Supporting Information

Selective and mild oxyfunctionalization of model polyolefins

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Experimental Section

Materials and Methods. All materials used were of reagent grade. Pyrrole was distilled before use. Squalane and a cyclohexane solution of the polymer substrate were purified by stirring over H_2SO_4, followed by the neutralization of the organic layer by washing with a saturated solution of Na_2CO_3. The organic layer was dried over $MgSO_4$ and passed through a column of neutral alumina. The filtrate was concentrated using rotary evaporation. The alkane substrates were analyzed by ^1H NMR and IR spectroscopy, in addition to, GC-MS to ensure purity.[1]

^1H, $^{13}C\{^1H\}$ and DEPT ^{13}C NMR spectra were recorded on a Varian 300-VXR spectrometer and a Unity VAC-300 autosampler instrument. NMR samples were dissolved in either deuterated chloroform or methylene chloride (Cambridge Isotope Laboratories). IR spectra were recorded on a Nicolett Magna-IR 550 spectrometer. Samples were prepared as a thin film by evaporation of methylene chloride solution on NaCl plates. UV-visible spectra were collected on a Spectronic Genesys 5 spectrophotometer. FAB-MS spectra were obtained on a VG Analytical 7070E-HF mass spectrometer. GC-MS spectra were collected using a 6890 Series Agilent GC System equipped with an Agilent 5973 Network Mass Selective Detector. The GC system is outfitted with HP-5MS cross-linked (5 %) phenylmethylsiloxane column, 30 m x 0.25 mm x 0.25 μm film thickness, using high purity helium as the carrier gas. Size exclusion chromatography analyses were obtained using a Hewlett Packard Series 1100 liquid

chromatograph equipped with three Jordi polydivinylbenzene columns of 10^4, 10^2, and 500 Å and a HP 1047A refractive index detector at 35 °C. Tetrahydrofuran was the mobile phase and the flow rate was set at 1.0 mL/min. The instrument was calibrated using polystyrene standards. Thermal characterization of polymers was conducted using a Perkins Elmer Pyris 1 differential calorimeter under helium atmosphere using a heating rate of 10 °C/min. Elemental analyses were conducted by Atlantic Microlab.

Synthesis of Manganese *meso*-(tetra-2,6-dichlorophenylporphyrin) Acetate [Mn(TDCPP)OAc]. Mn(TDCPP)OAc was prepared in 2 steps. First, the free base porphyrin, H_2TDCPP was synthesized following a modified Lindsey procedure.[2,3] Freshly distilled pyrrole (2.17 mL, 31.3 mmol) and 2,6-dichorobenzaldehyde (5.54 g, 31.3 mmol) were dissolved in 1.8 L of CH_2Cl_2 in a 2-L, 3-necked flask equipped with a magnetic stir bar, a rubber septum, and a condenser with N_2 inlet. The reaction was flushed with N_2 for 10 minutes, and $BF_3{\cdot}OEt_2$ (1.17 mL, 9.2 mmol) was added with a syringe. The reaction was stirred at room temperature for 2 h under N_2, after which, the solution was brought slowly to a gentle reflux, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (5.44 g, 23.5 mmol) was added as a powder. The reaction was stirred at a gentle reflux for 30 minutes. The reaction mixture was cooled, concentrated, and the product was washed with methanol until the filtrate was clear to remove impurities. The purple product was further purified by column chromatography (neutral alumina, CH_2Cl_2). (1.71 g, 25 % yield). ^{1}H NMR ($CDCl_3$, δ in ppm relative to TMS): 8.66 (s, 8 H Pyr), 7.73 (m, AB_2, 12 H Ph), -2.51 (s, broad, 2 NH Pyr). UV/vis (CH_2Cl_2, nm) 370, 418, 508, 592. FAB-LRMS Calcd for $[C_{44}H_{22}N_4Cl_8]^{\cdot+}$: 885.9, Found: 886.1.

