Supporting Information

Catalytic hydroxylation of polyethylenes

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1. General

All reactions were conducted under inert atmosphere in a nitrogen-filled glovebox or with standard Schlenk techniques, unless otherwise specified. Vessels used in air-free reactions were oven-dried prior to use. Vials used as a reaction vessel were sealed with Teflon-lined cap. Silica-gel chromatography was performed with Silicycle SiliaFlash P60 silica gel. Toluene, tetrahydrofuran, and dichloromethane were purged with nitrogen and dried with an Innovative Pure-Solv solvent purification system. Anhydrous dimethylsulfoxide, dimethylformamide, dioxane, and N-methylpyrrolidone, 1,2,4-trichlorobenzene, acetonitrile were purchased from Acros Organics. Anhydrous 1,2-dichlorobenzene and 1,2-dichoroethane were purchased from Aldrich. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. $^{13}$CPBA was purchased from Aldrich and the content of active oxygen was determined by iodometric titration (Org. Synth. 1970, 50, 15). The hydroxylation of polyethylenes was conducted with commercial low molecular weight polyethylene (Aldrich, $M_w = 4.3$ kg/mol, $M_n = 1.7$ kg/mol, PDI = 2.63), low-density polyethylene (LDPE, Aldrich, $M_w = 88.1$ kg/mol, $M_n = 10.2$ kg/mol, PDI = 8.65), high-density polyethylene (HDPE, AlfaAeser, $M_w = 114.7$ kg/mol, $M_n = 10.3$ kg/mol, PDI = 11.2) and linear low-density polyethylene (LLDPE, Aldrich, $M_w = 122.9$ kg/mol, $M_n = 23.6$ kg/mol, PDI = 5.2). For the polymerization of graft copolymers and blends, the following materials and methods were employed: The e-caprolactone was dried over calcium hydride overnight, collected by vacuum distillation, and stored in a dry box. The tin(II) 2-ethylhexanoate was dried over 3Å molecular sieves and stored in a dry box. The low-density polyethylene (LDPE, Aldrich, $M_w = 88.1$ kg/mol, $M_n = 10.2$ kg/mol, PDI = 8.65) and polycaprolactone (Aldrich, $M_w = 14.0$ kg/mol, $M_n = 10.0$ kg/mol, PDI = 1.40, according to manufacturer) were purchased from Aldrich and used directly in the melt blends. The PE-g-PCL graft co-polymer used for the blends contained an average of 1.8 PCL arms/100 ethylene monomers; the average DP of PCL calculated from $^1H$ NMR spectroscopy for this material were 95.3, and the $M_n$ and PDI determined by GPC analysis were 43.7 kg/mol and 6.09, respectively. The blends were created by mixing low-density polyethylene and polycaprolactone with or without PE-g-PCL as compatibilizer for 1 h in 1,2-dichlorobenzene at 140 °C under N$_2$ atmosphere, followed by evaporation of solvent at 180 °C for 20 min under stream of nitrogen. The morphology of the blends was investigated using scanning electron microscopy (SEM). The surfaces of cryofractured samples were PCL-etched in hot acetone. High temperature size exclusion chromatography (SEC) analyses were obtained using a PolymerChar chromatograph equipped with PLgel 10um Mixed-B column and IR-5 detector. The mobile phase was 1,2,4-trichlorobenzene and the flowrate was set at 2.0 mL/min at 160 °C. The instrument was calibrated using Agilent PS-1 and PS-2 standards. The samples were prepared in TCB by heating at 170 °C for 2 hour with an injection concentration of 1.0 mg/mL. Differential Scanning Calorimetry (DSC) measurements were made on a TA Discovery Series instrument using temperature scan from -90 °C to 220 °C at a scan rate of 10 °C/min. NMR spectra were recorded on a Bruker AVQ-500 or Bruker DPX-500 spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) relative to residual solvent peaks rounded to the nearest 0.01 for proton and 0.1 for carbon (ref: CHCl$_3$ [1$^H$: 7.26, 13$^C$: 77.16], CHCl$_2$-CHCl$_2$ [1$^H$: 6.0, 13$^C$: 73.78], MeOH [1$^H$: 3.31, 13$^C$: 49.0], DMSO [1$^H$: 2.50, 13$^C$: 39.5]). Coupling constants (J) were reported in Hz. IR spectra were recorded with a Bruker Vertex 80 FTIR spectrometer, the spectra were reported in cm$^{-1}$. Scanning electron microscopy was performed on cryofractured, acetone etched specimens using a Hitachi TM-
1000 scanning electron microscope. The HRMS of Ni catalyst were measured with ESI using the apparatus LTQ Orbitrap XL by Thermo (room temperature, DCM). The water contact-angles were measured using ramé-hart Model A100 instrument at 25 °C. The film for contact-angles measurement were prepared with 10 mg/ml solution of polymer in 1,2-DCB.

2. Synthesis of Nickel complexes

\[
\begin{align*}
\text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O} & \xrightarrow{L, \text{NaBPh}_4} \text{MeOH, 25 °C, 12 h} \quad [\text{Ni}(L)_x \text{X}_y]([\text{BR}_4])_m \\
1: [\text{Ni}^{II}(\text{bisoxa})_3][\text{BPh}_4]_2 & \quad 5: [\text{Ni}^{II}(\text{Phen})_3][\text{BPh}_4]_2 \\
2: [\text{Ni}^{II}(\text{tpy})_2][\text{BPh}_4]_2 & \quad 6: [\text{Ni}^{II}(2,9-\text{Me}_2\text{Phen})_2(\text{OAc})][\text{BPh}_4] \\
3: [\text{Ni}^{II}(\text{bpy})_3][\text{BPh}_4]_2 & \quad 7: [\text{Ni}^{II}(\text{Me}_3\text{Phen})_3][\text{BPh}_4]_2 \\
4: [\text{Ni}^{II}(\text{Bu}_2\text{bpy})_3][\text{BPh}_4]_2
\end{align*}
\]

**General procedure:** Ni(OAc)_2 \cdot 4\text{H}_2\text{O} (1.0 equiv) and ligand L (3.0 equiv) were dissolved in methanol (c = 0.025 M). The resulting reaction mixture was stirred for 2 hours at room temperature. Subsequently, NaBPh_4 was added in one portion, and the mixture was stirred for another 12 hours at room temperature. The formed precipitate was filtered, washed with water, ethanol, and hexane. The resulting solid was dissolved in DCM dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was recrystallized from the solvent stated for each complex below.

**[Ni(bisoxa)]_3[BPh_4]_2 (1):** Following the general procedure after recrystallization from ethanol/acetone mixture the product was isolated as purple solid in 77% yield. HRMS m/z (ESI+) calcd for C_{51}H_{62}BN_6NiO_6\text{[M-BPh}_4\text{]}^+: 923.4172, found 923.4153; elemental analysis (%) calcd for C_{75}H_{82}B_2N_6NiO_6: C 72.42, H 6.65, N 6.76, found C 72.15, H 6.81, N 6.89; IR (neat, cm\(^{-1}\)) v 3034, 2984, 1649, 1477, 1117, 704.

