Electronic Supplementary Information Flame retardant phosphonate-functionalised polyethylenes

Nichabhat Blake, Zoë R. Turner, Jean-Charles Buffet, and Dermot O'Hare*

Chemistry Research Laboratory, Department of Chemistry, University of Oxford, 12 Mansfield Road, OX1 3TA Oxford, UK. E-mail: dermot.ohare@chem.ox.ac.uk

Table of Contents

1. General details and instrumentation	S2
2. Experimental details	S4
2.1. Solution-phase copolymerisation of ethylene and bromoalkene studies	S4
2.2. Post-polymerisation modification	S4
2.2.1. Reaction of poly(ethylene)-co-(11-bromo-1-undecene) and $P(O^{i}Pr)_{3}$	S4
2.2.2. Reaction of poly(ethylene)-co-(11-bromo-1-undecene) and $P(OPh)_3$	S5
3. NMR spectroscopy	S6
4. FT-IR spectroscopy	S26
5. Gel permeation chromatography (GPC)	S34
6. Differential scanning calorimetry (DSC)	S37
7. Thermogravimetric analysis (TGA)	S42
8. Powder X-ray diffraction	S43
9. References	S43

1. General details and instrumentation

General procedures

Air- and moisture-sensitive compounds were manipulated under an inert atmosphere of nitrogen, using standard Schlenk line techniques¹ on a dual manifold vacuum/nitrogen line or in an MBraun Labmaster 100 glovebox.

Hexane and toluene were dried using an MBraun SPS 800 solvent purification system, stored over a potassium mirror, and degassed under partial vacuum before use. Xylene was used as received.

1,1,2,2-tetrachloroethane- d_2 (Sigma Aldrich) was used as supplied for polymer samples.

Solution NMR spectroscopy

NMR spectra were recorded using a Bruker Avance III NMR (11.75 T, 499.9 MHz). The polymer samples (*ca.* 40 mg) were dissolved at 130 °C in 1,1,2,2-tetrachloroethane- d_2 with chromium(III) acetylacetonate (3 mg mL⁻¹). Spectra were recorded at 403 K unless otherwise stated and referenced internally to the residual *protio* solvent resonance. Chemical shifts, δ , are reported in parts per million (ppm) relative to tetramethylsilane (δ = 0 ppm).

Infrared spectroscopy

Fourier-transform infrared (FTIR) spectra were measured using a Bruker VERTEX 80 spectrometer with an incompartment diamond ATR accessory (DuraSamplIR II^{TM}). A background spectrum was run before the samples and subtracted from the sample spectra. IR data are reported in wavenumbers within the range of 4,000–400 cm⁻¹.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC 4000 System within a temperature range of 30–180 °C at a rate of 20 °C min⁻¹. Polymer samples were sealed in 100 μ L aluminium crucibles. An empty crucible was used as a reference, and the DSC was calibrated using indium and zinc.

Thermogravimetric analysis

Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere and a synthetic air ($O_2:N_2 = 20:80$) atmosphere using a Perkin Elmer TGA 8000. The weight change was recorded from 50 to 800 °C at a rate of 20 °C min⁻¹.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) analysis was performed by S. Roberts on a PANAnalytical X'Pert Pro Diffractometer in scanning mode using Cu Ka radiation ($\alpha 1 = 1.540598$ Å, $\alpha 2 = 1.544426$ Å) in reflection mode at 40 kV and 40 mA. The polymer samples were packed on stainless steel holders which can result in peaks at 43.36, 44.29, and 50.51° but which did not interfere with the analysis. Signals between 2h = 3-70° were recorded with step size 0.0167°.