In a second step, the metallation reaction,[2,4,5] a 1-L, 3-necked flask equipped with a reflux condenser, a thermometer, and a magnetic stir bar, was charged with 500 mL *N,N*-

dimethylformamide (DMF), H_2TDCPP (0.56 g, 0.62 mmol) and 2,4,6-collidine (10 mL, 75.6 mmol). The reaction was heated to reflux under N_2, and $Mn(OAc)_2 \cdot 4H_2O$ (50 g, 289 mmol) was added. The reaction was stirred at reflux for 21 h, monitoring the metallation reaction by UV/visible spectroscopy. The reaction mixture was cooled, and the product was precipitated in brine (0 ºC). The product was collected by vacuum filtration and was washed with cold distilled water. Mn(TDCPP)OAc was purified by Soxhlet extraction with hexanes, followed by extraction of the desired product with methylene chloride, and subsequent column chromatography (neutral alumina, 100 % CH_2Cl_2 followed by 100 % methanol) to provide better yields. The red-brown fraction was collected and concentrated by rotary evaporation (0.34 g, 54 % yield). The crude product was previously purified by column chromatography, followed by recrystallization, but the yields were very low. In those cases, the product was recrystallized by adding a small volume of hexane to a hot concentrated solution of the product in CH_2Cl_2. The flask was placed in the refrigerator at 5 ºC for several days and shiny black crystals were collected (low yields). [Mn(TDCPP)OAc employed in these oxyfunctionalization reactions was not recrystallized.] ^{1}H NMR (CD_2Cl_2, δ in ppm): 8.32 (*p*-H Ph), 7.6 (*m*-H Ph), -22 (H Pyr). UV/vis (CH_2Cl_2, λ in nm) 232, 268, 328sh, 349sh, 370, 398sh, 475, 583, 610sh. [Note: The absorbances at 232 and 268 nm are due to residual solvent (DMF) and 2,4,6-collidine, respectively.] FAB-HRMS Calcd for $[C_{44}H_{20}N_4Cl_8Mn]^+$: 938.85766, Found: 938.85788. Recycling Mn(TDCPP)OAc has been reported with high yields and only a minimal decrease in activity.[6]

Oxidation of Adamantane. This procedure was adapted from previous work demonstrating the oxyfunctionalization of small molecule alkanes using the Mn(TDCPP)X (X = Cl, OAc)/imidazole system with sodium periodate as the oxidant.[7] A 10-mL test tube equipped with a magnetic stir bar was charged with the catalyst, Mn(TDCPP)OAc (3.1 mg, 3.09 μmol),

the cocatalyst, imidazole (1.9 mg, 0.027 mmol), a phase transfer catalyst, benzyldimethyltetradecylammonium chloride (BDTAC) (0.0506 g, 0.125 mmol), adamantane (34.7 mg, 0.255 mmol) and 1 mL CH_2Cl_2. The oxidant, $NaIO_4$ (0.265 g, 1.24 mmol) was added to the reaction mixture as a solution in 12.5 mL distilled water. The test tube was sealed by a screw cap or a rubber septum. (The reaction is not air sensitive.) The biphasic mixture was stirred vigorously for 24 h at room temperature. The lower methylene chloride layer of the reaction was collected and washed three times in a separatory funnel with distilled water before drying over magnesium sulfate. The mixture was filtered, and the isolated dry organic layer was concentrated using rotary evaporation. The reaction mixture was analyzed by GC-MS and ^1H NMR spectroscopy and compared with analyses of authentic samples. Yields were calculated by adding an internal standard, decane, to the GC-MS sample: adamantane (16 %, 84 % conversion), 1-adamantanol (42 %), 2-adamantanone (42 %). [A control reaction revealed there was no reaction in the absence of Mn(TDCPP)OAc.]

Optimization Study for Oxidation of Adamantane. The reactions were performed on small scale, and the reaction variables were not rigorously investigated, but this study provided insight into the effect of changing the reaction conditions. The first study examined the effect of changing the concentration of the oxidant, $NaIO_4$. The optimum experiment for the oxidation study was $[NaIO_4]_0/[admanatane]_0$ at approximately five-fold. Optimization of the nitrogen base was studied in the second set of experiments using the optimized quantity of oxidant determined from the first series of reactions. The optimum experiment for the nitrogen base study was $[N\text{-}base]_0/[Mn(TDCPP)OAc]_0$ in the range of 10-16 equivalents. Optimal results were obtained when $[BDTAC]_0/[Mn(TDCPP)OAc]_0$ was approximately 40. Similar results were reported with a different phase transfer catalyst, tricaprylmethylammonium chloride using this ratio as well.