**[Ni(tpy)]_2[BPh_4]_2 (2):** Following the general procedure, after recrystallization from acetonitrile, the product was isolated as brown solid in 81% yield. HRMS m/z (ESI+) calcd for C_{55}H_{60}BN_6Ni^+: 843.2912, found 843.2894; elemental analysis (%) calcd for C_{78}H_{82}B_2N_6Ni: C 80.51, H 5.37, N 7.22, found C 80.43, H 5.30, N 7.17; IR (neat, cm\(^{-1}\)) v 3050, 2981, 1597, 1444, 703.
[Ni(bpy)$_3$](BPh)$_4$ (3): Following the general procedure, after recrystallization from acetonitrile, the product was isolated as grey solid in 74% yield. HRMS m/z (ESI+) calcd for C$_{54}$H$_{42}$BN$_6$Ni$^+$ [M-BPh$_4$]$^+$: 845.3069, found 845.3053; elemental analysis (%) calcd for C$_{78}$H$_{64}$B$_2$N$_6$Ni: C 80.37, H 5.53, N 7.21, found C 80.13, H 5.36, N 7.19; IR (neat, cm$^{-1}$) ν 3030, 1600, 1577, 1472, 1061, 703.

[Ni(Bu$_2$bpy)$_3$](BPh)$_4$ (4): Following the general procedure, after recrystallization from acetone, the product was isolated as beige solid in 83% yield. HRMS m/z (ESI+) calcd for C$_{78}$H$_{64}$BN$_6$Ni$^+$ [M-BPh$_4$]$^+$: 1181.6825, found 1181.6797; elemental analysis (%) calcd for C$_{102}$H$_{112}$B$_2$N$_8$Ni: C 81.55, H 7.51, N 5.59, found C 81.51, H 7.44, N 5.52; IR (neat, cm$^{-1}$) ν 3053, 2965, 1612, 1480, 1019, 701.

[Ni(phen)$_3$](BPh)$_4$ (5): Following the general procedure, after recrystallization from acetone, the product was isolated as beige solid in 60% yield. HRMS m/z (ESI+) calcd for C$_{68}$H$_{64}$BN$_6$Ni$^+$ [M-BPh$_4$]$^+$: 917.3069, found 917.3069; elemental analysis (%) calcd for C$_{84}$H$_{64}$B$_2$N$_6$Ni: C 81.51, H 5.21, N 6.79, found C 81.84, H 5.20, N 6.67; IR (neat, cm$^{-1}$) ν 3051, 1580, 1477, 868, 723, 703.

[Ni(2,9-Me$_2$phen)$_2$OAc](BPh)$_4$ (6): Following the general procedure, after recrystallization from acetonitrile, the product was isolated as pale blue solid in 73% yield. HRMS m/z (ESI+) calcd for C$_{38}$H$_{27}$Ni$_4$O$_2$$^+$ [M-BPh$_4$]$^+$: 533.1482, found 533.1475; elemental analysis (%) calcd for C$_{48}$H$_{47}$BN$_6$Ni$_6$O$_2$: C 75.99, H 5.55, N 6.56, found C 75.79, H 5.82, N 7.30; IR (neat, cm$^{-1}$) ν 3055, 1619, 1496, 1154, 939, 702.

[Ni(Me$_4$phen)$_3$](BPh)$_4$ (7): Following the general procedure, after recrystallization from acetone, the product was isolated as pink solid in 66% yield. HRMS m/z (ESI+) calcd for C$_{72}$H$_{68}$BN$_6$Ni$^+$ [M-BPh$_4$]$^+$: 1085.4947, found 1085.4910; elemental analysis (%) calcd for C$_{98}$H$_{84}$B$_2$N$_2$: C 82.00, H 6.31, N 5.98, found C 81.80, H 6.33, N 6.41; IR (neat, cm$^{-1}$) ν 3054, 3028, 2981, 1524, 1425, 1014, 700.

3. Oxidation of cyclohexane

Typical procedure for the oxidation of cyclohexane with Ni complexes: Cyclohexane (7.5 equiv) and $^6$CPBA (1.0 equiv) were dissolved in the mixture of dichloromethane and acetonitrile (3/1, c = 0.5 M). To this solution was added a stock solution of the Ni catalyst 1-7 (0.1 mol %, the concentration of the stock solution is 10 mg/ml in DCM/CH$_3$CN). The resulting solution was stirred at room temperature for 19 h. Dodecane was then added as an internal standard. The yields of the products were determined by $^1$H NMR spectroscopy.
Table S1. Oxidation of cyclohexane by Ni(OAc)$_2$ H$_2$O

| Entry | Ligand | Yield of C$_6$H$_{11}$OH : C$_6$H$_{11}$Cl : C$_6$H$_{10}$(O) : ε-CL$^a$ |
|-------|--------|-----------------------------------------------------------------|
| 1     | -      | traces                                                          |
| 2     | L7     | 49 : 4 : 2 : 1                                                  |
| 3     | L8     | 51 : 2 : 1 : 4                                                  |
| 4     | L9     | 48 : 2 : 1 : 3                                                  |
| 5     | L10    | traces                                                          |
| 6     | L11    | traces                                                          |
| 7     | L12    | 22 : - : - : -                                                 |
| 8     | L13    | traces                                                          |
| 9     | L14    | traces                                                          |
| 10    | L15    | 18 : - : - : -                                                 |

Standard conditions: Cyclohexane (7.5 equiv.), mCPBA (1.0 equiv.), Ni(OAc)$_2$ H$_2$O (0.1 mol%), Ligand (0.3 mol%) in DCE (0.5 M) at 50 °C under nitrogen atmosphere, the reactions were conducted in closed vials sealed with Teflon-lined cap; $^a$Yield based on $^a$mCPBA determined by GC analysis with $^a$C$_{12}$H$_{26}$ as internal standard.

4. Oxidation of n-octadecane
Typical procedure for the oxidation of n-octadecane: n-octadecane (1.0 equiv) and Ni catalyst 7 (0.4 mol%) were dissolved in dichloroethane (c = 0.1 M). To this solution was added mCPBA (4.0 equiv) and the vial was sealed with Teflon-lined cap. The resulting reaction mixture was stirred at 80 °C for 3 h under nitrogen atmosphere. The yields of the products were determined by 1H NMR spectroscopy using nitromethane or dibromomethane as internal standard.