Gel permeation chromatography

Gel permeation chromatography (GPC) was performed by L. Thobru, S. Herum, and R. Jenssen (Norner AS, Norway) on a high-temperature gel permeation chromatography with an IR5 infrared detector (GPC-IR5). Samples were prepared by dissolution in 1,2,4-trichlorobenzene (TCB) containing 300 ppm of 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) at 160 °C for 90 minutes and then filtered with a 10 μ m SS filter before being passed through the GPC column. The samples were run under a flow rate of 0.5 mL min⁻¹ using TCB containing 300 ppm of BHT as mobile phase with 1 mg mL⁻¹ BHT added as a flow rate marker. The GPC column and detector temperature were set at 145 and 160 °C respectively.

Bromine analysis

Bromine analyses were carried out in duplicate by S. Dhupper (Exeter Analytical UK Ltd.) using an oxygen combustion technique followed by the Hypochlorite Amplification method.

Microscale combustion calorimetry

Microscale combustion calorimetry (MCC) tests were carried out in triplicate by C. Chong and S. Kumar (Interscience Fire Laboratory). The tests were carried out following the procedure specified in ASTM D 7309-19 standard test method for "Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry".

Commercially supplied materials

Dichloro[*rac*-ethylenebis(indenyl)]zirconium(IV) (Strem chemicals) was stored in the glovebox and used as received. 11-Bromo-1-undecene (Fluorochem), 7-Bromo-1-heptene, 6-Bromo-1-hexene, 5-Bromo-1-pentene (Sigma Aldrich) and 1-docecene (Alfa Aesar) were freeze-pump-thaw degassed and stored over pre-activated 3 Å molecular sieves. Triisopropyl phosphite and triphenyl phosphite (Sigma Aldrich) were used as received. Low density polyethylene (powder, 500 micron, Alfa Aesar) was used as received. Aluminium hydroxide (Sigma Aldrich) was used as received.

2. Experimental Details

2.1 Solution-phase copolymerisation of ethylene and bromoalkene studies

A stock solution of the catalyst in toluene was prepared at a concentration of 1 mg mL⁻¹. 1000 equivalents of MAO were added to a 150 mL Rotaflo ampoule and washed with 10 mL hexanes. 0.5 mL stock solution (0.5 mg) was added to the ampule along with a further 34.5 mL hexanes. Bromoalkene (4.56 mmol) was added into a side-arm of a Rotaflo ampoule followed by a 5 mL hexanes solution of TIBA with [bromoalkene]₀:[TIBA]₀ = 10:1. The vessel was sealed and was pumped onto a vacuum line and degassed under reduced pressure. It was cycled a further three times using an ethylene purge while the reaction was brought to temperature in an oil bath with the stirring was set at 1000 rpm. The stopcock was opened to ethylene at a pressure of 2 bar and the timer was started. On completion of the run, the vessel was closed to ethylene and degassed. The copolymerisation solution was stirred with 100 mL HCl/IPA solution (2.5 %v/v) then filtered on a glass sintered frit (porosity 3) and washed with 2 × 50 mL pentane. The polymer sample was dried under vacuum at 90 °C for 18 h.

¹H NMR ($C_2D_2CI_4$, 499.9 MHz, 403 K): 3.49 (2H, t, ³*J* = 6.58 Hz, C*H*₂Br), 1.97 (2H, p, ³*J* = 6.82 Hz, C*H*₂CH₂Br), 1.39 (br s, (C*H*₂)_n) ppm.

Inverse gated ¹³C{¹H} NMR (C₂D₂Cl₄, 151.0 MHz, 393 K): 37.21 (C10), 33.59 (C9 and C11), 32.90 (C1), 32.37 (C2), 29.51, 29.42, 28.86, 28.77 (C5, C6, C7, C13), 29.01 (CH₂ of PE), 28.13 (C4), 27.64 (C3), 26.32, 26.27 (C8, C12) ppm.