Oxidation of PEP Analog – Squalane. This procedure was adapted from previous work demonstrating the oxyfunctionalization of small molecule alkanes using the Mn(TDCPP)X (X = Cl, OAc)/imidazole system with various oxidants.[2,6-9] A 250-mL round bottom flask equipped with a magnetic stir bar was charged with Mn(TDCPP)OAc (31.2 mg, 30.9 μmol), imidazole (22.1 mg, 0.320 mmol), BDTAC (0.508 g, 1.26 mmol), squalane (0.526 g, 1.24 mmol), and 5 mL CH_2Cl_2. The oxidant, Oxone® (1.5922 g, 2.59 mmol) was added to the reaction as a solution in 50 mL 0.25 M phosphate buffer, pH =7. The flask was sealed with a rubber septum. (The reaction is not air sensitive.) [8] or $NaIO_4$[7] can also be used as oxidants to achieve similar results.) The biphasic mixture was stirred vigorously for 2 days. The reaction was monitored by NMR spectroscopy. After two days, the lower methylene chloride layer of the reaction was collected and washed three times in a separatory funnel with distilled water before drying over magnesium sulfate. [No functionalized squalane products were identified in the aqueous washes by TLC.] The mixture was filtered, and the isolated dry organic layer was concentrated using rotary evaporation. TLC and subsequent column chromatography (silica gel: pentane 100 % to 1:1 pentane/diethyl ether) revealed a complex mixture of products that were not completely separable. Fractions were analyzed by IR, ^1H, ^{13}C, and DEPT ^{13}C NMR spectroscopy. DEPT ^{13}C NMR experiments revealed all hydroxylated products were tertiary alcohols. (Mass yield: 0.3603 g, 29 % (based on 1.24 g crude product), including 0.16 g unreacted squalane, 70 % conversion). The following products reported below were nearly pure fractions (i.e. The range of R_f values was narrow). The remainder of the products were mixtures whose characterization data was not included.

Recovered starting material (eluted 100 % pentane, 0.161 g) residual product by TLC, R_f = 0.74; pentane:Et_2O::5:1) ^{13}C NMR ($CDCl_3$, δ in ppm) 39.5, 37.5, 32.9, 28.1, 27.6, 24.9, 24.6, 22.8, 22.7, 19.8. ^1H NMR ($CDCl_3$, δ in ppm) 1.6-1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9.

Group **S1**: (R_f = 0.74-0.58; pentane:Et_2O::5:1, 0.026 g, 7.2 % of product mass, eluted 10:1 pentane:Et_2O) ^{13}C NMR ($CDCl_3$, δ in ppm) 54.0, 46.4, 39.4, 37.3, 37.1, 32.8, 28.0, 27.5, 24.9, 24.5, 22.7, 21.0, 19.8. ^1H NMR ($CDCl_3$, δ in ppm) 2.8, 2.6, 2.4, 1.6, 1.5, 1.3, 1.2, 1.1, 0.9, 0.8. Anal. Calcd. for $C_{30}H_{60}O$: C, 82.49; H, 13.85; O, 3.66, Found: C, 77.40; H, 12.98; O, 5.02.

Group **S2**: (R_f = 0.29-45; pentane:Et_2O::5:1, 0.058 g, 16.1 % of product mass, eluted 10:1 pentane:Et_2O) ^{13}C NMR ($CDCl_3$, δ in ppm) 72.9, 42.2, 39.6, 37.7, 37.5, 37.1, 32.8, 29.7, 28.2, 27.9, 27.0, 24.9, 24.5, 24.3, 22.7, 19.8. ^1H NMR ($CDCl_3$, δ in ppm) 3.5, 1.5, 1.4, 1.3, 1.2, 1.1, 0.9, 0.8, 0.7. Anal. Calcd. for $C_{30}H_{62}O$: C, 82.11; H, 14.24; O, 3.65, Calcd for $C_{30}H_{62}O_2$: C, 79.15; H, 13.74; O, 7.04, Found: C, 80.50; H, 13.95; O, 4.34.

