Towards Degradable Polyethylene: End-functionalised Polyethylene (PE-X) and PE-I/LDPE blends from Iron-Catalysed Chain Growth of ZnEt₂ with Ethylene

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Experimental Details

General

All experiments with moisture or air sensitive compounds were carried out under nitrogen using standard Schlenk techniques. A MBraun Labmaster DP nitrogen filled glovebox was used to store and handle compounds and reagents. NMR solvents were freeze-pump-thaw degassed, dried and stored in a gas-tight ampule over 3 Å molecular sieves in the glovebox. All glassware was dried overnight at 150 °C. Toluene was dried using an Innovative Technology Pure Solvent SPS-400 Column and subsequently stored over 3 Å molecular sieves. Dipentyl zinc,¹ and iron complex 1,² were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used without further purification.

Characterisation

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 400 MHz instrument at 298 K. If not indicated otherwise, NMR spectra were taken in CDCl₃ as the solvent and in 5 mm Norell NMR tubes. All air sensitive compounds were analysed in air-sealed Young's NMR tubes and prepared inside the glovebox. Solvent peaks were used as internal references for ¹H, ¹³C, ¹¹B and ³¹P chemical shifts (ppm). The following abbreviations

are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet. NMR experiments were conducted on a Bruker DRX-400 MHz, AV-400 MHz and Bruker AV 500 MHz AVANCE III HD spectrometer using TopSpin 3.2 and equipped with a z-gradient bbo/5 mm tunable Smart Probe and a GRASP II gradient spectroscopy accessory providing a maximum gradient output of 53.5G/cm (5.35G/cmA). Analysis of polymer samples were caried out at 120 °C in a mixture of 1,2,4-trichlorobenzene/CD₂Cl₄ (70/30 v/v). Quantitative ¹³C NMR spectra are measured at 120 °C using the experiment zgig30, an inverse-gated decoupled ¹³C (decoupling only during acquisition but not during the delay time to eliminate nOe enhancement) with a 30 degree ¹³C pulse. The delay time is 40s and acquisition time ~0.46s. ¹H NMR spectra were collected at 120 °C with normal conditions - delay of 0.5s and acquisition time of ~3.6s.

Mass spectrometry was measured using a Micromass Autospec Premier in low resolution mode. IR spectroscopy measurements were conducted on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Raman analysis was conducted on a Thermo-Fischer DXR 2xi using a Raman Imaging Microscope. Lasers were set at 24.1 mW, pulsing at an exposure time of 10 Hz. 35 scans were conducted per scan on average.

Elemental analyses were carried out by the Science and Technical Support Unit at London Metropolitan University or MEDAC LTD.

Differential scanning calorimetry (DSC) measurements were performed using a Perkin Elmer DSC 4000 and a sample mass of approximately 5 mg under a nitrogen atmosphere with a heating cycle of 10 °C/min from 0 to 200 °C and followed by a cooling cycle at the same rate from 200 to 0 °C. Then the samples were reheated at the same rate for a second heating cycle to 200 °C. Only the second cycle is reported.

Secondary electrons imaging and focussed ion beam FIB machining were performed using an Auriga Zeiss scanning electron microscope (SEM) at 20 kV. All samples were gold-plated before analysis. The ion beam for FIB micro machining was at 54° with respect to the electron beam and was only used for milling, not for imaging. The sample was milled with a Ga⁺ ion beam current of 4 nA with an acceleration voltage of 30 keV. The cross-sectioned face was then polished with a low beam current (5 pA) prior to the imaging in SEM mode. An Oxford Instruments INCA EDX was used for chemical analysis.