Bromine (duplicate analysis): 9.65 and 9.71 wt%

2.2 Post-polymerisation modification

2.2.1 Reaction of poly(ethylene)-co-(11-bromo-1-undecene) and P(O'Pr)₃

In a 50 mL Rotaflo ampoule equipped with a magnetic stir bar, poly(ethylene)-co-(11-bromo-1-undecene) with 5.80 mol% comonomer incorporation level (2.0 g, 2.9 mmol of Br group) was added. The copolymer was heated at 130 °C until melted. Triisopropyl phosphite (35.8 mL, 145.1 mmol, 50 equiv.) was added and the reaction was refluxed at 180 °C for 6 h. The reaction solution was allowed to cool down at RT and precipitated with pentane then filtered on a glass sintered frit (porosity 3) and washed with 2×50 mL pentane. The resultant functionalised copolymer was dried under vacuum at 90 °C for 18 h.

¹H NMR (C₂D₂Cl₄, 499.9 MHz, 403 K): 4.74 (2H, m, O=P(OC**H**Me₂)₂), 1.77–1.68 (4H, m, C**H**₂C**H**₂O=P(OⁱPr)₂), 1.39 (br s, (C**H**₂)_n) ppm.

Inverse gated ¹³C{¹H} NMR ($C_2D_2Cl_4$, 151.0 MHz, 393 K): 68.92 (C14, ² J_{CP} = 6.57 Hz), 37.23 (C10), 33.58 (C9, C11), 29.89 (C3, ³ J_{CP} = 14.96 Hz), 29.51, 28.48 (C4, C5, C6, C7), 29.01 (CH₂ of PE), 26.68 (C1, ¹ J_{CP} = 140.80 Hz), 26.32 (C8, C12), 23.40 (C15), 22.01 (C2, ² J_{CP} = 5.39 Hz) ppm.



³¹P{¹H} NMR (C₂D₂Cl₄, 202.4 MHz, 403 K): 29.5 (O=**P**(O^{*i*}Pr)₂) ppm.

Bromine (duplicate analysis): 0.29 and 0.23 wt%

2.2.2 Reaction of poly(ethylene)-co-(11-bromo-1-undecene) and P(OPh)₃

In a 50 mL Rotaflo ampoule equipped with a magnetic stir bar, poly(ethylene)-co-(11-bromo-1-undecene) with 5.11 mol% comonomer incorporation level (2.0 g, 2.7 mmol of Br group) was added. The copolymer was heated at 130 °C until melted. Triphenyl phosphite (34.8 mL, 132.6 mmol, 50 equiv.) was added and the reaction was stirred at 200 °C for 72 h. The reaction solution was allowed to cool down at RT and precipitated with pentane then filtered on a glass sintered frit (porosity 3) and washed with 2×50 mL pentane. The resultant functionalised copolymer was dried under vacuum at 90 °C for 18 h.

¹H NMR (C₂D₂Cl₄, 499.9 MHz, 403 K): 7.39–7.28 (10H, m, O=P(OC₆H₅)₂), 2.16 (2H, m, CH₂O=P(OPh)₂), 1.88 (2H, m, CH₂CH₂O=P(OPh)₂), 1.39 (br s, (CH₂)_n) ppm.

Inverse gated ¹³C{¹H} NMR ($C_2D_2CI_4$, 151.0 MHz, 393 K): 150.31 (C14, ${}^2J_{CP}$ =9.13 Hz), 129.02 (C16), 124.27 (C17), 119.95 (C15, ${}^3J_{CP}$ = 4.36 Hz), 37.25 (C10), 33.59 (C9, C11), 29.74 (C3, ${}^3J_{CP}$ = 15.43 Hz), 29.52, 28.73, 28.39 (C5, C5, C6, C7), 29.01 (CH₂ of PE), 26.33 (C8, C12), 25.75 (C1, ${}^{1}J_{CP}$ = 139.26 Hz), 21.76 (C2, ${}^{2}J_{CP}$ = 5.63 Hz) ppm.



³¹P{¹H} NMR (C₂D₂Cl₄, 202.4 MHz, 403 K): 25.2 (O=**P**(OPh)₂) ppm.