Group **S3**: (R_f = 0.18, 0.46; pentane:Et_2O::5:1, 0.0468 g, 13 % of product mass, eluted 5:1 pentane:Et_2O) ^{13}C NMR ($CDCl_3$, δ in ppm) 71.1, 44.3, 39.4, 37.7, 37.5, 32.0, 29.8, 29.4, 28, 27.5, 24.9, 24.5, 22.7, 21.9, 19.8. ^1H NMR ($CDCl_3$, δ in ppm) 1.5, 1.4, 1.3, 1.2, 1.1, 0.9, 0.8. Anal. Calcd. for $C_{30}H_{62}O$: C, 82.11; H, 14.24; O, 3.65, Calcd for $C_{30}H_{60}O_2$: C, 79.58; H, 13.36; O, 7.07, Found: C, 80.02; H, 13.72; O, 4.17.

Group **S4**: (R_f = 0.02; pentane:Et_2O::5:1, 0.0136 g, 3.8 % of product mass, eluted 100 % CH_2Cl_2) ^{13}C NMR ($CDCl_3$, δ in ppm) 73.0, 71.2, 44.3, 42.0, 39.6, 37.7, 37.4, 37.3, 37.1, 32.8, 29.8, 29.2, 28.0, 27.7, 27.4, 27.0, 26.5, 24.8, 24.5, 22.8, 22.7, 21.9, 21.7, 19.8. ^1H NMR ($CDCl_3$, δ in ppm) 3.5, 2.6, 2.4, 2.1, 1.5, 1.4, 1.3, 1.2, 1.1, 0.9, 0.8. Anal. Calcd. for $C_{30}H_{60}O_2$: C, 79.58; H, 13.36; O, 7.07, Calcd for $C_{30}H_{60}O_3$: C, 76.86; H, 12.90; O, 10.24, Found: C, 73.76; H, 12.22; O, 8.60.

By analogy, FAB-HRMS of one isolated fraction from a different run using NaOCl as the oxidant provided a peak for $[C_{30}H_{62}O + Na]^+$ at 461.4655, calculated: 461.46984, which is proof for a monohydroxylated squalane molecule. High resolution FAB-MS another product obtained from separate reaction using $NaIO_4$ as the oxidant confirmed the presence of the molecular ion, $[C_{30}H_{62}O_2 + Na]^+$, at 477.4650, calculated: 477.46475, consistent with the dihydroxylated products. (Other products were not identified using mass spectrometry.)

The following observations were based on reactions monitored by ^{13}C NMR spectroscopy. Control reactions ran without oxidant or Mn(TDCPP)OAc resulted in no reaction. For a control reaction in the absence of squalane, no new peaks were observed in the crude NMR spectra; thus the new chemical shifts are assigned to functionalized squalane product. In general, other reactions that were run with *tert*-butyl pyridine in place of imidazole were less successful, and sometimes failed to work at all. In the case of the oxidant, increasing the amount of $NaIO_4$ seemed to have little affect on the reaction, whereas, increasing the amount of Oxone® seemed to produce more product in the same reaction time. Also, varying the concentration of BDTAC in the reaction did not seem to affect the reactions where imidazole was the nitrogen base.

Oxyfunctionalization of a Low-Molecular-Weight Model Polyolefin, poly(ethylene-*alt*-propylene) (PEP). The Mn(TDCPP)OAc/imidazole system described above in the squalane and adamantane sections using Oxone® as the oxidant was used for the post-polymerization modification of poly(ethylene-*alt*-propylene) (PEP). In a typical reaction, a 250-mL round bottom flask equipped with a magnetic stir bar was charged with Mn(TDCPP)OAc (43.6 mg, 43.5 μmol), imidazole (29.4 mg, 0.435 mmol), BDTAC (0.7072 g, 1.75 mmol), PEP (M_n = 5 kg/mol) (1.0815 g, 0.235 mmol, 15.45 mmol monomer), and 10 mL CH_2Cl_2. The oxidant, Oxone® (1.79 g, 2.91 mmol) was added to the reaction as a solution in 60 mL 0.25 M phosphate

buffer, pH =7. The flask was sealed by a rubber septum. (The reaction is not air sensitive.) The biphasic reaction mixture was stirred vigorously for 5 days at room temperature. The reaction was monitored by ^{13}C NMR spectroscopy. After five days, the lower methylene chloride layer of the reaction was collected and washed three times in a separatory funnel with distilled water before drying over magnesium sulfate. The mixture was filtered, and the isolated dry organic layer was concentrated using rotary evaporation (2.4489 g). SEC analysis of the crude reaction provided an M_n of 8.8 kg/mol relative to polystyrene standards and a PDI of 1.1. TLC and subsequent column chromatography of the crude reaction (silica gel: pentane 100 % to 1:1 pentane/diethyl ether) revealed a complex mixture of products that were not completely separable. Mass yield: 1.12 g, 46 %. (Unreacted PEP recovered, 0.1635 g, 16 % of original PEP, 84 % conversion)