Table S2. Oxidation of n-octadecane by Ni complexes

| Entry | Catalyst | A18 : K18 : Cl18 : E18 | TONb |
|-------|----------|-------------------------|------|
| 1c    | -        | 62 : 13 : 18 : 7        | 32%d |
| 2     | 1        | 62 : 17 : 21 : -        | 404  |
| 3     | 2        | 65 : 14 : 17 : 4        | 367  |
| 4     | 3        | 66 : 14 : 20 : -        | 381  |
| 5     | 4        | 69 : 16 : 15 : -        | 403  |
| 6     | 5        | 68 : 6 : 26 : -         | 390  |
| 7     | 6        | 68 : 9 : 18 : 5         | 366  |
| 8     | 7        | 75 : 13 : 12 : -        | 408  |
| 9     | 8c       | 65 : 13 : 22 : -        | 385  |

Standard conditions: nC18H38 (1.0 equiv), mCPBA (1.0 equiv), DCE (0.5 M), at 80 °C, under nitrogen atmosphere, the reactions were conducted in closed vials sealed with Teflon-lined cap; cRatio of alcohol (A), ketone (K) and chloroalkyl (Cl) functionalities calculated from the 1H NMR spectrum using CH2Br2 as internal standard; dTON=(alcohol + ketone + ε-CL)/catalyst; eWithout catalyst; fYield of alcohol + Yield of ketone + Yield of ε-CL based on mCPBA; g[Ni(TPA(OAc)(H2O))(BPh4)2], TPA = tris(2-pyridylmethyl)amine.
Table S3. Oxidation of \textit{n}-octadecane with Ni complexes with excess of \textit{m}CPBA

| Entry | Catalyst | TF (%)$^a$ | $A_{18}$ : $K_{18}$ : $Cl_{18}$ : $E_{18}$ $^b$ |
|-------|----------|-----------|---------------------------------|
| 1$^c$ | -        | 24        | 50 : 17 : 29 : 4                |
| 2$^{c,d}$ | -        | 47        | 38 : 9 : 11 : 32                |
| 3     | 1        | 68        | 34 : 31 : 35 : -                |
| 4     | 2        | 24        | 67 : 17 : 16 : -                |
| 5     | 3        | 54        | 42 : 30 : 35 : -                |
| 6     | 4        | 55        | 44 : 27 : 29 : -                |
| 7     | 5        | 63        | 44 : 24 : 32 : -                |
| 8     | 6        | 30        | 60 : 13 : 27 : -                |
| 9     | 7        | 66        | 55 : 21 : 24 : -                |
| 10$^d$ | 7        | 82        | 50 : 26 : 24 : -                |
| 11    | 8$^e$    | 63        | 35 : 24 : 41 : -                |

Standard conditions: $^a$C$_{18}$H$_{38}$ : $^m$CPBA : [Ni(Me$_2$Phen)$_3$](BPh$_4$)$_2$ = 1 : 4 : 4×10$^{-3}$, DCE (0.5 M), at 80 °C, under nitrogen atmosphere for 5 min, the reactions were conducted in closed vials sealed with Teflon-lined cap; $^c$Total yield of alcohol, ketone, chloroalkyl and ester functionalities based on $^a$C$_{18}$H$_{38}$, calculated from the $^1$H NMR spectrum using CH$_2$Br$_2$ as internal standard; $^d$Ratio of alcohol (A), ketone (K) and chloroalkyl (Cl) functionalities calculated from the $^1$H NMR spectrum using CH$_2$Br$_2$ as internal standard; $^e$Without catalyst; $^f$Reaction time = 3 h; $^{[Ni(TPA(OAc)(H$_2$O))(BPh$_4$)$_2$, TPA = tris(2-pyridylmethyl)amine.
5. Oxidation of low-molecular-weight polyethylene

Typical procedure for the Ni-catalyzed oxidation of low-molecular-weight polyethylene (Aldrich, $M_w = 4.3$ kg/mol, $M_n = 1.7$ kg/mol, PDI = 2.63): In an N$_2$-filled glove box, low-molecular-weight polyethylene (310 mg, 11.1 mmol), [Ni(Me$_4$phen)$_3$][BPh$_4$]$_2$ (1.15 mg in 115 μL of DCE, 0.79 μmol), and mCPBA (197 mg, 0.79 mmol) were suspended in DCE (10 mL) in a vial equipped with a magnetic stir bar sealed with Teflon-lined cap. The vial was placed in a heating block at 80 °C for 3 h (Attention! CO$_2$ is released). The reaction mixture was cooled to room temperature and 10 mL of MeOH were added. The precipitate was filtered, washed with methanol (10 mL), and dried at 50 °C under vacuum for 12 h to give 277 mg (89% yield) of oxidized polyethylene (PE-OH). The amounts of alcohol, ketone, and chloroalkyl were determined by $^1$H NMR (TCE-d$_2$) spectroscopy at 80 °C. The molecular weights of the functionalized polymer PE-OH were determined by high temperature GPC. The thermal properties of the oxidized polymers were determined by DSC. $^1$H NMR (500 MHz, C$_2$D$_2$Cl$_4$) δ 3.95 (C$_H$Cl), 3.62 (C$_H$OH), 2.41 (t, $J = 8.6$ Hz, C$_H$_2COC$_H$_2), 1.77, 1.64, 1.50, 1.35, 1.23, 0.97, 0.84. $^{13}$C NMR (126 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 71.8 (C$_H$OH), 43.5, 42.5, 38.3, 37.4, 33.9, 33.5, 31.6, 29.9, 29.51, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 26.7, 26.2, 25.4, 23.9, 23.8, 22.8, 22.3, 13.7, 13.7.

Table S4. Effect of temperature on the oxidation of low molecular weight polyethylene

| Entry | T(°C) | TF | A : K : Cl | ($M_w, M_n, PDI$) | $T_m$ (°C) |
|-------|-------|----|------------|-------------------|------------|
| 1     | 80    | 2.0| 70 : 6 : 24| 4.4, 1.9, 2.37    | 103.4      |
| 2     | 90    | 2.4| 68 : 6 : 26| 4.0, 1.7, 2.43    | 92.0       |
| 3     | 100   | 2.8| 63 : 6 : 31| 4.9, 1.8, 2.77    | 92.0       |
| 4     | 120   | 2.9| 60 : 5 : 34| 4.0, 1.7, 2.46    | 90.8       |