3. NMR spectroscopy



Figure S1 ¹H NMR spectrum ($C_2D_2Cl_4$, 499.9 MHz, 403 K) of poly(ethylene)-co-(5-bromo-1-pentene) with comonomer incorporation level = $(2/2)/[(2/2)+{(242.6-5)/4}]*100 = 1.66 \text{ mol}\%$.



Figure S2 ¹H NMR spectrum ($C_2D_2CI_4$, 499.9 MHz, 403 K) of poly(ethylene)-co-(6-bromo-1-hexene) with comonomer incorporation level = $(2/2)/[(2/2)+{(357.7-7)/4}]*100 = 1.13 mol\%$.



Figure S3 ¹H NMR spectrum ($C_2D_2Cl_4$, 499.9 MHz, 403 K) of poly(ethylene)-co-(7-bromo-1-heptene) with comonomer incorporation level = $(2/2)/[(2/2)+{(142.1-9)/4}]*100 = 2.92 \text{ mol}\%$.



Figure S4 Stacked ¹H NMR spectra ($C_2D_2CI_4$, 499.9 MHz, 393 K) of poly(ethylene)-co-(11-bromo-1-undecene) from ethylene/11-bromo-1-undecene copolymerisation using [TIBA]₀:[11-bromo-1-undecene]₀ = 2 (top) or 0 (bottom)



Figure S5 ¹H NMR spectrum ($C_2D_2Cl_4$, 499.9 MHz, 403 K) of poly(ethylene)-co-(11-bromo-1-undecene) (PE-Br) with comonomer incorporation level = $(2/2)/[(2/2)+\{(82-17)/4\}]*100 = 5.80 \text{ mol}\%$.



Figure S6 COSY NMR spectrum ($C_2D_2CI_4$, 499.9 MHz, 403 K) of PE-Br



Figure S8 Inverse gated ¹³C{¹H} NMR spectrum (C₂D₂Cl₄, 151.0 MHz, 393 K) of PE-Br (full spectrum)



Figure S9 Inverse gated ${}^{13}C{}^{1}H$ NMR spectrum (C₂D₂Cl₄, 151.0 MHz, 393 K) of poly(ethylene)-co(11-bromo-1-undecene) (PE-Br)



Figure S10 Inverse gated ¹³C{¹H} NMR spectrum (C₂D₂Cl₄, 151.0 MHz, 393 K) of PE-Br with assignment



Figure S11 ¹H NMR spectrum ($C_2D_2Cl_4$, 499.9 MHz, 403 K) of poly(ethylene)-co-(1-dodecene) with comonomer incorporation level = $(3/3)/[(3/3)+{(75.6-21)/4}]*100 = 6.80 \text{ mol}\%$.



Figure S12 Inverse gated ${}^{13}C{}^{1}H$ NMR spectrum (C₂D₂Cl₄, 125.7 MHz, 403 K) of poly(ethylene)-co-(1-dodecene) with assignment



Figure S14 ¹H{³¹P} NMR spectrum ($C_2D_2Cl_4$, 499.9 MHz, 403 K, top) and ¹H NMR spectrum ($C_2D_2Cl_4$, 499.9 MHz, 403 K, bottom) of PE-PO(OⁱPr)



Figure S16 COSY NMR spectrum ($C_2D_2CI_4$, 499.9 MHz, 403 K) of PE-PO(O'Pr)₂



Figure S17 ¹H-¹³C HSQC NMR spectrum (C₂D₂Cl₄, 499.9 MHz, 403 K) of PE-PO(O'Pr)₂(full spectrum)



Figure S18 ¹H-¹³C HSQC NMR spectrum (C₂D₂Cl₄, 499.9 MHz, 403 K) of PE-PO(OⁱPr)₂ (selected region)







Figure S21 Inverse gated ¹³C{¹H} NMR spectrum (C₂D₂Cl₄, 151.0 MHz, 393 K) of PE-PO(OⁱPr)₂ with assignment



