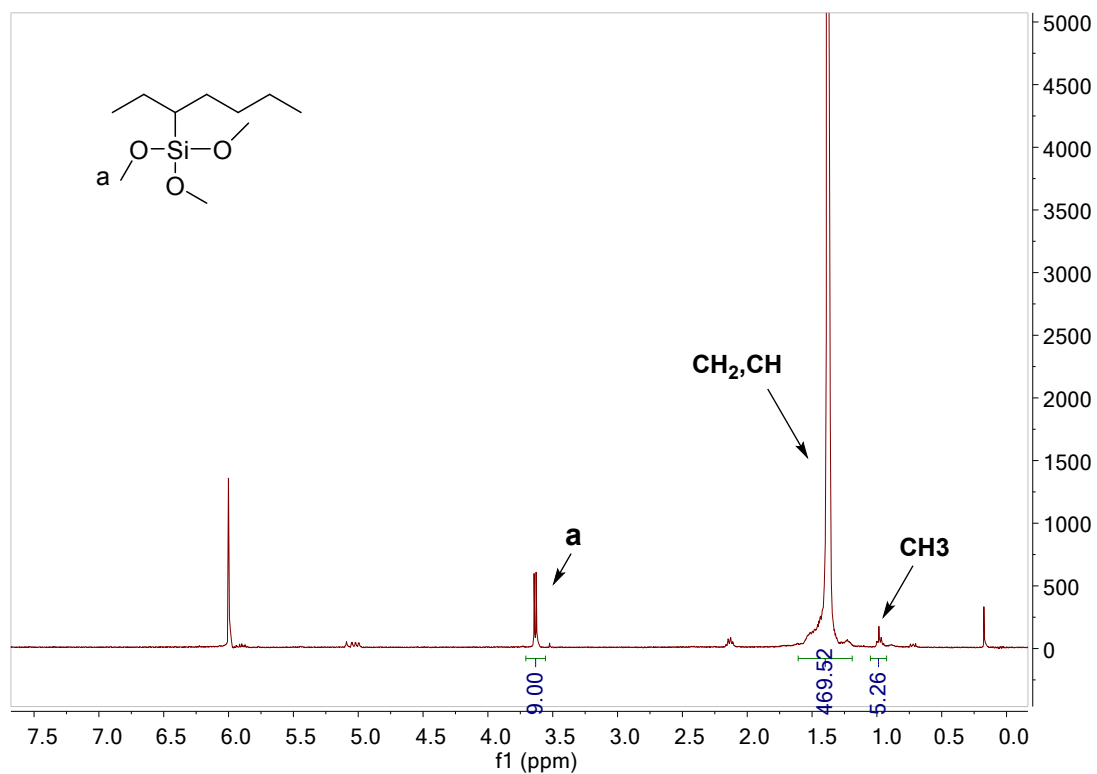


**Figure S6.** <sup>1</sup>H NMR spectrum of the polymer from Table 1, Entry 3. (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 120 °C)

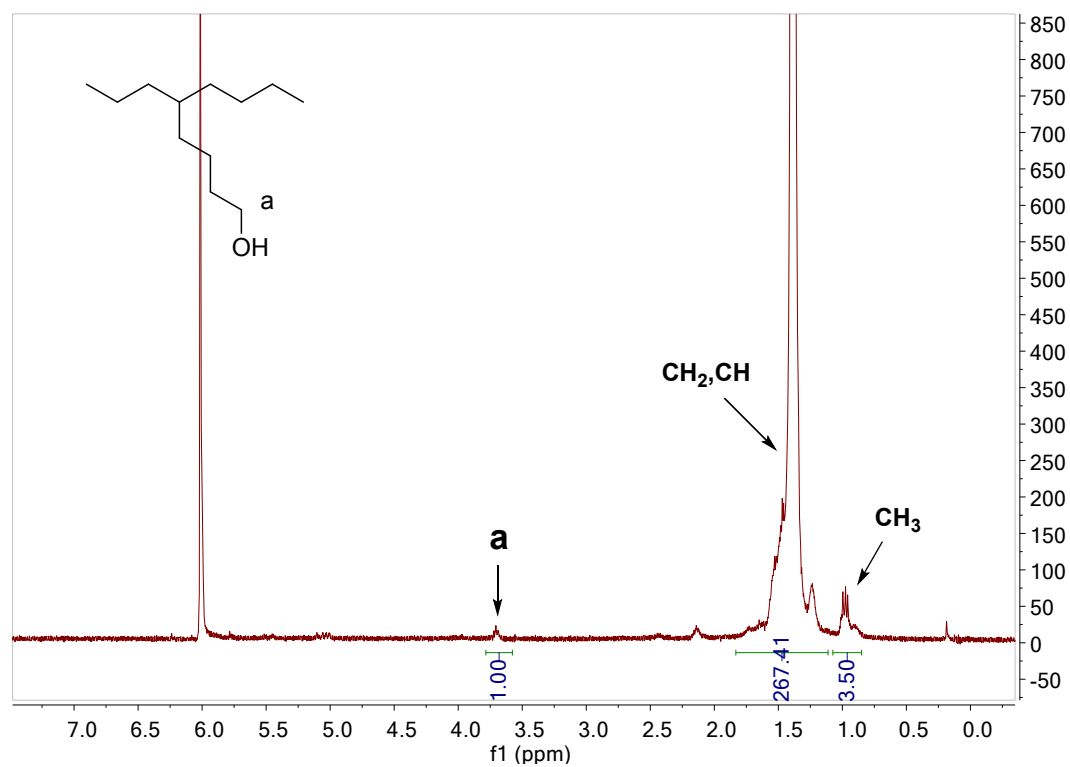


**Figure S7.** <sup>1</sup>H NMR spectrum of the polymer from Table 1, Entry 4. (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 120 °C)

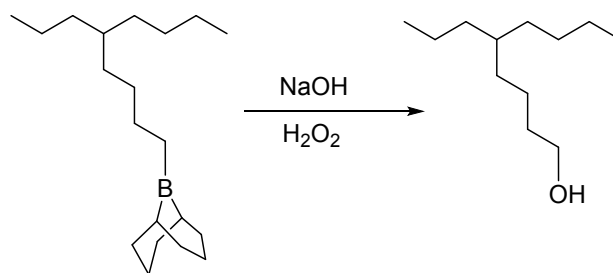




**Figure S8.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 5. ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $120^\circ\text{C}$ )

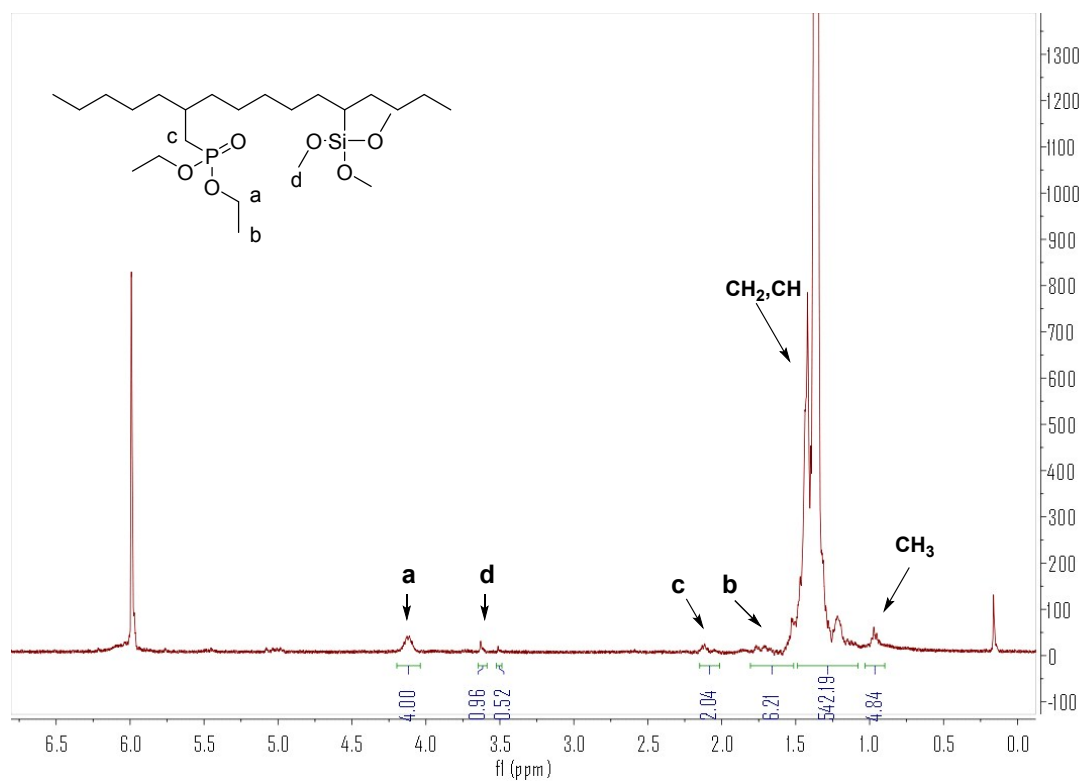


**Figure S9.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 6. ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $120^\circ\text{C}$ )