Standard conditions: Starting low molecular weight polyethylene (low-MW PE) with $M_w = 4.3$ kg/mol, $M_n = 1.7$ kg/mol and PDI = 2.63, $T_m = 105.1$ °C, ratio ethylene monomer : mCPBA : [Ni(Me$_4$phen)$_3$][BPh$_4$]$_2$ = 100 : 7.25 : 7.25*10$^{-3}$ in DCE (monomer concentration 1.1 M), under N$_2$ atmosphere for 3h. $^a$Temperature in °C. $^b$TF = A + Cl + K + E, the sum of all functionalities per 100 monomer units, where A, Cl, K, E = alcohol, chloroalkyl, ketone, ester functionalities per 100 monomer units respectively, calculated from the $^1$H NMR spectrum. $^c$Ratio of alcohol (A), ketone (K) and chloroalkyl (Cl) functionalities calculated from the $^1$H NMR spectrum. $^d$Number and weight average molecular weight in g/mol determined by high temperature size exclusion chromatography with 1,24-TCB as eluent at 160 °C. $^e$Melting temperature determined by differential scanning calorimetry. $^f$PDI = polydispersity index, $M_w/M_n$. DCE = 1.2 dichloroethane.
Table S5. Effect of concentration on the oxidation of low molecular weight polyethylene

| Entry | C (M) | TF | A : K : Cl : E | (M<sub>w</sub>, M<sub>n</sub>, PDI) | T<sub>m</sub> (°C) |
|-------|-------|----|----------------|-------------------------------|-------------|
| 1     | 1.1   | 2.0| 70:6:24: -     | 4.4, 1.9, 2.37               | 103.4       |
| 2     | 2.8   | 2.3| 80:8:12: -     | 4.0, 1.8, 2.24               | 95.9        |
| 3     | 11.0  | 2.6| 86:7:7: -      | 4.0, 1.8, 2.21               | 95.7        |
| 4     | 22.0  | 3.0| 88:5:5:2       | 4.1, 1.9, 2.14               | 95.0        |

Standard conditions: Starting low molecular weight polyethylene (low-MW PE) with M<sub>w</sub> = 4.3 kg/mol M<sub>n</sub> = 1.7 kg/mol and PDI = 2.63, T<sub>m</sub> = 105.1 °C, ratio ethylene monomer : mCPBA : [Ni] = 100 : 7.25 : 7.25 x 10<sup>-3</sup> in DCE, under N<sub>2</sub> atmosphere for 3h at 80 °C. *Monomer concentration (M), *TF = A + Cl + K + E, the sum of all functionalities per 100 monomer units, where A, Cl, K, E = alcohol, chloroalkyl, ketone, ester functionalities per 100 monomer units respectively, calculated from the <sup>1</sup>H NMR spectrum. *Ratio of alcohol (A), ketone (K) and chloroalkyl (Cl) functionalities calculated from the <sup>1</sup>H NMR spectrum. *M<sub>w</sub>, M<sub>n</sub>, PDI of functionalized polyethylene. *Melting temperature determined by differential scanning calorimetry. M<sub>n</sub> and M<sub>w</sub> = number and weight average molecular weight in g/mol determined by high temperature size exclusion chromatography with TCB as eluent at 160 °C. PDI = polydispersity index, M<sub>w</sub>/M<sub>n</sub>, DCE = 1,2 dichloroethane.

Figure S1 High temperature size exclusion chromatography of (a) low-MW PE and (b) oxidized low-MW PE (Table S6, entry 4) in the presence of Ni catalyst 7 and (c) oxidized low-MW PE in the absence of Ni catalyst (Table S6, entry 6)
### Table S6 Effect of ratio monomer/CPBA on oxidation of low molecular weight polyethylene

| Entry | Monomer : $^m$CPBA$^a$ | TF$^b$ | A : K : Cl : E$^c$ | $(M_w, M_n, PDI)^d$ | $T_m^e$ |
|-------|------------------------|--------|---------------------|----------------------|--------|
| 1     | 100 : 7.2              | 2.6    | 86 : 7 : 7 : -      | 4.0, 1.8, 2.21       | 95.7   |
| 2     | 100 : 10.8             | 3.6    | 85 : 9 : 6 : -      | 4.2, 2.0, 2.11       | 91.6   |
| 3     | 100 : 14.5             | 4.8    | 80 : 10 : 8 : 2     | 4.3, 2.1, 2.08       | 88.2   |
| 4     | 100 : 21.7             | 5.0    | 76 : 13 : 9 : 2     | 4.6, 2.1, 2.20       | 87.6   |
| 5     | 100 : 28.9             | 5.5    | 74 : 13 : 11 : 2    | 4.7, 2.2, 2.14       | 82.7   |
| 6$^f$ | 100 : 28.9             | 3.1    | 35 : 5 : 6 : 5      | 3.9, 1.6, 2.51       | 84.9   |
| 7$^e$ | 100 : 14.5             | 4.5    | 76 : 11 : 13 : 2    | 3.7, 1.8, 2.02       | 82.4   |

Standard conditions: Starting low molecular weight polyethylene (low-MW PE) with $M_w = 4.3$ kg/mol, $M_n = 1.7$ kg/mol and PDI = 2.63, $T_m = 105.1$ °C, ratio $^m$CPBA : [Ni(Me$_4$Phen)$_3$][BPh$_4$]$_2$ = 1 : $10^{-3}$ in DCE (monomer concentration 11 M), under N$_2$ atmosphere for 3h at 80 °C. $^a$Monomer : $^m$CPBA ratio (M). $^b$TF = A + Cl + K + E, the sum of all functionalities per 100 monomer units, where A, Cl, K, E = alcohol, chloroalkyl, ketone, ester functionalities per 100 monomer units respectively, calculated from the $^1$H NMR spectrum. $^c$Ratio of alcohol (A), ketone (K) and chloroalkyl (Cl) functionalities calculated from the $^1$H NMR spectrum. $^d$Melting temperature determined by differential scanning calorimetry. $^e$Ratio of alcohol (A), ketone (K) and chloroalkyl (Cl) functionalities calculated from the $^1$H NMR spectrum. $^f$M$_w$, M$_n$, PDI of functionalized polyethylene. $^g$Reaction carried out without [Ni(Me$_4$Phen)$_3$][BPh$_4$]$_2$, C(monomer) = 1.1 M. $^h$Reaction carried out with [Ni(TPA(OAc)(H$_2$O))[BPh$_4$]$_2$ (TPA = tris(2-pyridylmethyl)amine) instead of [Ni(Me$_4$Phen)$_3$][BPh$_4$]$_2$. $^i$M$_n$ and M$_w$ = number and weight average molecular weight in g/mol determined by high temperature size exclusion chromatography with TCB as eluent at 160 °C. PDI = polydispersity index, $M_w$/$M_n$, DCE = 1,2 dichloroethane.