Figure S22 ¹H NMR spectrum (C₂D₂Cl₄, 499.9 MHz, 403 K) of PE-PO(OPh)₂



Figure S24 1 H- 31 P HMBC NMR spectrum (C₂D₂Cl₄, 499.9 MHz, 403 K) of PE-PO(OPh)₂



Figure S26 HSQC NMR spectrum (C₂D₂Cl₄, 499.0 MHz, 393 K) of PE-PO(OPh)₂



Figure S27 Inverse gated ¹³C{¹H} NMR spectrum (C₂D₂Cl₄, 151.0 MHz, 393 K) of PE-PO(OPh)₂ (full spectrum)



Figure S28 Inverse gated ¹³C{¹H} NMR spectrum (C₂D₂Cl₄, 151.0 MHz, 393 K) of PE-PO(OPh)₂



Figure S29 Inverse gated ¹³C{¹H} NMR spectrum (C₂D₂Cl₄, 151.0 MHz, 393 K) of PE-PO(OPh)₂ with assignment



Figure S30 Stacked ¹H NMR spectra ($C_2D_2Cl_4$, 600.0 MHz, 393 K) of PE-PO(OPh)₂ (blue), PE-PO(OⁱPr)₂ (green) and poly(ethylene)-co-(11-bromo-1-undecene) (red)



Figure S31 Stacked inverse gated ${}^{13}C{}^{1}H$ NMR spectra ($C_2D_2Cl_4$, 151.0 MHz, 393 K) of PE-PO(OPh)₂ (blue), PE-PO(OⁱPr)₂ (green) and poly(ethylene)-co-(11-bromo-1-undecene) (red). The resonances at 32.8 and 32.4 ppm corresponding to CH_2CH_2Br and CH_2CH_2Br shown in the inverse gated ${}^{13}C{}^{1}H$ NMR spectrum of PE-Br (red) were not observed from the inverse gated ${}^{13}C{}^{1}H$ NMR spectra of PE-PO(OPh)₂ (blue) and PE-PO(OⁱPr)₂ (green)



Figure S32 Stacked ¹H NMR spectra ($C_2D_2Cl_4$, 499.9 MHz, 393 K) of poly(ethylene)-co-(11-bromo-1-undecene) (a) and aliquots from post-polymerisation modification of poly(ethylene)-co-(11-bromo-1-undecene) and $P(O^{i}Pr)_3$ collected at 48, 24, 6 and 3 h (b, c, d and e respectively). **Reaction temperature was at 130 °C.**



Figure S33 Stacked ¹H NMR spectra ($C_2D_2CI_4$, 499.9 MHz, 393 K) of poly(ethylene)-co-(11-bromo-1-undecene) (a) and aliquots from post-polymerisation modification of poly(ethylene)-co-(11-bromo-1-undecene) and $P(O'Pr)_3$ collected at 48, 24, 6 and 3 h (b, c, d and e respectively). **Reaction temperature was at 180 °C.**



Figure S34 ¹H NMR spectrum of ($C_2D_2CI_4$, 499.9 MHz, 393 K) of aliquot collected after 3 h from postpolymerisation modification of poly(ethylene)-co-(11-bromo-1-undecene) and P($O^{i}Pr$)₃. **Reaction temperature was at 180** °C. The ¹H NMR spectrum shows 97% conversion of the bromide group to the phosphonate group.