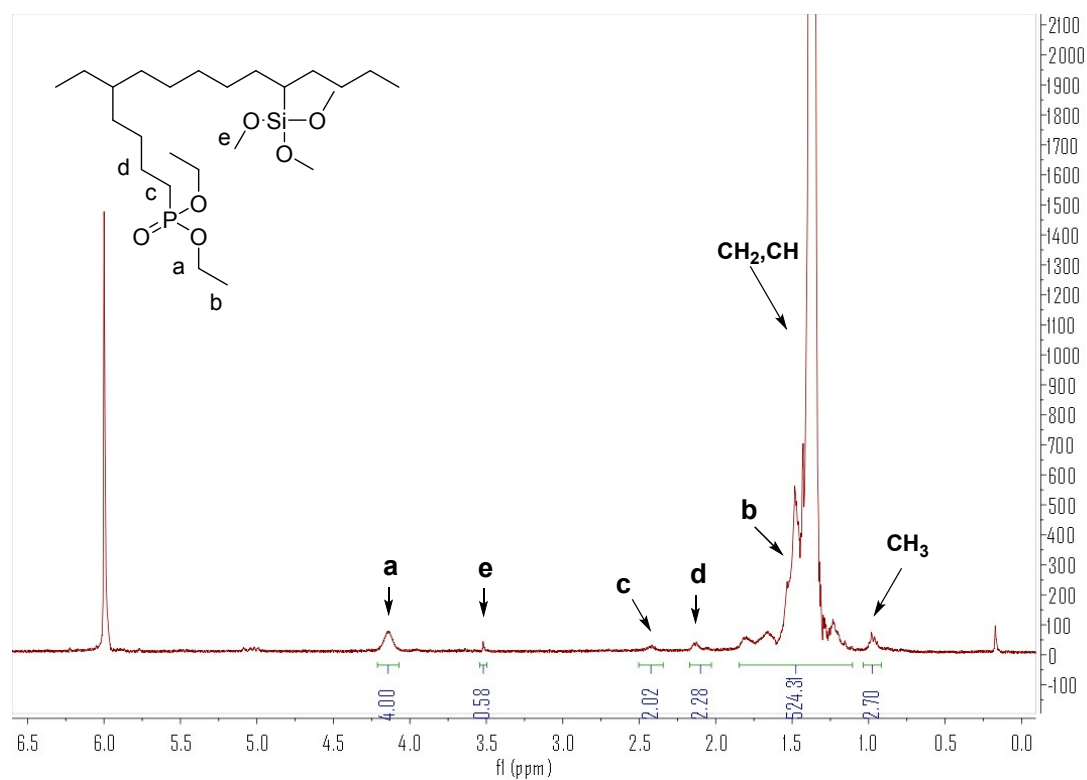


Scheme S2. Oxidation of Poly(E-co-B1).

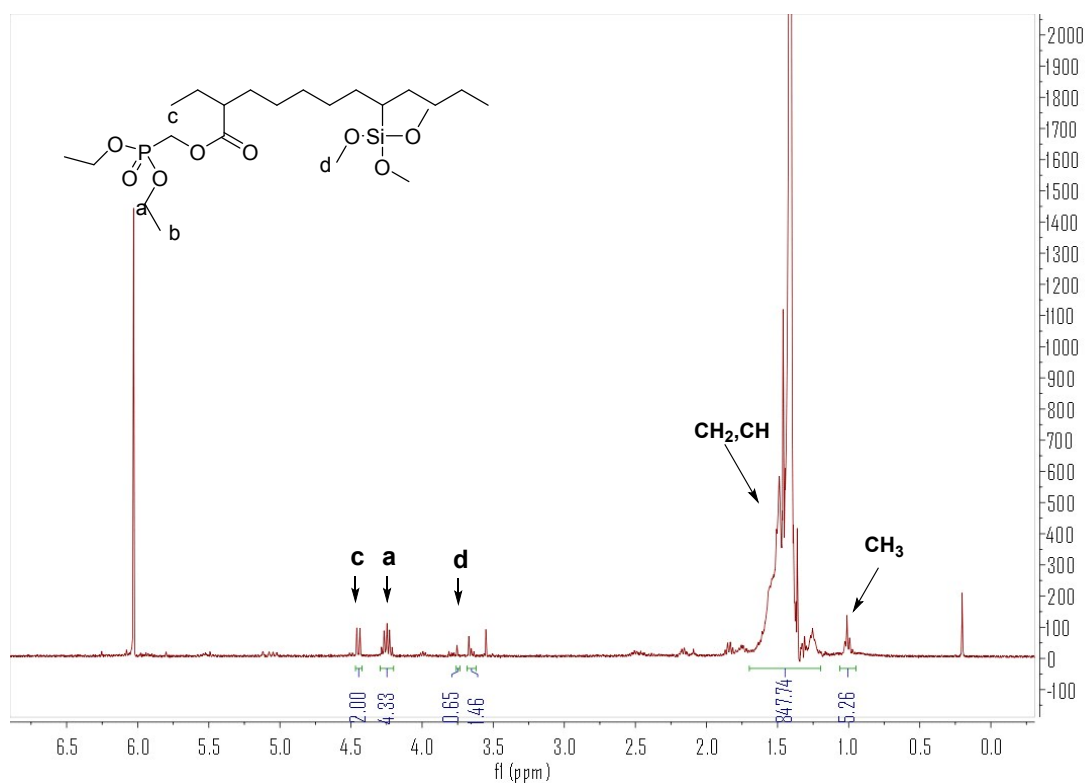
The  $^1\text{H}$  NMR spectrum of Poly(E-co-B1) is broad and difficult to analyze. Therefore, the copolymer was oxidized for analysis.<sup>2</sup> **Oxidation of Poly(E-co-B1):** The copolymer was dissolved in toluene to make a 2-3% solution at 110 °C. A desired amount of 6N NaOH solution (1.3 mol/mol of Poly(E-co-B1)) was degassed and added to it. Then,  $\text{H}_2\text{O}_2$  (30% aqueous solution, 3.9 mol/mol of Poly(E-co-B1)) was added dropwise. The mixture was stirred at 110 °C for 12-16 h. After the reaction, toluene was evaporated under vacuum, the white polymer was washed several times with EtOH and dried at 80 °C for 24 h under vacuum.



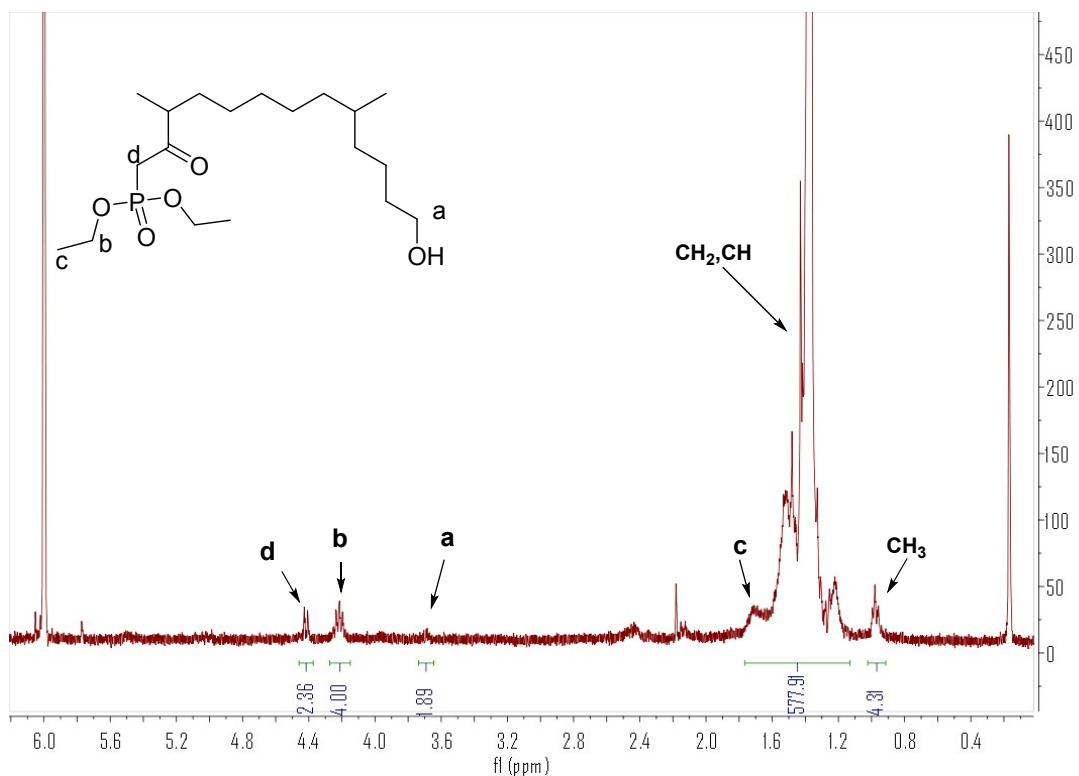
**Figure S10.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 7. ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 120 °C)