6. Oxidation of low-density polyethylene

Typical procedure for the Ni-catalyzed oxidation of low-density polyethylene (Aldrich, $M_w = 88.1$ kg/mol, $M_n = 10.2$ kg/mol, PDI = 8.65): In a N$_2$ filled glove box, low-density polyethylene (310 mg, 11.1 mmol) was suspended in DCE (1.0 mL) in a vial equipped with a magnetic stir bar and sealed with Teflon-lined cap. The resulting suspension was heated in DCE (1.0 mL) at 120 °C for 2 h until formation of a homogenous solution. After cooling to room temperature [Ni(Me$_4$phen)$_3$][BPh$_4$]$_2$ (2.3 mg in 230 μL of DCE, 16 μmol) and $m$-CPBA (395 mg, 1.59 mmol) were
added. The resulting mixture was stirred at room temperature for 5 min, and then the vial was placed in the heating block at 80 °C for 3 h (Attention! CO₂ is released). The reaction mixture was cooled to room temperature, and 10 mL of MeOH were added. The precipitate was filtered, washed with methanol (10 mL), and dried at 50 °C under vacuum for 12 h to give 292 mg (94% yield) of oxidized low-density polyethylene (LDPE-OH). The amounts of alcohol, ketone, and chloroalkyl were determined by ¹H NMR (TCE-d₂) spectroscopy at 100 °C. The molecular weights of the functionalized polymer LDPE-OH were determined by high temperature GPC. The thermal properties of oxidized polymers were determined by DSC. ¹H NMR (500 MHz, C₂D₂Cl₄) δ 3.95 (CHCl), 3.63 (CHOH), 2.41 (t, J = 7.4 Hz, CH₂COCH₂), 1.79, 1.62, 1.47, 1.35, 1.23, 0.97, 0.84. ¹³C NMR (126 MHz, C₂D₂Cl₄) δ 71.8 (CHOH), 64.0 (CHCl), 42.5, 38.3, 37.4, 33.9, 33.5, 32.1, 31.6, 29.9, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 26.7, 26.3, 26.3, 25.4, 23.8, 23.4, 22.8, 22.3, 13.7, 13.7.

Table S7 Oxidation of LDPE

| Entry | Variation from std conditions⁵ | TF⁵ | A : K : Cl : E | (Mₚ, Mₙ, PDI)⁵ | Tₘ (°C)⁶ |
|-------|-------------------------------|-----|---------------|----------------|----------|
| 1     | -                             | 2.4 | 82 : 9 : 9 : - | 99.6, 12.7, 7.82 | 108.8    |
| 2     | C = 5.5 M                     | 2.3 | 75 : 15 : 10 : - | 100.0, 10.9, 9.14 | 114.6    |
| 3     | 90 °C                         | 4.0 | 75 : 11 : 14 : - | 84.4, 10.2, 8.28 | 112.8    |
| 4     | Ni catalyst 8, 90 °C          | 2.9 | 58 : 12 : 9 : 21 | 62.9, 8.3, 7.56 | 112.2    |
| 5     | C = 5.5 M, 90 °C              | 4.4 | 74 : 9 : 17 : - | 118.3, 10.9, 10.82 | 102.1    |
| 6     | No Ni, 90 °C                  | 3.9 | 28 : 20 : 3 : 49 | 15.3, 4.8, 3.2 | 96.0     |

⁵Standard conditions: Starting low-density polyethylene (LDPE) with Mₚ = 88.1, Mₙ = 10.2 and PDI = 8.65, Tₘ = 111.9 °C, ratio ethylene monomer : CPBA : [Ni(Me₄Phen)₃][BPh₄]₂ = 100 : 14.5 : 14.5*10⁻³ in DCE (11.0 M), under N₂ atmosphere for 3h at 80 °C. TF = A + Cl + K + E, the sum of all functionalities per 100 monomer units, where A, Cl, K, E = alcohol, chloroalkyl, ketone, ester functionalities per 100 monomer units respectively, calculated from the ¹H NMR spectrum. ¹Ratio of alcohol (A), ketone (K) and chloroalkyl (Cl) functionalities calculated from the ¹H NMR spectrum. ²Mₚ, Mₙ, PDI of functionalized polyethylene. ³Melting temperature determined by differential scanning calorimetry. Mₚ and Mₙ = number and weight average molecular weight in g/mol determined by high temperature size exclusion chromatography with TCB as eluent at 160 °C. PDI = polydispersity index, Mₚ/Mₙ. DCE = 1,2 dichloroethane.
Figure S2 $^1$H NMR spectra of (a) LDPE in TCE-$d_2$ at 100 °C, (b) hydroxylated low density polyethylene in the presence of Ni catalyst 7 in TCE-$d_2$ at 100 °C (Entry 3, Table S7) and (c) hydroxylated low density polyethylene in the absence of Ni catalyst 7 in TCE-$d_2$ at 100 °C (Entry 6, Table S7).
7. Oxidation of high-density polyethylene

**Typical procedure for the Ni-catalyzed oxidation of high-density polyethylene** (HDPE, AlfaAeser, $M_w = 114.7$ kg/mol, $M_n = 10.3$ kg/mol, PDI = 11.2): In a N$_2$ filled glove box, high-density polyethylene (310 mg, 11.1 mmol) was suspended in 1,2,4-TCB/DCE (1/1, 4 mL) in a vial equipped with a magnetic stir bar and sealed with Teflon-lined cap. The resulting suspension was heated 120 °C for 12 h until a homogenous solution formed. After cooling to room temperature, [Ni(Me$_4$Phen)$_3$][BPh$_4$] (4.6 mg in 460 μL of DCE, 32 μmol) and m-CPBA (395 mg, 1.59 mmol) were added. The resulting mixture was stirred at room temperature for 5 min, and then the vial was placed in the heating block at 80 °C for 3 h. (Attention! CO$_2$ is released). The reaction mixture was cooled to room temperature, and 10 mL of MeOH were added. The precipitate was filtered, washed with methanol (10 mL), and dried at 50 °C under vacuum for 5 h to give 305 mg (98% yield) of oxidized high-density polyethylene (HDPE-OH). The amounts of alcohol, ketone, and chloroalkyl were determined by $^1$H NMR (TCE-d$_2$) spectroscopy at 100 °C. The molecular weights of the functionalized polymer HDPE-OH were determined by high temperature GPC. The thermal properties of oxidized polymers were determined by DSC. $^1$H NMR (500 MHz, C$_2$D$_2$Cl$_4$) δ 3.95 (CHCl), 3.63 (CHOH), 2.41 (t, $J$ = 7.4 Hz, CH$_2$COCH$_2$), 1.79, 1.51, 1.35, 0.97. $^{13}$C NMR (126 MHz, C$_2$D$_2$Cl$_4$) δ 71.8 (CHOH), 64.0 (CHCl), 42.5, 38.3, 37.4, 33.9, 33.5, 29.9, 29.4, 29.0, 26.7, 26.2, 25.4, 23.8, 22.8, 22.3, 13.7.