PEP starting material. ^{1}H NMR ($CDCl_3$, δ in ppm) 1.7, 1.4, 1.3, 1.2, 1.1, 0.72, 0.70. ^{13}C NMR ($CDCl_3$, δ in ppm) 44.3, 39.4, 37.5, 35.2, 35.0, 34.5, 34.0, 33.2, 33.0, 29.3, 27.9, 28.5, 25.0, 24.8, 24.5, 22.7, 19.7, 19.6, 19.3, 19.2, 19.0.

Group **P1.** (R_f = 0.71-0.84; pentane:Et_2O::5:1, 0.3974 g, 35 % of product mass, eluted 10:1 pentane:Et_2O) ^{13}C NMR ($CDCl_3$, δ in ppm) 72.9, 44.3, 42.3, 39.5, 37.6, 37.5, 35.1, 33.3, 32.9, 29.2, 27.9, 24.9, 24.6, 19.8, 19.7, 19.3, 19.1, 14.2. ^{1}H NMR ($CDCl_3$, δ in ppm) 6.5, 6.3, 6.2, 5.9, 5.8, 5.3, 5.1, 5.0, 3.5, 2.6, 2.5, 2.2, 1.7, 1.6, 1.4, 1.3, 1.2, 1.1, 0.9, 0.8, 0.7. SEC M_n = 8.7 kg/mol, PDI = 1.1.

Group **P2.** (R_f = 0.42-0.52; pentane:Et_2O::5:1, 0.1328 g, 12 % of product mass, eluted 10:1 pentane:Et_2O) ^{13}C NMR ($CDCl_3$, δ in ppm) 73.0, 44.3, 42.3, 39.4, 37.5, 35.1, 35.0, 34.4, 34.0, 33.3, 29.8, 29.4, 29.2, 28.0, 27.8, 27.1, 24.6, 22.8, 22.7, 21.4, 19.9, 19.4, 19.3, 19.1. ^{1}H NMR ($CDCl_3$, δ in ppm) 2.6, 1.7, 1.4, 1.3, 1.2, 1.1, 0.9, 0.8, 0.7. SEC M_n = 8.8 kg/mol, PDI = 1.1.

Group **P3.** (R_f = 0.09-0.15; pentane:Et_2O::5:1, 0.1057g, 10 % of product mass, eluted 5:2 pentane:Et_2O) ^{13}C NMR ($CDCl_3$, δ in ppm) 73.0, 44.3, 42.3, 39.4, 37.5, 35.1, 33.3, 32.9, 29.8, 29.3, 27.8, 27.0, 24.6, 22.8, 21.4, 19.9, 19.8, 19.4, 19.3, 19.1. ^{1}H NMR ($CDCl_3$, δ in ppm) 2.6, 1.7, 1.4, 1.3, 1.2, 1.1, 0.9, 0.8, 0.7.

Group **P4.** (R_f = 0.03-0.05; pentane:Et_2O::5:1, 0.0730 g, 7 % of product mass, eluted 5:2 and 2:1 pentane:Et_2O) ^{13}C NMR ($CDCl_3$, δ in ppm) 73.0, 44.3, 42.3, 39.4, 37.6, 35.1, 34.6, 33.3, 32.9, 29.7, 29.3, 28.1, 27.9, 27.5, 27.0, 24.6, 22.8, 22.7, 21.4, 19.8, 19.4, 19.3, 19.1. ^{1}H NMR ($CDCl_3$, δ in ppm) 2.6, 2.2, 1.7, 1.4, 1.3, 1.2, 1.1, 0.9, 0.8, 0.7. SEC M_n = 8.6 kg/mol, PDI = 1.1.