Figure S35 Stacked ¹H NMR spectra ($C_2D_2CI_4$, 499.9 MHz, 393 K) of poly(ethylene)-co-(11-bromo-1-undecene) (a) and PE-PO(OPh)₂ (b), PE-Br-PO(OPh)₂_80% (c), PE-Br-PO(OPh)₂_70% (d) and PE-Br-PO(OPh)₂_50% (e)



Figure S36 Stacked ¹H NMR spectra (CDCl₃, 400.2 MHz, 298 K) of triisopropyl phosphite (top) and the filtrate from post-polymerisation modification of poly(ethylene)-co-(11-bromo-1-undecene) and $P(O^{i}Pr)_{3}$ which volatiles were removed using rotary evaporator(bottom)



Figure S37 Stacked ³¹P{¹H} NMR spectra (CDCl₃, 162.0 MHz, 298 K) of triisopropyl phosphite (top) and the filtrate from post-polymerisation modification of poly(ethylene)-co-(11-bromo-1-undecene) and $P(O^{i}Pr)_{3}$ which volatiles were removed using rotary evaporator(bottom)



Figure S38 Stacked ¹H NMR spectra (CDCl₃, 400.2 MHz, 298 K) of triphenyl phosphite (top) and the filtrate from post-polymerisation modification of poly(ethylene)-co-(11-bromo-1-undecene) and P(OPh)₃ which volatiles were removed using rotary evaporator(bottom)



Figure S39 Stacked ³¹P{¹H} NMR spectra (CDCl₃, 162.0 MHz, 298 K) of triphenyl phosphite (top) and the filtrate from post-polymerisation modification of poly(ethylene)-co-(11-bromo-1-undecene) and $P(OPh)_3$ which volatiles were removed using rotary evaporator(bottom)

4. FT-IR spectroscopy



Figure S40 FT-IR spectrum of poly(ethylene)-co-(11-bromo-1-undecene)



Figure S41 FT-IR spectrum of PE-PO(OⁱPr)₂



Figure S42 FT-IR spectrum of PE-PO(OPh)₂



Figure S43 Stacked FT-IR spectra of poly(ethylene)-co-(11-bromo-1-undecene) (black), $PE-PO(O^{i}Pr)_{2}$ (red) and $PE-PO(OPh)_{2}$ (blue)



Figure S44 FT-IR spectrum of LDPE:PE-PO(OⁱPr)₂ (90:10 wt%)



Figure S45 FT-IR spectrum of LDPE:PE-PO(OⁱPr)₂ (95:5 wt%)



Figure S46 FT-IR spectrum of LDPE:PE-PO(OⁱPr)₂ (99:1 wt%)



Figure S47 Stacked FT-IR spectra of LDPE:PE-PO(O[/]Pr)₂ 90:10 wt% (black), 95:5 wt% (red) and 99:1 wt% (blue)



Figure S48 FT-IR spectrum of LDPE:PE-PO(OPh)₂ (90:10 wt%)



Figure S49 FT-IR spectrum of LDPE:PE-PO(OPh)₂ (95:5 wt%)



Figure S50 FT-IR spectrum of LDPE:PE-PO(OPh)₂ (99:1 wt%)



Figure S51 Stacked FT-IR spectra of LDPE:PE-PO(OPh)₂ 90:10 wt% (black), 95:5 wt% (red) and 99:1 wt% (blue)



Figure S52 FT-IR spectrum of LDPE:ATH (90:10 wt%)



Figure S53 FT-IR spectrum of LDPE:ATH:PE-PO(OⁱPr)₂ (80:10:10 wt%)



Figure S54 FT-IR spectrum of LDPE:ATH:PE-PO(OPh)₂ (80:10:10 wt%)



Figure S55 FT-IR spectrum of LDPE

5. Gel permeation chromatography (GPC)



Figure S56 GPC traces for poly(ethylene)-co-(11-bromo-1-undecene) obtained from ethylene/11-bromo-1undecene copolymerisations using 0.2 mM **Zr** as a catalyst, MAO as a cocatalyst and scavenger with [Al]₀:[Zr]₀ = 1000:1, [11-bromo-1-undecene]₀ = 91 mM, 2 bar of ethylene, 70 °C, 0.5 h. **[TIBA]₀:[11-bromo-1-undecene]₀ = 0** (black, M_w = 29,400, M_w/M_n = 3.4), **0.1** (blue, M_w = 36,900, M_w/M_n = 4.4) and **2** (red, M_w = 5800, M_w/M_n = 4.2).