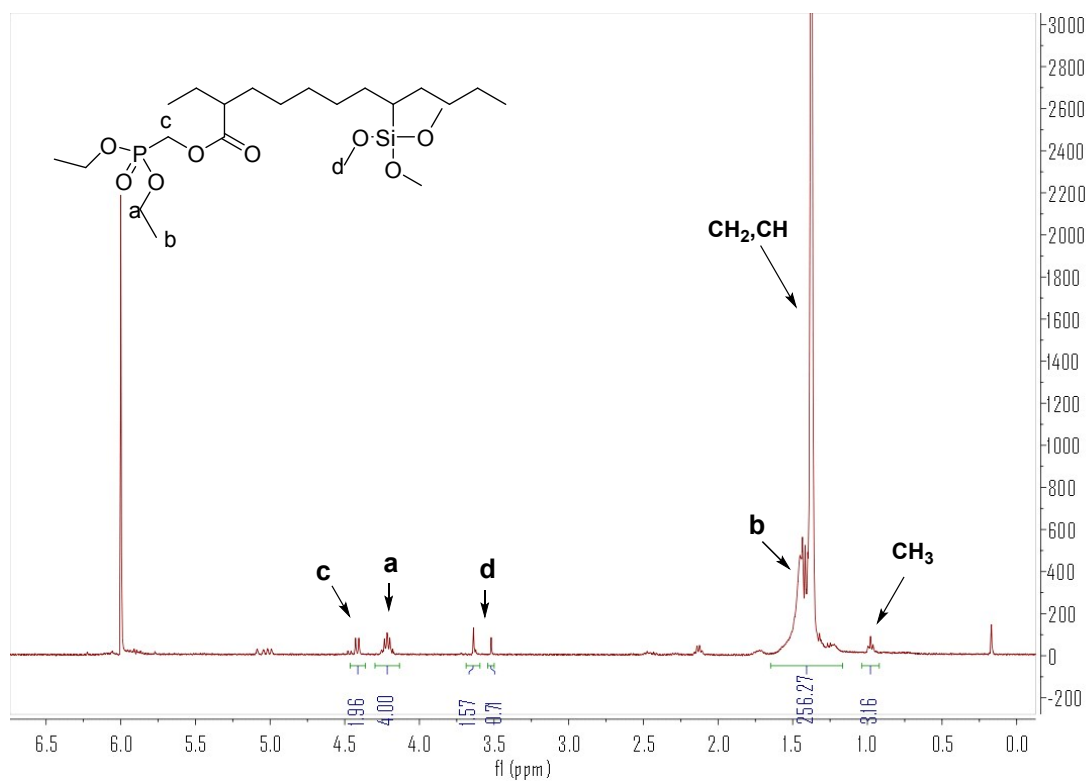
**Figure S11.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 8. ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 120  $^\circ\text{C}$ )



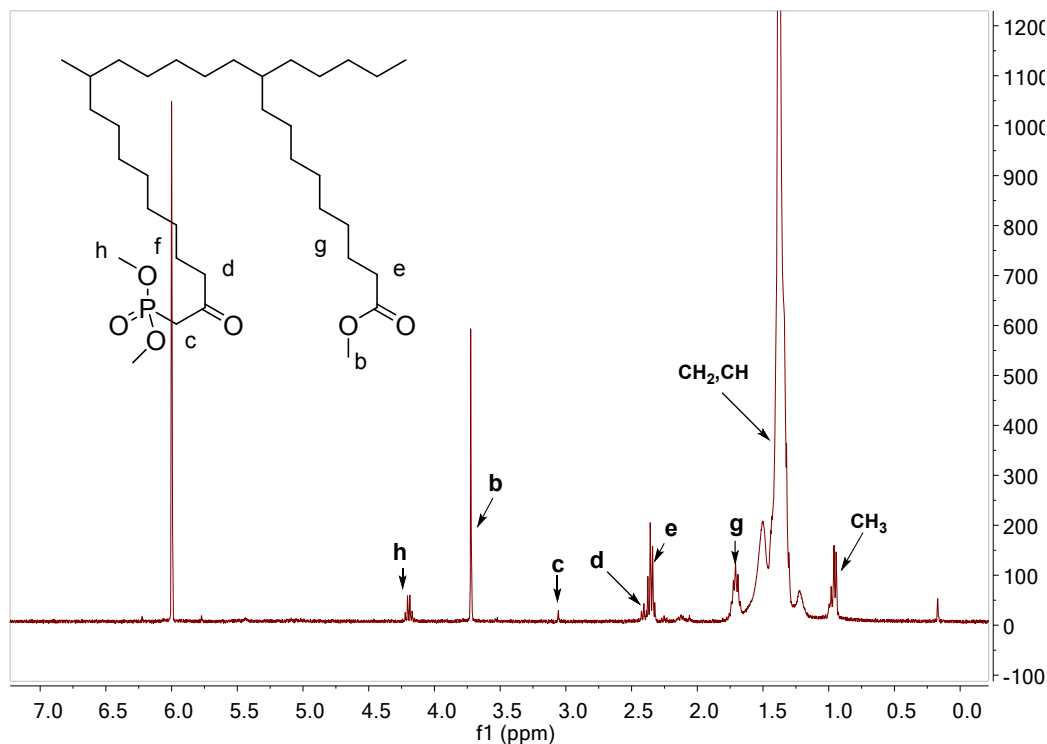
**Figure S12.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 9. ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 120  $^\circ\text{C}$ )



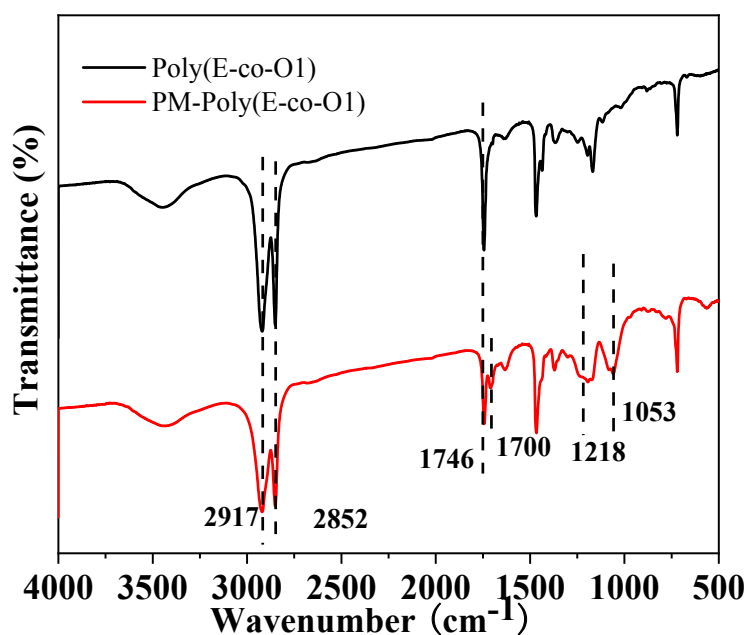
**Figure S13.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 10. ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 120  $^\circ\text{C}$ ). **Oxidation of Poly(E-co-P3-co-B1):** Similar procedure as Poly(E-co-B1) was employed except Poly(E-co-P3-co-B1) was used.



**Figure S14.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 11. ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 120  $^\circ\text{C}$ )



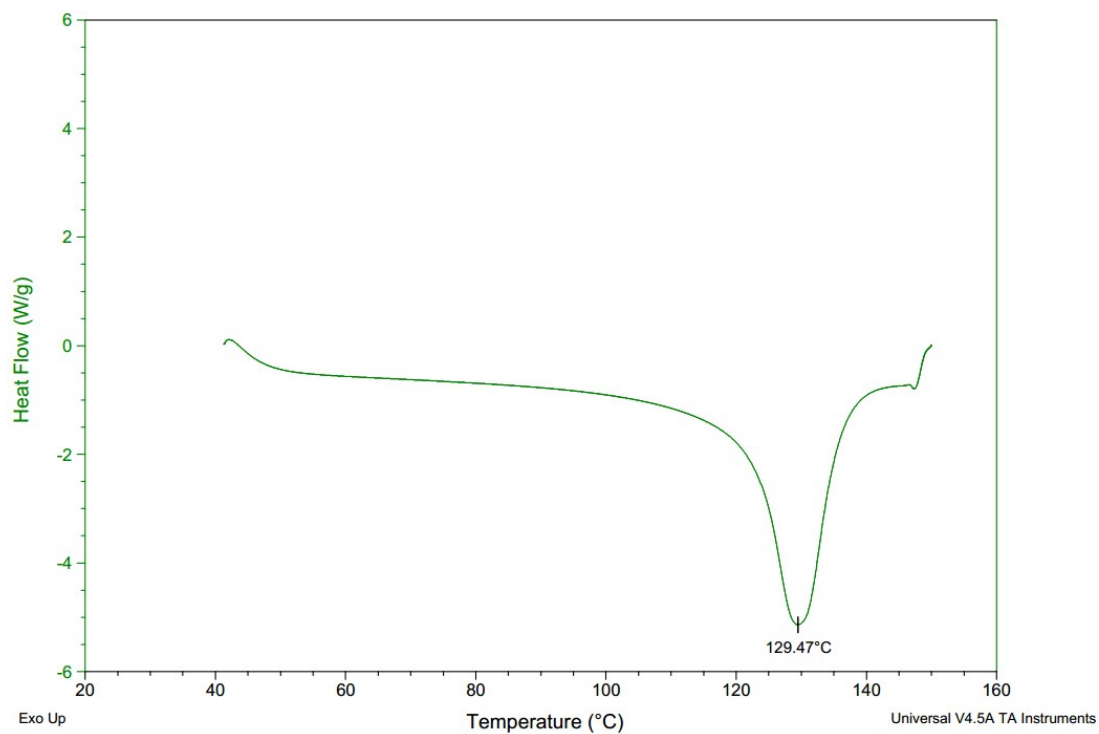
**Figure S15.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 13. ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 120  $^\circ\text{C}$ )