Group **P5.** (R_f = 0.02; pentane:Et_2O::5:1, 0.0889 g, 8 % of product mass, eluted 2:1 pentane:Et_2O) ^{13}C NMR ($CDCl_3$, δ in ppm) 73.0, 44.3, 42.3, 39.5, 37.5, 35.1, 34.6, 33.2, 32.8, 29.8, 29.2, 28.0, 27.8, 27.0, 24.6, 22.8, 22.7, 21.4, 19.9, 19.4, 19.3, 19.1. ^{1}H NMR ($CDCl_3$, δ in ppm) 4.9, 3.5, 2.6, 2.5, 2.2, 1.7, 1.4, 1.3, 1.2, 1.1, 0.9, 0.7. SEC M_n = 8.6 kg/mol, PDI = 1.1.

Various control reactions identified that the reaction was not active, or was substantially retarded, in the absence of imidazole. In general, reactions with imidazole were better than those performed with 4-*tert*-butyl pyridine, which sometimes resulted in no reaction at all. It was observed by ^{13}C NMR spectroscopy, that new chemical shifts due to products appeared sooner in a reaction with a ratio of phase transfer catalyst to manganese catalyst equal to 40 (2 days) versus a ratio equal to 2 (several weeks). It was also observed that products were identified over shorter reactions times with an increase in catalyst concentration.[10] Reactions with NaOCl as the oxygen donor were successful as well, but required longer reaction times.[8] Whereas, reactions with $NaIO_4$ did not provide any oxygenated products.[7] Additionally, no new chemical shifts were observed when the reaction was run in the absence of PEP substrate, indicating the new chemical shifts observed in a standard reaction are due to functionalized PEP products.

Experiments at 50 °C. A series of experiments were run to investigate the effect of increasing the reaction temperature and the concentration of Oxone® relative to monomer on the polymer oxyfunctionalization reaction. The reactions were performed in sealed, high pressure glass reactors, and heated in an oil bath. The experiment was otherwise performed as described above for PEP. Experimental details can be found in the footnotes of Tables S1 and S2. First, the effect of increasing the temperature was studied. Two parallel reactions were set up, and one was heated to 50 °C while the other reaction was run at room temperature. Each day, the reaction was cooled and an aliquot containing about 70 mg of reaction mixture was removed, worked up as described above, and analyzed by SEC, ^{1}H and ^{13}C NMR and IR spectroscopy. Using higher concentrations for NMR spectroscopy, it was observed that the reaction does in fact reach reasonable conversions well before the normal five day reaction time frame. [Previously, smaller aliquots were taken from the reaction, and under our NMR experimental conditions, the signal to noise ratio prevented detection of the product.]

In a separate series of experiments, the initial concentration of Oxone® relative to the initial concentration of monomer was varied in five reactions performed in sealed, high pressure glass vessels, which were heated at 50 °C for 43 h. The reactions were cooled and worked up in the usual way. The experimental results and details are summarized in Table S2.

Oxyfunctionalization of a High-Molecular-Weight Model PEP. The oxyfunctionalization of high-molecular-weight (SEC M_n = 62 kg/mol, PDI = 1.1) was performed in a sealed, high pressure glass reactor. The reactor was charged with Mn(TDCPP)OAc (19.5 mg, 19.0 μmol), imidazole (12.4 mg, 0.18 mmol), BDTAC (0.2814 g, 0.696 mmol), 50 kg/mol PEP (0.4998 g, 7.14 mmol monomer), 10 mL $CHCl_3$, in addition to a solution of Oxone® ((1.1026 g, 1.79 mmol) in 36 mL 0.25 M phosphate buffer, pH = 7). The reaction was stirred at

room temperature for 3 days, and then worked up as described for the low-molecular-weight example. The functionalized material (hexanes/Et_2O: 2.5:1) was isolated from the unreacted product (100 % hexanes) by column chromatography (silica gel). The products were isolated by rotary evaporation and dried overnight under vacuum at 50 ºC. Mass yield: 0.2926 g, 27 %. (Unreacted PEP recovered, 0.0023 g, > 99 % conversion). Characterization of the products was consistent with the low-molecular-weight PEP. SEC analysis provided a number-average molecular weight of 63.7 kg/mol relative to polystyrene standards, and a PDI of 1.1.