**Table S8 Oxidation of HDPE**

| Entry | Variation from std conditions$^a$ | TF$^b$ | A : K : Cl : E$^c$ | ($M_w$, $M_n$, PDI)$^d$ | $T_m$ (°C)$^e$ |
|-------|-------------------------------|--------|-------------------|-----------------------|----------------|
| 1     | -                             | 2.3    | 60 : 19 : 21 : -  | 127.7, 10.8, 11.86    | 125.9          |
| 2     | No Ni                         | 0.7    | 14 : 28 : - : 58  | 55.3, 8.6, 6.41       | 126.6          |

$^a$Standard conditions: Starting high-density polyethylene (HDPE) with $M_w = 114.7$ kg/mol, $M_n = 10.3$ kg/mol and PDI = 11.2, $T_m = 127.4$ °C, ratio ethylene monomer : m-CPBA : [Ni(Me$_4$Phen)$_3$][BPh$_4$]$_2$ = 100 : 14.5 : 29 *10$^3$ in DCE/1,2,4-TCB(1/1, 2.8 M), under N$_2$ atmosphere for 3h at 80 °C. $^b$TF = A + Cl + K + E, the sum of all functionalities per 100 monomer units, where A, Cl, K, E = alcohol, chloroaalkyl, ketone, ester functionalities per

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**Figure S3** High temperature size exclusion chromatography of (a) LDPE and (b) oxidized LDPE (Table S7, entry 2) and (c) oxidized LDPE in the absence of Ni catalyst (Table S7, entry 7)
100 monomer units respectively, calculated from the $^1$H NMR spectrum. ^{1}Ratio of alcohol (A), ketone (K) and chloroalkyl (Cl) functionalities calculated from the $^1$H NMR spectrum. ^{2}M_n, M_w, PDI of functionalized polyethylene. ^{3}Melting temperature determined by differential scanning calorimetry. $M_n$ and $M_w$ = number and weight average molecular weight in g/mol determined by high temperature size exclusion chromatography with TCB as eluent at 160 °C. PDI = polydispersity index, $M_w/M_n$. DCE = 1,2 dichloroethane.

Figure S4 High temperature size exclusion chromatography of (a) HDPE, (b) oxidized HDPE (Table S8 entry 1) and (c) oxidized HDPE in the absence of Ni catalyst (Table S8, entry 2)

8. Oxidation of linear low-density polyethylene

Typical procedure for the Ni-catalyzed oxidation of linear low-density polyethylene (LLDPE, Aldrich, $M_w = 122.9$ kg/mol, $M_n = 23.6$ kg/mol, PDI = 5.2): In a N$_2$ filled glove box, high-density polyethylene (310 mg, 11.1 mmol) was suspended in 1,2,4-TCB/DCE (1/3, 4 mL) in a vial equipped with a magnetic stir bar and sealed with Teflon-lined cap. The resulting suspension was heated 120 °C for 12 h until formation of a homogenous solution. After cooling to room temperature [Ni(Me$_4$phen)$_3$](BPh$_4$)$_2$, $m$CPBA in 1,2,4-TCB, 80 °C, N$_2$ PE monomer: $m$CPBA : [Ni] = 100 : 14.5 : 14.5 *10$^{-3}$ C(monomer) = 2.8 M were added. The resulting mixture was stirred at room temperature for 5 min, and then the vial was placed in the heating block at 80°C for 3 h. (Attention! CO$_2$ is released). The reaction mixture was cooled to room temperature and 10 mL of MeOH were added. The precipitate was filtered, washed with methanol (10 mL), and dried at 50 °C.
under vacuum for 12 h to give 308 mg (99%) of oxidized low-density polyethylene (LDPE-OH). The amounts of alcohol, ketone, and chloroalkyl were determined by $^1$H NMR (TCE-$d_2$) spectroscopy at 100 °C. The molecular weights of the functionalized polymer PE-OH were determined by high temperature GPC. The thermal properties of oxidized polymers were determined by DSC. $^1$H NMR (500 MHz, C$_2$D$_2$Cl$_4$) 3.95 (CHCl), 3.63 (CHOH), 2.41 (t, $J = 7.4$ Hz, CH$_2$COCH$_2$), 1.79, 1.51, 1.35, 0.97. $^{13}$C NMR (126 MHz, C$_2$D$_2$Cl$_4$) δ 71.8 (CHOH), 64.0 (CHCl), 42.5, 39.0, 38.4, 37.4, 33.4, 29.9, 29.4, 29.2, 29.0, 26.7, 26.3, 26.1, 25.4, 23.8, 10.8.

**Table S9 Oxidation of LLDPE**

| Entry | Variation from std conditions$^a$ | TF$^b$ | A : K : Cl : E$^c$ | ($M_w, M_n, PDI)^d$ | $T_m$ (°C)$^e$ |
|-------|----------------------------------|--------|-------------------|---------------------|----------------|
| 1     | -                                | 2.8    | 68 : 16 : 16 : -  | 117.3 , 19.4, 6.04  | 121.6         |
| 2     | No Ni                            | 2.1    | 17 : 22 : 18 : 43 | 25.2, 7.4, 3.42     | 122.5         |

$^a$Standard conditions: Starting linear low-density polyethylene (LLDPE) with $M_w = 122.9$ kg/mol, $M_n = 23.6$ kg/mol and PDI = 5.2, $T_m = 122.3$ °C, ratio ethylene monomer : $^{10}$CPBA : [Ni(Me$_4$Phen)$_3$][BPh$_4$]$_2$ = 100 : 14.5 : 14.5*10$^{-3}$ in DCE/1,2,4-TCB(3/1, 2.8 M), under N$_2$ atmosphere for 3h at 80 °C; $^b$TF = A + Cl + K + E, the sum of all functionalities per 100 monomer units, where A, Cl, K, E = alcohol, chloroalkyl, ketone, ester functionalities per 100 monomer units respectively, calculated from the $^1$H NMR spectrum. $^c$Ratio of alcohol (A), ketone (K) and chloroalkyl (Cl) functionalities calculated from the $^1$H NMR spectrum. $^d$Melting temperature determined by differential scanning calorimetry. $M_w$ and $M_n$ = number and weight average molecular weight in g/mol determined by high temperature size exclusion chromatography with TCB as eluent at 160 °C. PDI = polydispersity index, $M_w$/$M_n$. DCE = 1,2 dichloroethane.

**Figure S5** High temperature size exclusion chromatography of (a)
LLDPE, (b) oxidized LLDPE (Table S9, entry 1) and (c) oxidized LLDPE in the absence of Ni catalyst (Table S9, entry 2)

9. Synthesis of low-density polyethylene-graft-polycaprolactone

**Typical procedure for the synthesis of PE-g-PCL:** To generate the PE-g-PCL materials, we used the functionalized low-density polyethylene, LDPE-OH obtained from the reaction with mCPBA in the presence of [Ni(Me₄Phen)₃][BPh₄]₂ (Table S9, Entry1). The LDPE-OH used to graft PCL contained 1.8 hydroxyl functionalities per 100 monomer units and a total of 2.4 functionalities per 100 monomer units (alcohol : ketone : Cl = 82 : 9 : 9).

The molecular weight parameters were $M_w = 99.6$ kg/mol, $M_n = 12.7$ kg/mol, and PDI = 7.82. In a N₂ filled glove box LDPE-OH (50 mg, 0.032 mmol of -OH), ε-caprolactone (355 μL, 3.20 mmol), tin(II) 2-ethylhexanoate (1.3 mg, 3.2 μmol), and DCE (1 mL) in a vial equipped with a magnetic stir bar and sealed with Teflon-lined cap. The resulting suspension was heated at 100 °C for 40 h, during which time the formation of a gel was observed. After cooling to room temperature, the reaction mixture was dissolved in 10 ml of acetone at 50 °C for 30 min. The reaction mixture was cooled to room temperature, and 10 mL of MeOH were added. The precipitate was filtered, washed with methanol (10 mL), and dried at 50 °C under vacuum for 12 h to give 308 mg of PE-g-PCL.