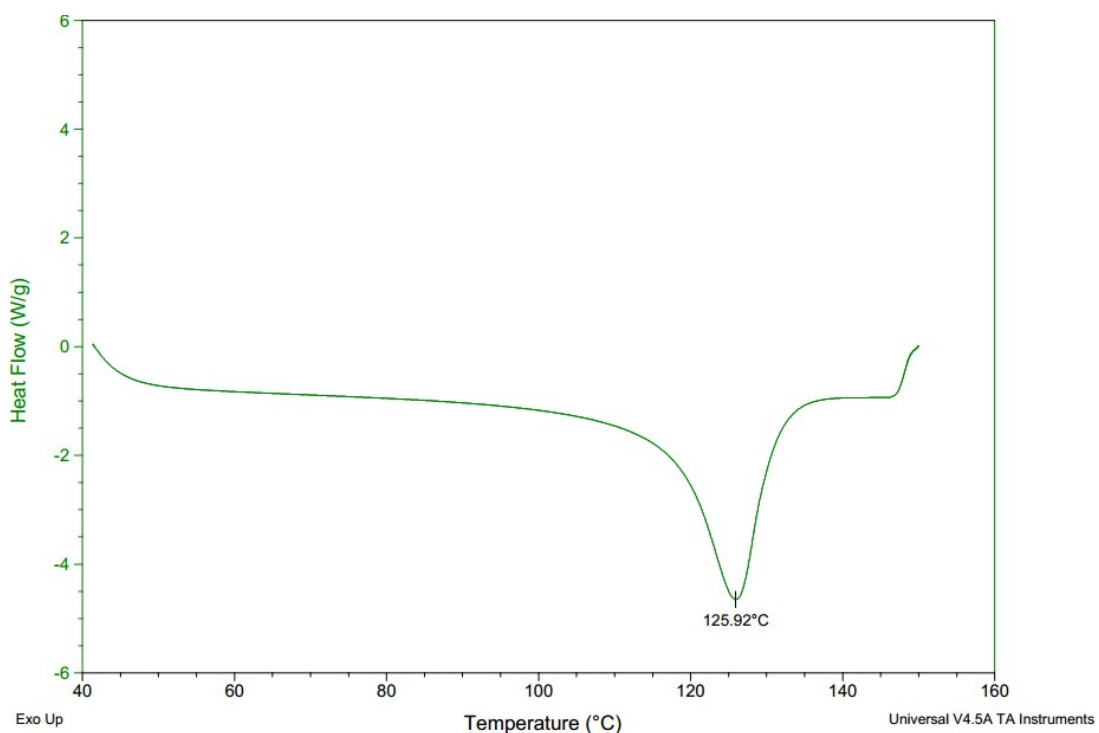
**Figure S16.** FT-IR spectrum of the polymer from Table 1, Entry 13.

Despite the characteristic peak of polyethylene, the peak at  $1053\text{ cm}^{-1}$  was ascribed to P-O-C groups, the characteristic peak of P=O stretching vibration was overlapped with **Poly(E-co-O1)** at around  $1218\text{ cm}^{-1}$ , the peak at  $1700\text{ cm}^{-1}$  was ascribed to C=O group, which means dimethyl methanephosphonate was successfully access to the main chain of polyethylene backbone. While peak at  $1750\text{ cm}^{-1}$  indicating ester group still exist, which means this method can't react completely.

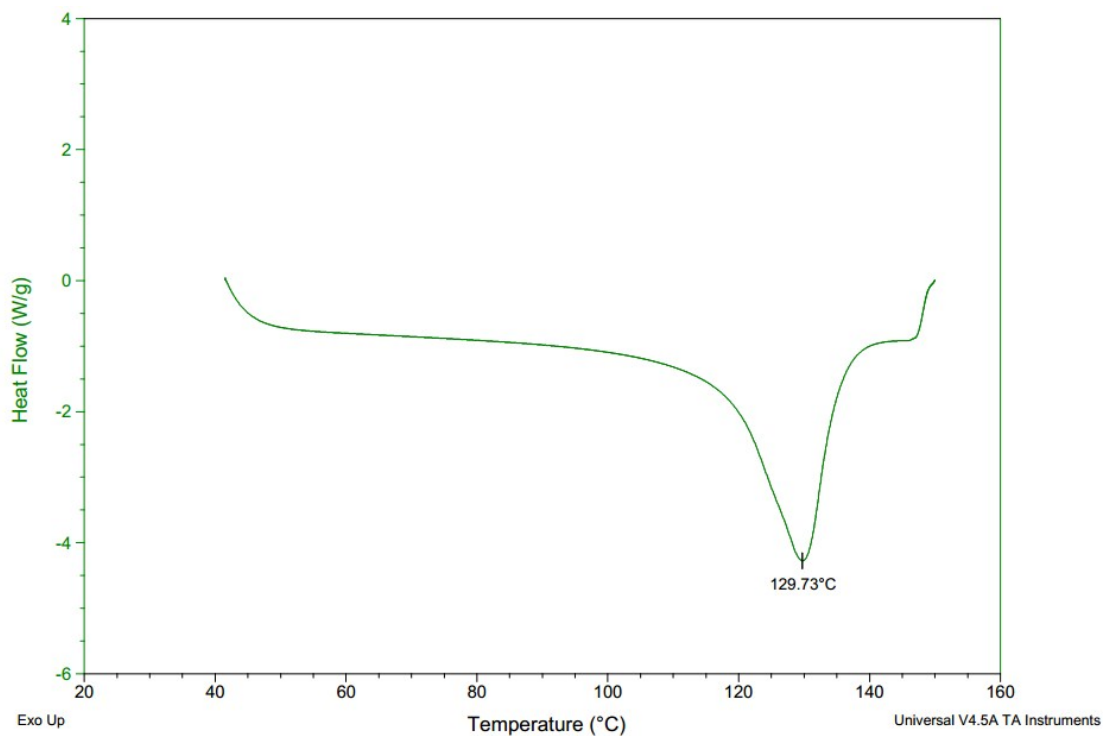
## 4.2 DSC of polymers



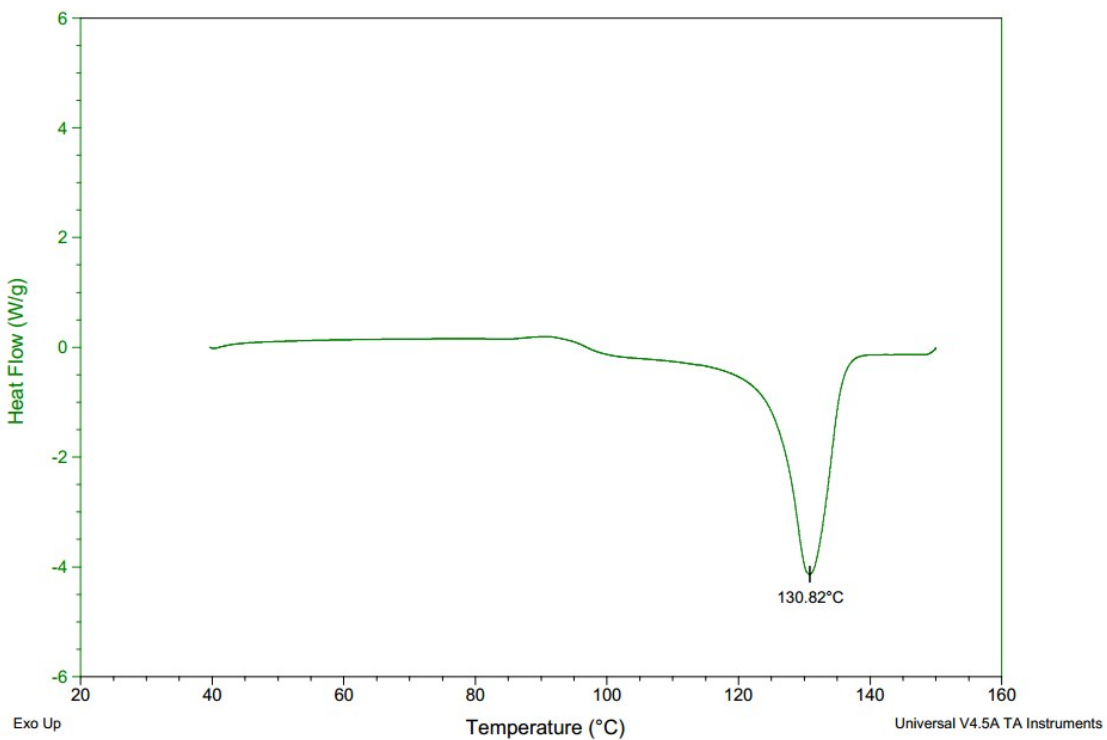
**Figure S17.** DSC data of the polymer (table 1, entry 2).