Preparation of Zn(PE)₂



(2,6-diacetylpyridinebis(2,6-diisopropylanil))FeCl₂ (1) (6.5 mg, 0.01 mmol) was placed in 5 ml toluene resulting in a blue suspension. After the addition of 100 equivalents of MMAO (0.93 ml of 7 wt% sol. in toluene), the solution turned orange. To the orange solution was added ZnEt₂ dissolved in 25 ml of toluene (3 mmol, 2.63 ml of 15 wt.% solution in toluene), resulting in a yellow solution. The polymerisation was started by the addition of ethylene (1 bar(g)) at room temperature. After the desired time (typically less than 1 hour), the polymerisation was stopped by closing the ethylene supply and the resulting precipitate was filtered resulting in 1.94 g of Zn(PE)₂ polymer, after multiple washes with toluene under N₂. Contamination with PE due to partial hydrolysis during workup is often observed, and it is recommended to convert Zn(PE)₂ *in situ*, without isolation. ¹H-NMR (400 MHz, d₈-toluene, 100 °C): δ 1.53 (m, ZnCH₂CH₂), 1.36 (CH₂), 0.83 (CH₃), 0.30 (t, *J* = 8Hz, ZnCH₂). ¹³C NMR (400 MHz, d₈-toluene, 100 °C): δ 3.1.53 (m, ZnCH₂CH₂), 1.36 (CH₂), 2846 (vCHs), 1467 (δ CH₂), 1379 (δ CH₃), 717 (δ CH₂), 625 (ρ ZnCH₂).



Figure S1. FT-IR Spectrum of Zn(PE)₂.



Figure S2. ¹H NMR spectrum of ZnPE₂ (together with PE) in d⁸-toluene at 373K.



Figure S3. ¹³C{¹H} NMR spectrum of ZnPE₂ (together with PE) in in d⁸-toluene at 373K.

Reaction of dipentyl zinc with oxygen.



A solution of dipentyl zinc (10 mg) in d^8 -toluene in a J Young NMR tube was saturated with oxygen (1 bar) and heated to 80 °C for 2 hours. The reaction was analysis by ¹H and ¹³C NMR spectroscopy.



Figure S4. ¹H NMR spectrum of [Zn(C₅H₁₁)(OC₅H₁₁)]_n (400 MHz, d⁶-benzene, 298K).



Figure S5. ¹³C $\{^{1}H\}$ NMR spectrum of $[Zn(C_{5}H_{11})(OC_{5}H_{11})]_{n}$ in d⁶-benzene at 298K.

Reaction of Zn(PE)₂ with oxygen.

Zn(PE)₂ (0.200 g, 0.196 mmol, Zn($C_{34}H_{69}$)₂) was suspended in 10 ml toluene. The mixture was pressurised with air (1 bar, anhydrous synthetic air, mixture of 80 % N₂ and 20 % O₂) and stirred vigorously for two hours at 80 °C. The reaction was quenched by the addition of the reaction mixture to 100 ml methanol containing 1 ml of 1M aqueous HCl solution. The precipitate was filtered, washed and dried to yield the PE-OH product (0.181 g, 93 % yield). The product was analysed by ¹H and ¹³C NMR, which indicated 57 % OH-functionalisation to C₃₄H₆₉OH, the remainder being C₃₄H₇₀.

Reaction of dipentyl zinc with sulfur.

Elemental sulfur (5.3 mg, 0.29 mmol) was dissolved in d⁸-toluene in a J Young NMR tube. Dipentyl zinc (50 μ L, 0.29 mmol) was added with ice cooling. The reaction was left to proceed at room temperature and monitored by NMR spectroscopy.



Figure S6: ¹H-NMR spectrum of C_5H_{11} -S_k- C_5H_{11} (k= 1-8) formed upon reaction of dipentylzinc with sulfur (Zn:S= 1:1). * = unknown impurities. (400 MHz, d₈-toluene at 298K).

Preparation for PE-S_k-PE



(2,6-diacetylpyridinebis(2,6-diisopropylanil))FeCl₂ (1) (26.3 mg, 0.04 mmol) was placed in 10 ml toluene resulting in a blue suspension. After the addition of 100 equivalents of MMAO (3.7 ml of 7 wt% sol. in toluene) at RT, the solution turned orange. To the orange solution was added Zn(Et)₂ dissolved in 120 ml of toluene (12 mmol, 10.7 ml of 15 wt.% solution in toluene, 1.1 M), resulting in a yellow solution. The polymerisation was started by the addition of ethylene (1 bar(g)) at room temperature. After 1 h, the polymerisation was stopped by closing the ethylene supply and the resulting suspension exposed to N₂ to remove residual ethylene from the solution. Sulphur (S₈, 1.54 g, 48 mmol, 4 eq.) was added to the solution at RT and the solution was kept at 60 °C for 24h. The resulting polymer was cooled to RT, precipitated in methanol, filtered and dried under vacuum to result in a yellow powder (6.16 g, 8.2 mmol based on C₂₂H₄₅S₄C₂₂H₄₅, 69% yield). ¹H-NMR (400 MHz, d₈-toluene, 25 °C): δ 2.70 ppm (t, 0.67 H, ³J_{H-H} = 7.3 Hz, CH₂-S₃), δ 2.54 ppm (t, 0.60 H, ³J_{H-H} = 7.4 Hz, CH₂-S₂), δ 2.40 ppm (t, 0.15