$^1$H NMR (500 MHz CDCl₃) δ 4.84 (C₉H₄OC(O)), 4.04 (t, $J = 6.7$ Hz, C₉H₂εOH), 3.63 (t, $J = 6.6$ Hz, C₉H₂OC(O)), 2.29 (t, $J = 7.5$ Hz, OC(O)C₉H₂a), 1.66 - 1.52 (C₉H₂gCH₃CH₉aCH₂OC(O)), 1.49, 1.36 (p, $J = 7.9$ Hz, CH₂CH₉gCH₂CH₂OC(O)), 1.23, 0.86.

$^{13}$C NMR (126 MHz, CDCl₃) δ 173.5 (CO), 74.2 (C₉H₄OC(O)), 64.1 (C₉H₂εOC(O)), 34.1 (OC(O)CH₉a), 32.3, 29.7 (CH₂, PE), 28.3 (CH₉aOC(O)), 26.7, 25.5 (CH₂CH₉aCH₂OC(O)), 24.6 (CH₂CH₉aCH₂CH₂OC(O)), 14.2, 11.9.

**Table S10. Synthesis of polyethylene-graft-polycaprolactone**

| Entry | Initiatorᵃ | [Sn]₀ : [OH]₀ : [ε-CL]₀ | DPᵇ | $(M_n$, $M_n$, PDI)c | $T_{g₁}$, $T_{m₁}$, $T_{m₂}$ (°C)d |
|-------|-------------|-----------------|-----|----------------|---------------------|
|       |             |                 |     |                 |                     |

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ᵃ Initiator = Sn(2-ethylhexanoate)
ᵇ DP = Degree of Polymerization
ᶜ $(M_n$, $M_n$, PDI) = Molecular Weight Parameters
ᵈ $T_{g₁}$, $T_{m₁}$, $T_{m₂}$ = Glass Transition, Melting Point 1, Melting Point 2
1 LDPE-OH 0.1 : 1 : 30 29.1 123.1, 20.7, 5.95 -59.1, 50.8, 99.8
2 LDPE-OH 0.1 : 1 : 50 47.9 195.1, 38.4, 5.08 -57.3, 54.6, 99.0
3 LDPE-OH 0.1 : 1 : 100 95.3 266.9, 43.7, 6.09 -59.3, 60.0, 97.1
4 HDPE-OH 0.1 : 1 : 100 93.1 232.5, 37.5, 6.19 -61.5, 60.9, 121.5

*LDPE-OH = hydroxylated low density polyethylene with \(M_w = 99.6\) kg/mol, \(M_n = 12.7\) kg/mol and PDI = 7.82. \(T_m = 108.8\) °C, 1.8 hydroxyl functionalities per 100 monomer units and a total of 2.4 functionalities per 100 monomer units (A : K : Cl = 82 : 9 : 9), HDPE-OH = hydroxylated high density polyethylene with \(M_w = 102.7\) kg/mol, \(M_n = 12.4\) kg/mol and PDI = 8.3, \(T_m = 129.1\) °C, 1.2 hydroxyl functionalities per 100 monomer units and a total of 2.2 functionalities per 100 monomer units (A : K : Cl = 58 : 20 : 22). *\(\beta\)DP= the average degree of polymerization of PCL calculated from the \(^1\)H NMR spectrum. *\(M_n\) and \(M_w = \text{number and weight average molecular weight of functionalized polyethylene in kg/mol determined by high temperature size exclusion chromatography. PDI = polydispersity index } M_w/M_n; \) *Melting temperature determined by differential scanning calorimetry (DSC). *Reaction conducted at 120 °C.

**Figure S6** \(^1\)H NMR of (a) hydroxylated low density polyethylene (LDPE-OH) in TCE-\(d_2\) at 100 °C and (b) Polyethylene-polycaprolactone graft co-polymer (PE-g-PCL) in CDCl\(_3\) at rt.
Mechanisms proposed in the literature for oxidation of cyclohexane with Ni-CPBA systeme.
11. ORTEP diagrams of Ni complexes 7

**Figure S7** [Ni(Me₄phen)₃](BPh₄)₂ (7)

X-ray crystal structure of compound 7 was deposited in the Cambridge Crystallographic Data Centre: CCDC 1519144.
12. Electrochemical data

Figure S8 Cyclic voltamogram of Ni complexes 1-7

Table S11 Cyclic voltammetry data of Nickel complexes

| Ni complexes | E_{1/2}(Ni^{II}/Ni^{III}) | E_{pa}(Ni^{II}/Ni^{III}) | E_{pc}(Ni^{II}/Ni^{III}) |
|--------------|---------------------------|--------------------------|--------------------------|
| [Ni(bisoxa)_3](BF_4)_2 | -                         | -                        | 1.39                     |
| [Ni(ppy)_2](BF_4)_2     | 1.28                      | 1.32                     | 1.23                     |
| [Ni(bpy)_3](BF_4)_2     | 1.39                      | 1.42                     | 1.33                     |
| [Ni('Bu_2bpy)_3](BF_4)_2 | 1.24                      | 1.45                     | 1.03                     |
| [Ni(phen)_3](BF_4)_2    | 1.41                      | 1.45                     | 1.36                     |
| [Ni(2,9-Me_2phen)_2OAc](BF_4) | -                        | 1.37                     | -                        |
| [Ni(Me_4phen)_3](BF_4)_2 | 1.15                      | 1.19                     | 1.11                     |

*Cyclic voltammograms were obtained with a glassy carbon working electrode (3 mm dia.), silver wire quasi-reference electrode, and platinum wire counter electrode. Voltammograms were referenced using ferrocene as an internal standard. Cyclic voltammetry of Nickel complexes (1 mM) was performed in acetonitrile containing n-Bu_4NPF_6 (0.1 M) as a supporting electrolyte, under nitrogen atmosphere at 25°C. Scan rate = 100 mV s\(^{-1}\); All redox potentials are expressed to the ferrocene/ferrocenium couple (Fc/Fc\(^+\)).
13. UV data for Ni complexes 1-7

![Figure S9 UV spectra of Ni complexes 1-7](image)