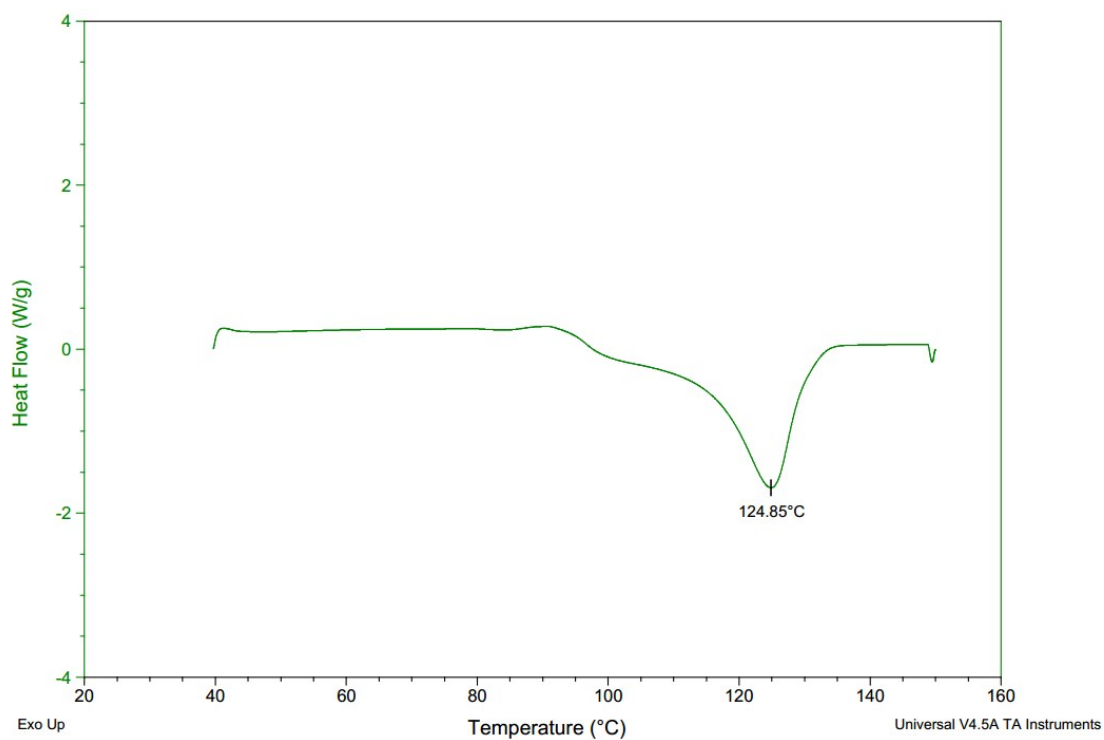
**Figure S18.** DSC data of the polymer (table 1, entry 3)



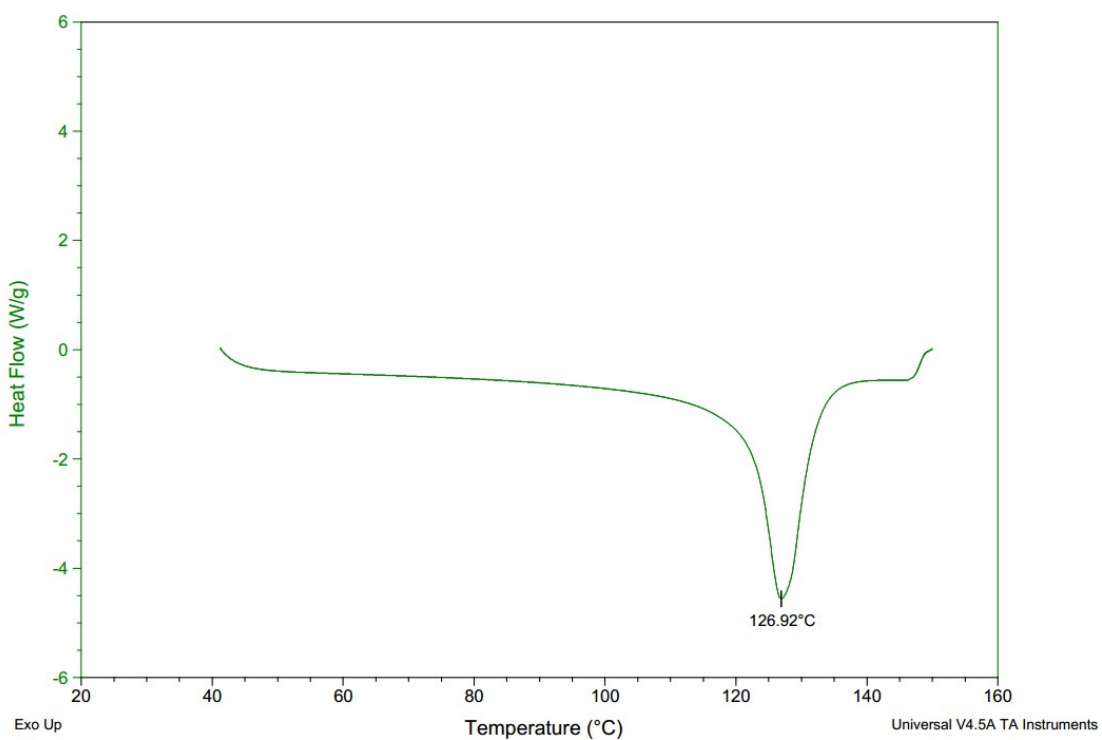
**Figure S19.** DSC data of the polymer (table 1, entry 4)