Determination of the Average Degree of Oxyfunctionalization. The average number of hydroxyl groups per chain was determined by a second step modification of the hydroxylated PEP products.[11,12] Chemical determinations were made based on reaction of acetyl chloride with the hydroxyl groups on the polymer chain.[13] The functionalized product (10 mg, 0.14 mmol monomer (based on PEP)) was dissolved in CH_2Cl_2. Since the number of hydroxyl groups was unknown, a large excess of acetyl chloride (40 μL, 0.56 mmol) and pyridine (40 μL, 0.49 mmol) were added using a syringe. The reaction was stirred overnight at room temperature. The unreacted acetyl chloride was quenched by the addition of a saturated solution of $NaHCO_3$. The reaction was washed with additional $NaHCO_3$ solution three times, concentrated, and purified through a short column of alumina using 5:1 hexanes:Et_2O as the mobile phase. The purified solution was dried over $MgSO_4$, concentrated, and dried under vacuum at 50 ºC for approximately 18 h. The products were characterized using ^1H NMR spectroscopy. The average number of hydroxyl groups per chain was estimated by calculating the ratio of the integrated intensity of the methyl protons of the acetyl group near 2 ppm relative to the integrated intensity of the polymer, which was determined based on the number of protons per repeat unit and the number of repeat units per polymer chain (10 H per repeat unit and ca. 70 repeat units per chain),

or calculated on a per 100 backbone carbon basis, 4 backbone carbons per repeat unit. (The *sec*-butyl end group was not resolved for end-group analysis.)

Table S1. Study on the effect of temperature on the oxyfunctionalization of 5 kg/mol PEP.[a]

Reaction Time (days)	Room Temperature						50 °C					
	# OH / Chain[b]	# OH / 100 C[b]	T_g (°C)	M_n[c] (kg/mol)	PDI[c]	Conv[d] (%)	# OH / Chain[b]	# OH / 100 C[b]	T_g (°C)	M_n[c] (kg/mol)	PDI[c]	Conv[d] (%)
1	2.6	0.9	-	8.3	1.14	97	20.3	7.3	-	7.8	1.25	-
2	2.0	0.7	-	8.1	1.07	-	0.30	0.1	-	7.7	1.15	95
3	2.8	1.0	-	8.3	1.16	92	3.6	1.3	-	7.7	1.26	98
4	-	-	-	8.1	1.07	-	-	-	-	7.4	1.13	99
5	1.8	0.6		8.2	1.15	97	2.8	1.0		7.4	1.15	-
6	2.0	0.7	-59	8.2	1.10	90	-	-	-			-
7	-	-	-	-	-	-	-	-	-	7.6	1.12	-
10	-	-	-	-	-	-	2.0	0.7	-57	7.6	1.11	-

[a]Reaction conditions: Mn(TDCPP)OAc (34 mg, 34.3 μmol) and Oxone®:monomer:BDTAC:imidazole:Mn::66:400:40:10:1 in 10 mL CH_2Cl_2 and 65 mL 0.25 M phosphate buffer, pH =7. [b]Average value determined from ^{1}H NMR analysis of acetylated functionalized product; ca. 70 repeat units per chain, 4 backbone carbons per repeat unit. [c]Determined from SEC analysis of the crude aliquot. [d]Based on recovered PEP relative to the crude aliquot.

Table S2. Study on the effect of the concentration of Oxone® on the oxyfunctionalization of 5 kg/mol PEP.[a]

$[Oxone^{®}]_0/[monomer]_0$	# OH / chain[b]	# OH / 100 C[b]	T_g (°C)	M_n[c] (kg/mol)	PDI[c]	Conversion[d] (%)
0.08	1.9	0.7	-60	8.2	1.11	95
0.16	2.5	0.9	-60	7.5	1.11	-
0.33	1.5	0.5	-54	8.5	1.32	97
0.72	4.8 (12.8)[e]	1.7 (4.6)[e]	-49	6.9	1.18	98
0.91	6.2	2.2	-	2.0	2.29	99

[a]Reaction conditions: Mn(TDCPP)OAc (18 mg, 18 μmol) and monomer:BDTAC:imidazole:Mn::400:40:10:1 in 10 mL CH_2Cl_2 and 0.25 M phosphate buffer, pH =7, reaction time 43 h. [b]Average value determined from ^{1}H NMR analysis of acetylated functionalized product; ca. 70 repeat units per chain, 4 backbone carbons per repeat unit. [c]Determined from SEC analysis. [d]Based on recovered PEP relative to the starting material. [e]Calculated from elemental analysis.

References

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