H, ${}^{3}J_{\text{H-H}} = 7.4 \text{ Hz}$, CH₂-S₁), δ 1.63 ppm (m, 2H, CH₂-CH₂-S_k), δ 1.34 ppm (br. s, 36H, , -CH₂-), δ 0.92 ppm (t, 3H, ${}^{3}J_{\text{H-H}} = 6.96 \text{ Hz}$, -CH₃). 13 C-NMR (400 MHz, d₈-toluene, 25 °C): δ 32.43 (S_kCH₂CH₂), 29-93-30.31 (CH₂), 23.18 (CH₂CH₃), 14.36 (CH₃) (S_kCH₂ was not observed, probably due to various values for k). 1 H NMR data corresponds to previously reported data for PE-S_k-PE obtained by a different method.³

Elemental analysis of PE-S_k-PE ($C_{22}H_{45}S_kC_{22}H_{45}$) by combustion analysis revealed a combined 82.7 % for carbon and hydrogen. Considering an average chain length of C_{22} and assuming the remainder is sulphur, an average value for k can be calculated and was found to be 4.03. Examples for different k values can be seen in Table S1.

Table S1: Calculated elemental composition of PE-Sk-PE (C22H45SkC22H45).

S_k	C [wt.%]	H [wt.%]	S [wt.%]
k= 3	73.87	12.68	13.44
k= 4	70.70	12.14	17.16
k= 5	67.80	11.64	20.57
k= 6			



Figure S7. ¹H NMR spectra of PE-S_k-PE before and after heating at 80°C for 1 hour in d^8 -toluene, indicating a lowering of the k-value after heating.



Figure S8: Raman spectrum of PE-S_k-PE (k= 4.03, top) and HDPE (bottom), showing v(C–S) at 744 cm⁻¹.



Figure S9. ¹³C-NMR spectrum of PE-S_k-PE in d_8 -toluene at 298K. (signals for a are not observed due to different values of k).

Preparation of PE-I

Zn(PE)₂ (28 mg, 0.028 mmol, Zn(C₃₄H₆₉)₂) was suspended in 10 ml toluene. A solution of iodine (14.2 mg, 0.056 mmol, 2 equiv.) in 5 ml of toluene was added to the mixture over 1h at room temperature. The reaction was kept at 60 °C for 1 h. The reaction was quenched by the addition of the reaction mixture to 20 ml methanol and 1 ml of 1M aqueous HCl solution. The precipitate was filtered and dried to yield the product polymer (16 mg, 48 % yield). The product was analysed by ¹H which indicated 84 % iodine-functionalisation. ¹H-NMR (400 MHz, CDCl₃, 25 °C): δ 3.19 ppm (t, 2H, ³*J*_{H-H} = 7 Hz, C*H*₂-I), 1.82 ppm (m, 2H, C*H*₂-CH₂-I), 1.25 ppm (s, 67H, -C*H*₂-), 0.88 ppm (t, 3H, ³*J*_{H-H} = 7 Hz, -C*H*₃).



Figure S10. ¹H NMR spectrum of C₄₇H₉₅I in 1,2,4-trichlorobenzene/CD₂Cl₄ at 393 K.



trichlorobenzene/CD₂Cl₄ recorded at 393 K.



Figure S12. Degree of functionalization of PE-I, as a function of chain length, determined by ¹H NMR analysis at 120 °C in C₂D₂Cl₄/1,2,4-trichlorobenzene. CCG conditions: Catalyst **1** (10 μ mol), MAO (100 Equiv.), ZnEt₂ (Zn/Fe ratio: 300), 30 °C, 1 bar ethylene in toluene. In order to obtain different chain lengths, reactions are quenched at different time intervals by the addition of I₂.