**Figure S20.** DSC data of the polymer (table 1, entry 5)

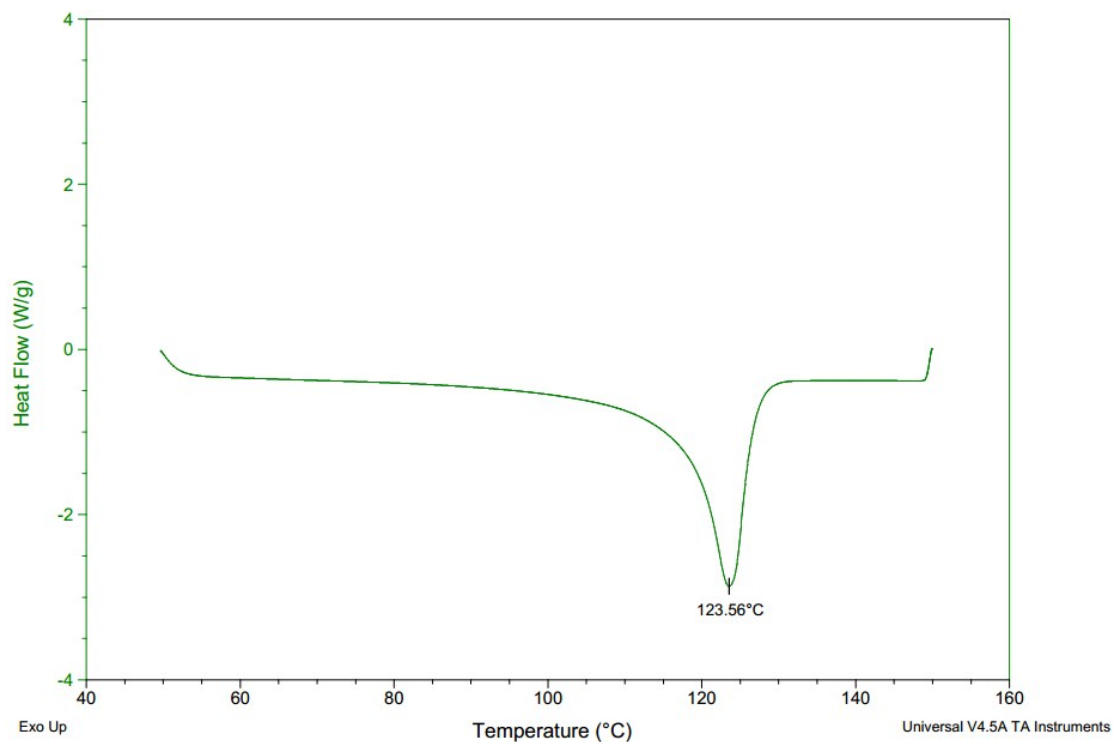


**Figure S21.** DSC data of the polymer (table 1, entry 6)

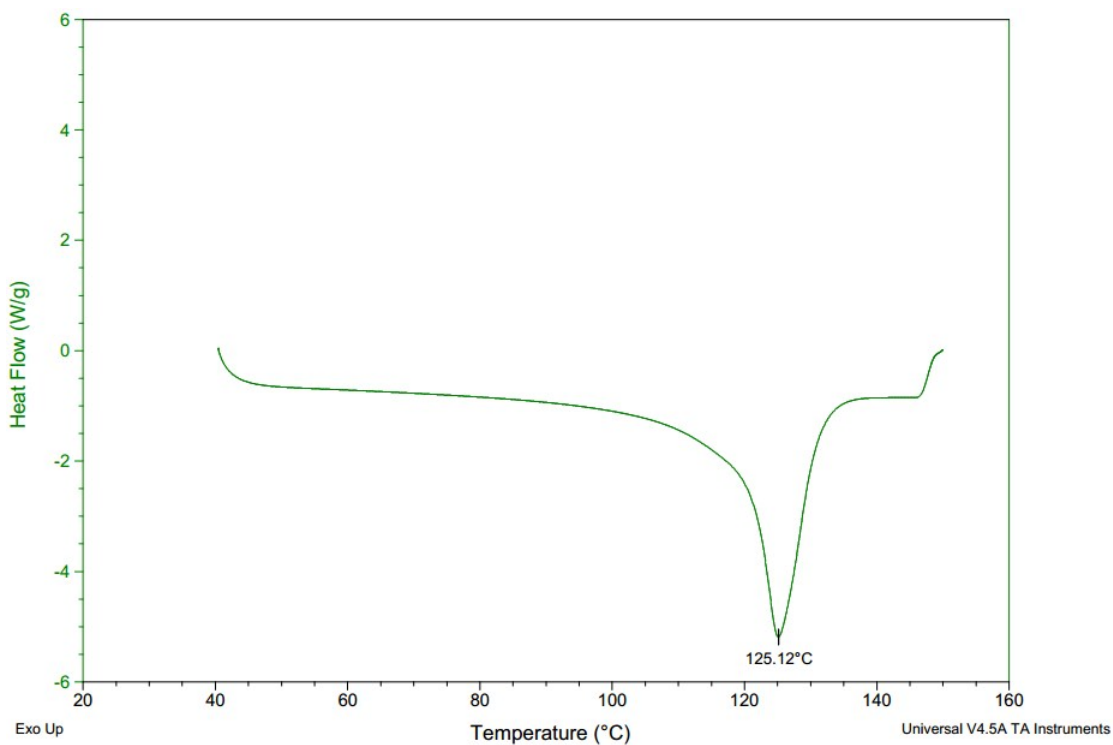


**Figure S22.** DSC data of the polymer (table 1, entry 7)

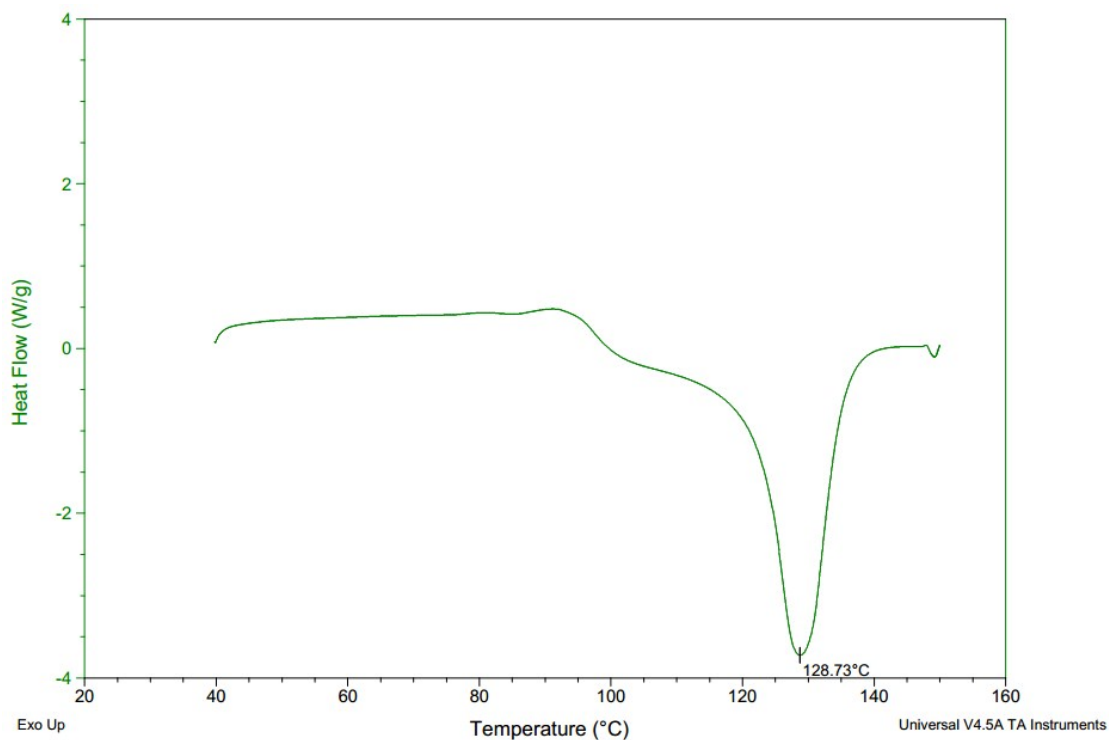




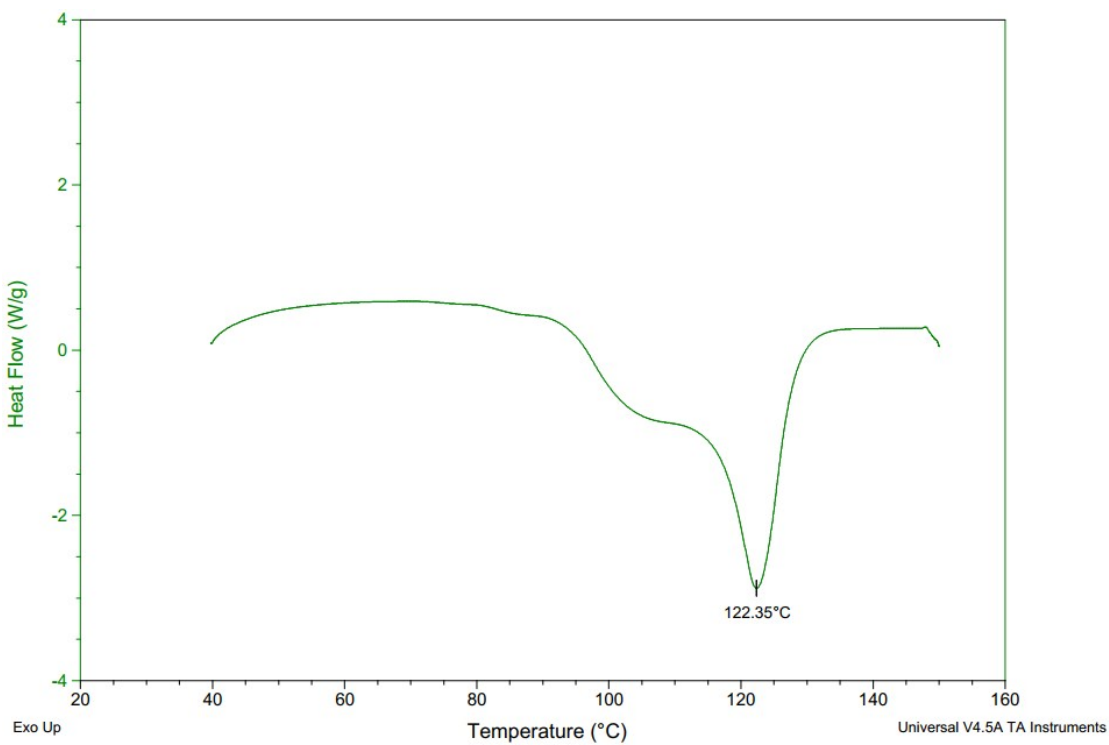
**Figure S23.** DSC data of the polymer (table 1, entry 8)



**Figure S24.** DSC data of the polymer (table 1, entry 9)



**Figure S25.** DSC data of the polymer (table 1, entry 10)



**Figure S26.** DSC data of the polymer (table 1, entry 11)

### 4.3 GPC of polymers

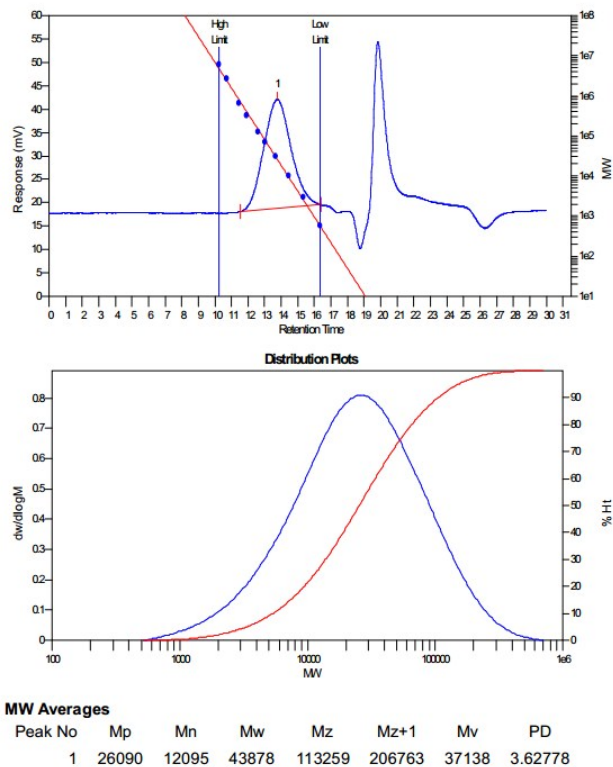


Figure S27. GPC trace of the polymer (table 1, entry 2).