Figure S57 GPC traces for poly(ethylene)-co-(bromoalkene) obtained from copolymerisations of ethylene with 11-bromo-1-undecene (black, $M_w = 36,900$, $M_w/M_n = 4.4$), 7-bromo-1-heptene (red, $M_w = 52,100$, $M_w/M_n = 5.9$), 6-bromo-1-hexene (blue, $M_w = 30,100$, $M_w/M_n = 5.3$) and 5-bromo-1-pentene (green, $M_w = 53,600$, $M_w/M_n = 4.5$). Conditions: 0.2 mM **Zr** as a catalyst, MAO as a cocatalyst and scavenger with [Al]₀:[Zr]₀ = 1000:1, [11-bromo-1-undecene]₀ = 91 mM, [TIBA]₀:[11-bromo-1-undecene]₀ = 0.1, 2 bar of ethylene, 70 °C, 0.5 h.



Figure S58 GPC traces and SCB profiles of poly(ethylene)-co-(bromoalkene) obtained from copolymerisations of ethylene with 7-bromo-1-heptene (black, $M_w = 52,100$, $M_w/M_n = 5.9$), 6-bromo-1-hexene (red, $M_w = 30,100$, $M_w/M_n = 5.3$) and 5-bromo-1-pentene (blue, $M_w = 53,600$, $M_w/M_n = 4.5$).



Figure S59 GPC traces and SCB profiles of poly(ethylene)-co-(1-dodecene) (black, $M_w = 21,600$, $M_w/M_n = 3.9$) and poly(ethylene)-co-(11-bromo-1-undecene) (red, $M_w = 27,400$, $M_w/M_n = 4.3$). Conditions: 0.2 mM **Zr** as a catalyst, MAO as a cocatalyst and scavenger with [Al]₀:[Zr]₀ = 1000:1, [comonomer]₀ = 182 mM, [TIBA]₀:[comonomer]₀ = 0.1, 2 bar of ethylene, 70 °C, 0.5 h.



Figure S60 GPC trace of PE-PO($O^{i}Pr$)₂ (M_{w} = 15,600, M_{w}/M_{n} = 6.0).



Figure S61 GPC traces of PE-PO(OPh)₂_50% (black, $M_w = 22,100$, $M_w/M_n = 3.1$), PE-PO(OPh)₂_70% (red, $M_w = 52,200$, $M_w/M_n = 9.8$) and PE-PO(OPh)₂_80% (blue, $M_w = 21,800$, $M_w/M_n = 4.0$).

6. Diffrential scanning calorimetry (DSC)







Figure S67 DSC 2nd heating curve of PE-PO(OⁱPr)₂



Figure S71 DSC 2nd heating curve of LDPE:PE-PO(O^{*i*}Pr)₂ (99:1 wt%)



Figure S75 DSC 2nd heating curve of LDPE:ATH (90:10 wt%) (ND320)





Figure S 77 DSC 2nd heating curve of LDPE:ATH:PE-PO(OPh)₂ (80:10:10 wt%) (ND325)





7. Thermogravimetric analysis (TGA)



Figure S79 TGA curve of poly(ethylene)-co(11-bromo-undecene) performed under an air atmosphere with a heating rate of 20 °C min⁻¹



Figure S80 DTG curve of poly(ethylene)-co(11-bromo-undecene) performed under an air atmosphere with a heating rate of 20 $^{\circ}$ C min⁻¹

8. Powder X-ray diffraction



Figure S81 Powder XRD patterns of poly(ethylene)-co(11-bromo-1-undecene) (blue), PE-PO(O'Pr)₂ (red) and PE-PO(OPh)₂ (black)

9. References

1. D. F. Shriver and M. A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, Wiley, 2 edn., 1986.