**Table S12 UV-Vis data of Ni complexes 1-7**

| Ni complexes<sup>a</sup> | $3^3A_g \rightarrow 3^3T_{1g}(F)$<sup>b</sup> | $3^3A_g \rightarrow 3^3T_{2g}$<sup>c</sup> | $3^3A_g \rightarrow 3^3E_{1g}$<sup>c</sup> |
|--------------------------|------------------|------------------|------------------|
| [Ni(bisoxa)$_2$](BPh$_4$)$_2$ (1) | 552 (5) | 890 (6) | 762 (2.3) |
| [Ni(tpy)$_2$](BPh$_4$)$_2$ (2) | 510 (13) | 790 (24) | 873 (16) |
| [Ni(bpy)$_2$](BPh$_4$)$_2$ (3) | 519 (10) | 783 (4) | 860 (2) |
| [Ni(4,4'-Bu$_2$bpy)$_2$](BPh$_4$)$_2$ (4) | 522 (14) | 784 (7) | 857 (5) |
| [Ni(phen)$_2$](BPh$_4$)$_2$ (5)<sup>d</sup> | 516 (12) | 785 (7) | 847 (6) |
| [Ni(2,9-Me$_2$phen)$_2$(OAc)](BPh$_4$) (6) | 615 (10) | 892 (3) | 802 (1) |
| [Ni(Me$_4$Phen)$_2$](BPh$_4$)$_2$ (7) | 524 (11) | 784 (6) | 854 (4) |

<sup>a</sup>In DCM/CH3CN (1/1, 0.15 M) at 28 °C; <sup>b</sup>$\lambda_{\text{max}}$ in nm; <sup>c</sup>$\varepsilon$ in M<sup>-1</sup>cm<sup>1</sup>. <sup>d</sup>In DCM/CH3CN(1/1, 0.3 M).
14. SEM images of LDPE-PCL blends

![SEM images of LDPE-PCL blends](image)

**Figure S10** SEM images of cryofractured and PCL-etched surfaces of (a) 80/20 LDPE/PCL, (b) 80/20/5 LDPE/PCL/PE-g-PCL and (c) 80/20/10 LDPE/PCL/PE-g-PCL

15. Wetting measurements

![Wetting measurements](image)

**Figure S11** Water droplets on (a) the control LDPE (b) hydroxylated LDPE
16. Copies of 1H and 13C NMR spectra

AB496-A1-100C-TCE.1.fid
1H starting parameters (zg30)
DRX-500 TBFIC
10/30/13 CGC

\[ \eta_w = 4.3, \eta_n = 1.7 \]

\[ \text{PDI} = 2.63 \]

\[ \text{C(\text{monomer})} = 11.0 \text{ M} \]

\[ \text{[Ni}^{\text{II}}(\text{Me}_3\text{Phen})_3](\text{BPh}_2)_2\text{CPOA} \]

DCE, 80 °C, N₂

\[ \text{[Ni]} = 100 ; \text{14.5 ; 14.5 \times 10^{-3}} \]

\[ \text{CPBA} \]

AB-PE1.1.fid
1H starting parameters (zg30)
DRX-500 TBFIC
10/30/13 CGC

\[ \eta_w = 4.3, \eta_n = 1.7 \]

\[ \text{PDI} = 2.63 \]
\[
\text{M}_w = 4.3, \text{M}_n = 1.7 \\
PDI = 2.63
\]
LDPE
$M_w = 88.1, M_n = 10.1$
FDI = 8.65

$[\text{Ni(Me₄Phen)}]_3[BPH₄]_{2-n} \cdot n\text{CPBA}$
DCE, 90 °C, N₂

PE monomer : n CPBA
$[\text{Ni}] = 100 \cdot 14.5, 14.5 \cdot 10^{-3}$
$C(\text{monomer}) = 5.5 \text{ M}$
[Ni(Me₅Phen)₃][BPh₄]₂ + CPBA
DCE, 90 °C, N₂

LDPE
Mₚ = 88.1, Mₙ = 10.1
PDI = 0.05

PE monomer : CPBA : [Ni] = 100 : 14.5 : 14.5 * 10⁻³
C(monomer) = 5.5 M

A K Cl E

f1 (ppm)
0 5 10 15 20 25 30 35 40 45 50
95 90 85 80 75 70 65 60 55
HDPE

$M_w = 114.7 \text{ kg/mol}$
$M_n = 10.3 \text{ kg/mol}$
$PDI = 11.2$

$\text{[Ni(Me$_2$PPh$_3$)$_2$Cl] (3Ph)$_2$CPBA}$

DCE/1,2,4-TCB, 80 °C, N$_2$

PE monomer: α CPBA $[Ni] = 100 : 14.5 \times 10^{-3}$

C (monomer) = 2.8 M

AB1162-carbon.13.fid

AB-HDPE.13.fid
AB1108-B1-13s-100C-TCE.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC

LLDPE
$M_w = 122.9$ kg/mol
$M_n = 23.6$ kg/mol
PDI = 5.2

$[\text{Ni}([\text{Me}_{2}\text{Phen}]_2)[\text{BPh}_4]_2]_{\text{PE}}$ CPBA
DCE/1,2,4-TCB, 80 °C, N$_2$
PE monomer : CPBA : [Ni] = 100 : 14.6 : 14.5 $\times 10^{-3}$
C (monomer) = 2.8 M

A K Cl E

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

LLDPE
$M_w = 122.9$ kg/mol
$M_n = 23.5$ kg/mol
PDI = 3.2

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

S29
**AB1108-A1-a.13.fid**

**LLDPE**

\[ M_w = 122.9 \text{ kg/mol} \]

\[ M_n = 23.6 \text{ kg/mol} \]

\[ PDI = 5.2 \]

**[Ni(η5-Phen)]_2[BF_4]_2 \cdot \alpha\text{CPBA}**  
**DCE/1,2,4-TCB, 30 °C, N_2**  
**[N] = 100:14.5:14.6 \times 10^{-9} \]**  
**C(monomer) = 2.8 M**

![Chemical structures and peaks](image1)

**AB-PE5.13.fid**

**LLDPE**

\[ M_w = 122.9 \text{ kg/mol} \]

\[ M_n = 23.6 \text{ kg/mol} \]

\[ PDI = 5.2 \]

![Chemical structures and peaks](image2)
NONi(II) catalyst, 13CPBA
DCE, 90 °C, N2
PE monomer : 13CPBA : [Ni] = 100 : 14.5 : 14.5 x 10^-3
C(monomer) = 6.5 M

LOPE
Mn = 83.1, Mw = 10.1
PDI = 0.65

AB-PE3.1.1/fid
1H starting parameters (2430)
DRX-500 TBIC
10/30/13 CGC

LOPE
Mn = 83.1, Mw = 10.1
PDI = 0.65
LDPE-g-PCL
17. Copy of IR Spectrum of LDPE-g-PCL
18. Copy of DSC plots

Figure S12 DSC plot of low MW PE-OH
Figure S13 DSC plot of LDPE-OH
Figure S14 DSC plot of HDPE-OH

Enthalpy (normalized): 132.01 J/g
Onset x: 115.214 °C
Peak temperature: 126.934 °C
Figure S15 DSC plot of LLDPE-OH

(080) AB-1108

Peak temperature: 121.564 °C
Enthalpy (normalized): 78.371 J/g
Onset x: 96.783 °C
Figure S16 DSC plot of LDPE-g-PE