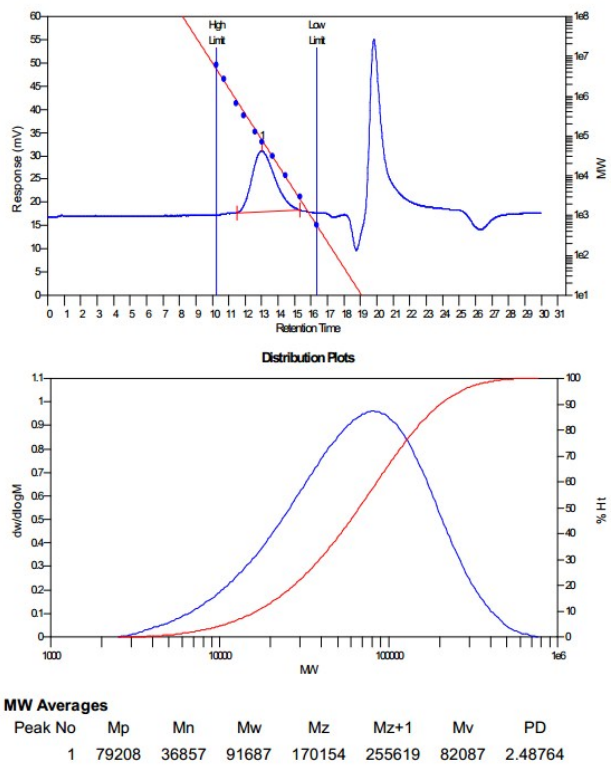


Figure S28. GPC trace of the polymer (table 1, entry 3).

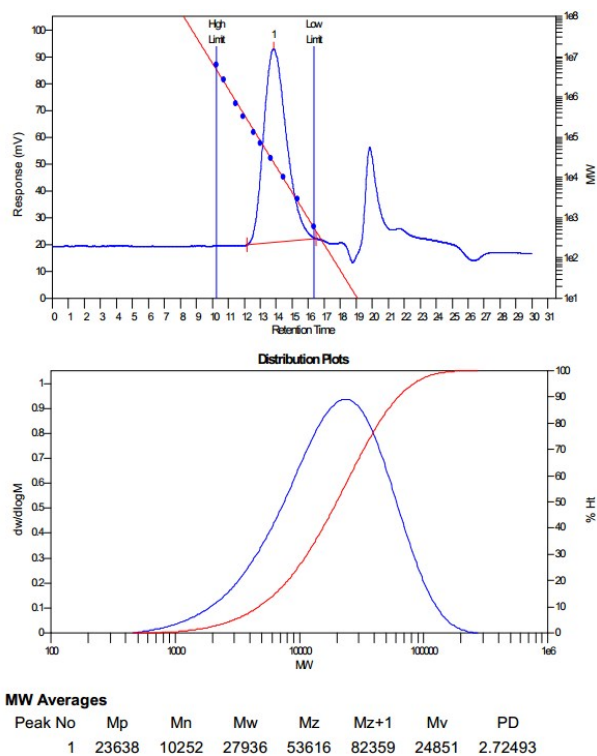


Figure S29. GPC trace of the polymer (table 1, entry 4).

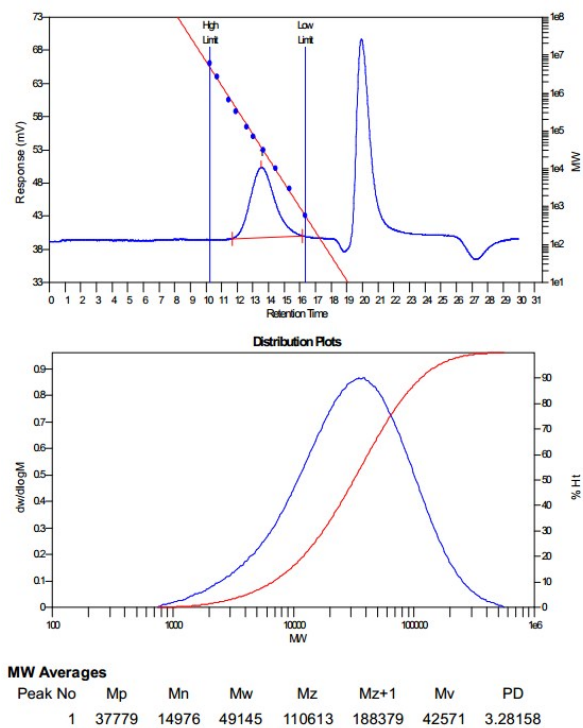


Figure S30. GPC trace of the polymer (table 1, entry 5).

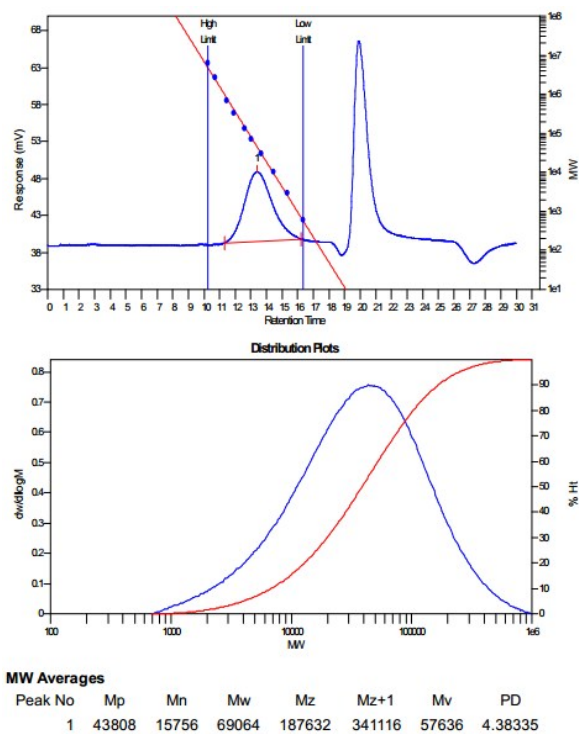


Figure S31. GPC trace of the polymer (table 1, entry 6).

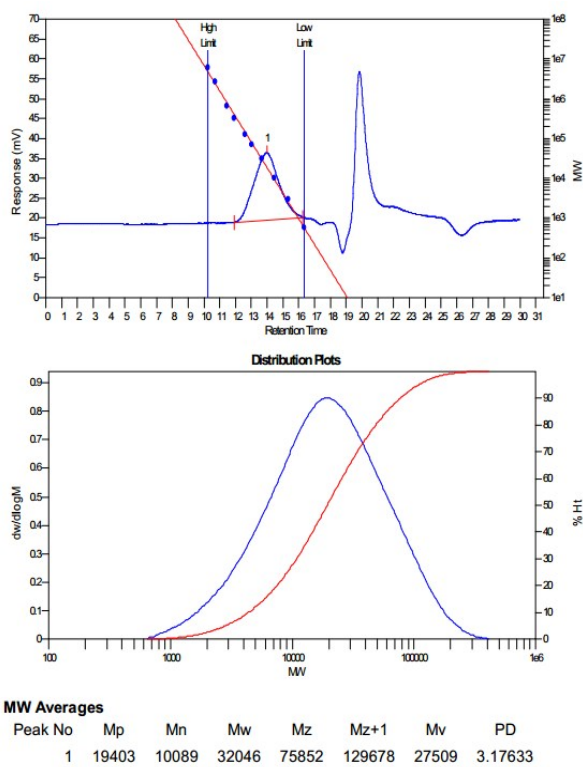


Figure S32. GPC trace of the polymer (table 1, entry 7).