Figure S13. Variation of average chain length of PE-I with time, as determined by ¹³C NMR analysis. CCG conditions: Catalyst **1** (10 μ mol), MAO (100 Equiv.), ZnEt₂ (Zn/Fe ratio: 300), 30 °C, 1 bar ethylene in toluene. Reaction quenched with I₂ at given time interval.



Figure S14. GC-FID analysis of PE-I product distributions. Pure $C_{12}H_{25}I$ (green) was used as a reference. CCG conditions: Catalyst **1** (10 µmol), MAO (100 Equiv.), ZnEt₂ (Zn/Fe ratio: 300), 30 °C, 1 bar ethylene in toluene. Reaction quenched with I₂ at given time interval.



Figure S15. ATR FT-IR spectrum of C₄₀H₈₁I.



Figure S16. ATR FT-IR spectra of various alkyl iodides, used for the calibration of chain length determination.



Figure S17. Calibration curve for average chain length determination by IR for PE-I using the ratio of peak integrations for v(C-H)/v(C-I) (the ratio of 7/2 shown in Figure S13).

Preparation of PE-Br



Zn(PE)₂ (14 mg, 0.014 mmol, Zn($C_{34}H_{69}$)₂) was suspended in 10 mL toluene. Elemental bromine (1.4 µl, 0.028 mmol, 2 equiv. dissolved in 5 mL toluene) was added to the mixture over 1 h at room temperature. The reaction was stirred for 1 h and quenched by the addition of 10 mL methanol containing 1 mL of HCl solution (1M). The precipitate was filtered and dried to yield the product polymer (13.9 mg, 87 % yield). The product was analysed by ¹H and ¹³C NMR which indicated $C_{34}H_{69}$ Br with 74 % bromo-functionalisation.



Solution Blending of PE-I/LDPE

To prepare the PE-I/LDPE blends in solution, a round bottom flask was charged with 1.0 g of LDPE and 15.0 ml of toluene. A second-round bottom flask was charged with 0.1 PE-I and 5 ml of toluene. Both flasks were stirred for 30 min at 110 °C under reflux and then mixed and kept stirring for 30 minutes at 110 °C. The mixture was left to cool slowly to room temperature, filtered and dried in a vacuum oven overnight, producing 1.05 g of white powder (95% yield).

Melt Blending of PE-I/LDPE

The PE-I/LDPE blends were prepared using a co-rotating twin-screw extruder (Eurolab XL, Thermo Fisher Scientific, Karlsruhe, Germany) equipped with a 16 mm diameter screw. The extruder has a length-to-diameter ratio of 25, and a screw speed of 15 rpm was used during processing for the first cycle, 30 rpm of the second cycle and 50 rpm for the third cycle. For the fabrication of PE-I/LDPE blends, the feeding zone of the extruder was set to be 130 °C while the temperatures of the four subsequent mixing zones were all kept at 130 °C. A die temperature of 130 °C was used in the fabrication of these materials.

All extrudates were then pelletized (Haake VariCut, Thermo Fisher Scientific, Karlsruhe, Germany) and injection-molded (Haake MiniJet Pro Piston Injection Molding System, Thermo Fisher Scientific, Karlsruhe, Germany) into rectangular (80 mm × 13 mm × 3 mm)-shaped test specimens. A mold temperature of 40 °C was used. For the injection molding of PE-I/LDPE, the barrel temperature was set at 130°C. All samples were injection-molded at an injection pressure of 640 bar for 8 s, followed by a post-pressure of 640 bar for a further 60 s.



Figure S20. Experimental⁴ and calculated⁵ melting points of linear alkyl iodides $C_nH_{2n+1}I$ as a function of chain length n.



Figure S21. TGA analysis of C₁₈H₃₇-I and LDPE.



Figure S22. FT-IR spectrum of the polymer blend obtained from melt blending LDPE with 10 wt% $C_{70}H_{141}$ -I.



Figure S23. DSC analysis of PE-I/LDPE blends with different PE-I chain lengths, obtained through melt blending. Measurements shown were taken during the second heating cycle.

References

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