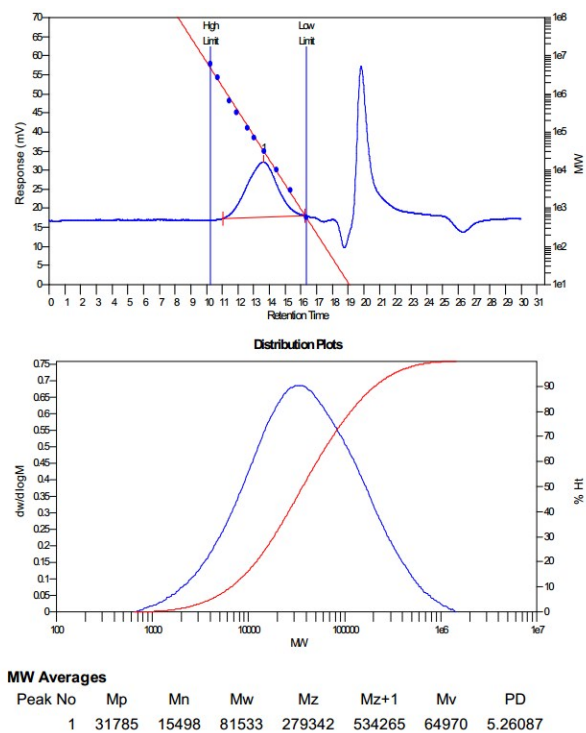


Figure S33. GPC trace of the polymer (table 1, entry 8).

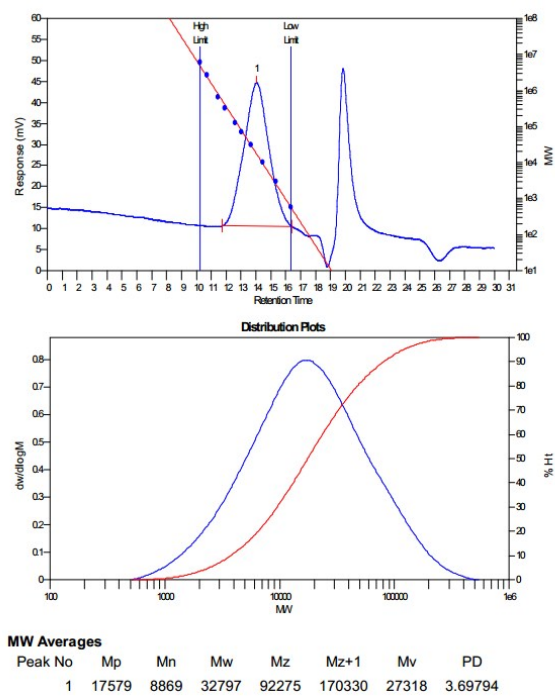


Figure S34. GPC trace of the polymer (table 1, entry 9).

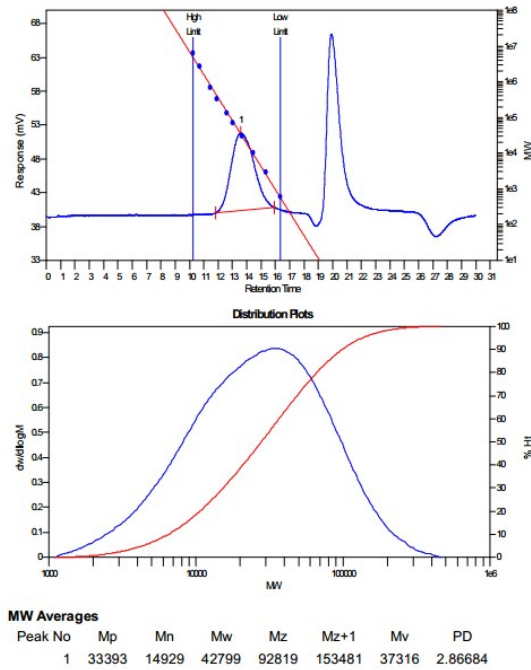


Figure S35. GPC trace of the polymer (table 1, entry 10).

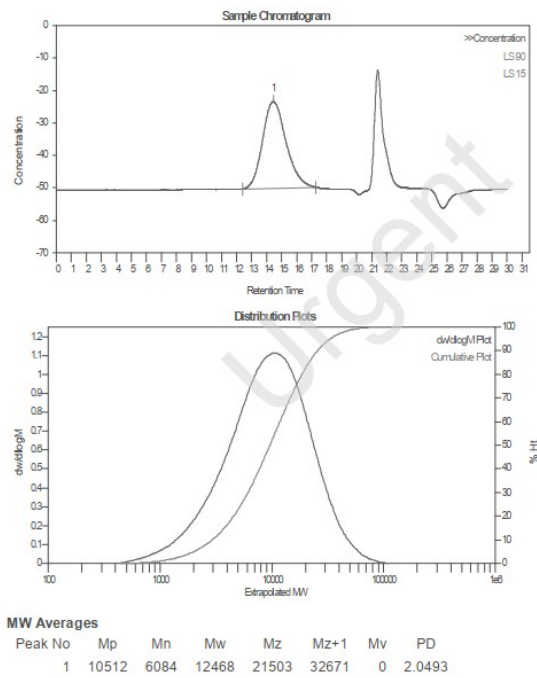
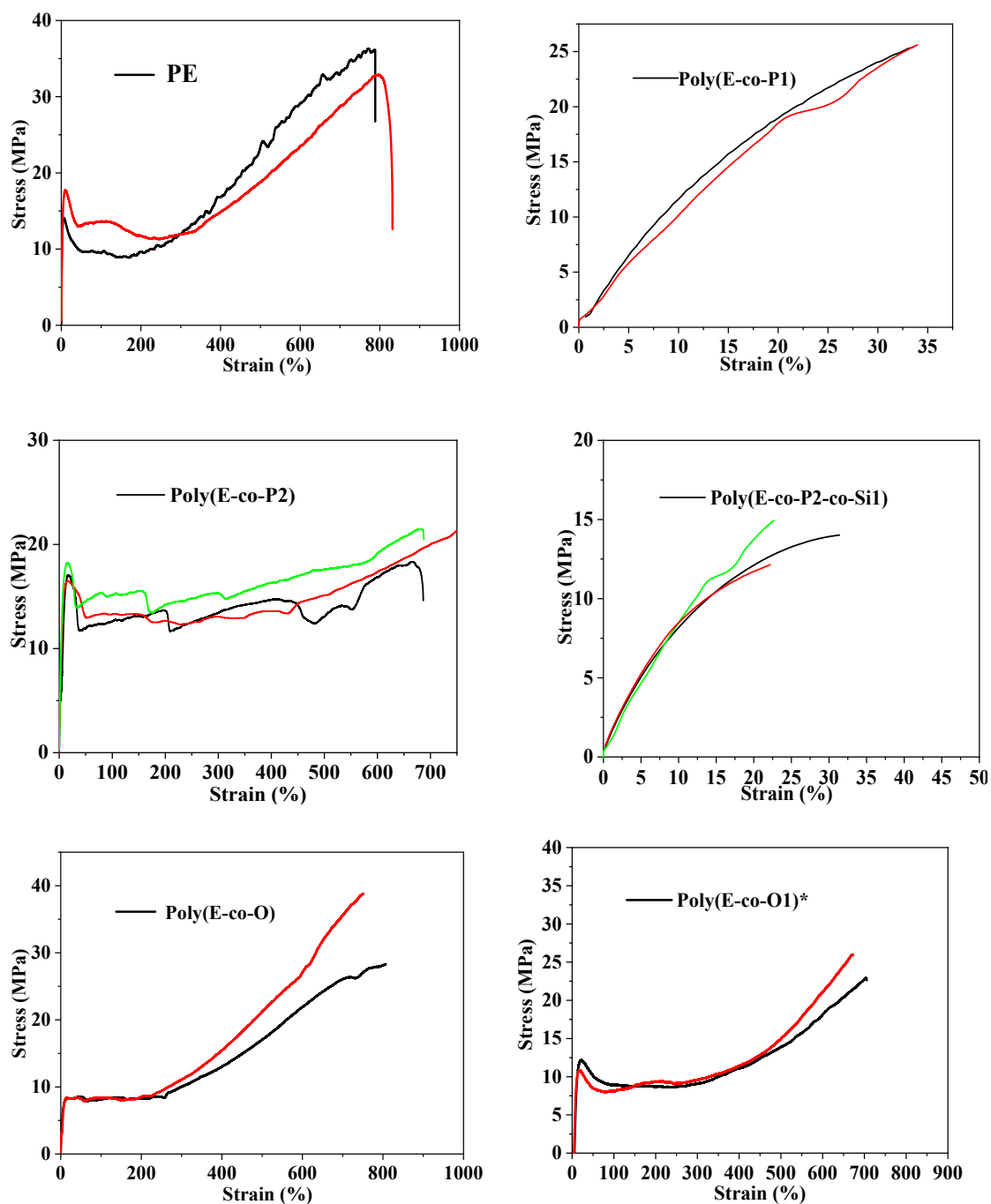


Figure S36. GPC trace of the polymer (table 1, entry 11).

## 5. Tensile tests of the polymer products



**Figure S37.** Stress vs. strain curves at 25 °C of the polymer products. Results on multiple specimens are shown for reproducibility.



## 6. Reference

1. Marvin, L.; Ihor, k.; Olivier, C.; Mathias, D. Straightforward Xanthate-Mediated Synthesis of Functional  $\gamma$ -Thiolactones and Their Application to Polymer Synthesis and Modification. *Macromolecules*. 2017, *50*, 3524-3531.
2. Ramakrishnan, S.; Berluche, E.; Chung, T. C. Functional Group Containing Copolymers Prepared by the Ziegler-Natta Process. *Macromolecules*. 1990, *23*, 378-382.